

# Porphyrin-based homogeneous catalysts for the CO<sub>2</sub> cycloaddition to epoxides and aziridines

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**ABSTRACT:** The direct insertion of carbon dioxide (CO<sub>2</sub>) into three-membered rings, such as epoxides and aziridines, represents a relevant strategy to obtain cyclic carbonates and oxazolidinones, which are two useful classes of fine chemicals. The synthesis of these compounds can be efficiently catalyzed by a combination of metal porphyrin complexes and various co-catalysts in homogeneous systems. The catalytic efficiency of these systems is discussed herein by taking into account both the characteristics of the metals and the nature of the co-catalysts, either when used as two-component systems or when combined in bifunctional catalysts. Moreover, mechanistic proposals of the CO<sub>2</sub> cycloaddition processes are reported to provide a rationale of catalytic cycles in order to pave the way for designing more active and efficient catalytic procedures.

**KEYWORDS:** porphyrin, oxazolidinones, cyclic carbonates, CO<sub>2</sub>, homogeneous systems.

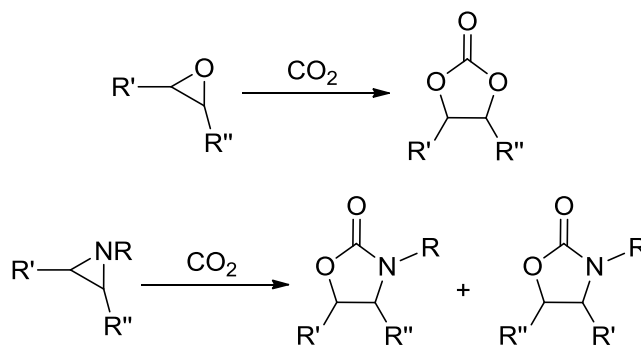
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## 1. Introduction

During the past two centuries the global effects of human activities have contributed to damaging our environment, and now academic and industrial scientific communities are working intensively together to find solutions to reduce or even reverse the ecosystem degradation trends. In this

context, many efforts are currently devoted to replacing linear economic syntheses of fine chemicals, based on the “take-make-consume-throw away” philosophy, with circular economic procedures which are “restorative and/or regenerative” by intention and design. Circular economic procedures can be adapted to the chemical valorization of carbon dioxide (CO<sub>2</sub>) whose over-production is responsible for several major environmental concerns. The utilization of CO<sub>2</sub>, as a renewable C1 building block in ‘*benign by design*’ syntheses of added-value compounds, represents one of the most important challenges for the scientific community [1-4].

Among all the organic transformations, which occur by Carbon Capture and Conversion (CCC) processes, the 100% atom-efficient cycloaddition of CO<sub>2</sub> to three-membered rings, such as epoxides and aziridines (Scheme 1), is an attractive methodology for the synthesis of cyclic carbonates [5, 6] and oxazolidinones [7], which are widely used as raw materials for the preparation of chemicals and pharmaceutical compounds [8, 9].



**Scheme 1.** Synthesis of cyclic carbonates and oxazolidinones by CO<sub>2</sub> cycloaddition to epoxides and aziridines, respectively.

The CO<sub>2</sub> insertion into epoxides and aziridines is well-mediated by several homogeneous and heterogeneous catalytic species [10-17], which are essential for optimizing the process sustainability by applying eco-friendly experimental conditions, such as low catalytic loadings, low reaction temperatures and low CO<sub>2</sub> pressures.

Out of all the available systems for performing CCC processes, porphyrin-based catalysts are very promising due to the unique chemo-physical properties of this class of aza-macrocycles. In fact, the catalytic activity of porphyrin species in promoting the *conversion* of CO<sub>2</sub> into cyclic carbonates and oxazolidinones, can be coupled with their capacity to efficiently *capture* CO<sub>2</sub>, when arranged in frameworks (e.g. metal-organic frameworks MOFs and covalent-organic frameworks COFs), which are capable of absorbing large quantities of gases in a confined space.

It is important to remind that the high chemical stability of porphyrin systems assures high TON (turnover number) and TOF (TOF = turnover frequency) values which in turn increases the

sustainability of porphyrin-based methodologies. In addition, the great chemical versatility of porphyrins permits the introduction of opportune functional groups onto the skeleton in order to create bifunctional catalysts which are able to contemporarily activate CO<sub>2</sub> and the organic substrate.

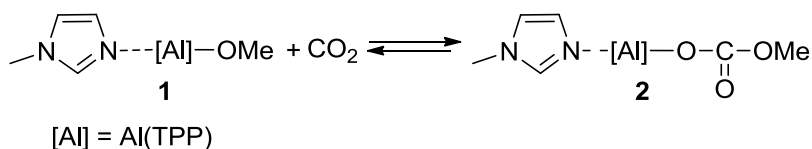
Thus, in this review we would like to give an overview of the catalytic ability of porphyrin-based homogeneous complexes in promoting the cyclic carbonate and oxazolidinone formations. The catalytic activity of heterogeneous porphyrin systems [18] as well as the porphyrin-catalyzed copolymerization of epoxides and CO<sub>2</sub> forming polycarbonates will not be addressed here.

Finally, we sincerely apologize in advance if some important contributions have been unintentionally omitted.

## 2. Synthesis of Cyclic Carbonates.

### 2.1. Main group metal porphyrin catalysts ( $M = Al^{III}, Mg^{II}, Sn^{II}, Sn^{IV}, Bi^{III}$ ).

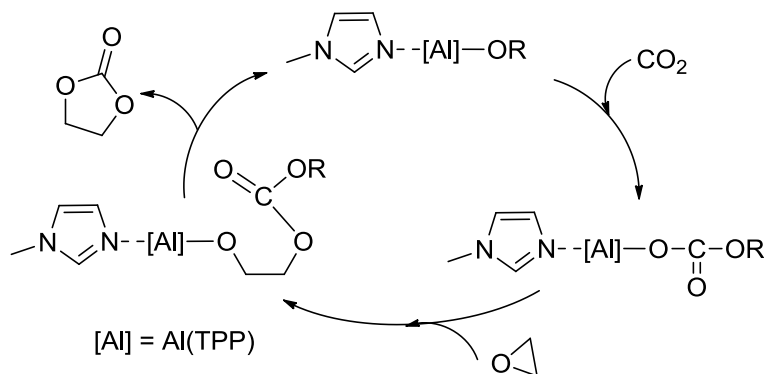
The first example of porphyrin-catalyzed synthesis of cyclic carbonates was reported by S. Inoue and co-authors in 1978 [19] who described the catalytic activity of aluminum (III) alkoxide porphyrins in promoting the cycloaddition of carbon dioxide to propylene oxide forming propylene carbonate. Inoue and co-authors proposed that (TPP)Al(OR) complexes (TPP = dianion of tetraphenyl porphyrin) were very reactive towards CO<sub>2</sub>, in the presence of 1-methylimidazole (NMI), yielding corresponding aluminum (III) complexes bearing a carbonate axial ligand, which was formed by inserting carbon dioxide into the Al-OR bond. The so-formed (TPP)Al(OCOOR) complexes, whose molecular structures were formulated on the basis of spectroscopic data [20], reacted well with epoxides forming cyclic carbonates. In particular, Inoue and co-authors published that Al(TPP)(OMe) (**1**) complex reacted with CO<sub>2</sub> yielding corresponding aluminum (III) complex **2** bearing, as the axial ligands, NMI and the carbonate group (Scheme 2).



**Scheme 2.** Formation of Al(TPP)(OCOOMe)(NMI) (**2**).

The reaction of Al(TPP)(OMe) (**1**) with carbon dioxide was monitored by IR infrared spectroscopy which revealed, only in the presence of NMI, the formation of the new carbonyl absorption at 1697 cm<sup>-1</sup>, which was attributed to the inserted carbon dioxide group. The so-formed complex **2** was sufficiently reactive towards epoxide to easily form the corresponding cyclic

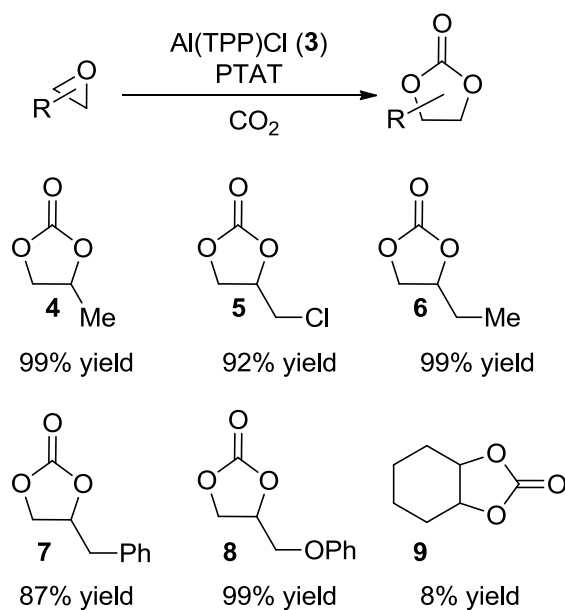
carbonate. The mechanism reported in Scheme 3 was formulated on the basis of spectroscopic data by using an aluminum porphyrin complex which, showing a long poly(oxyalkylene) chain as the axial ligand, was highly soluble in organic solvents and suitable to be used for spectroscopic studies [20].



**Scheme 3.** Suggested mechanism of the cyclic carbonate formation.

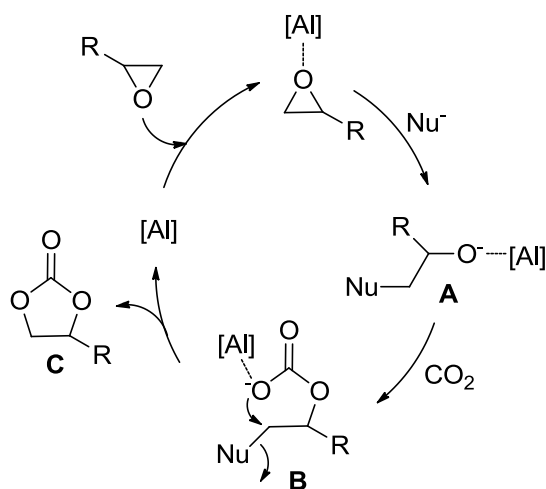
More recently, H. Jing and co-authors [21] studied the catalytic activity of aluminum porphyrins, showing the general formula  $\text{Al(III)(porphyrin)X}$  ( $\text{X} = \text{Cl}^-, \text{F}^-, \text{Br}^-, \text{I}^-, \text{OAc}^-$ ) for promoting the cyclic carbonate synthesis in the presence of Lewis basic co-catalysts. Catalytic activities of these complexes strongly depended on the nature of both X axial ligand and co-catalyst. The best catalytic performances were observed in the presence of the  $\text{Al(TPP)Cl}$  (**3**)/phenyltrimethyl ammonium tribromide (PTAT) combination, in a ratio of 1:2, because  $\text{Br}_3^-$  is a very good nucleophile and leaving group. In addition to that, the Cl axial ligand conferred the best Lewis acidity to aluminum which seems determinant in assuring good catalytic activities.

The  $\text{Al(TPP)Cl}$  (**3**)/PTAT system was employed for the synthesis of compounds shown in Scheme 4, which were obtained by using epoxide as the reaction solvent,  $P_{\text{CO}_2} = 1.0 \text{ MPa}$  and  $T = 25^\circ\text{C}$ .



**Scheme 4.** Synthesis of cyclic carbonates catalyzed by Al(TPP)Cl (**3**)/PTAT system.

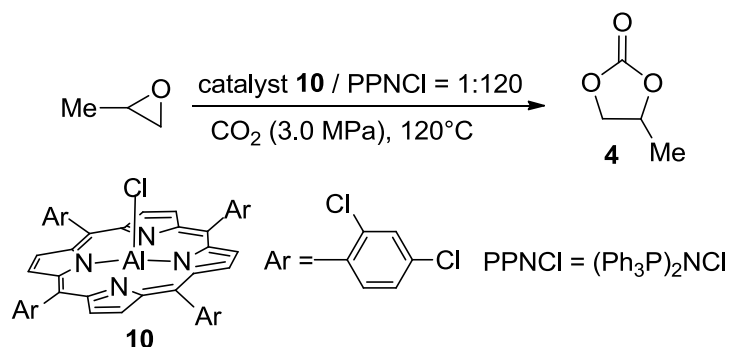
Considering that the catalytic productivity is strongly related to the Lewis acidity of the metal center and the nucleophilic power of the co-catalyst, the authors suggested the mechanism shown in Scheme 5 for the cyclic carbonate formation.



**Scheme 5.** Mechanism of the Al(TPP)Cl (**3**)/PTAT-catalyzed synthesis of cyclic carbonates.

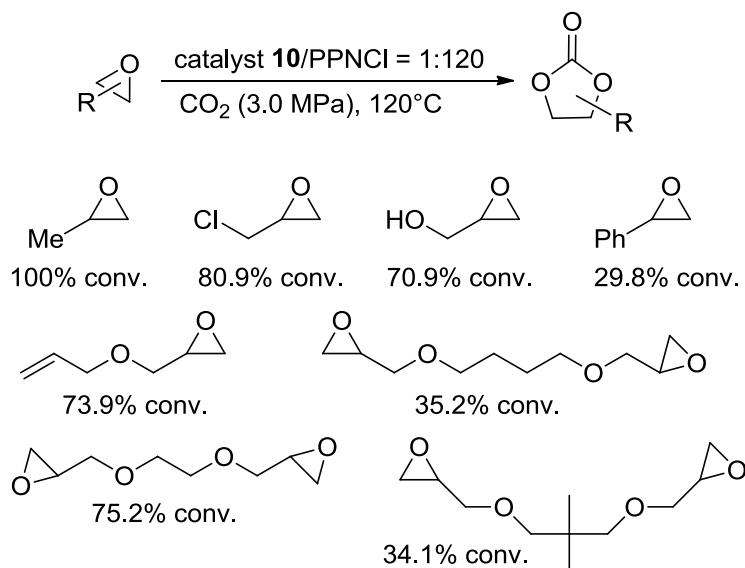
The coordination of the Lewis acid aluminum center to the oxygen atom of epoxide favors the nucleophilic attack of the anion of the co-catalyst which forms, by a ring-opening reaction, species **A**. The reaction of CO<sub>2</sub> with the very reactive intermediate **A** would yield **B** that, thanks to a ring-closure reaction, generates the desired cyclic carbonate **C** and restores the original aluminum catalyst.

In order to improve the catalytic performance of aluminum-based porphyrin catalysts, Y. Qin, X. Wang and co-authors [22] studied the steric and electronic effect of porphyrin ligand on the catalytic activity of Al(III)(porphyrin)X (X = Cl<sup>-</sup>, OTs<sup>-</sup> (Ts = *p*-toluenesulfonyl), OTf<sup>-</sup> (Tf = trifluoromethanesulfonyl)) complexes which were employed in the presence of various co-catalysts. Good catalytic activities were observed by using aluminum compounds showing electron deficient ligands, which enhanced the Lewis acidity of the metal center. In particular, porphyrin complex **10**, bearing 2,4(Cl)<sub>2</sub>C<sub>6</sub>H<sub>3</sub> substituents onto the four *meso* positions of the ligand and the electronegative chlorine atom as the axial ligand X, was very efficient in the CO<sub>2</sub> cycloaddition to propylene oxide forming **4**. This model catalytic reaction was run in the presence of TBAB (tetrabutyl ammonium bromide), PPNI, PPNBr and PPNCl (PPN<sup>+</sup> = bis (triphenylphosphoranylidene)ammonium cation) as the co-catalyst in order to investigate their influence on the reaction productivity. Collected data indicated that **10**-catalyzed synthesis of cyclic carbonate **4** (Scheme 6) was very efficient when performed in the presence of PPNCl, which displays a bulky, non-coordinating cation and a nucleophilic anion with high nucleophilicity.



**Scheme 6.** Catalyst **10**/PPNCl-catalyzed synthesis of cyclic carbonate **4**.

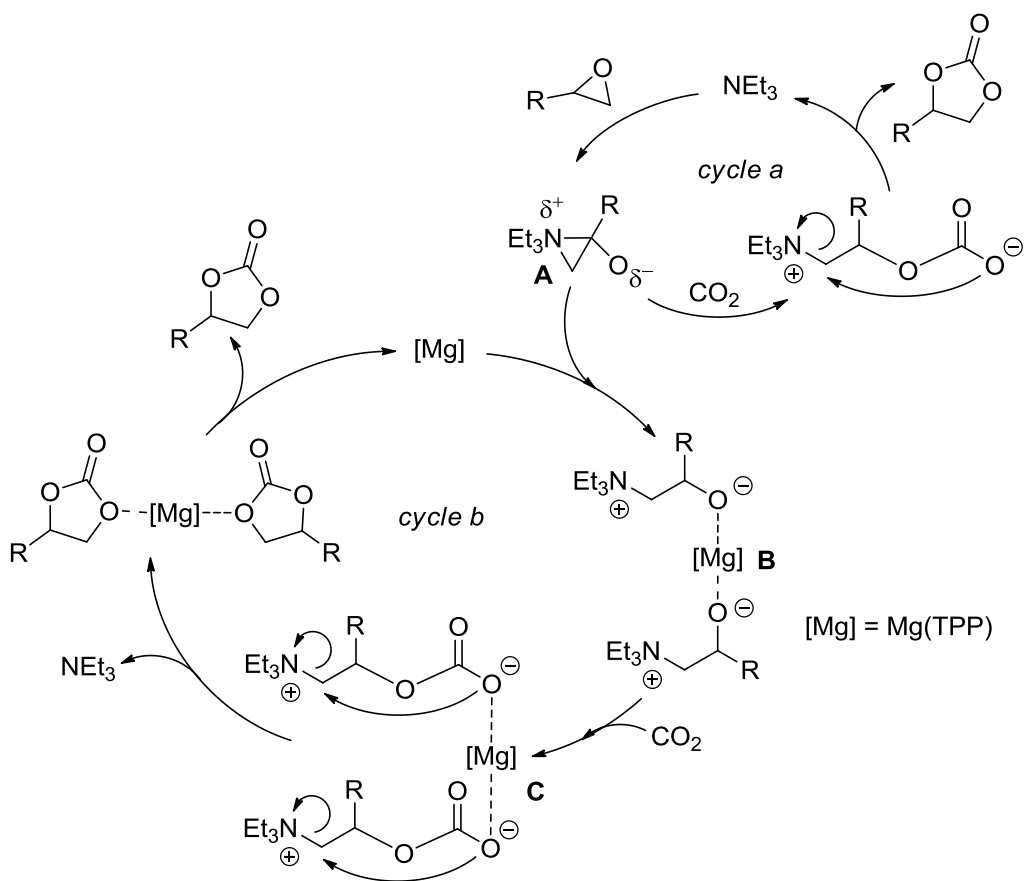
The catalytic **10**/PPNCl system was used in solvent-free conditions (epoxide was used as the reaction solvent) to synthesize several cyclic carbonates with very good epoxide conversions (Scheme 7). It is important to underline that the catalyst was stable enough to be reused at least four consecutive times without losing its catalytic activity.



**Scheme 7.** Epoxide conversions of the catalyst **10**/PPNCl-catalyzed synthesis of cyclic carbonates.

The mechanism of the reaction catalyzed by the binary Al<sup>III</sup>(porphyrin)/PPNX system was recently investigated by using DFT calculations [23]. The first approach of the study was the determination of the energetic profile of the reaction performed in the presence of the sole aluminum catalyst **10**. DFT calculations revealed that the ring-opening process of epoxide requires the very high electronic energy of 58.2 kcal/mol, to definitely clarify the indispensable role of a nucleophilic co-catalyst. In agreement with the commonly suggested three-step mechanism, P. Li and Z. Cao studied the ring-opening, CO<sub>2</sub>-insertion, and ring-closure steps of the catalytic cycle in the presence of **10**/PPNX (X = Cl<sup>-</sup>, Br<sup>-</sup> and I<sup>-</sup>) catalytic system. The theoretical study disclosed that the rate-determining step of the reaction is the ring-opening event and the calculation of free energy barriers suggested that the co-catalyst activity increases in the order PPNCl > PPNBr > PPNI in accordance with the nucleophilicity of chloride, bromide and iodide as well as in agreement to experimental results. It is important to underline that the bulky PPN cation determines the reaction regioselectivity because it drives the nucleophilic attack onto the less substituted carbon atom of epoxide. The subsequent CO<sub>2</sub>-insertion and ring-closure steps are exoergonic processes.

In view of the dependence of the catalytic activity towards the Lewis acidity of the metal center, magnesium porphyrins were less active than aluminum analogues. Mg(TPP) complex (**11**) catalyzed the cycloaddition of CO<sub>2</sub> to epichloridrin forming cyclic carbonate **5** in yields up to 98% by using triethylamine (TEA) as the co-catalyst [24]. Even if it is well known that amines, such as TEA, can be responsible for the epoxide ring-opening affording the corresponding alkoxide **A**, which in turn can convert into cyclic carbonate (Scheme 8, *cycle a*), the presence of Mg(TPP) was required in order to achieve cyclic carbonates in good yields.

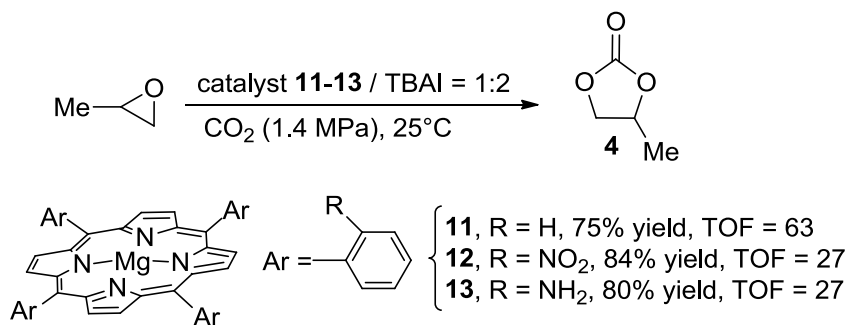


**Scheme 8.** Proposed mechanism of the cyclic carbonate formation catalyzed by Mg(TPP) (**11**)/TEA system.

The beneficial effect of magnesium porphyrin complex **11** was probably due to the formation of intermediate **B** (Scheme 8, *cycle b*), in which alkoxide, deriving from **A**, can be stabilized by axial coordination to the magnesium ion. Complex **B** would react with two CO<sub>2</sub> molecules affording the cyclic carbonate after a cyclization reaction, during which the starting magnesium porphyrin complex **11** and TEA are regenerated. The reaction productivity was very reliant on experimental parameters and the best catalytic efficiency was obtained by running the reaction for 8 hours at 140°C and under 1.5 MPa CO<sub>2</sub> pressure.

The introduction of either electron-withdrawing (Scheme 9, complex **12**) or electron-donating groups (Scheme 9, complex **13**) on the porphyrin skeleton did not result in a positive catalytic outcome due to the steric hindrance of the substituents [21].





**Scheme 9.** Magnesium porphyrin-catalyzed synthesis of cyclic carbonate **4**.

The DFT investigation of cycloadditions, catalyzed by Mg(TPP) (**11**)/TBAI combination, was undertaken to shed some light on the catalytic mechanism [25]. The study indicated, in analogy to what was proposed for aluminum-catalyzed reactions (Scheme 5) that the catalytic cycle occurs in four steps. The reaction starts with the epoxide coordination to Mg(TPP), which is followed by the ring-opening of epoxide due to the nucleophilic attack of iodide. Next, the insertion of carbon dioxide into the metal-oxygen bond occurs and finally, the cyclic carbonate is formed by a  $S_N2$ -type ring-closing process which represents the rate-determining step of the mechanism. When the epoxide substrate shows two differently substituted carbon atoms, the regioselectivity of both the ring-opening and ring-closing processes is mainly governed by steric factors and both events occur at the less encumbered carbon atom. Only when epoxides are mono-substituted with a strong electron-donating group, electronic factors become determinant and the ring-opening and closing reactions occur at the more substituted carbon atom.

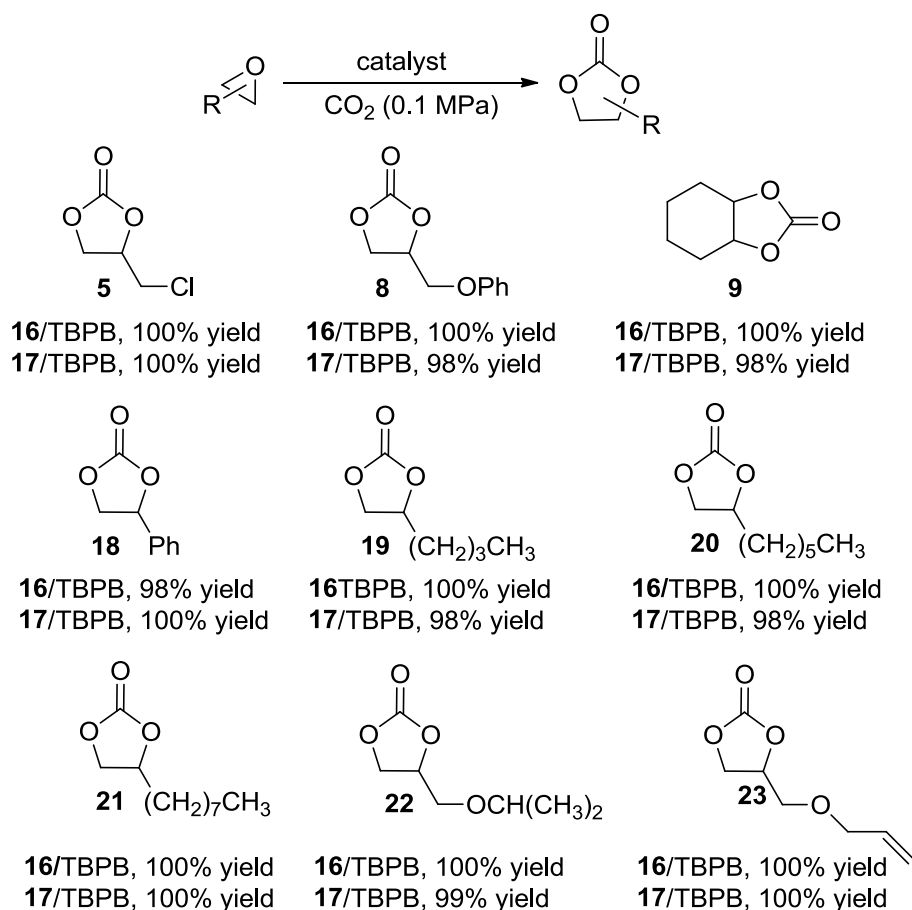
The mechanism of magnesium porphyrin-catalyzed reactions was also investigated in the presence of PPNCl, which is more sterically hindered than TBAI [23]. The study indicated a different energetic profile in which the ring-opening step, instead of the ring-closing, is the rate-determining step in accordance with the minor influence of sterically hindered co-catalysts on the final ring-closure event.

The dependence of the catalytic performance on the Lewis acidity of the porphyrin metal was confirmed by comparing the activities of  $\text{Sn}^{\text{II}}$ (porphyrin) complexes to those of  $\text{Sn}^{\text{IV}}$ (porphyrin) $\text{X}_2$  derivatives. As expected,  $\text{Sn}^{\text{IV}}$ (TPP) $\text{Cl}_2$  (**14**) was more active than  $\text{Sn}^{\text{II}}$ (TPP) (**15**), by using 4-dimethyl ammoniumpyridine (DMAP) as the co-catalyst, in the coupling reaction of propylene oxide and  $\text{CO}_2$  forming **4** [21]. The desired propylene carbonate (**4**) was obtained in 99% yield (TOF = 794) (TOF = turnover frequency) in the presence of **14**, and in 51% yield (TOF = 202) when complex **15** was the employed catalyst. The activity of  $\text{Sn}^{\text{IV}}$ (TPP) $\text{Cl}_2$  (**14**)/DMAP catalytic system was tested in the cycloaddition of  $\text{CO}_2$  with several epoxides in a catalyst/co-catalyst ratio of

1:5, by using the substrate as the reaction solvent,  $P_{\text{CO}_2} = 1.4 \text{ MPa}$  and  $T = 150^\circ\text{C}$ . Several cyclic carbonates were synthesized; in particular compounds **4-8** (Scheme 2) were obtained in very high yields (79%-99%), whilst compound **9** was isolated in the low yield of 20%, probably due to the high steric hindrance of the bicyclic ring.

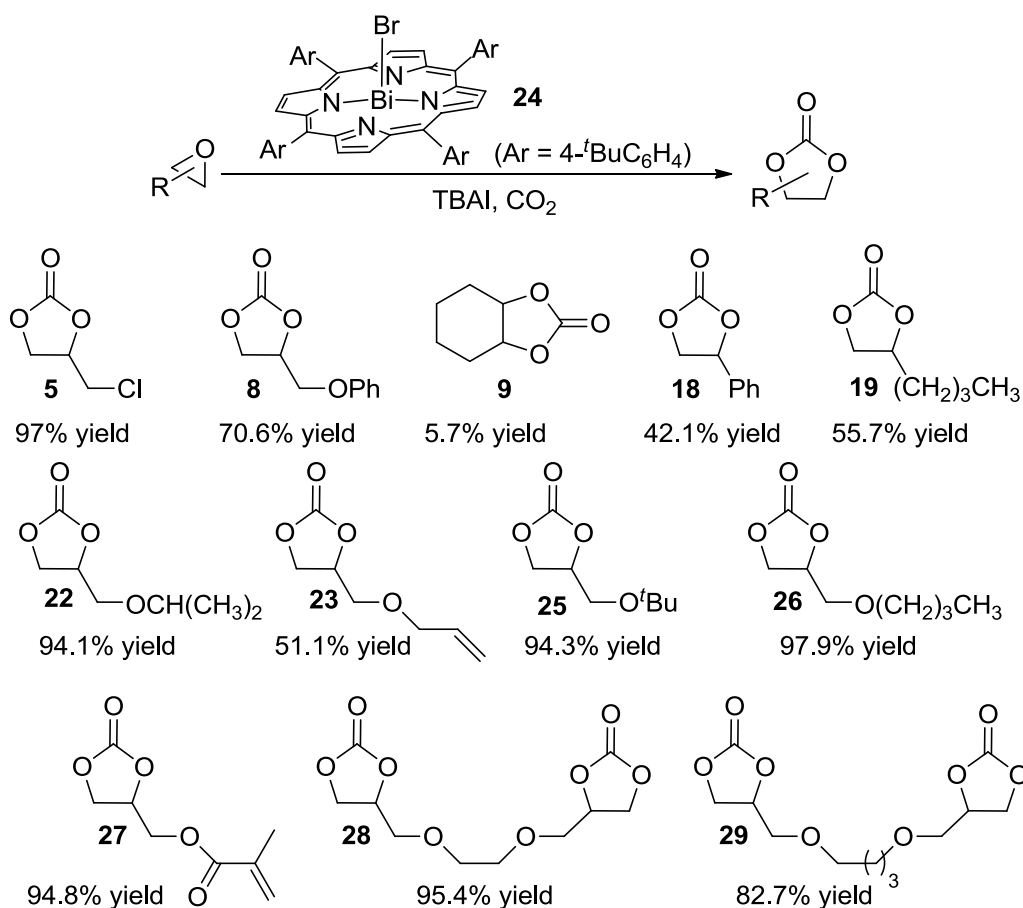
The catalytic efficiency of  $\text{Sn}^{\text{IV}}(\text{porphyrin})\text{X}_2$  complexes was investigated by changing the nature of the axial ligand X, and very good results were achieved by employing  $\text{Sn}^{\text{IV}}(\text{TPP})(\text{OTf})_2$  (**16**) [26] and  $\text{Sn}^{\text{IV}}(\text{TPP})(\text{ClO}_4)_2$  (**17**) [27]. Both complexes were used in combination with tetrabutylphosphonium bromide (TBPB) as the co-catalyst, in the **16**/TBPB ratio of 1:50 and **17**/TBPB ratio of 1:20, respectively. In both cases the study of the reaction scope (Scheme 10) revealed an excellent applicability of the catalytic system by using dimethylformamide (DMF) as the reaction solvent under atmospheric  $\text{CO}_2$  pressure. The very good performances were ascribed to the electron-withdrawing nature of the axial ligands  $\text{OTf}^-$  and  $\text{ClO}_4^-$  which, by increasing the electron-deficiency of tin(IV) metal, optimizes the interaction between the active metal and epoxide substrate.

Among all the halide quaternary ammonium and phosphonium salts tested as co-catalysts, TBPB was the most active species due to the poor electrostatic interaction between the very bulky cation and an anion whose nucleophilicity is maximized. Both **16** and **17** catalysts displayed an excellent chemical stability as proven by the retention of almost identical catalytic activity after ten consecutive catalytic reactions.



**Scheme 10.** Synthesis of cyclic carbonates catalyzed by Sn<sup>IV</sup>(TPP)(OTf)<sub>2</sub> (**16**)/TBPB and Sn<sup>IV</sup>(TPP)(ClO<sub>4</sub>)<sub>2</sub> (**17**)/TBPB systems.

Among porphyrin complexes of main group metals, bismuth derivatives were poorly employed as catalysts of the cycloaddition of CO<sub>2</sub> to epoxides, even if they are a non-toxic class of catalysts. Recently, several Bi<sup>III</sup>(porphyrin)X complexes were synthesized and tested as catalysts for the synthesis of cyclic carbonates under solvent-free conditions and by using tetrabutylammonium iodide (TBAI) as the reaction co-catalyst [28]. The screening of the catalytic activity of different porphyrin complexes, as well as the optimization of experimental conditions, was performed by using propylene oxide as a model substrate. The best yield in propylene carbonate **4** was reached by using the bismuth complex **24**, under atmospheric CO<sub>2</sub> pressure (0.1 MPa), at 90°C with a catalyst/co-catalyst ratio of 1:12. These experimental conditions were effective for the synthesis of various cyclic carbonates, which are shown in Scheme 11.

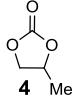
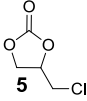
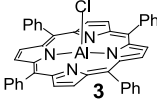
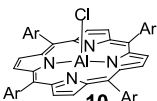
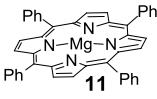
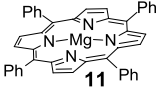
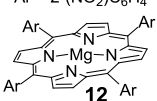
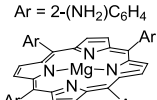
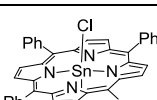
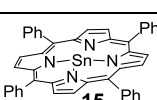
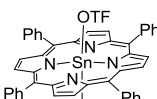
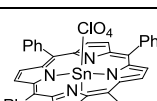
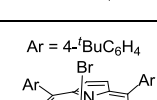


**Scheme 11.** Synthesis of cyclic carbonates catalyzed by  $\text{Bi}^{\text{III}}(\text{porphyrin})\text{Br}$  (**24**)/TBAI system.

On the basis of kinetic studies, the authors suggested a mechanism very similar to that proposed for aluminum-catalyzed reactions (Scheme 5). Collected data indicated that the coordination of epoxide to the bismuth porphyrin activates the substrate and favors the nucleophilic attack of iodide with the consequent ring-opening reaction and the following  $\text{CO}_2$  insertion. Thus, the desired cyclic carbonate product can be formed by a  $\text{S}_{\text{N}}2$ -type ring-closing process, during which the porphyrin catalyst is restored.

The performance of main group porphyrin catalysts, in promoting the synthesis of cyclic carbonates **4** and **5**, is summarized in Table 1.

**Table 1.** Catalytic activities of complexes **3**, **10-17** and **24** in promoting the synthesis of compounds **4** and **5**.

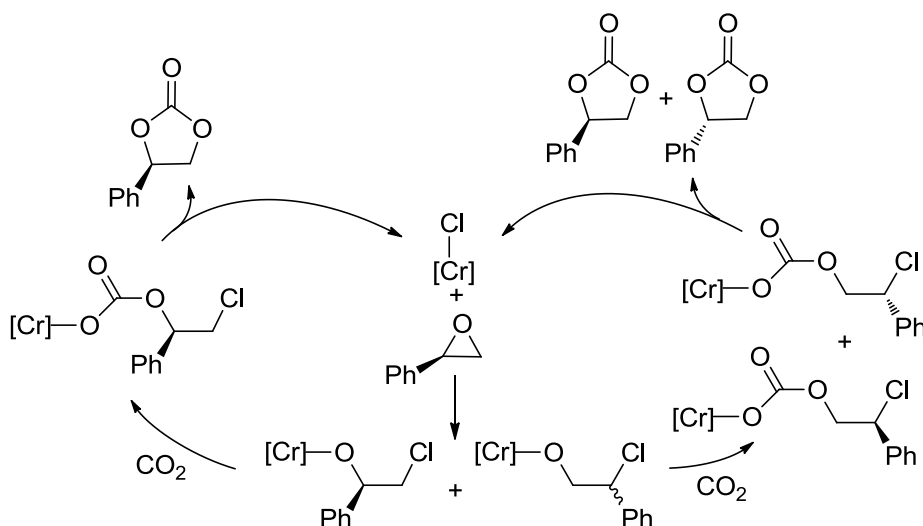
entry [ref.]	main group porphyrin/co-catalyst	mol% cat.	P <sub>CO2</sub> (MPa)	T (°C)	solvent		
1 [21]	 <b>3</b> / PTAT = 1:2	0.05	1.0	25	epoxide	99% yield 5 h	92% yield 12 h
2 [22]	Ar = 2,4-(Cl) <sub>2</sub> C <sub>6</sub> H <sub>3</sub>  <b>10</b> / PPNCI = 1:120	0.001	3.0	120	epoxide	100% yield 1 h	80.9% yield 1 h
3 [24]	 <b>11</b> / TEA = 1:1.25	0.01	1.5	140	epoxide	not reported	98% yield 8 h
4 [21]	 <b>11</b> / TBAI = 1:2	0.05	1.4	25	epoxide	75% yield 24 h	not reported
5 [21]	Ar = 2-(NO <sub>2</sub> )C <sub>6</sub> H <sub>4</sub>  <b>12</b> / TBAI = 1:2	0.05	1.4	25	epoxide	84% yield 62 h	not reported
6 [21]	Ar = 2-(NH <sub>2</sub> )C <sub>6</sub> H <sub>4</sub>  <b>13</b> / TBAI = 1:2	0.05	1.4	25	epoxide	80% yield 60 h	not reported
7 [21]	 <b>14</b> / DMAP = 1:5	0.025	1.4	150	epoxide	99% yield 5 h	not reported
8 [21]	 <b>15</b> / DMAP = 1:5	0.025	1.4	150	epoxide	51% yield 10 h	not reported
9 [26]	 <b>16</b> / TBPB = 1:50	2	0.1	50	DMF	not reported	100% yield 5 h
10 [27]	 <b>17</b> / TBPB = 1:20	2	0.1	50	DMF	not reported	100% yield 11 h
11 [28]	Ar = 4- <sup>t</sup> BuC <sub>6</sub> H <sub>4</sub>  <b>24</b> / TBAI = 1:12	0.2	0.1	90	epoxide	not reported	97% yield 6 h

As reported in Table 1, the synthesis of cyclic carbonates was usually solvent-free and epoxide was used as the reaction solvent. No one catalyst efficiently worked by using the ideal experimental condition of ambient temperature under atmospheric CO<sub>2</sub> pressure. When atmospheric CO<sub>2</sub> pressure (0.1 MPa) was applied, the temperature of 50°C and a large co-catalyst amount were required to afford desired products in good yields (Table 1, entries 9 and 10). On the other hand, when reactions were run at 25°C, the minimum CO<sub>2</sub> pressure of 1.0 MPa was necessary to assure the cyclic carbonate formation. It is important to note that when a low catalytic loading was employed (Table 1, entry 2), the enormous catalyst/co-catalyst ratio of 1:120 was needed to indicate the importance of the co-catalyst in the cyclic carbonate formation.

## 2.2 Transition metal porphyrin catalysts ( $M = Cr^{III}, Cr^{VI}, Co^{II}, Mn^{III}, Ru^{IV}$ and $V^{IV}$ ).

The catalytic activity of transition metal porphyrin complexes in the CO<sub>2</sub> cycloaddition to epoxides was first investigated in 1995 by W. J. Kruper and co-authors [29], by using chromium porphyrin complexes Cr<sup>III</sup>(TTP)Cl (**30**) (TTP = dianion of tetra-*p*-tolyl porphyrin) and Cr<sup>IV</sup>(TTP)O (**31**) as the reaction catalysts. The synthesis of seven cyclic carbonates from both acyclic and cyclic epoxides was performed in a steel autoclave under 5.0 MPa CO<sub>2</sub> pressure, at moderate temperatures (60 °C-130 °C) and by employing either NMI or DMAP as the co-catalyst. Collected data indicated similar catalytic activities for **30** and **31** catalytic species. The lack of the formation of cyclic carbonate, when reactions were performed in the presence of the sole chromium porphyrin, revealed that the presence of both chromium complex and the co-catalyst is required for the transformation of epoxides into corresponding cyclic carbonates in good yields (84%-100% yield).

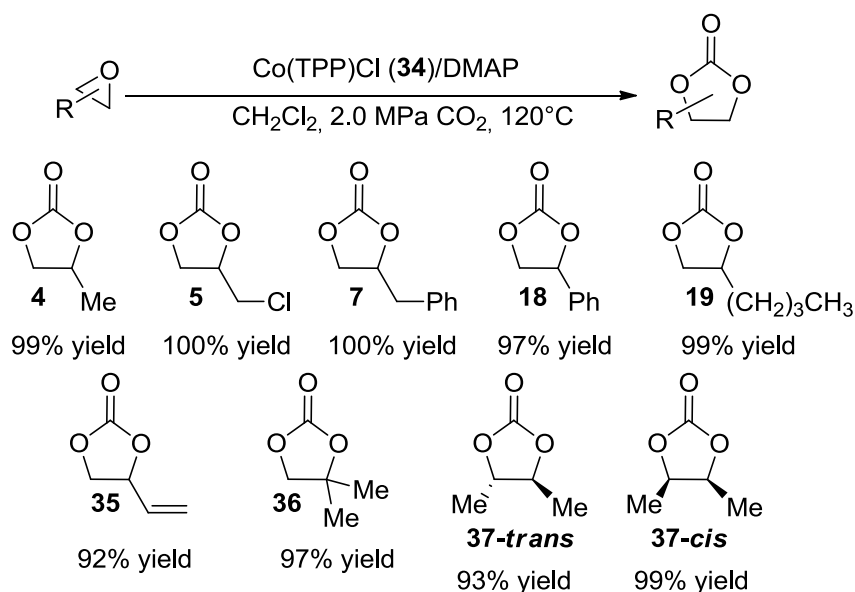
Analogously to that reported above for main group metal-catalyzed reactions (Scheme 5), a first coordination of epoxide to the metal center was also proposed for chromium-catalyzed CO<sub>2</sub> cycloadditions. The substrate activation by the metal makes the ring-opening reaction possible with the consequent insertion of the CO<sub>2</sub> molecule. The stereochemistry of the transformation of styrene oxide into styrene carbonate **18**, catalyzed by Cr<sup>III</sup>(TPP)Cl (**32**)/PPNCl system, was investigated by NMR spectroscopy, polarimetry and chiral HPLC, by employing enantiomeric pure *R*-styrene oxide as the reaction substrate [30]. Achieved experimental data indicated that the ring-opening process occurred by a nucleophilic attack at both the methylene and methine carbons and, considering that the latter mainly occurred without retention of the configuration, the CO<sub>2</sub> cycloaddition to *R*-styrene oxide resulted in the formation of both enantiomers of styrene carbonate **18** (Scheme 12).



**Scheme 12.** Mechanisms of the reaction of *R*-styrene oxide with CO<sub>2</sub>.

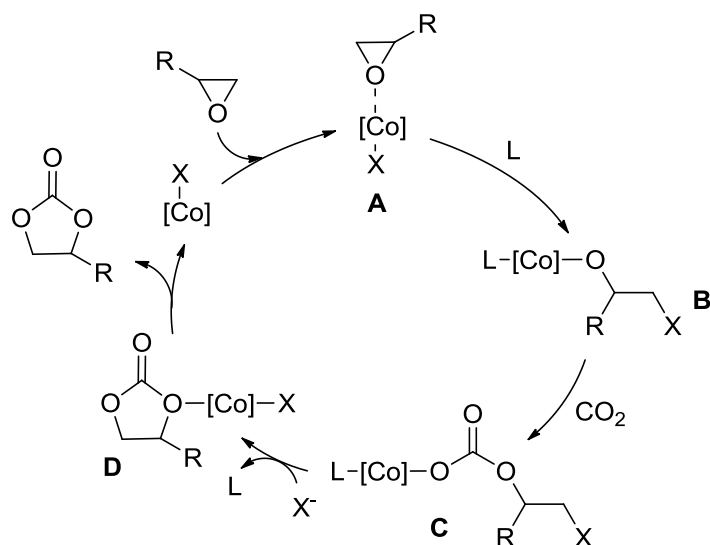
In order to increase the solubility of chromium (III) porphyrin catalysts in compressed CO<sub>2</sub>, porphyrin ligands were functionalized by introducing fluorinated groups onto the skeleton [31]. Resulting fluorinated chromium complexes were very active in catalyzing the reaction between CO<sub>2</sub> and cyclohexene oxide leading, in the presence of PPNCl as the co-catalyst, the corresponding copolymer as the mayor product (91%-99% yield) and cyclic carbonate **9** was formed only in traces (1%-9% yield).

Considering that the performance of catalysts, which are active in CO<sub>2</sub> cycloadditions, is strongly related to the Lewis acidity of the metal, the scientific community has turned its attention towards transition metals which present several accessible oxidation states in order to fine-tune the acidity of the active center. In this contest, S. T. Nguyen and co-authors investigated the catalytic activity of commercially available Co<sup>II</sup>(TPP) (**33**) and Co<sup>III</sup>(TPP)Cl (**34**) complexes [32]. The slight catalytic activity of complex **33** prompted the authors to study the efficiency of the more acidic Co<sup>III</sup>(TPP)Cl (**34**) in the presence of DMAP as the co-catalyst. The system was active in synthesizing cyclic carbonate products in very high yields; both terminal and internal disubstituted epoxides were reactive yielding desired products with retention of the configuration. The catalytic activity of **34** was optimized by performing a model reaction under different CO<sub>2</sub> pressures and using several **34**/DMAP ratios. Compounds reported in Scheme 13 were obtained by using **34**/DMAP ratio of 1:5 (except compounds **36** and **37** which were synthesized by using **34**/DMAP = 1:2 and 1:3, respectively), 2.0 MPa of CO<sub>2</sub>, at 120°C and applying a large excess of epoxide substrate in CH<sub>2</sub>Cl<sub>2</sub> reaction solvent (Scheme 13).



**Scheme 13.** Synthesis of cyclic carbonates catalyzed by Co(TPP)Cl (**34**)/DMAP system.

The catalytic activity of Co<sup>III</sup>(TPP)Cl (**34**) has been analyzed by screening different CO<sub>2</sub> pressures and catalyst/DMAP ratios, and this study allowed the authors to hypothesize a reaction mechanism which was very similar to that proposed by Inoue and co-authors when aluminum porphyrin/NMI system was used as the catalytic system (Scheme 3).



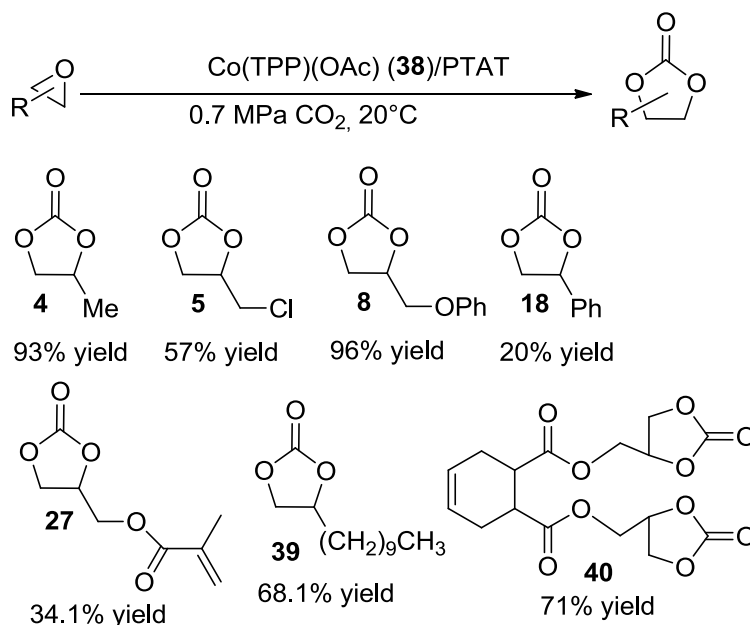
**Scheme 14.** Suggested mechanism for the cycloaddition catalyzed by Co(TPP)Cl (**34**)/DMAP system.

As reported in Scheme 14, the first step of the suggested mechanism is the coordination of epoxide to the metal center which provokes the ring-opening reaction with the consequent formation of metal alkoxide intermediate **B**. Thus, the insertion of carbon dioxide into the cobalt-oxygen bond of **B** originates **C** which can be converted into the desired compound by a ring-



closing process. The authors reported that the catalytic efficiency decreased at high DMAP and CO<sub>2</sub> concentrations. The cobalt center can be deactivated by the presence of a large amount of Lewis base due to the saturation of the active metal, while high CO<sub>2</sub> concentrations can reduce the quantity of the available co-catalyst by forming a zwitterionic DMAP-CO<sub>2</sub> complex. The dependence of the Co(TPP)Cl (**34**) catalytic efficiency on experimental conditions and catalyst/co-catalyst ratio was also investigated by performing a kinetic study of the propylene carbonate **4** synthesis which confirmed the occurrence of inhibiting processes at high CO<sub>2</sub> and/or co-catalyst concentrations [33].

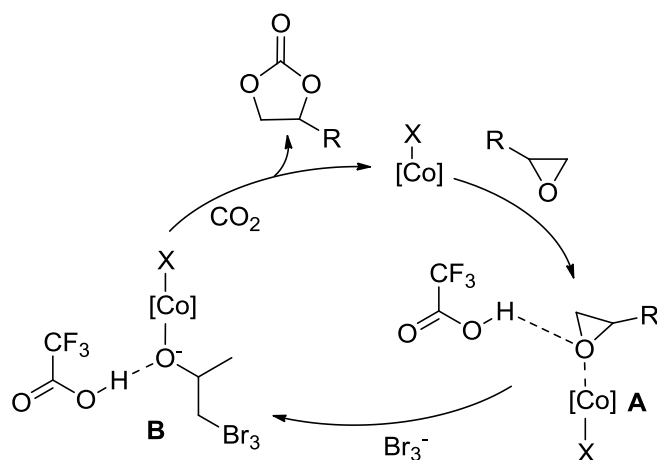
The catalytic activity of cobalt (III) porphyrin complexes was also investigated by H. Jing and co-authors by using different cobalt complexes in combination with either PTAT or TBAB, as the co-catalyst (catalyst/co-catalyst = 1:2), in order to compare the nucleophilic activity of Br<sub>3</sub><sup>-</sup> and Br<sup>-</sup>, respectively [34]. The model coupling reaction of CO<sub>2</sub> with propylene oxide, giving **4**, was efficiently promoted by Co<sup>III</sup>(TPP)(OAc) (**38**) and occurred in higher yields when performed in the presence of PTAT rather than TBAB. This can be due to the superiority of Br<sub>3</sub><sup>-</sup> of PTAT, as a nucleophilic and leaving group, with respect to that of Br<sup>-</sup>, of TBAB (Scheme 15). Reactions were run under 0.7 MPa of CO<sub>2</sub> at 20°C.



**Scheme 15.** Synthesis of cyclic carbonates catalyzed by Co(TPP)(OAc) (**38**)/PTAT system.

The catalytic activity of Co (III) porphyrin complexes/PTAT system was enhanced by adding a Brønsted acid which, as revealed by a kinetic study, decreased the activation energy of the catalytic reaction thanks to a supplementary substrate activation due to hydrogen bindings [35]. The catalytic activity of Co(TCPP)(CF<sub>3</sub>COO) (**41**) (TCPP = dianion of tetra(4-carboxyphenyl)porphyrin) was

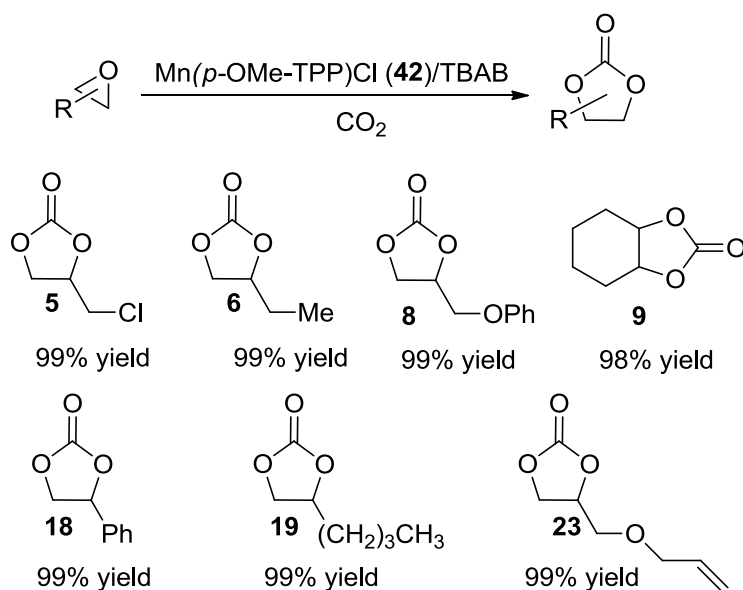
studied in the presence of trifluoroacetic acid ( $\text{CF}_3\text{COOH}$ ), which favored the reaction according to the proposed mechanism, where the hydrogen bond between the Brønsted acid and the oxygen atom of the epoxide renders the substrate more reactive towards the nucleophilic attack (Scheme 16).



**Scheme 16.** Proposed mechanism for the positive assistance of a Brønsted acid in the cobalt-catalyzed  $\text{CO}_2$  cycloaddition.

Recently, chiral basket-handle porphyrin-Co(III) complexes were tested, in a two-component system with tetrabutylammonium chloride (TBACl), to synthesize enantiomeric pure cyclic carbonates [36]. Even if this is the first example of an asymmetric synthesis of cyclic carbonates promoted by chiral metal porphyrin complexes, a moderate enantioselectivity was observed and enantiomeric excesses up to 56.0% were obtained.

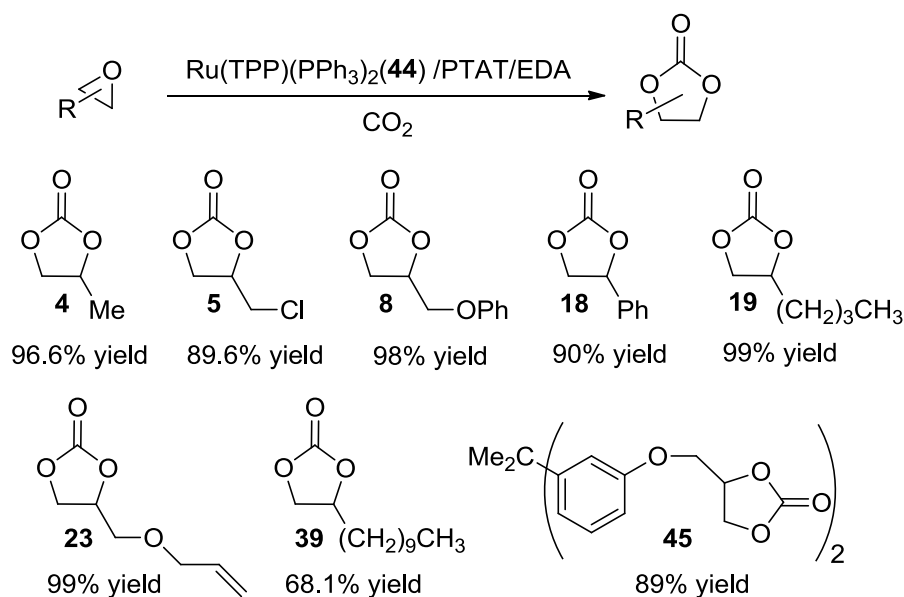
Very good results in terms of reaction sustainability were achieved by employing the catalytic  $\text{Mn}(p\text{-OMe-TPP})\text{Cl}$  (**42**)/TBAB ( $p\text{-OMe-TPP}$  = dianion of tetra(4-metossiphenyl) porphyrin) system which was active with both terminal and internal epoxides at ambient  $\text{CO}_2$  pressure and moderate temperature ( $70^\circ\text{C}$ ) [37]. Several cyclic carbonates were synthesized (Scheme 17), including cyclic carbonate **9** which is often formed in very low yields by the  $\text{CO}_2$  cycloaddition with the corresponding epoxide (see Schemes 4 and 11).



**Scheme 17.** Reaction scope of the reaction catalyzed by Mn(*p*-OMe-TPP)Cl (**42**)/TBAB system.

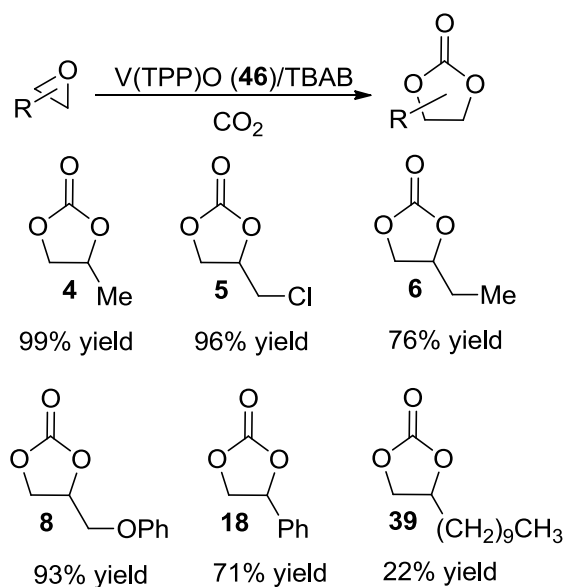
The authors proposed a mechanism very similar to those reported above for Al(TPP)Cl (**3**)/PTAT (Scheme 5), Cr(TPP)Cl (**32**)/PPNCl (Scheme 12) and Co(TPP)Cl (**34**)/DMAP (Scheme 14) systems. Complex Mn(*p*-OMe-TPP)Cl (**42**) showed a very good chemical stability, as proven by the very limited activity loss after recycling the catalyst for four consecutive times.

Ruthenium (II) porphyrin complexes are not acidic enough to activate epoxides and in fact, the transformation of propylene oxide into **4** occurred in the very low yield of 14% when conducted in the presence of Ru(TPP)(PPh<sub>3</sub>)Cl (**43**)/PTAT system [34]. In view of these results, H. Jing and co-authors performed cycloaddition reactions by adding an oxidant, namely ethydiazoacetate (EDA), to the reaction medium [38]. EDA can be responsible for the oxidation of ruthenium (II) to ruthenium (IV) with the consequent increase of the Lewis acidity of the active metal center. In fact, the system Ru<sup>II</sup>(TPP)(PPh<sub>3</sub>)<sub>2</sub> (**44**)/PTAT, which was completely inactive in the synthesis of propylene carbonate (**4**), resulted as very efficient upon the addition of EDA in an equimolar amount with respect to the ruthenium complex. This system was effective for the synthesis of different cyclic carbonates under 0.67 MPa CO<sub>2</sub>, at 50°C, by employing epoxide as the reaction solvent and the Ru<sup>II</sup>(TPP)(PPh<sub>3</sub>)<sub>2</sub> (**44**)/PTAT/EDA ratio of 1:2:1 (Scheme 18).



**Scheme 18.** Synthesis of cyclic carbonate catalyzed by Ru<sup>II</sup>(TPP)(PPh<sub>3</sub>)<sub>2</sub>(**44**)/PTAT/EDA system.

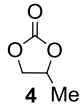
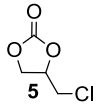
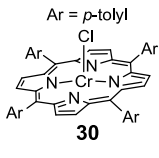
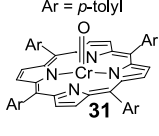
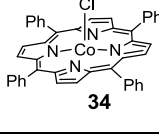
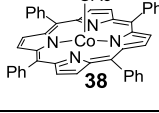
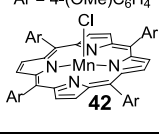
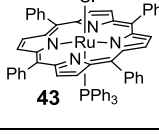
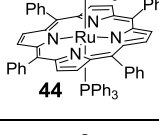
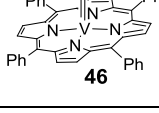
As largely discussed above, the acidic nature of the metal catalyst is determinant in assuring good reaction productivity. In this context, the activity of vanadium (IV) porphyrin derivatives was investigated in the presence of several co-catalysts and by testing different values of CO<sub>2</sub> pressures, temperatures, reaction times and catalyst/co-catalyst ratios. D. Bai and co-authors reported the use of V<sup>IV</sup>(TPP)O (**46**)/TBAB system for the synthesis of compounds shown in Scheme 19 by applying 1.4 MPa CO<sub>2</sub> pressure, 150°C and the **46**/TBAB ratio of 1:2 [39].



**Scheme 19.** Synthesis of cyclic carbonate catalyzed by V(IV)(TPP)O (**46**)/TBAB system.

Data reported above on the catalytic activity of transition metal porphyrins is shown in Table 2.

**Table 2.** Catalytic activities of complexes **30**, **31**, **34**, **38**, **42-44** and **46** in promoting the synthesis of compounds **4** and **5**.

entry [ref]	transition metal porphyrin/co-catalyst	mol% cat.	P <sub>CO<sub>2</sub></sub> (MPa)	T (°C)	solvent		
1 [29]	Ar = <i>p</i> -tolyl  <b>30</b> / DMAP = 1:10	0.07	5.0	60	epoxide	100% yield 40 h	100% yield 18 h
2 [29]	Ar = <i>p</i> -tolyl  <b>31</b> / NMI = 1:10	0.07	5.0	80	epoxide	95% yield 48 h	not reported
3 [32]	 <b>34</b> / DMAP = 1:5	0.4	2.0	120	CH <sub>2</sub> Cl <sub>2</sub>	99% yield 1 h	100% yield 1 h
4 [34]	 <b>38</b> / PTAT = 1:2	0.1	0.7	20	epoxide	93% yield 4.6 h	57% yield 7.5 h
5 [37]	Ar = 4-(OMe)C <sub>6</sub> H <sub>4</sub>  <b>42</b> / TBAB = 1: 1.3	1.8	0.1	70	epoxide	not reported	99% yield 4 h
6 [34]	 <b>43</b> / PTAT = 1:2	0.1	0.7	25	epoxide	not reported	14% yield 3 h
7 [38]	 <b>44</b> / PTAT / EDA = 1:2:1	0.5	0.67	50	epoxide	96.6% yield 1.5 h	89.6% yield 1.5 h
8 [39]	 <b>46</b> / TBAB = 1:2	0.05	1.4	150	epoxide	99% yield 5 h	96% yield 4 h

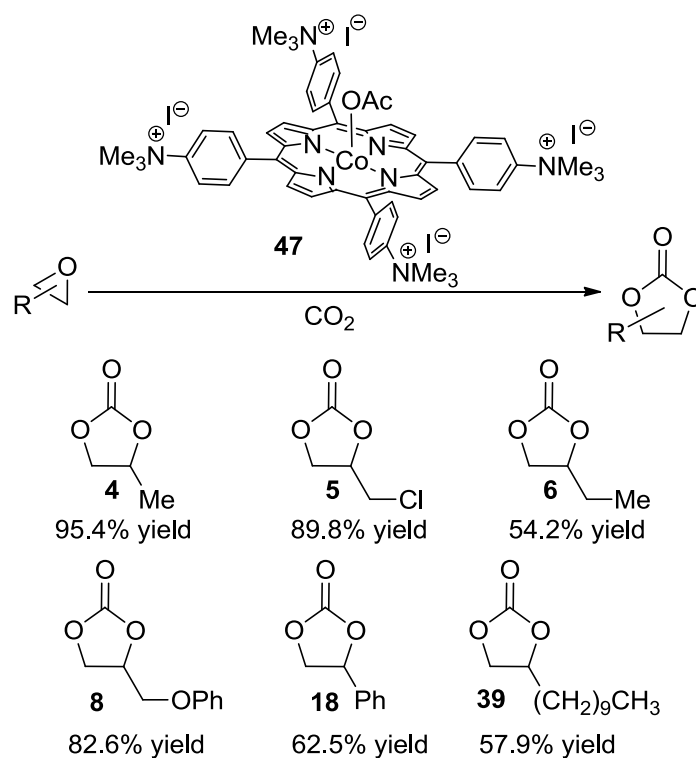
The comparison of these results with those reported in Table 1 revealed that the synthesis of compounds **4** and **5** occurred with a comparable efficiency either in the presence of main group or transition metal porphyrins. The convenient CO<sub>2</sub> pressure/reaction temperature combination of 0.67 MPa/50°C was responsible for the formation of **4** and **5** in the presence of 0.5 mol% of

ruthenium catalyst **44** (Table 2, entry 7). Cyclic carbonates were also obtained in good yields under atmospheric CO<sub>2</sub> pressure by operating at 70°C and using 1.8 mol% of catalyst **42** (Table 2, entry 5). As already reported in Table 1, the reactions were usually performed by using epoxide as the solvent.

#### 2.4. Bifunctional Metal Porphyrin Complexes

As largely reported above, cycloaddition reactions always require the contemporary presence of a Lewis acid center, such as a metal porphyrin complex, and a Lewis basic co-catalyst. In order to optimize the catalytic efficiency, these two active species can be combined into a unique molecule which displays a bifunctional nature. This class of catalysts can contemporarily furnish the metal center, placed into the tetrapyrrolic core, to coordinate the epoxide molecule and the nucleophilic agent to attack the activated epoxide ring.

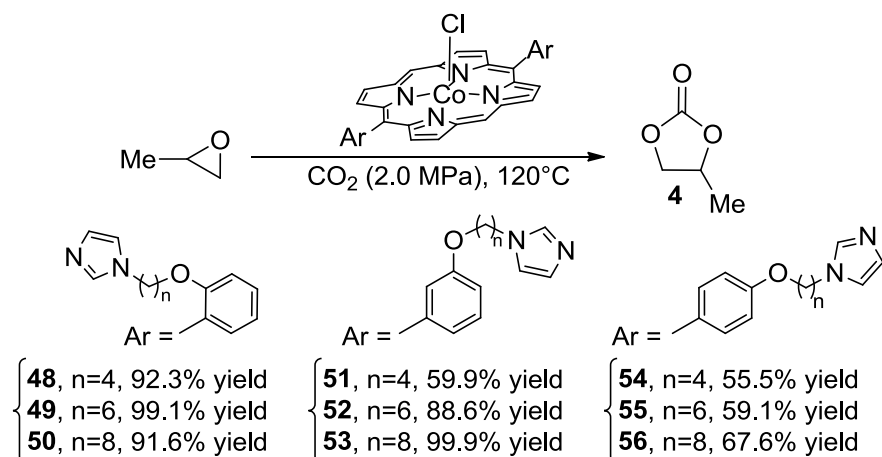
The first example of bifunctional metal porphyrins, employed for the coupling of epoxides with CO<sub>2</sub> to obtain cyclic carbonates, was reported by H. Jing and co-authors in 2010 [40]. Different bifunctional metal porphyrin complexes, with the general formula M<sup>III</sup>(TTMAPP)I<sub>4</sub>(X) (TTMAPPI<sub>4</sub> = dianion of tetra-(*p*-*N,N,N*-trimethylphenylammonium iodide)porphyrin) were synthesized. All of them show the trimethyl ammonium iodide functionality on the *para* positions of the *meso*-aryl porphyrin substituents, delivering the nucleophilic iodide ion for the ring-opening reaction of epoxide. The catalytic activity of a numbers of M<sup>III</sup>(TTMAPP)I<sub>4</sub>(X) was investigated in the model coupling reaction of CO<sub>2</sub> with propylene oxide, giving cyclic carbonate **4**, by using 0.05 mmol of the catalyst under 0.67 MPa of CO<sub>2</sub> at 80°C. Regarding the employed metals, the most active metal was cobalt (III) followed by, in respective order, Mn (III) > Fe (III) > Cr (III); while the most active catalyst showed OAc<sup>-</sup> as the X axial ligand. Generally speaking, X axial ligand of this class of metal porphyrin catalysts are ordered in increasing activity as the following: OAc<sup>-</sup> > I<sup>-</sup> > Cl<sup>-</sup> > Br<sup>-</sup> > OTs<sup>-</sup> > CF<sub>3</sub>COO<sup>-</sup> > CCl<sub>3</sub>COO<sup>-</sup>. The most active catalyst Co<sup>III</sup>(TTMAPP)I<sub>4</sub>(OAc) (**47**) was employed to study the reaction scope which revealed the potential of the proposed catalytic system (Scheme 20).



**Scheme 20.** Study of the scope of the  $\text{Co}^{\text{III}}(\text{TTMAPP})\text{I}_4(\text{OAc})$  (**47**)-catalyzed reaction.

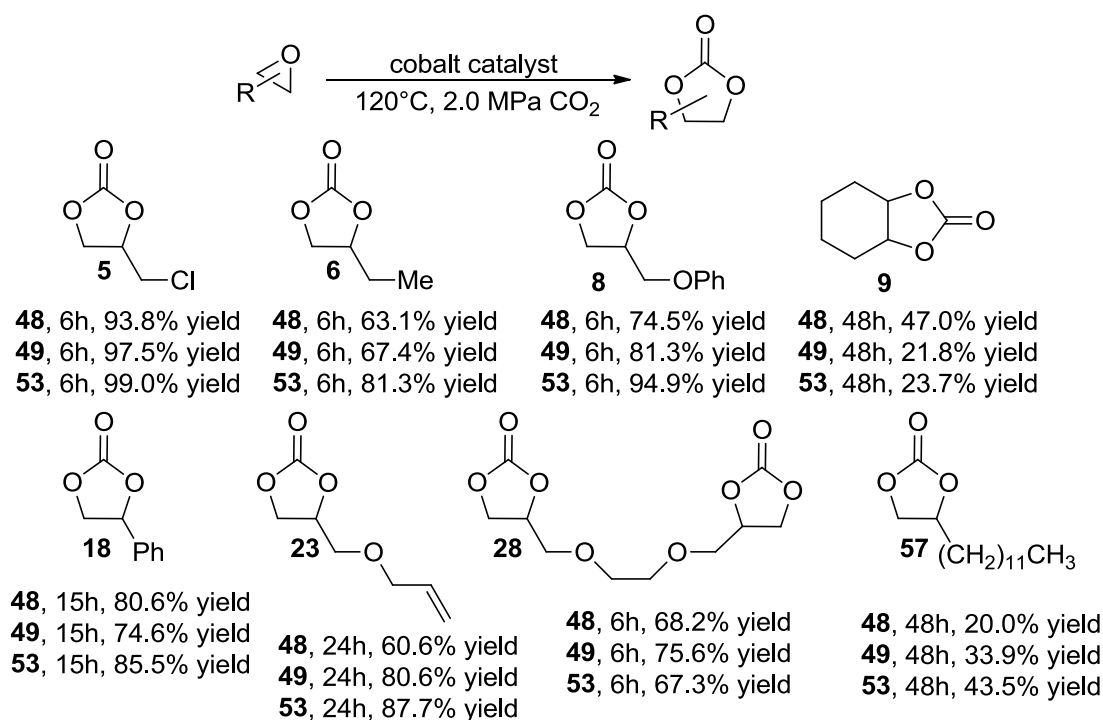
It should be noted that the good chemical stability of catalyst **47** permitted its recycling for five consecutive times in the synthesis of cyclic carbonate **4**, with a very small decrease of the catalytic efficiency.

Later, in 2016, the same authors proposed the synthesis and study of the catalytic activity of another bifunctional derivative of a  $\text{Co}(\text{III})$  porphyrin, which was obtained by grafting imidazole moieties onto the porphyrin framework [41]. The cycloaddition reaction of propylene oxide and  $\text{CO}_2$ , yielding cyclic carbonate **4**, was used as the model reaction to study the activity of the catalysts **48-56**, which show different length of the alkoxyimidazole chains located in *ortho*, *meta* or *para* positions of the *meso*-aryl ring of the porphyrin ligand.



**Scheme 21.** Synthesis of compound **4** catalyzed by complexes **48-56**

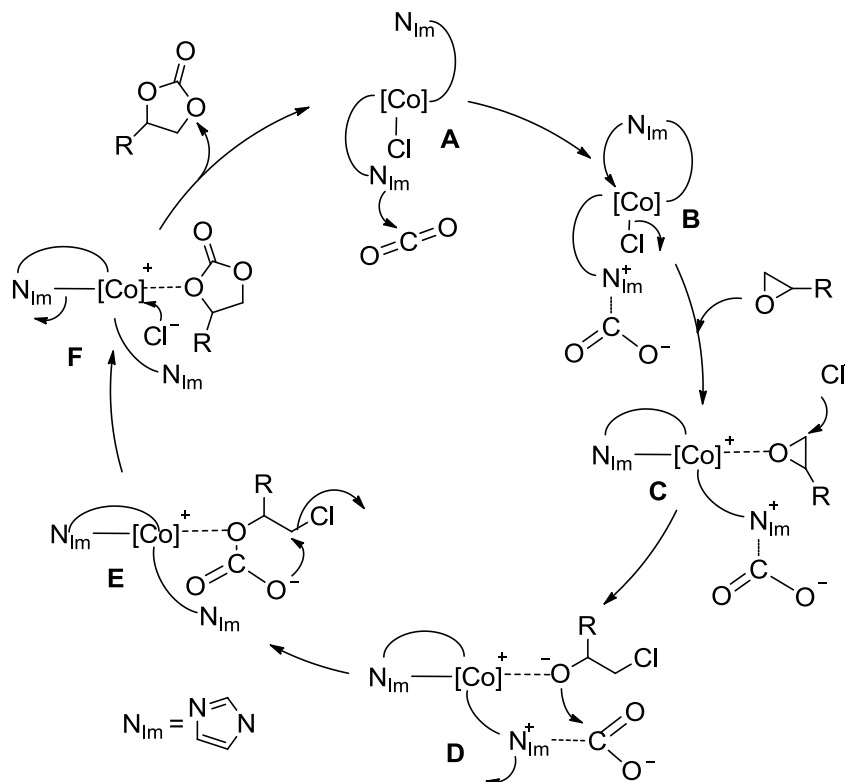
The experimental conditions of the synthesis of cyclic carbonate **4** were optimized by using catalyst **53** at different propylene oxide concentrations, reaction temperatures and CO<sub>2</sub> pressures. The best conditions of P<sub>CO<sub>2</sub></sub> = 2.0MPa, 120°C and 0.1 mol% of catalyst were then employed to perform the study of the reaction substrates scope by using **48**, **49** and **53** catalysts (Scheme 22); the achieved results indicated that the reaction did not performed well by using bulky and hindered substrates for steric reasons.



**Scheme 22.** Synthesis of cyclic carbonates catalyzed by complexes **48**, **49** and **53**.



On the basis of preliminary kinetic studies, the authors suggested the tri-synergistic catalytic mechanism showed in Scheme 23.

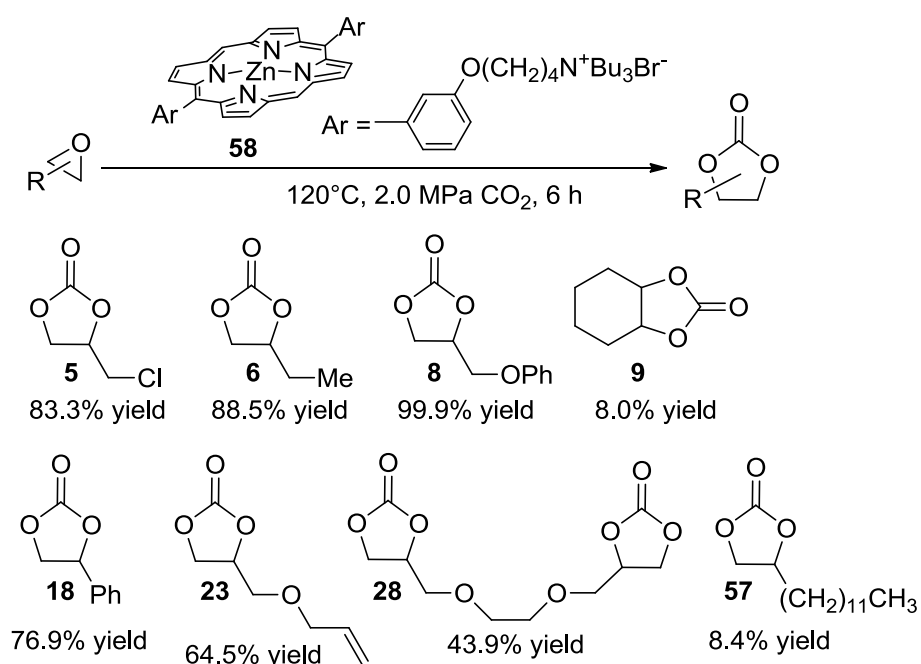


**Scheme 23.** Proposed mechanism for the cycloaddition of epoxide and CO<sub>2</sub> catalyzed by cobalt porphyrin catalysts **48-56**.

The proposed mechanism starts with the approaching of one imidazole group towards the cobalt center causing the release of the axial chloride ion and subsequently, the reaction of the other imidazole group with CO<sub>2</sub> molecule forms the zwitterionic adduct **B**. This latter compound can coordinate and activate epoxide towards the nucleophilic attack of the chloride giving, by a ring-opening process, the metal alkoxide intermediate **D**. Finally, an intramolecular nucleophilic reaction forms **E** which releases the desired cyclic carbonate with the contemporary regeneration of the original catalyst **A**.

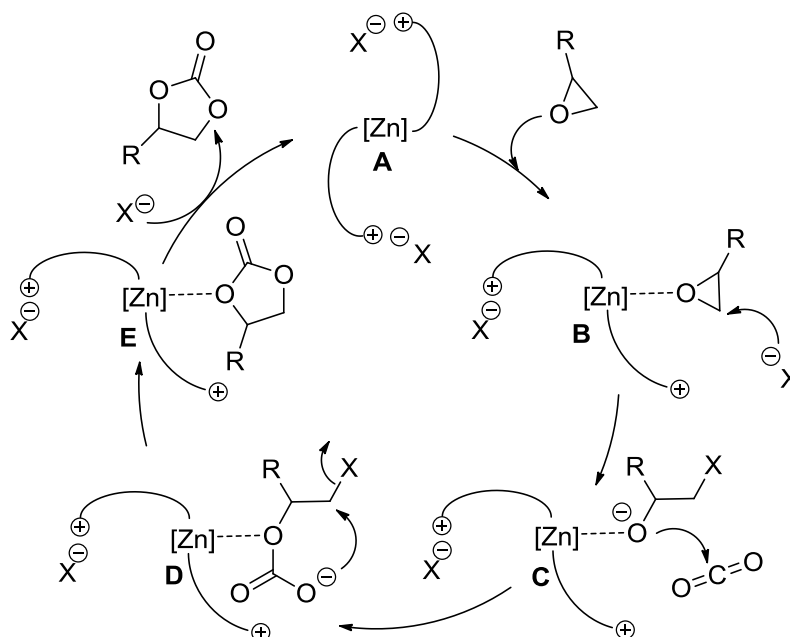
Zn<sup>II</sup>(porphyrin)/co-catalyst binary systems were scarcely used to promote the CO<sub>2</sub> cycloaddition with epoxides due to their modest catalytic activity; either low epoxide conversions (34% by using Zn(TPP)) [31] or TOF values (11.11 h<sup>-1</sup> by using Zn(*p*-OMe-TPP)) [37] were usually observed. In view of these results, the catalytic activity of bifunctional zinc complexes was investigated in order to evaluate possible positive synergic effects due to the linkage of the nucleophilic agent on the porphyrin skeleton of the zinc catalyst.

Accordingly, zinc porphyrin complexes were functionalized by placing ammonium ionic liquids (MPILs) on *para*, *meta* and *ortho* positions of *meso*-aryl substituents of the porphyrin ligand [42]. Several zinc catalysts, experimental conditions and MPILs, showing different halogen anions, were screened in the reaction of propylene oxide with CO<sub>2</sub> forming compound **4**. Once the best conditions for this reaction were defined, the very efficient catalyst **58**, which presents the most suitable structure for the epoxide activation, was employed for the study of the reaction scope under 2.0 MPa CO<sub>2</sub> pressure at 120 °C and in a solvent-free conditions. It is important to note that complex **58** presents MPILs groups on *meta* positions of *meso*-aryl groups in order to assure the most effective interaction between the nucleophilic anion of the ammonium group and the epoxide, which is coordinated to the zinc metal center.



**Scheme 24.** Synthesis of cyclic carbonates catalyzed by complex **58**

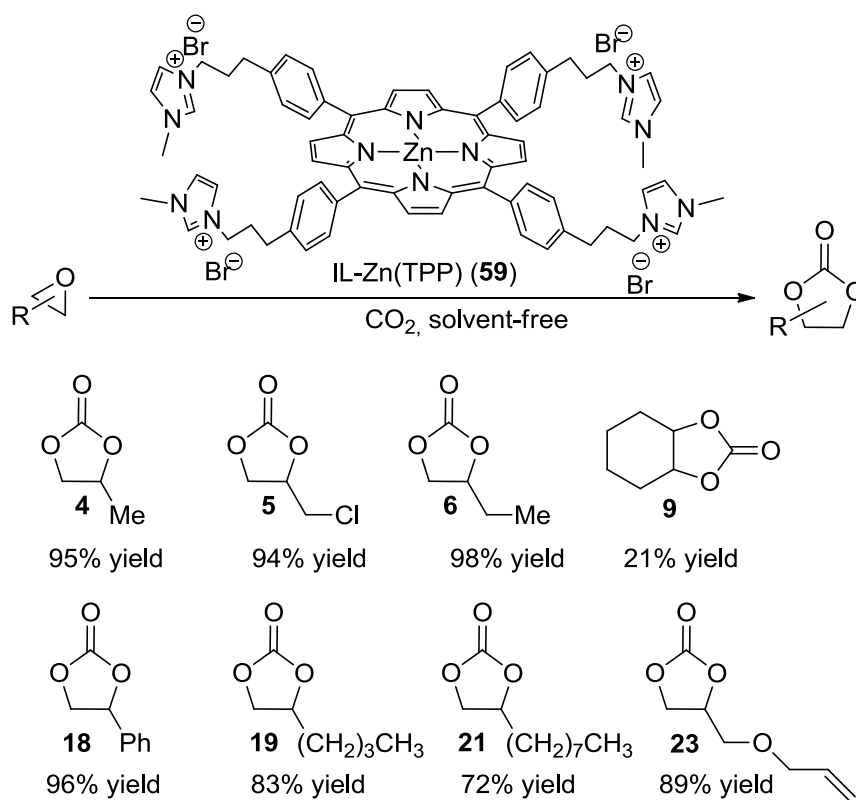
It should be underlined that compound **4** was obtained in 72.3% yield instead of 99.9% yield, by using the binary Zn(DPP)/TBAB (DPP = dianion of 5,15-diphenyl porphyrin) system, in the same experimental conditions employed for the **58**-catalyzed reaction. This result pointed out that ammonium moieties on the porphyrin skeleton and the zinc metal into the porphyrin core cooperatively act in a bifunctional catalyst by increasing the CO<sub>2</sub> solubility and favoring the interaction between activated epoxide and the nucleophilic agent. A possible mechanism of the **58**-catalyzed reaction is reported in Scheme 25.



**Scheme 25.** Proposed mechanism for the cyclic carbonate formation catalyzed by complex **58**.

As reported for the cobalt-catalyzed reaction, the authors proposed that the activation of epoxide, by coordination to the Lewis acid zinc metal, yields intermediate **B**, which can be attacked by the nucleophilic anion at the less substituted carbon atom, forming the metal alkoxide **C**. This latter intermediate would be nucleophilic enough to react with  $\text{CO}_2$  to generate **D** which, by a ring-closing process, releases the final product and the catalyst into the reaction medium.

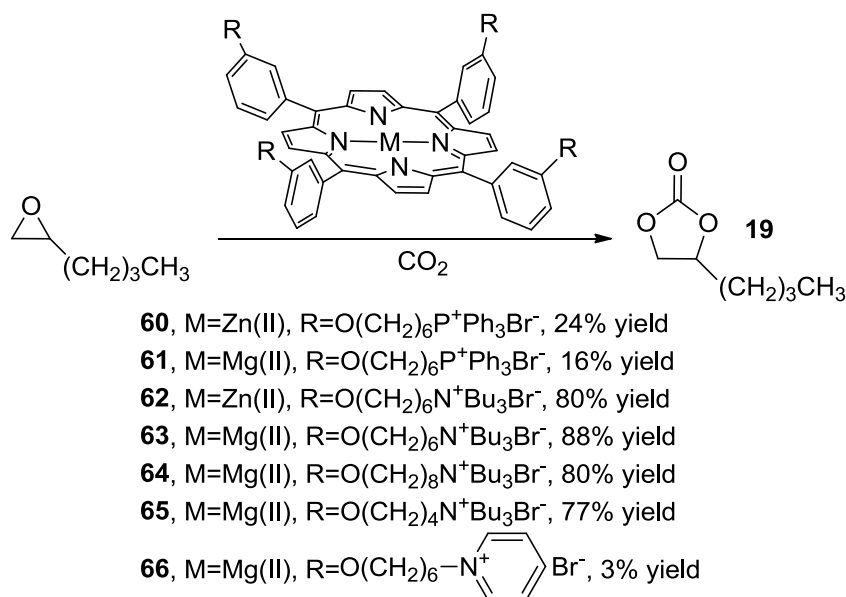
Very recently, H. Ji and co-authors [43] reported the functionalization of  $\text{Zn}(\text{TPP})$  with the ionic liquid 1-butyl-3-methylimidazolium bromide ( $[\text{BMim}]\text{Br}$ ) to form IL- $\text{ZnTPP}$  (**59**) complex whose catalytic activity was investigated and fine-tuned by using it to promote the synthesis of cyclic carbonate **4**, as the model reaction. In the best experimental conditions of 0.1 mol% of catalyst,  $60^\circ\text{C}$ , 2.0 MPa of  $\text{CO}_2$  and solvent-free medium, catalyst **59** was employed for the synthesis of various cyclic carbonates, which were obtained in good yields, except compound **9**, due to the scarce reactivity of more hindered internal epoxides (Scheme 26). It should be mentioned that complex **59** was sufficiently stable to be reused for ten consecutive times without losing its catalytic efficiency.



**Scheme 26.** Synthesis of cyclic carbonates catalyzed by complex IL-ZnTPP **59**

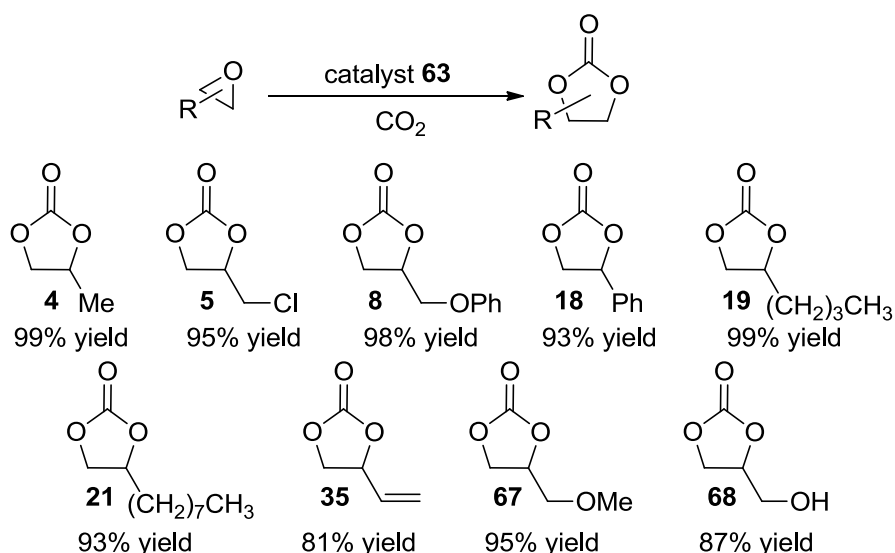
The mechanistic proposal for **59**-catalyzed reactions is very similar to those reported for other bifunctional catalysts (see Scheme 21). The first step of the reaction would be the coordination of epoxide to Lewis acid zinc metal which activates the three-membered ring towards the nucleophilic attack of the anion located on the porphyrin periphery. Next, the so-formed metal alkoxide would react with CO<sub>2</sub> and finally, a ring-closing event produces the final cyclic carbonate product.

The activity of zinc (II) bifunctional porphyrins was extensively investigated and compared with that of magnesium (II) counterparts by T. Ema and co-workers. In 2012 this group published the synthesis and the study of the catalytic activity of a class of bifunctional zinc and magnesium porphyrins showing tetraphenylphosphonium bromide (TPPB), TBAB, PTAT and DMAP nucleophilic moieties linked to alkyl chains which are placed onto the *meta* positions of the *meso*-aryl substituents [44]. Synthesized **60-66** catalysts were tested in the model reaction of 1,2-epoxyhexane with CO<sub>2</sub> yielding cyclic carbonate **19** (Scheme 27). It is very important to underline that the use of a binary Mg(TPP)/TBAB system afforded compound **19** in very low yields confirming the positive catalytic effect of the bifunctional catalyst.



**Scheme 27.** Synthesis of cyclic carbonate **19** catalyzed by complexes **60-66**.

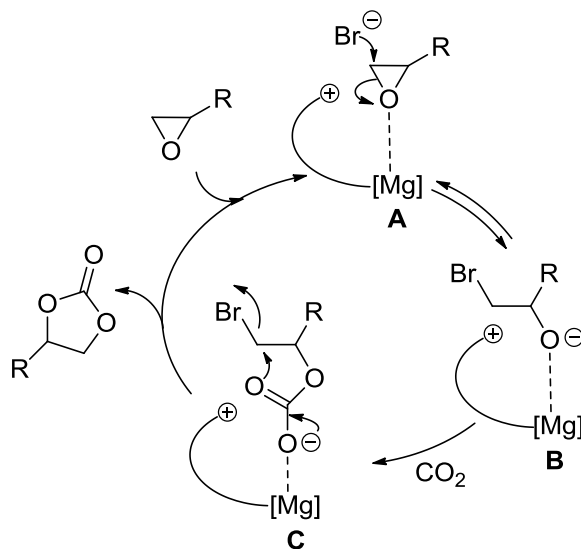
In view of the excellent catalytic performance of catalyst **63**, this complex was used to optimize experimental conditions and study the reaction scope, which was performed by using 0.005 mol% of the catalyst at 120°C and under 1.5 CO<sub>2</sub> MPa (Scheme 28). It should be noted that outstanding TON (turnover number) and TOF values, up to 103000 and 12000 h<sup>-1</sup> respectively, were reached by using this catalyst.



**Scheme 28.** Synthesis of cyclic carbonates catalyzed by complex **63**

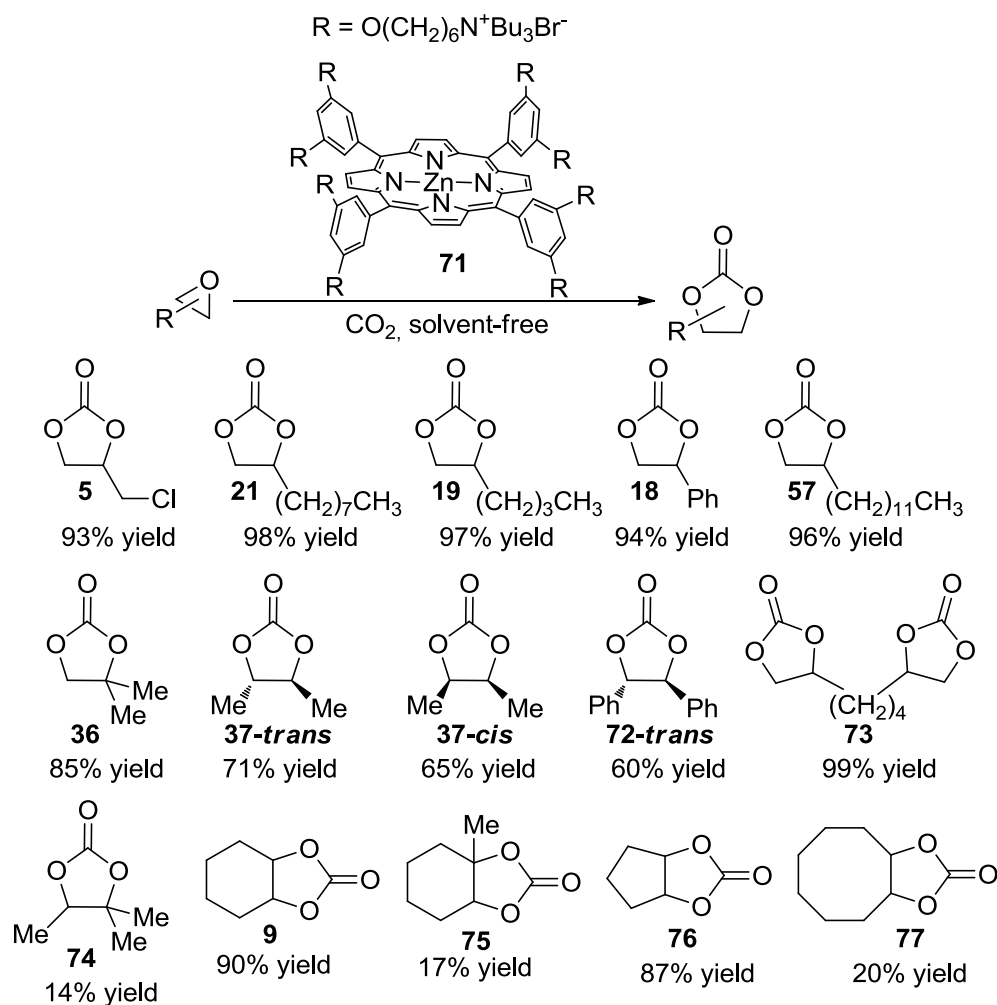
The suggested mechanism for **63**-catalyzed reactions was in accordance to what was previously proposed for other bifunctional-catalyzed systems. The epoxide coordinates the metal center before being attacked by bromide forming the metal-alkoxy derivative **B** which is very reactive towards

CO<sub>2</sub>. The so-formed intermediate **C** can then be involved in a ring-closing reaction which releases bromide and cyclic carbonate. Consequently, the catalyst can be regenerated to form, with a new epoxide molecule, compound **A** (Scheme 29).



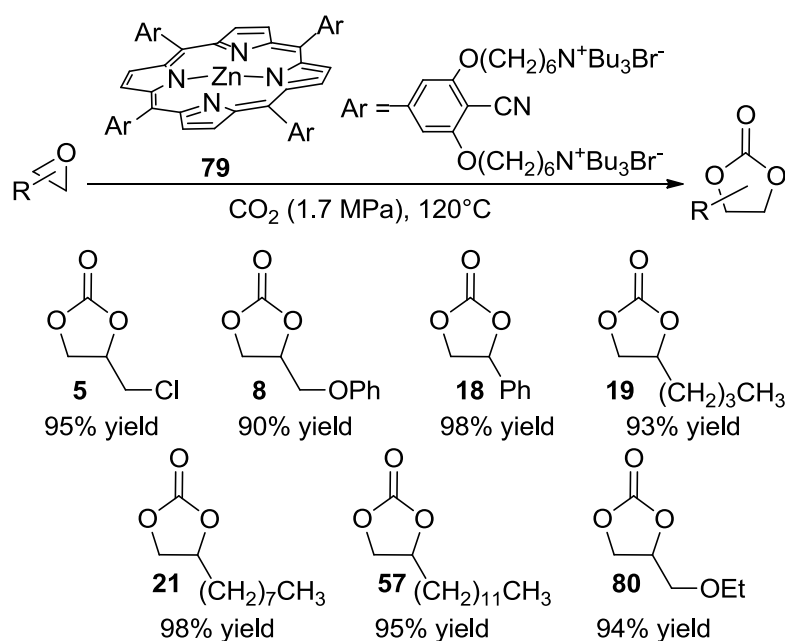
**Scheme 29.** Proposed mechanism of the **63**-catalyzed synthesis of cyclic carbonates.

Considering the very good results achieved, T. Ema and co-workers studied how the catalytic activity can be influenced by the position in which nucleophiles are located on aryl substituents. In addition to that, the relationship between the number of arms and the catalytic efficiency was also investigated [45]. Therefore, besides catalyst **62**, in which *m*-(O(CH<sub>2</sub>)<sub>6</sub>N<sup>+</sup>Bu<sub>3</sub>Br<sup>-</sup>)C<sub>6</sub>H<sub>4</sub> aryl groups are present on *meso* positions of the tetrapyrrolic core (Scheme 27), other two zinc complexes, showing the same functional group -O(CH<sub>2</sub>)<sub>6</sub>N<sup>+</sup>Bu<sub>3</sub>Br<sup>-</sup> either on the *ortho* (complex **69**) or *para* (complex **70**) position of the *meso* aryl group, were synthesized. The comparison of the catalytic activities of complexes **62**, **69** and **70** in promoting the synthesis of compound **19**, revealed that complex **62** performed the best probably due to the optimal orientation of nucleophilic arms which favors the ring-opening reaction of epoxide. Subsequently, in order to increase the number of nucleophilic agents on the porphyrin skeleton, zinc complex **71**, showing eight O(CH<sub>2</sub>)<sub>6</sub>N<sup>+</sup>Bu<sub>3</sub>Br<sup>-</sup> groups on *meta* positions of *meso* aryl porphyrin groups, was synthesized and tested in catalysis. Complex **71** was very efficient in catalyzing the synthesis of numerous cyclic carbonates (Scheme 30) in very good yields by using catalytic loadings up to 0.005 mol %, 1.7 CO<sub>2</sub> MPa and 120°C. Reactions also occurred by using low reactive internal epoxides and *trans*-epoxides, which were converted into **37-trans** and **72-trans** cyclic carbonates with an excellent stereocontrol. In addition, complex **71** was active at the very low temperature of 20°C and under atmospheric pressure in the synthesis of compound **19**.



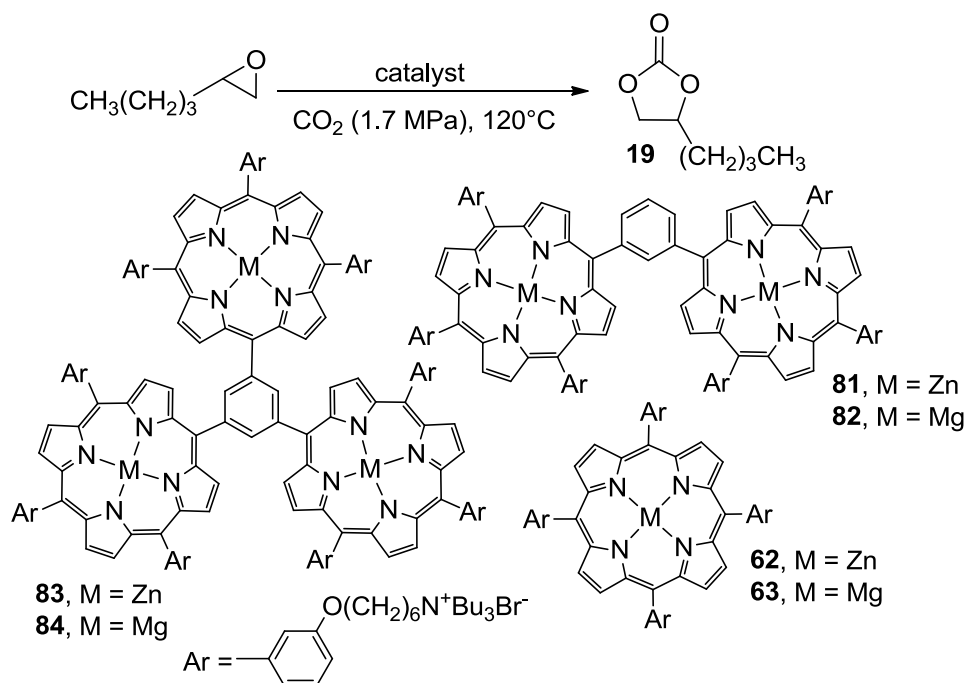
**Scheme 30.** Study of the scope of the **71**-catalyzed reaction between epoxides and CO<sub>2</sub>.

In order to better study the dependence of the catalytic activity of zinc complexes on the number of nucleophilic arms, T. Ema and co-authors synthesized catalyst **78** bearing twelve O(CH<sub>2</sub>)<sub>6</sub>N<sup>+</sup>Bu<sub>3</sub>Br<sup>-</sup> nucleophiles on *meta* and *para* positions of *meso* aryl substituents [46]. Catalyst **78** was less active than **71** because the electron-donating O(CH<sub>2</sub>)<sub>6</sub>N<sup>+</sup>Bu<sub>3</sub>Br<sup>-</sup> group on the *para* position decreased the Lewis acidity of the zinc atom with the consequent decrease of the ability of the metal in the epoxide coordination. Thus, the O(CH<sub>2</sub>)<sub>6</sub>N<sup>+</sup>Bu<sub>3</sub>Br<sup>-</sup> on the *para* position of complex **78** was replaced with the electron-withdrawing cyano group and the resulting complex **79** displayed a very good catalytic activity (TOF up to 42000h<sup>-1</sup>) in the synthesis of compounds reported in Scheme 31.



**Scheme 31.** Synthesis of cyclic carbonate catalyzed by complex **79**.

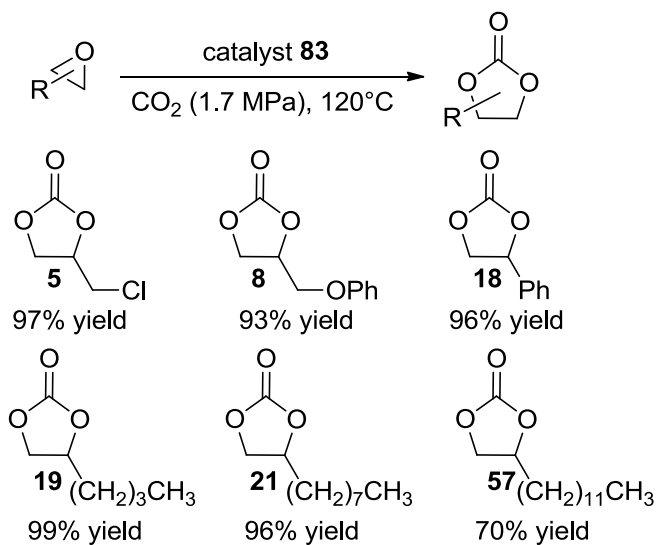
Another approach for the creation of bifunctional catalysts is the synthesis of multi-porphyrin systems which have more active metal sites and several nucleophilic functionalities in the same molecule. This strategy was carried out in order to synthesize dimers and trimers zinc and magnesium porphyrins **81-84**, and the comparison of the activities of **62**, **63**, **81-84** complexes displayed compounds **83** and **84** as the most active in the synthesis of **19** (Scheme 32) [47].



**Scheme 32.** Synthesis of cyclic carbonate **19** catalyzed by complexes **62**, **63**, **81-84**.



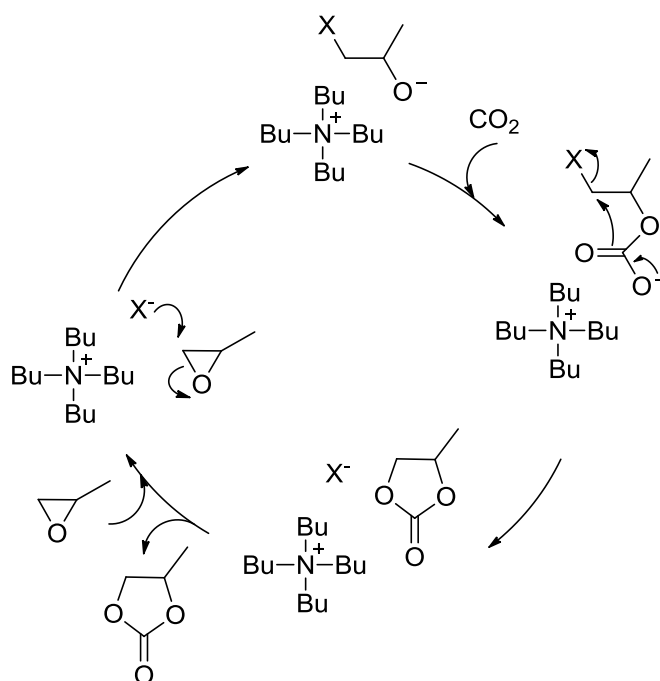
The most active catalyst, **83**, was employed to investigate the potential of the methodology by testing the reaction of a number of epoxides with CO<sub>2</sub>. Achieved results are listed in Scheme 33.



**Scheme 33.** Synthesis of cyclic carbonate catalyzed by complex **83**.

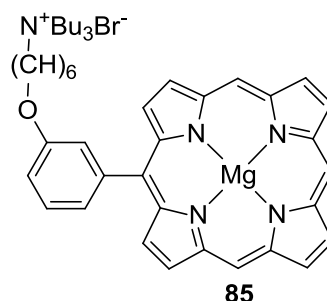
The outstanding TON and TOF values of 220000 and 46000 h<sup>-1</sup> respectively, were registered for **84** and 310000 and 40000 h<sup>-1</sup>, for **83**.

The mechanism of the cyclic carbonate synthesis promoted by magnesium and zinc bifunctional catalysts was deeply investigated by using DFT calculations. T. Ema and co-authors first studied the energy profiles of the synthesis of propylene carbonate **4** in the presence of TBAX alone, in order to clarify the role of the porphyrin catalyst in the reaction [48]. This study revealed that the rate-determining step of the cycle is the ring-opening reaction and the lowest energy barrier of 23.3 kcal/mol was calculated for TBACl. On the other hand, when the reaction was performed in the presence of TBAB and TBAI, the energy barriers resulted in 26.5 kcal/mol and 27.2 kcal/mol, respectively. The mechanism, proposed on the basis of DFT calculations, is reported in Scheme 34.



**Scheme 34.** Mechanism of TBAX-catalyzed synthesis of **4**.

Next, the DFT study was performed in the presence of the mono-substituted porphyrin **85** (Figure 1) to speed up calculations. The energy profile of the reaction confirmed the mechanism reported in Scheme 29 for **63**-catalyzed cycloaddition [49].



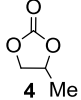
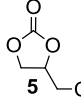
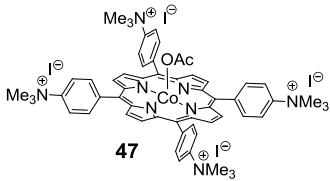
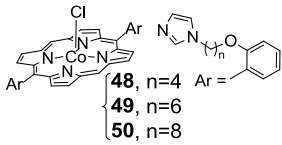
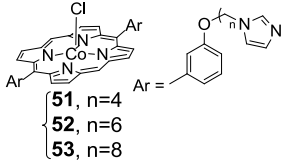
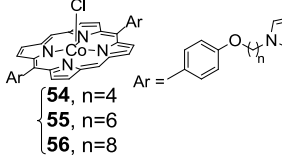
**Figure 1.** Structure of mono-substituted porphyrin **85**.

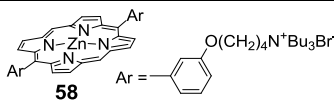

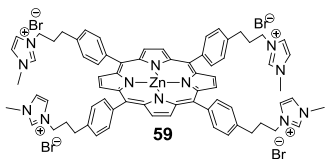
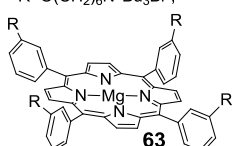
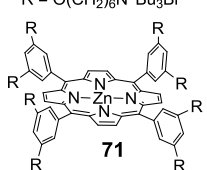
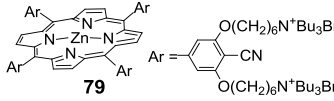

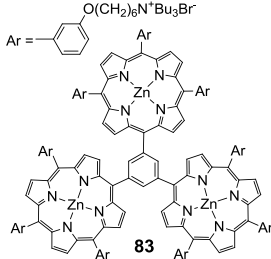
DFT calculations showed that the ring-opening process is still the rate-determining step of the cycle however, lower activation energies were calculated for this step and, when bromide is the counter ion of the ammonium salt, the smallest activation energy of 13.5 kcal/mol was obtained. This positive result was attributed to the cooperation between the metal into the tetrapyrrolic core and the nucleophilic periphery, where the flexible ammonium cation plays a beneficial role during the entire catalytic cycle by stabilizing anionic intermediates and driving the whole process.

The most opportune position for the nucleophilic arms on the porphyrin skeleton is already discussed above by comparing catalytic activities of complexes **62**, **69**, **70** which bear the  $O(CH_2)_6N^+Bu_3Br^-$  group on the *meta*, *ortho* or *para* positions of the *meso* aryl substituent, respectively. From a theoretical point of view, the rate-determining step of the process is the ring-opening of the epoxide wherever the ammonium salt is located [45]. However, DFT calculations highlighted that when the alkyl chain is on the *meta* position of the *meso* aryl group, the activation energy is lower than in the other two cases, due to the occurrence of a concave conformation which is well suitable for the electrostatic stabilization of bromide. In addition, when the ammonium functionality is located on the *meta* position, it can modulate its conformation for the stabilization of anionic intermediates, better than when on the *para* or *ortho* positions.

Results referring to the catalytic activity of bifunctional metal porphyrins are summarized in Table 3.

**Table 3.** Catalytic activities of complexes **47-56**, **58**, **59**, **63**, **71**, **79** and **83** in promoting the synthesis of compounds **4** and **5**.

entry [ref]	bifunctional metal porphyrin	mol% cat.	P <sub>CO2</sub> (MPa)	T (°C)	solvent	 <b>4</b> Me	 <b>5</b> Cl
1 [40]	 <b>47</b>	0.1	0.67	80	epoxide	95.4% yield 5 h	89.8% yield 6 h
2 [41]	 <b>48</b> , n=4 <b>49</b> , n=6 <b>50</b> , n=8	0.001	2.0	120	epoxide	92.3% yield 6 h, cat <b>48</b> 99.1% yield 6 h, cat <b>49</b> 91.6% yield 6 h, cat <b>50</b>	93.8% yield 6 h, cat <b>48</b> 97.5% yield 6 h, cat <b>49</b>
3 [41]	 <b>51</b> , n=4 <b>52</b> , n=6 <b>53</b> , n=8	0.001	2.0	120	epoxide	59.9% yield 6 h, cat <b>51</b> 88.6% yield 6 h, cat <b>52</b> 99.9% yield 6 h, cat <b>53</b>	99.0% yield 6 h, cat <b>53</b>
4 [41]	 <b>54</b> , n=4 <b>55</b> , n=6 <b>56</b> , n=8	0.001	2.0	120	epoxide	55.5% yield 6 h, cat <b>54</b> 59.1% yield 6 h, cat <b>55</b> 67.6% yield 6 h, cat <b>56</b>	not reported

5 [42]	 <b>58</b> Ar = 	0.002	2.0	120	epoxide	99.9% yield 5 h	83.3% yield 6 h
6 [43]	 <b>59</b>	0.1	2.0	60	epoxide	95% yield 8 h	94% yield 8 h
7 [44]	R = O(CH <sub>2</sub> ) <sub>6</sub> N <sup>+</sup> Bu <sub>3</sub> Br <sup>-</sup> ,  <b>63</b>	0.005	1.5	120	epoxide	99% yield 6 h	95% yield 6 h
8 [45]	R = O(CH <sub>2</sub> ) <sub>6</sub> N <sup>+</sup> Bu <sub>3</sub> Br <sup>-</sup> ,  <b>71</b>	0.01	1.7	120	epoxide	not reported	93% yield 9 h
9 [46]	 <b>79</b> Ar = 	0.005	1.7	120	epoxide	not reported	95% yield 12 h
10 [47]	 <b>83</b>	0.002	1.7	120	epoxide	not reported	97 % yield 12 h

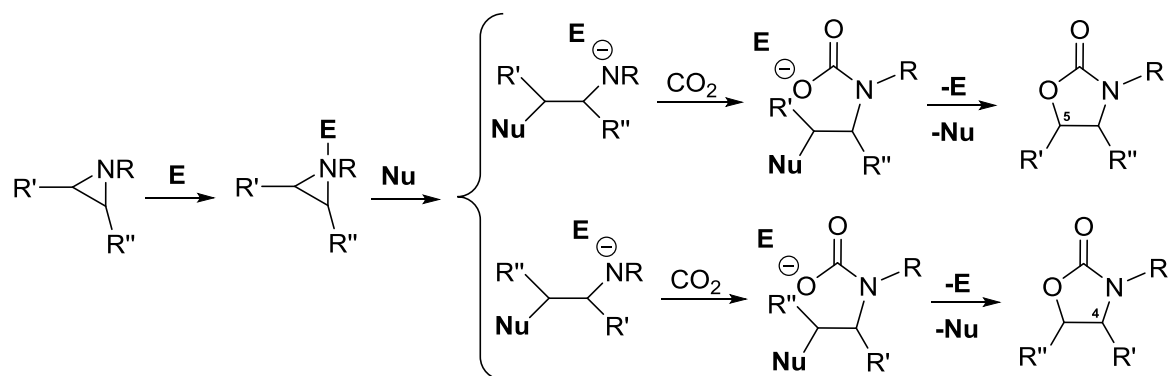
As already stated, the use of bifunctional porphyrins avoid the presence of co-catalytic species, which are often employed in a large amount. As reported in Table 3, both main group and transition metal bifunctional porphyrins are good promoters which can be used in very low catalytic loadings (up to 0.001 mol%). In all reported cases, reactions were run at moderate to high-temperatures (60-120 °C) and under reasonable CO<sub>2</sub> pressures (up to 2.0 MPa).

### 3. Synthesis of oxazolidinones.

The cycloaddition reaction of CO<sub>2</sub> into three-membered rings, such as aziridines, can be exploited for the synthesis of oxazolidinones. Even if aziridines are structurally analogous to epoxides, the cycloaddition reaction of CO<sub>2</sub> to aziridines has been investigated less than the parallel reaction giving cyclic carbonates. To the best of our knowledge only two examples [43, 50] are

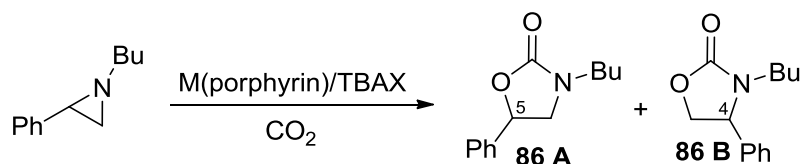
reported in which porphyrin-based catalysts were used to promote the cycloaddition of CO<sub>2</sub> to aziridines in homogeneous systems.

It is important to note that the reaction of CO<sub>2</sub> with epoxide generates only one corresponding cyclic carbonate (Scheme 1), while the CO<sub>2</sub> cycloaddition to an aziridine molecule can produce two different regioisomers depending where, between the two differently substituted carbon atoms, the aziridine ring-opening reaction takes place (Scheme 35).



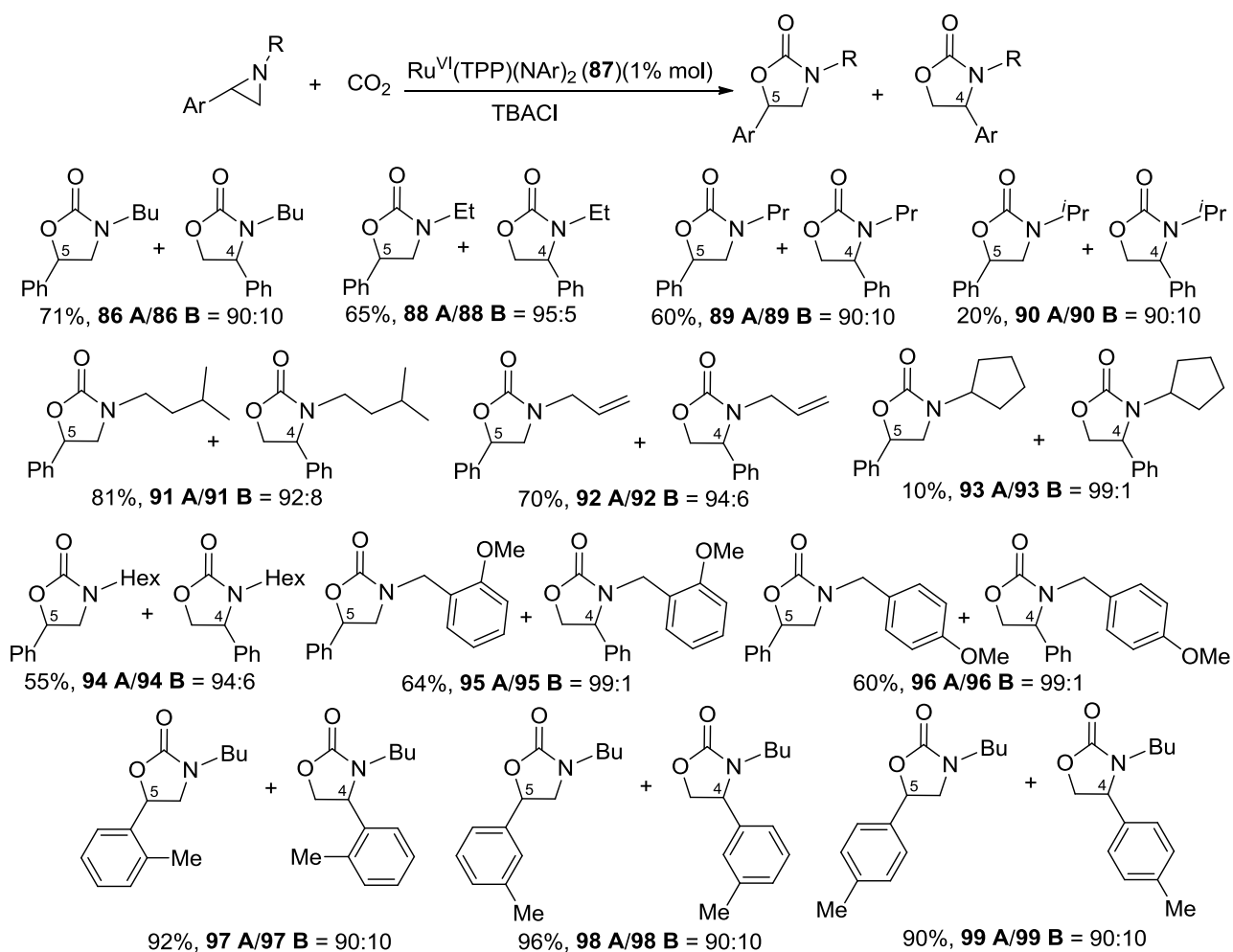
**Scheme 35.** Formation of oxazolidinones by CO<sub>2</sub> cycloaddition to aziridines.

In 2018, E. Gallo and co-authors investigated the catalytic activity of different metal porphyrin complexes by using the model reaction between 1-butyl-2-phenyl aziridine and carbon dioxide in the presence of TBAX (X = F<sup>-</sup>, Cl<sup>-</sup>, Br<sup>-</sup>, I<sup>-</sup>) salts as co-catalysts (Scheme 36) [50].



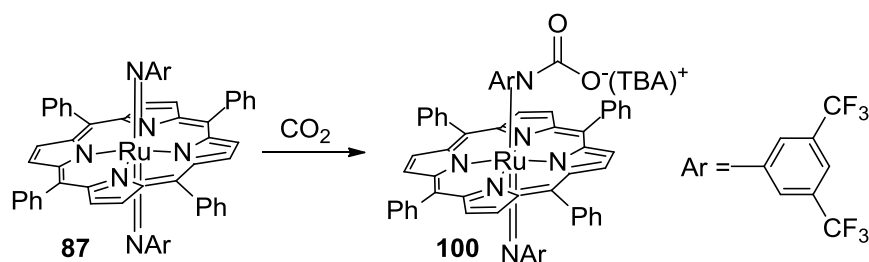
**Scheme 36.** Formation of oxazolidinones **86 A** and **86 B** by CO<sub>2</sub> cycloaddition to 1-butyl-2-phenyl aziridine.

The screening revealed the Ru<sup>VI</sup>(TPP)(NAr)<sub>2</sub> (**87**)/TBACl (Ar = 3,5-(CF<sub>3</sub>)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>) combination was a very active catalytic system, by applying the catalytic ratio Ru(TPP)(NAr)<sub>2</sub>/TBACl/aziridine = 1:10:100 under 0.6 MPa of CO<sub>2</sub> at 100°C. Good results in terms of yield (71%) and regioselectivity were obtained and the 5-substituted isomer **86 A** was isolated as the major isomer (**86 A**/**86 B** ratio = 90:10). The catalytic system Ru<sup>VI</sup>(TPP)(NAr)<sub>2</sub> (**87**)/TBACl exhibited a broad substrates scope and it was used for the synthesis of various oxazolidinones (Scheme 37).



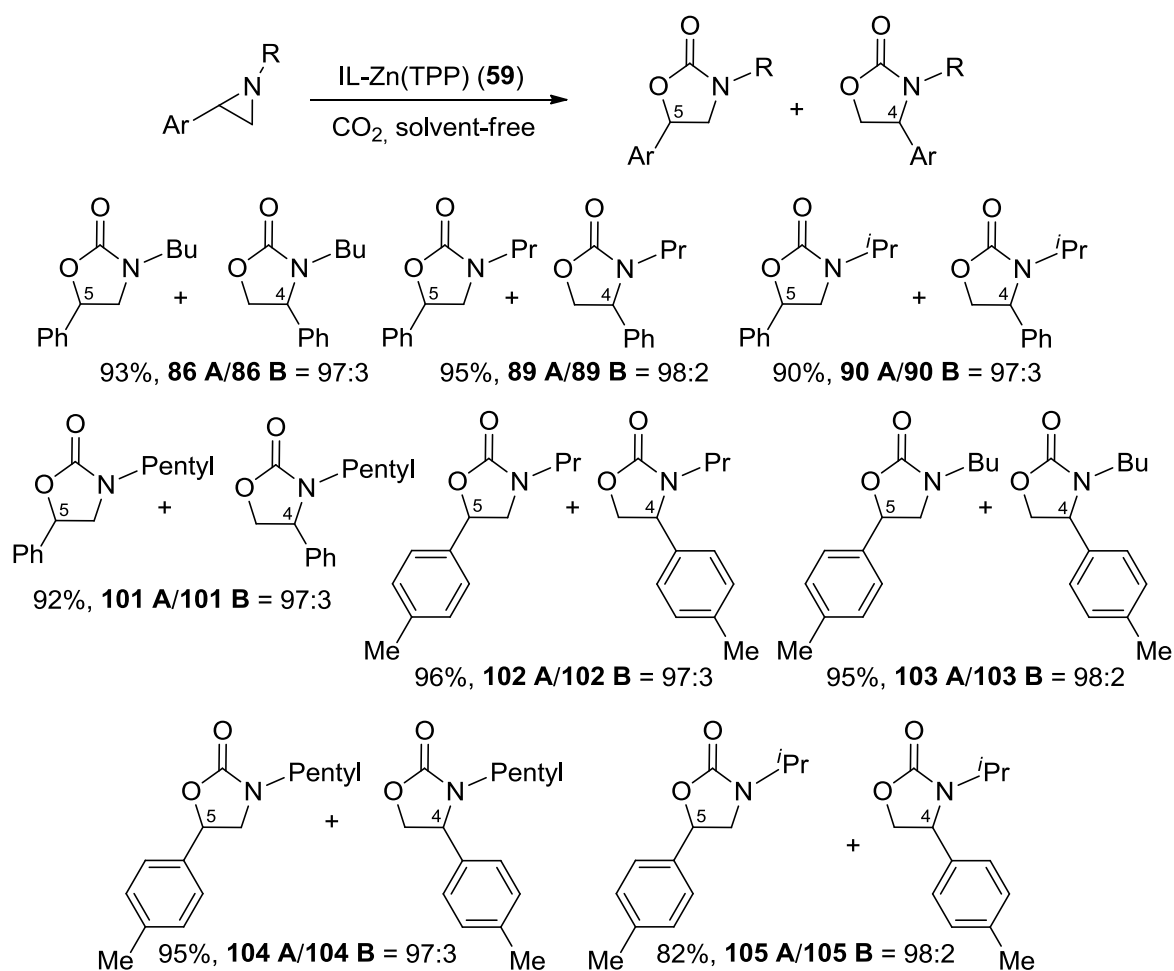
**Scheme 37.** Formation of oxazolidinones by CO<sub>2</sub> cycloaddition to aziridines catalyzed by Ru<sup>VI</sup>(TPP)(NAr)<sub>2</sub> (**87**)/TBACl system.

During a preliminary mechanistic study, undertaken to better figure out the nature of the ruthenium species involved in the catalytic cycle, complex [Ru<sup>V</sup>(TPP)(NAr)(NArCOO)](TBA) (**100**) (Scheme 38) was observed at the end of the catalytic reaction. The molecular structure of this complex was suggested on the basis of <sup>1</sup>H NMR, ESI-MS data and the IR(ATR) analysis revealed the presence of a stretching at 1604 cm<sup>-1</sup> which was attributed to the carbonyl group of the carbon dioxide. An unpublished DFT study indicated that the CO<sub>2</sub> molecule can interact with Ru<sup>VI</sup>(TPP)(NAr)<sub>2</sub> (**87**) complex thanks to the high electronic density on the nitrogen imido atom of the axial ligand bound to ruthenium atom.



**Scheme 38.** Synthesis of  $[\text{Ru}^{\text{V}}(\text{TPP})(\text{NAr})(\text{NArCOO})](\text{TBA})$  (**100**).

In the same year, H. Ji and co-authors [43] exploited the advantages of using bifunctional porphyrin systems to synthesize oxazolidinones by cycloaddition of  $\text{CO}_2$  with aziridines. The complex IL-ZnTPP (**59**), whose catalytic efficiency, as the promoter of the cyclic carbonate formation was discussed above (Scheme 26), was also tested in the model reaction of 1-butyl-2-phenyl aziridine with  $\text{CO}_2$  yielding oxazolidinones **86 A** and **86 B**. It is important to note that the reaction did not work well by using either [BMim]Br (30% of oxazolidinone) or Zn(TPP) alone (41% of oxazolidinone) nor by simply mixing Zn(TPP) and [BMim]Br species together in the 1:4 ratio, indicating that the incorporation of the co-catalyst into the porphyrin skeleton was necessary in order to achieve satisfactory catalytic results. Several 2-oxazolidinones were obtained in good yields (92%-97%) and regioselectivities by employing, under solvent-free conditions, 0.1 mol% of IL-ZnTPP (**59**) catalyst,  $90^\circ\text{C}$  and 2.0 MPa  $\text{CO}_2$  pressure (Scheme 39). In all the tested reactions 5-substituted oxazolidinone was isolated as the prominent isomer. Probably due to steric reasons, the reaction productivity decreased by increasing the length of the alkyl chain on the aziridine nitrogen atom.

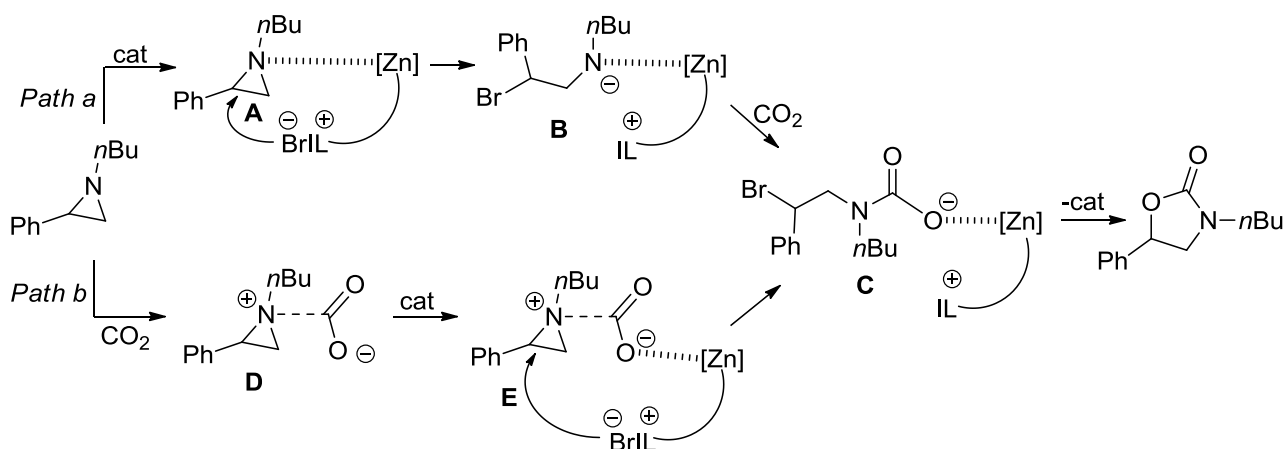


**Scheme 39.** Synthesis of oxazolidinones by the cycloaddition of CO<sub>2</sub> to aziridines catalyzed by IL-Zn(TPP) (**59**) complex.

The authors suggested two different mechanistic pathways for the IL-Zn(TPP)-catalyzed synthesis of oxazolidinones. The mechanism described in Scheme 40, *path a* is very similar to that reported for the IL-Zn(TPP) (**59**)-catalyzed synthesis of cyclic carbonates. The first step is the coordination of aziridine to the Lewis acid zinc metal and the formation of **A** is followed by an intramolecular nucleophilic attack of bromide ion on the more substituted aziridine carbon atom forming **B**. The consecutive reaction of intermediate **B** with CO<sub>2</sub> generates zinc alkoxide **C** which evolves into corresponding oxazolidinone by a ring-closing reaction. The second suggested mechanism (Scheme 40, *path b*) takes into account the pronounced Lewis basicity of aziridine molecule, which would be responsible for a relevant interaction with carbon dioxide, forming a CO<sub>2</sub>-aziridine adduct **D**. This species can coordinate IL-Zn(TPP) (**59**) compound by the oxygen atom of CO<sub>2</sub> yielding intermediate **E**. Next, an intramolecular nucleophilic reaction, mainly at the more substituted carbon atom of aziridine molecule, yields the same intermediate **C**, whose formation was also proposed in the *path a* (Scheme 40). The last step of the proposed mechanism is



the ring-closing reaction involving **C** which forms the desired 5-substituted oxazolidinone as the major product, and restores the catalytic species permitting the cycle to restart.



**Scheme 40.** Suggested mechanisms of the IL-Zn(TPP) (**59**)-catalyzed synthesis of oxazolidinones.

#### 4. Conclusion

This review provides an overview of the catalytic activity of metal porphyrin complexes in the direct insertion of CO<sub>2</sub> into three-membered rings, such as epoxides and aziridines, in homogenous systems. Various synthetic methodologies for obtaining cyclic carbonates and oxazolidinones were discussed and summarized; results highlighted the potential of porphyrin-based catalysts for performing CO<sub>2</sub> cycloadditions in very good yields and by using mild experimental conditions. The large number of papers which have been published up to now clearly indicates the high interest of the scientific community in developing active and sustainable methodologies for the CO<sub>2</sub> valorization by synthesizing fine chemicals. Finally, the most important mechanistic aspects of the synthesis of cyclic carbonates were discussed to shed some light on catalytic pathways in order to plan in the near future new and efficient methods for obtaining these high added-value compounds.

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