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FULL PAPER

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Abstract: A molecular cage consisting of two free-base porphyrins connected by four flexible linkers was metalated with Co(III) to afford in good yield a bimetallic catalyst. The catalytic activity of the bis-Co(III) porphyrin molecular cage **$(CoCl)_2$-1** was studied for the formation of cyclic carbonates from CO_2 and propylene oxide (PO) or styrene oxide (SO) with pyridine as cocatalyst. Various reaction parameters such as the molar ratio of the catalyst and the co-catalyst, the time of reaction, the temperature and CO_2 pressure were investigated. The molecular cage was shown to be a catalyst of high selectivity for the studied reactions and much more efficient to convert the epoxides to the corresponding cyclic carbonates than the monomeric Co(III)Cl *meso*-tetraphenylporphyrin (**CoCl-TPP**) model. When quantitative conversion of PO into propylene carbonate (PC) was reached (0.1 mol% catalyst, 1.2 mol% pyridine, 120 °C, 30 bar of CO_2) only 23% of PC was obtained with **CoCl-TPP** (0.2 mol%). This enhanced catalytic activity is attributed to the synergistic effect of the two metal sites incorporated in the framework of the molecular cage.

Introduction

The pocket structure of natural enzymes has prompted researchers to design various hollow structures with active components that could trap molecules and convert them into useful chemicals. Architectures incorporating metalloporphyrins[1] are particularly appealing due to the involvement of such complexes as catalysts in many enzymes. Among the reactions of interest, the conversion of CO_2 has received increasing attention in the scientific community since this gas is massively produced as waste from our fossil fuels-based economy and only partly consumed by plants through photosynthesis, leading to a detrimental impact on the environment. CO_2 as an abundant carbon source can be converted to various chemical feedstocks.[2] Among useful chemicals, cyclic carbonates are an important class of compounds as they are used as electrolytes for lithium batteries,[3] green solvents[4] and raw materials to produce carbamates, polyesters, polycarbonates and fine chemicals.[5] Cyclic carbonates are obtained from an atom economical reaction involving the coupling of CO_2 and epoxide, but the high thermodynamic stability of CO_2 requires large amounts of energy for its transformation on an industrial scale and the use of catalysts in high temperature and pressure conditions. Catalytic systems have been extensively reported. They involve either nucleophiles (organic bases, N-heterocyclic carbenes or anions of ammonium or phosphonium salts) or binary systems composed of metal complexes as Lewis acids activating the epoxide and of nucleophilic co-catalysts facilitating the epoxide-ring opening.[6] Several advances have been reported for performing this reaction under milder conditions, and the most efficient homogeneous catalysts working at ambient conditions, based on coordination compounds including metal salen complexes (salen: N,N'-bis(salicylidene)ethylenediamine) and metalloporphyrins were recently reviewed.[7]

Metalloporphyrins as robust and versatile complexes occupy a special position in this field since Inoue reported in the late seventies that aluminium(III) porphyrins as Lewis acids catalyse propylene carbonate and also polycarbonate synthesis in modest yields, in the presence of 1-methylimidazole as co-catalyst.[8] These pioneering results were followed by other trials with Al-porphyrins[9] and many other metal complexes of porphyrins (Co, Cr, Sn, Mn, Zn, Ru, V, Mg, Bi) showing improved efficiency under various conditions as recently reviewed by Gallo and co-workers.[10] Noteworthy, single-component bifunctional catalysts gathering a metalloporphyrin and a nucleophilic co-catalyst enabled increased performance with respect to the two-component systems.[11] Especially Zn(II) or Mg(II) complexes with eight pendant ammonium salts have led to outstanding catalytic performance in solvent free conditions at 120 °C and 17-30 bar of CO_2 thanks to the cooperative action of the metalloporphyrins to activate the epoxide and the nearby nucleophilic bromide to open the epoxide.[11c, 11f, 11g] Another advance made to improve the activity of catalyst/co-catalyst systems focused on the design of bimetallic catalysts in which the two metal centres could act in synergy. Several bimetallic catalysts[6d, 12] have proven increased performance compared to the mononuclear ones, especially in mild conditions : Bimetallic salen complexes and derivatives,[13] heteroscorpionate aluminium complexes[14] and bimetallic iron(III) complexes.[15] Nevertheless, only one report deals with catalysts

consisting of two and three linked metalloporphyrins for this reaction.[11d]

Compared to the developments made so far for improving this reaction, the advantages of preorganising the catalyst in a structural constrained environment mimicking the natural enzyme pocket is another challenging task that has not received much attention yet. Nevertheless, embedding the catalyst in macrocyclic [16] or cage structures[17] was shown to be an effective strategy to enhance the catalytic activity.

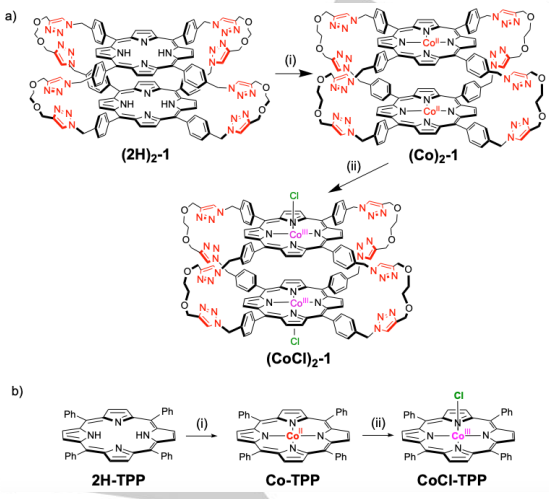
Herein, we investigate the catalytic activity of a covalent bis-Co(III) porphyrin cage **(CoCl)$_2$-1**, as a nanosized catalyst for the formation of cyclic carbonates from CO_2 and epoxides, using pyridine as co-catalyst. The cage preorganises two metalloporphyrins as catalytic sites in its framework and has an adaptable cavity size due to the flexibility of the four porphyrin linkers. This bimetallic hollow structure is attractive both for promoting a cooperative action of the preorganised metal centres and for the various possible interactions of the reactive species with the components of the cage which could have an impact on the energy barriers of the different reaction steps. The catalytic activity of the molecular cage is studied under different reaction conditions (i.e. molar ratio of the catalyst and the co-catalyst, time of reaction, temperature and CO_2 pressure) and compared with the monomeric cobalt(III) *meso*-tetraphenylporphyrin **CoCl-TPP** used as reference catalyst.

Results and Discussion

Synthesis and characterisation of molecular catalyst (CoCl)$_2$-1

Our choice for Co(III)Cl-porphyrins was motivated by their good Lewis acidic properties that enables epoxide activation,[11a, 11e, 17g, 18] the presence of axial chloride ligands as nucleophiles to cooperate to the epoxide ring-opening step[11e] and their chemical stability.

Cage **(CoCl)$_2$-1** was prepared from the previously reported free-base porphyrin cage **(2H)$_2$-1**,[19] according to slight modifications of published procedures describing the metalation of free-base porphyrins with cobalt(III) ions[18d, 18f, 20] (Scheme 1a).



Scheme 1. a) Synthesis of **(CoCl)$_2$-1**:[21] (i) $Co(OAc)_2$•$4H_2O$ (20 equiv), DMF, Ar, 150 °C, 2 h; (ii) HCl 37%, air, DCM/MeOH (9:1), 24 h, 86% ; b) Synthesis of **CoCl-TPP**: (i) $Co(OAc)_2$•$4H_2O$ (5 equiv), DMF, Ar, 150 °C, 1 h; (ii) HCl 37%, air, MeOH, 24 h, 93%.

The two porphyrins of cage **(2H)$_2$-1** were first metalated with Co(II) using an excess of $Co(OAc)_2$•$4H_2O$ in DMF at 150 °C. After cooling, air oxidation of cobalt(II) porphyrin cage **(Co)$_2$-1** was performed by stirring in presence of concentrated HCl for at least 24 h at room temperature. **(CoCl)$_2$-1** was isolated after purification in a good yield of 86 %. Both steps, cobalt(II) metalation of the porphyrins and oxidation to cobalt(III) porphyrins, were followed by UV-visible spectroscopy of an acidified aliquot in dimethyl sulfoxide (DMSO). Upon metalation, the Q bands of the protonated free base porphyrins of **(2H)$_2$-1** at 670 nm disappeared and Co(II) to Co(III) porphyrins oxidation was shown by a large red shift of the Soret band from 413 to 433 nm (see Figure S10-11). Cobalt(III) *meso*-tetraphenylporphyrin **CoCl-TPP**, used as reference catalyst, was obtained following the same procedure (Scheme 1b) and its characterisation was in accordance with literature data.[18f]

Cage **(CoCl)$_2$-1** was characterised by NMR spectroscopy and mass spectrometry. High resolution ESI-MS showed a main peak at m/z = 1167.3695 corresponding to the dicationic cage **(CoCl)$_2$-1** resulting from the loss of the two chloride ligands, the isotopic profile being in accordance with the calculated one at m/z = 1167.3684 (Figure S9). For ^{1}H NMR characterisation in $CDCl_3$ or CD_3OD, a few drops of pyridine-d_5 were required to solubilize the compound. The spectrum of cage **(CoCl)$_2$-1** shown in Figure 1 is consistent with the proposed structure, with an average C_4 symmetry as for the free-base porphyrin cage **(2H)$_2$-1**.[19] The absence of the NH pyrrolic signal of the free-base porphyrins attested the complete metalation of the porphyrin core. The main difference with the NMR spectra of previously described free base **(2H)$_2$-1** or **(Zn)$_2$-1** cages, is the absence of differentiation of protons on the *meso*-phenyl groups, pointing inside (o_{in}, m_{in}) or outside (o_{out}, m_{out}) the cavity and their close chemical shifts above 7 ppm. Cages **(2H)$_2$-1** or **(Zn)$_2$-1** have been shown to adopt a flattened conformation in the solid state and also in solution, based on the chemical shifts and differentiation of these phenyl protons. Here, the signals of o and m protons are broad, suggesting a slow rotation of the phenyl groups on the NMR time scale and their chemical shifts are in accordance with a remote position of the phenyl units from the shielding field of the opposite tetraphenylporphyrin core. In DCM/pyridine, cage **(CoCl)$_2$-1** is probably in an open conformation since the Co(III)Cl porphyrin can coordinate an additional axial Lewis base like pyridine[22] to adopt a hexacoordinated geometry which prevents close contact between the porphyrin macrocycles.

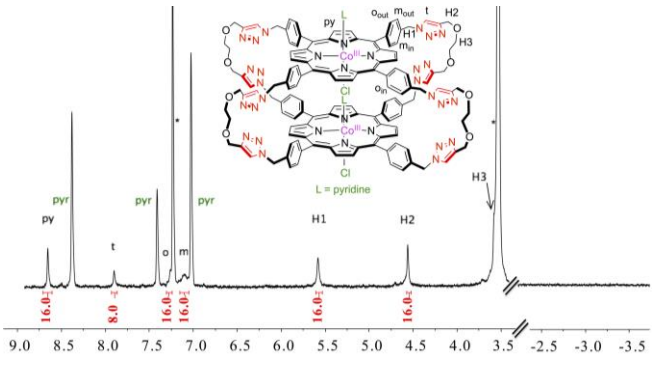


Figure 1. ^{1}H NMR ($CDCl_3$/1% pyridine-d_5, 300 MHz, 298 K) of cage **(CoCl)$_2$-1**.[23] *: Residual solvents. Pyr : pyridine.

The increased size of the cage **(CoCl)$_2$-1**, compared to that of **(Zn)$_2$-1**, was confirmed by NMR DOSY experiments (Figure S8). The calculated hydrodynamic radius obtained for **(CoCl)$_2$-1**, 12.4 ± 0.3 Å was higher than for **(Zn)$_2$-1**, 11.3 ± 0.6 Å.

Calculations performed at the DFT level of theory showed the high flexibility of the structure, several conformers having been identified in a small range of energy. The three identified conformations of lowest energy adopted by **(CoCl)$_2$-1** are shown in Figure 2. They correspond to structures with either the two axial chloride ligands pointing outside the cavity (out-out conformer, 2.7 kcal.mol^{-1}), or one axial ligand pointing inside the cavity and the other one outside (in-out conformer, 0.0 kcal.mol^{-1}), or two chloride anions pointing inside the cavity (in-in conformer, 1.8 kcal.mol^{-1}).

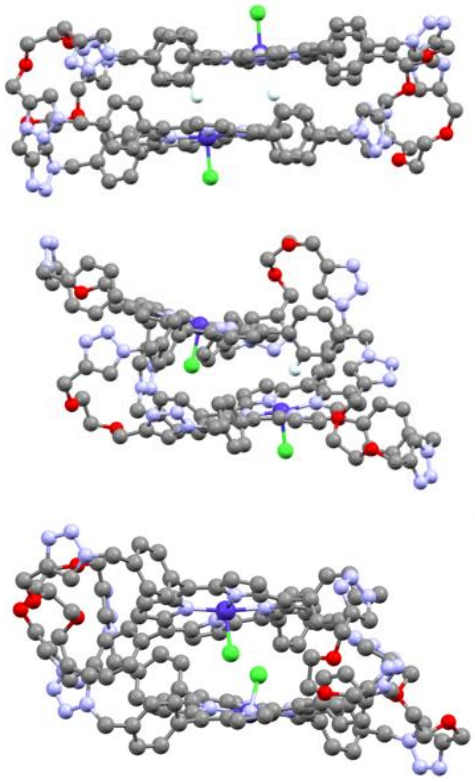


Figure 2. Optimized geometry of the lowest energy conformers out-out (top), in-out (middle) and in-in (bottom) of the (**CoCl)$_2$-1** complex. Only the H atom interacting with the cobalt(III) metal ions are shown, the others were removed for clarity.

For the out-out conformer, the distance between the mean planes of the porphyrins is around 3.9 Å, the porphyrin rings being almost parallel. Such evidence for π-π interactions between the rings is confirmed by the non-covalent interaction (NCI) analysis (see Figure S13). Furthermore, one hydrogen atom of a *meso*-phenyl ring of each metalloporphyrin points towards the axial vacant position of the cobalt(III) ion of the other metalloporphyrin (Co···H distance of 2.4 Å). The NCI analysis confirmed the presence of a van der Waals interaction between the Co(III) metal ion and the H atom. In the in-out conformer, the two porphyrin rings are no longer parallel, the interatomic distances between the pyrrolic rings varying from 3.4 to 5.4 Å. In this structure, π-π interactions between porphyrins pyrrolic rings still exist as well as a close contact Co···H of 2.7 Å involving the Co(III) having the axial chloride outside the cavity (Figure S14). In the in-in conformer, the presence of the axial chloride inside the cavity increases the distance between the porphyrins rings which vary from 3.6 to 6.6 Å, the structure being significantly distorted.

Calculations were also performed on the coordination of pyridine to the different conformers. Complexation to the in-out and to the in-in conformers barely affects the overall structure of the complex (Figure 3).

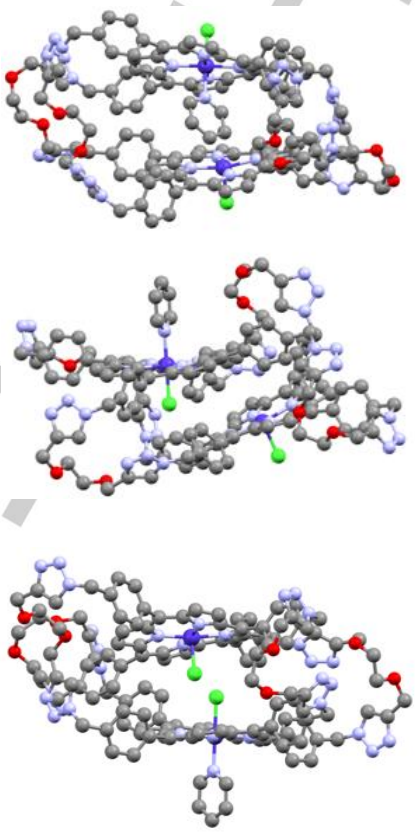


Figure 3. Optimized geometry of the out-out (top), in-out (middle) and in-in conformers (bottom) of the **(CoCl)$_2$-1** complexed with a pyridine. H atoms are hidden for clarity.

Pyridine coordination is strongly exergonic in the gas phase in the case of the in-out (ΔG = -20.9 kcal.mol^{-1}) and the in-in (ΔG = -16.1 kcal.mol^{-1}) conformers. Complexation to the out-out conformer is much less favourable. The vacant axial positions of the cobalt coordination sphere being inside the cavity, the molecule has to open, weakening the interactions between the two porphyrin rings. It results in both distortion of the overall structure (Figures 2-3) and a severe drop of the complexation energies, which is only of -2.1 kcal.mol^{-1}. This suggests that the active conformer for the catalysis has at least one chloride ligand inside the cavity and that pyridine coordination outside the cavity is favoured.

Catalytic activity of (CoCl)$_2$-1 in the synthesis of cyclic carbonates

The catalytic activity of cage **(CoCl)$_2$-1** was first investigated for the conversion of propylene oxide (PO) into propylene carbonate (PC) in the presence of a co-catalyst and in dichloromethane, as the cage is not soluble in this epoxide, precluding performing reactions in neat conditions. Reactions were carried out in a stainless-steel autoclave, at 120 °C and with a CO_2 pressure of 20 bar. Caution was taken to avoid water, since 10% of water in DCM was shown to catalyze the conversion of PO to PC in 12% yield. Accordingly, in anhydrous conditions, no conversion of PO

was obtained in the absence of catalyst (Table S1, Entry 1). The co-catalyst considered initially was DMAP, already used as such with **CoCl-TPP** as catalyst.[18a] Checking the activity of DMAP at 0.8 mol% without porphyrin catalyst led to a very high conversion to PC (91%) precluding its use as co-catalyst for the investigated reaction (Table S1, entry 2). Nevertheless, such high PO conversion with DMAP alone under similar conditions was confirmed by the study reported by Jones.[24]

Pyridine, a weaker nucleophile, was then selected. No conversion was observed in the presence of pyridine at 0.2 mol%. At 0.8 mol%, the conversion was 1% (Table S1, entry 3). Increasing the amount of pyridine did not lead to a high conversion and even when pyridine was used as solvent, PC was formed in only 8% yield in our reaction conditions (Table S1, entry 6). These results thus supported its use for the catalytic tests in presence of cage **$(CoCl)_2$-1** or **CoCl-TPP**.

The catalytic potential of cage **$(CoCl)_2$-1** was then evaluated in dichloromethane, with a low loading of 0.05 mol% and with 0.2 mol% of pyridine (2 equiv per porphyrin). In these conditions, PO was converted to PC in 20 % yield at 120 °C and 20 bar of CO_2 (Table 1, entry 2). After 24h, no other compound than PC and the PO starting material were detected by NMR, demonstrating the selectivity of **$(CoCl)_2$-1** as catalyst in these reaction conditions. Noteworthy, **$(CoCl)_2$-1** without additional co-catalyst was able to catalyse this reaction and gave PC in 13 % yield (Table 1, entry 1).

By increasing the co-catalyst amount to 0.6 mol% (6 equiv per porphyrin) a substantial yield increase to 38% was achieved (Table 1, entry 3). A more significant improvement was obtained by increasing the catalyst loading to 0.1 mol% while keeping 6 equiv of pyridine per porphyrin (1.2 mol%), the yield reaching 80 % (Table 1, entry 4). In these conditions, the reaction carried out with 0.2 mol% of the monomer **CoCl-TPP (**for an equal number of equivalents in Co(III) porphyrin catalyst) gave a four-time lower yield, 19% (Table 1, entry 5). For this model reaction, the TON calculated (95) is in adequacy with the one (71) reported earlier by Nguyen *et al.* in similar conditions (DCM, 120 °C, 17.2 bar).[18a] Therefore the increased activity obtained with cage **$(CoCl)_2$-1** strongly supports the fact that the two Co(III) porphyrins preorganised in a three-dimensional structure cooperate for this reaction, with the cage acting as a bimetallic catalyst.[25]

Table 1. Propylene carbonate synthesis from CO_2 and propylene oxide with various amounts of cobalt(III) porphyrins as catalysts and pyridine as co-catalyst.[a]

Entry	Catalyst (mol%)	Co-catalyst[b] (mol%)	Yield[c] (%)	TON[d]
1	**$(CoCl)_2$-1** (0.05)	-	13	260
2	**$(CoCl)_2$-1** (0.05)	0.2	20	400
3	**$(CoCl)_2$-1** (0.05)	0.6	38	760
4	**$(CoCl)_2$-1** (0.1)	1.2	80	800
5	**CoCl-TPP** (0.2)	1.2	19	95

[a] Conditions: propylene oxide (3.57 mmol, 1.1 M in DCM), 120 °C, 20 bar of CO2. [b] Pyridine. [c] Yields in PC, determined after 24 h by ^{1}H NMR spectroscopy using 1,2-dichloroethane as an internal standard; each test was conducted at least twice. [d] Moles of PC produced per mole of catalyst.

To further optimize the reaction, other reaction parameters such as the temperature and the CO_2 pressure were modified (Table 2). Increasing the temperature from 120 °C to 140 °C improved the conversion from 80% to 96% (Table 2, entries 1-2). Slightly increasing the CO_2 pressure from 20 to 25 bar at 120°C increased the yield to 97% and an almost quantitative yield of 99% was obtained with a pressure of 30 bar (Table 2 entries 3-4). Again, under these optimized reaction conditions, the model catalyst **CoCl-TPP** is much less active (23 %) than the cage **$(CoCl)_2$-1**) showing the positive outcome of the choice of a catalyst combining two Lewis acidic metal centres in a closed structure.

Table 2. Catalytic activity of cobalt(III) porphyrins/pyridine systems under different temperature and CO_2 pressure.[a]

Entry	Catalyst (mol%)	Temperature (°C)	P(CO_2) (bar)	Yield[b] (%)	TON[c]	TOF (h^{-1})
1	**$(CoCl)_2$-1** (0.1)	140	20	96	960	40
2	**$(CoCl)_2$-1** (0.1)	120	20	80	800	33
3	**$(CoCl)_2$-1** (0.1)	120	25	97	970	40
4	**$(CoCl)_2$-1** (0.1)	120	30	99	990	41
5	**CoCl-TPP** (0.2)	120	30	23	115	5
6	**CoCl-TPP** (0.2)	120	20	19	95	4

[a] Conditions: propylene oxide (3.57 mmol, 1.1 M in DCM), pyridine 1.2 mol%. [b] Yields in PC, determined after 24 h by ^{1}H NMR spectroscopy using 1,2-dichloroethane (1.26 mmol) as an internal standard; each test was conducted at least twice. [c] Moles of PC produced per mole of catalyst.

The activity of the cage **$(CoCl)_2$-1** was also compared to the model **CoCl-TPP** as a function of reaction time (Figure 4 and Table S2). In both cases, linear plots of yield (up to 80 or 70%) *versus* time were obtained. This linear relationship points to the high stability of the cage over the range of studied reaction times. The apparent rate constant of reaction (Table 3) was three times higher for **$(CoCl)_2$-1** ($8.89\ 10^{-4}\ s^{-1}$) than for the reference catalyst ($2.93\ 10^{-4}\ s^{-1}$) and even after a long reaction time of 68 h, the reaction was not completed with **CoCl-TPP**.

We also tested another substrate, styrene oxide (SO), a sterically more demanding reactant and studied the kinetics of the reaction of styrene carbonate (SC) formation. Again, conversion of SO was more efficient with **$(CoCl)_2$-1** than with the model catalyst **CoCl-TPP**, leading to a quantitative yield after 24 h, whereas only 50% of SC was formed with the model (Table 3). With **$(CoCl)_2$-1**, the conversion of SO was even faster than that of PO with apparent rate constants of k_{app} = $13.1\ 10^{-4}\ s^{-1}$ and $8.89\ 10^{-4}\ s^{-1}$ for SO and PO, respectively (Figure 4 and Table S2) and while SO was quantitatively converted at 24 h, only 80 % of PC was formed. Conversion of SO was also faster than that of PO with the model catalyst **CoCl-TPP**, but only 50 % of SC was formed after 24 h and 48 h were necessary to reach a quantitative reaction. These results confirm that the cage is more efficient than the model catalyst in the conversion of both PO and SO, in line with the conclusions drawn previously.

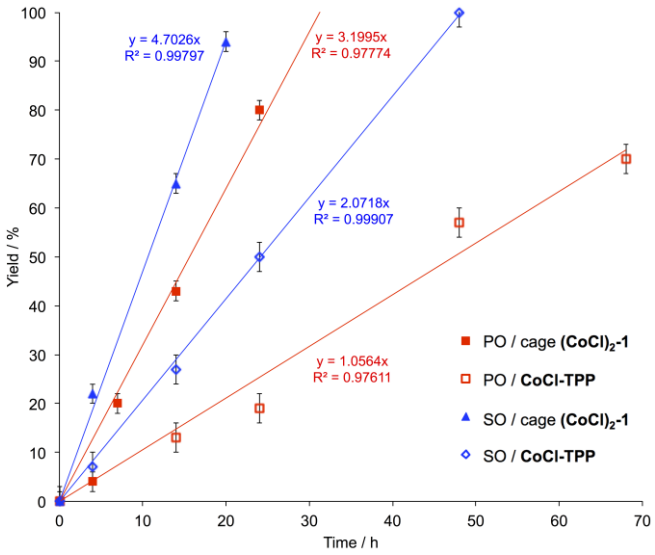


Figure 4. Kinetics of the conversion of styrene oxide (SO) or propylene oxide (PO) to the corresponding cycling carbonates catalysed by cage (**CoCl)$_2$-1** or reference porphyrin **CoCl-TPP**. Reactions conditions: SO or PO (3.57 mmol, 1.1 M in DCM), 0.2 mol% in porphyrin, pyridine 1.2 mol%, 120 °C, 20 bar.

Table 3. Yields of cyclic carbonates from CO_2 and epoxide after 24 h and apparent kinetic constants of cobalt(III) porphyrin/pyridine two-component catalytic systems.

Entry	Catalyst (mol%)	Sub-strate	Yield (%)	k_{app} (h^{-1})	k_{app} (10^{-4} s^{-1})	TON[a]	TOF (h^{-1})
1	**(CoCl)$_2$-1** (0.1)	PO	80	3.20	8.89	800	33.3
2	**CoCl-TPP** (0.2)	PO	19	1.06	2.93	95	3.96
3	**(CoCl)$_2$-1** (0.1)	SO	100	4.70	13.1	1000	41.7
4	**CoCl-TPP** (0.2)	SO	50	2.07	5.76	250	10.4

Conditions: epoxide (3.57 mmol, 1.1 M in DCM), pyridine 1.2 mol%, 120 °C, 20 bar of CO_2; Yields in cyclic carbonates, determined after 24 h by ^{1}H NMR spectroscopy using 1,2-dichloroethane as an internal standard; each test was conducted at least twice; k_{app} obtained as the slope of the linear regression of yield versus time. [a] Moles of PC produced per mole of catalyst.

Noteworthy, Ema and co-workers reported highly active bifunctional multi-metalloporphyrins catalysts in the context of cyclic carbonate formation from CO_2 and epoxides, in solvent-free conditions, with TON that reached 310000.[11d] The catalysts consisted of two or three trialkylammoniumbromide functionalised metalloporphyrins connected to a phenylene unit. In their conditions, using either the platform with two or three Mg(II)porphyrins at 0.0003 mol%, 120 °C, 17 bar of CO_2 and 24 h reaction, no evidence for cooperativity between the metal centres was found, the TOF values per metal centre being identical to or less than that of the monomeric bifunctional Mg(II)porphyrin catalyst.[6d] In the present study, performed in DCM for a homogeneous catalysis reaction, the TONs are much more modest. However, the cage acting as a bimetallic catalyst at 0.1 mol%,120 °C, 20 bar and 24 h of reaction improves the TON of PO and SO conversion by a factor of 8.4 and 4 respectively, relative to the reference at an identical concentration in metal centre (0.2 mol%) (Table 3). Even if these results cannot be directly compared, they show that gathering two metalloporphyrins in a flexible cage like-structure is a promising strategy to improve the catalytic activity compared to single metal centres arranged on a two-dimensional platform. In this respect, the face to face disposition of the two metal sites could favour their cooperativity within the cage. In addition, the intermediates species could be stabilized by weak interactions with the cage components, thanks to the flexibility of the structure.

Several mechanistic studies have been carried out with metalloporphyrins as Lewis acid catalysts associated to nucleophilic anions from ammonium salts or to N-heterocyclic bases (DMAP, N-methylimidazole, pyridine) forming either two-component or bifunctional single-component catalysts.[6d, 11e, 18c, 18e, 18h, 26] The generally accepted mechanism involves activation of the epoxide through coordination to the metal centre followed by ring-opening by nucleophilic attack on the less hindered epoxide carbon atom. The resulting coordinated alkoxide inserts CO_2 and intramolecular ring closure affords the cyclic carbonate regenerating the catalyst/cocatalyst system.[11c, 18e] The bimetallic Co(III)porphyrin cage offers several interesting features regarding such mechanism. Different hexacoordinated Co(III)Cl porphyrins with pyridine and epoxide as axial ligands can be involved in this reaction[18f, 22b, 27] and the distance between the two metal centres can be adjusted due to the flexible linkers.[19, 28] For the epoxide ring-opening step, a cooperative action of the two catalytic sites in which one axial chloride ligand promotes intramolecular ring opening of the epoxide bound to the other Co(III) site could account for the increased catalytic activity.[29] Noteworthy, whereas Co(III)porphyrins are not able to catalyse this reaction in absence of a co-catalyst, a yield of 13 % was obtained with the cage. Therefore, pyridine but also the eight triazoles of the linkers could play a role in activating CO_2 as reported for different Lewis bases[11e, 13b] and the triazoles could activate CO_2 in an intramolecular insertion step. Elucidation of the mechanism involved with this multicomponent cage will need further experiments combined with theoretical investigations.

Conclusion

In summary, we report the first example of a three-dimensional hollow structure with two Co(III)Cl porphyrins as catalytic sites for the synthesis of cyclic carbonates. This bimetallic molecular cage was prepared in high yield by Co(II) metalation of the two free-base porphyrins of the preformed cage, followed by their oxidation to Co(III)Cl porphyrins. The molecular cage was shown to catalyse, with high selectivity, the coupling of CO_2 and epoxides into cyclic carbonates. Despite its complexity, the cage is chemically stable at 120° C under 20-30 bar and converts at 0.1 mol%, PO or SO quantitatively in 24 h, using 1.2 mol% of pyridine as co-catalyst. Compared to the monomeric reference porphyrin **CoCl-TPP** used at identical concentration in metal site, the apparent rate constant for the conversion of PO with the bimetallic cage was three times higher, underlying the synergistic effect of the two metal centres organised in a closed structure. These promising results open the way to further optimise the intermolecular interactions of the bimetallic cage catalyst with the

substrates involved in the reaction through the modification of the Lewis acidic metal centres, their axial ligands and the linker components.

Experimental Section

Reagents and materials

All chemicals were of the best commercially available grade and used without further purification, except cobalt acetate which was recrystallised. $CHCl_3$ and CH_2Cl_2 were distilled over CaH_2 or P_2O_5 before use. Thin layer chromatography was carried out using aluminium sheets of silica gel (Merck, 60 F254). Column chromatography was carried out using silica gel (Merck, silica gel 60, 40-63 µm or 63-200) or aluminium oxide (Merck, aluminium oxide 90 standardized).

Instrumentation

Mass spectra were obtained using a Bruker MicroTOF spectrometer in electrospray mode (ES-MS).

Nuclear Magnetic Resonance (NMR) spectra for ^{1}H, ^{13}C were acquired on Bruker AVANCE 300, 400, 500, 600 spectrometers. The ^{1}H and ^{13}C spectra were referenced to residual solvent peaks. ($CDCl_3$, 7.24 and 77.16; CD_2Cl_2, 5.32 and 53.84; DMSO, 2.50 and 39.52; DMF, 8.03 and 163.15). Measures of self-diffusion coefficients were performed on a BRUKER 600 MHz spectrometer - Avance III, equipped with a DOTY (high strength z gradient probe DOTY Scientific, developing a pulse field gradient of 50 G/cm/A) or a BBI probe (Bruker BBI probe developing a pulse field gradient of 5 G/cm/A). The sample was thermostated at 298 K. Diffusion NMR data were acquired using a Stimulated Echo pulse sequence with bipolar z gradients. Limited Eddy current Delay was fixed to 5 ms. The diffusion time and the duration of the gradients were optimized for each sample. A recycling delay of 3 s was respected between scans. DOSY spectra were generated by the DOSY module of the software NMRNotebook, using Inverse Laplace Transform (ILT) driven by maximum entropy, to build the diffusion dimension. The diffusion coefficients were corrected by using DMF as an internal reference (η = 9.04 10^{-4} Pa.s and D_{DOTY} = 1.45 10^{-10} $m^2.s^{-1}$; D_{BBI} = 1.41 10^{-10} $m^2.s^{-1}$). The diffusion coefficients measured in different solvents (DMF-d_7/ pyridine-d_5 for **$(Zn)_2$-1**, CD_3OD/pyridine-d_5 for **$(CoCl)_2$-1**) were converted to hydrodynamic radii assuming a spherical model, in accordance to the Stokes-Einstein equation.[30]

UV-visible spectra were recorded on a Kontron Instruments UVIKON 860 spectrometer at 21°C with a 1 cm path cell.

Computational methods

All calculations were done with GAUSSIAN 09[31], version D01 using a mixed QM/QM ONIOM[32] approach. The porphyrin rings, the cobalt(III) cations, chloride anions and the ligands were treated at DFT level of theory (B3LYP functional) [33] with 6-31+G** basis set.[34] The linkers were treated with the semi-empirical PM6 method.[35] All calculations were done in gas phase. Dispersion corrections were introduced through Grimme's corrections.[36] All structures were fully optimised and the nature of the stationary point encountered was checked through a frequency calculation from which the Gibbs free energies were extracted. Weak interactions were analysed using the NCIPLOT package[37] on the GAUSSIAN wavefunction.

Synthesis of cage $(CoCl)_2$-1

$Co(OAc)_2$•$4H_2O$ (451 µmol, 112 mg, 20 equiv) was added to a stirred solution of cage **$(2H)_2$-1** (22.5 µmol, 50 mg, 1 equiv) in 22 mL of dry and degassed DMF. The reaction mixture was stirred at 150°C under argon, and the completion of the reaction was regularly checked by UV-visible, an aliquot of the reaction mixture (0.1 mL) was taken, poured in a vial and aqueous HCl 37% (2 drops), DCM (0.1 mL) and distilled water (0.1 mL) were added. The resulting purple precipitate of **$(CoCl)_2$-1** was filtered over cotton and washed with methanol (2 x 5 mL). To the solid solubilised in DMSO, two drops of HCl (37 wt.%) were added. The absence of non-metallated porphyrin in the aliquot was checked via UV-Visible by the absence at 670 nm of the Q band of protonated free-base porphyrin. If necessary, two additional equivalents of the cobalt salt were added to the reaction mixture and the progress of the reaction was checked again after 2 h. Once the metalation was completed, the reaction mixture was cooled to room temperature and HCl 37 wt.% (3 mL) was added.[18f] After 24 h under air, water was added to precipitate **$(CoCl)_2$-1**. The resulting purple solid was then filtered, washed with water to remove the unreacted $Co(OAc)_2$•$4H_2O$ until neutral pH and then washed with *n*-hexanes. Toluene was added to the solid and residual water was removed by evaporation of the heteroazeotropic mixture. The solid was dried at 50 °C under vacuum overnight to afford cage **$(CoCl)_2$-1** as a purple solid (19.4 µmol, 46.7 mg, 86 % yield). **^{1}H NMR** (500 MHz, methanol-d_4/*1%* pyridine-d_5): δ (ppm) 8.89 (16 H, s, H_{py}), 8.22 (8 H, s, H_t), 7.42 (16 H, br, H_o), 7.26 (16 H, br, H_m), 5.82 (16 H, s, H1), 4.71 (16 H, s, H2), 3.79 (16 H, s, H3). **^{1}H NMR** (500 MHz, $CDCl_3$/*1%* pyridine-d_5): δ (ppm) 8.67 (16 H, s, H_{py}), 7.91 (8 H, s, H_t), 7.27 (16 H, br, H_o), 7.11 (16 H, br, H_m), 5.58 (16 H, s, H1), 4.56 (16 H, s, H2), 3.57 (16 H, s, H3). **$^{13}C\{^{1}H\}$ NMR** (126 MHz, methanol-d_4/*1%* pyridine-d_5): δ (ppm) 146.4 (C_{12}), 143.3 (C_2), 140.5 (C_4), 137.3 (C_9), 136.7 (C_1), 135.1 (C_{5+7}), 127.7 (C_{6+8}), 125.8 (C_{11}), 119.9 (C_3), 70.9 (C_{14}), 65.0 (C_{13}), 54.4 (C_{10}). **HR-MS** (ESI) m/z: $[M\text{-}2Cl]^{2+}$ Calcd for $C_{128}H_{104}Co_2N_{32}Na_2O_8$/2 1167.3684; Found 1167.3695 (100). **UV-vis**: (DMSO) λ_{max} nm 433; 551; 589. **UV-vis**: (DCM/5% pyridine) λ_{max} nm 430; 544; 586.

General procedure for catalysed reactions

Reactions were performed in a 20 mL stainless-steel autoclave previously dried under vacuum at 100°C, equipped with a magnetic stir bar and purged with argon. In a typical run, the reactor under argon was charged with cage **$(CoCl)_2$-1** (8.60 mg, 3.57 µmol, 0.1 mol%) or **CoCl-TPP (**5.10 mg, 7.21 µmol, 0.2 mol%), degassed distilled dichloromethane (2.5 mL), propylene oxide (250 µL, 3.57 mmol), pyridine (3.5 µL, 43 µmol) and 1,2-dichloroethane (100 µL, 1.26 mmol) used as an internal standard. The reactor was placed at a pressure of CO_2 of approximately 10 bars at ambient temperature for 5 minutes before heating to the desired temperature (typically 120°C), the pressure adjusted (typically to 20 bars) and the reaction mixture stirred for the ascribed duration. The reaction was stopped by rapidly cooling the reactor in an ice bath. The pressure was then slowly released. The reaction mixture was transferred to a vial with dichloromethane. An aliquot was analysed by ^{1}H NMR spectroscopy in $CDCl_3$ and the conversion to cyclic carbonate was obtained using 1,2-dichloroethane as an internal standard (Figure S12). Each test was conducted at least twice. The mean value is reported. Standard deviations for TON/TOF are 2-3%. Quantities were adjusted when testing different conditions.

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Keywords: bimetallic catalyst • molecular cage • CO_2 conversion • cyclic carbonates • Co(III) porphyrin

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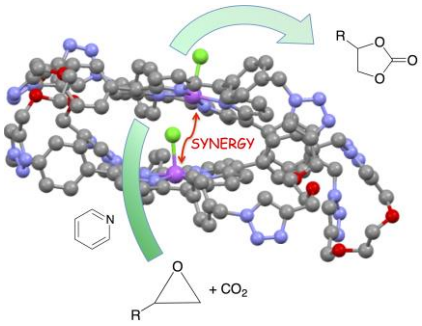

Synergistic action in a bimetallic nanosized catalyst: A bimetallic catalyst consisting of a flexible molecular cage with two Co(III) porphyrins is investigated to convert CO_2 and epoxides into cyclic carbonates. The preorganisation of the two metal centres in a closed structure favours their intramolecular cooperative action leading to superior catalytic performance than for a Co(III) *meso*-tetraphenylporphyrin.

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