Synthesis of Cyclic Carbonates by Ruthenium(VI) *Bis*-imido Porphyrin/TBACl-Catalysed Reaction of Epoxide with CO_2

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Dedicated to Professor Roberto Paolesse on the occasion of his 60th birthday.

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ABSTRACT: The catalytic activity of the ruthenium(VI) *bis*-imido porphyrin complex/TBACl binary system in promoting the CO_2 cycloaddition to epoxides forming cyclic carbonates is here reported. The system was very efficient in catalysing the conversion of differently substituted epoxides under mild experimental conditions (100 °C and 0.6 MPa of CO_2). Even if the sole TBACl resulted active under the optimised experimental conditions, the addition of ruthenium species was fundamental to maximising the reaction productivity both in terms of epoxide conversions and cyclic carbonate selectivities. A preliminary mechanistic study indicated a positive role of ruthenium imido nitrogen atom in activating carbon dioxide.

KEYWORDS: Homogeneous catalysis, ruthenium, cyclic carbonates, carbon dioxide, epoxides.

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INTRODUCTION

The increasing emission of carbon dioxide in the atmosphere, coming from anthropic activities, is responsible for many environmental issues, such as global warming [1] and ocean acidification. [2] Thus, the scientific community is currently working towards the chemical valorisation of carbon dioxide by transforming this greenhouse gas into high added-value compounds. This can determine a positive, albeit relatively small, impact on global CO_2 levels. [3-5] The limited use of carbon dioxide as a renewable C_1-building block in organic synthesis is due to its inherent thermodynamic stability; accordingly, a large energy input must generally be supplied for achieving the CO_2 activation. In order to use CO_2 as a feedstock under sustainable experimental conditions (avoiding the use of high temperatures, high CO_2 pressures and extremely reactive reagents), it is imperative to take full advantage of efficient catalytic systems for promoting the CO_2 conversion into fine-chemicals. [6]

Among all the CO_2-based organic transformations, the 100% atom-efficient cycloaddition of CO_2 to epoxides (Scheme 1) represents a valuable strategy for obtaining cyclic carbonates, which are extensively used as solvents in chemical processes [7-9] and batteries [10] and they are also employed as useful synthetic intermediates. [11, 12]

Insert Scheme 1

Several homogeneous and heterogeneous catalytic systems mediate the formation of cyclic carbonates starting from CO_2 and epoxides, and the most productive procedures require the contemporary presence of Lewis acid (M) and Lewis base (Nu^-) promoters. [13-16] One of the most validated mechanistic hypothesis proposes that the first coordination of an epoxide to the Lewis acidic metal is necessary for allowing the nucleophilic attack of the Lewis base to the three-membered ring. The so-obtained compound **A** is nucleophilic enough to attack carbon dioxide and the subsequent ring closure reaction forms the desired cyclic carbonate. Both the metal catalyst and the Lewis base are restored for repeating the catalytic cycle (Scheme 2).

Insert Scheme 2

Even if M is generally considered the reaction "catalyst" and the Lewis base is labelled as the 'co-catalyst', it is important to remember that while the Lewis acidic species is not usually active in the absence of the nucleophilic 'co-catalyst', the CO_2 cycloaddition can be catalysed by the sole Lewis base. [17] The DFT study of the TBAX-catalysed transformation of propylene oxide (PO) into propylene carbonate (PC) [18] suggested that the halide anion X^- is nucleophilic enough to attack the epoxide ring, thanks to the interaction of the TBA^+ cation with the epoxide oxygen atom. The so-formed intermediate undergoes the CO_2 insertion and the desired cyclic carbonate is formed by the following ring-closing reaction. However, the presence of the M catalyst is usually required for applying milder experimental conditions, improving the regioselectivity and speeding up the reaction.

Both homogeneous and heterogeneous porphyrin-based catalysts were seen to be very efficient in promoting the CO_2 cycloaddition to epoxide in the presence of the opportune co-catalyst (generally an ammonium salt). Regarding homogeneous systems, [19] many metal porphyrin catalysts were tested and good results were achieved by using either main group (Al, Mg, Sn, Bi) [20-25] or transition (Cr, Co, Mn, Ru and V) [26-31] metal derivatives. In addition, bifunctional metal catalysts were developed by inserting both Lewis acidic and nucleophilic moieties within the same molecular skeleton. Outstanding catalytic results were obtained in the presence of bifunctional metal porphyrin complexes showing an ammonium salt on the ligand periphery. [18, 32-34]

Albeit the acidic nature of the catalyst is usually necessary to maximise the reaction performance, we recently reported that the 'non-acidic' *bis*-imido porphyrin complex $Ru(TPP)(NAr)_2$ (**1**) (TPP = dianion of tetraphenyl porphyrin, Ar =3,5-$(CF_3)_2C_6H_3$), in combination with a tetrabutyl ammonium salt (TBAX), promoted the oxazolidinone synthesis by the cycloaddition of CO_2 to aziridines.[35] Although the reaction mechanism has not been studied in detail, preliminary results showed that the nitrogen atom of the axial imido ligand on the ruthenium centre may activate CO_2 molecule. The metal centre, being coordinatively saturated, doesn't interact with aziridine.

The good results obtained prompted us to test the catalytic activity of the $Ru(TPP)(NAr)_2$ (**1**)/TBAX binary system in the CO_2 cycloaddition to epoxides forming cyclic carbonates.

RESULTS AND DISCUSSION

The catalytic activity of Ru(TPP)$(NAr)_2$ (**1**) was first compared to that of other ruthenium complexes in the synthesis of cyclic carbonate **2**. Obtained data are reported in Table 1.

Insert Table 1

As shown in Table 1, the reaction occurred in the presence of TBACl alone and 74% of the starting epoxide was converted and the desired cyclic carbonate **2** was formed with 62% of selectivity after 8 hours at 100 °C under 0.6 MPa of CO_2 (Table 1, entry 1). The catalytic performance improved upon adding a ruthenium species to the catalytic reaction; when Ru(TPP)CO/TBACl system was used in the ratio reported in Table 1 (entry 2), the conversion increased from 74% to 77% and the cyclic carbonate selectivity from 62% to 99%. The epoxide conversion was further improved to 100% by replacing Ru(TPP)CO with Ru(TPP)$(NAr)_2$ (**1**), which mediated the formation of the desired product **2** with 99% of reaction selectivity. The compared systems mediated the synthesis of **2** by different mechanisms, which involve the sole TBACl containing both nucleophilic (Cl^-) and electrophilic (TBA^+) components (Table 1, entry 1) or the Lewis acid/base system as in the case of Ru(TPP)CO/TBACl combination (Table 1, entry 2). The beneficial effect of catalyst **1** (Table 1, entry 3) on the reaction productivity indicated the occurrence of a reaction mechanism in which the presence of a coordinatively unsaturated and '*acidic*' metal centre is not required. In fact, the presence of the two imido axial ligands on the ruthenium atom doesn't allow the coordination, and consequent epoxide activation, onto the central metal.

The chemical stability of the catalytic Ru(TPP)$(NAr)_2$ (**1**)/TBACl system, under the experimental conditions employed, was tested to investigate the recyclability of the catalyst. The synthesis of cyclic carbonate **2** was performed three consecutive times by adding the suitable amount of epoxide, after each complete consumption, to the initial catalytic mixture. As shown in entry 4 of Table 1, the catalytic performance was completely maintained indicating the lack of decomposition processes of the employed catalyst. Next, in order to investigate a possible scale-up of the Ru(TPP)$(NAr)_2$ (**1**)/TBACl-mediated procedure, the synthesis of **2** was executed by using 1.0 g of the starting epoxide (Table 1, entry 5). We were delighted to observe a complete retention of the reaction productivity, which paves the way to some practical applications of the procedure.

While the reaction efficiency was completely maintained when the catalyst Ru(TPP)$(NAr)_2$ (**1**) was replaced by Ru(TPP)$(NAr')_2$ (**3**) (Ar' = 3,5-$(NO_2)_2C_6H_3$) (Table 1, entry 6), a slight decrease of the epoxide conversion was observed when more sterically encumbered porphyrin ligands were employed. In fact, the complete conversion of the epoxide was not achieved regardless of the electronic characteristics of the porphyrin ring. However, the very high epoxide conversions of 93% and 95% were obtained in the presence of Ru(F_{20}TPP)$(NAr)_2$ (**4**) (F_{20}TPP = dianion of tetrapentafluorophenyl porphyrin) (Table 1 entry 5) and Ru(TMP)$(NAr)_2$ (**5**) (TMP = dianion of tetramesityl porphyrin), respectively. This result indicated that the steric hindrance of the porphyrin skeleton is more influent than its electronic nature in determining the catalytic efficiency of the methodology.

In view of the good catalytic results achieved by using Ru(TPP)$(NAr)_2$ (**1**)/TBACl binary system, this combination was employed for the synthesis of cyclic carbonates **6-12**, which was also performed in the presence of TBACl alone to better appreciate the influence of the ruthenium porphyrin catalyst (Table 2). In order to improve the solubilisation of CO_2 in the reaction medium, the reactions mediated by the sole TBACl were executed in THF where a better catalytic

performance in the synthesis of **2** was observed. When working in THF, the epoxide conversion increased from 74% (Table 1, entry 1) to 91% (Table 2, entry 1), while the cyclic carbonate selectivity remained the same (62% *vs* 63%) supporting the importance of maximising the CO_2 solubility in the reaction solvent to amplify the catalytic efficiency.

Unfortunately, we were forced to replace THF with benzene, as the reaction solvent, when catalyst **1** was employed in combination with TBACl, due to the poor chemical stability of the ruthenium species in coordinating solvents, such as THF. As shown in Table 2, even if the catalytic performances were always maximised by adding $Ru(TPP)(NAr)_2$ (**1**), the positive effect was strongly related to the nature of the starting epoxide. When epoxide was *mono*-substituted with a $-CH_2$(EWD) group (Table 2, entries 1-3), the reaction worked well both in the presence of TBACl and $Ru(TPP)(NAr)_2$ (**1**)/TBACl binary system. Compounds **2** (Table 2, entry 1), **6** (Table 2, entry 2) and **7** (Table 2, entry 3) were obtained with the complete conversion of the starting epoxide and with very high similar selectivities (94% - 99%) in the presence of the $Ru(TPP)(NAr)_2$ (**1**)/TBACl combination.

Insert Table 2

The positive effect of the $Ru(TPP)(NAr)_2$ (**1**) addition was more clearly observed in the synthesis of **8** (Table 2, entry 4), which involved an epoxide showing an electron-donating substituent on the three-membered ring. In this case, albeit the complete epoxide conversion was observed either in the presence or in the absence of catalyst **1**, the addition of the ruthenium species was responsible for an increase of the reaction selectivity from 27% to 65%. Next, the catalytic influence of the steric hindrance on the epoxide ring was investigated. The presence of a phenyl substituent on the starting epoxide did not hamper the formation of the corresponding cyclic carbonate **9** (Table 2, entry 5) in good selectivities. A moderate improvement of the reaction productivity was registered by running the reaction in the presence of $Ru(TPP)(NAr)_2$ (**1**)/TBACl instead of TBACl alone. When more sterically encumbered substrates were employed, the effect of the ruthenium catalyst was less evident. The synthesis of compound **10** (Table 1, entry 6) occurred with low selectivities both in the presence or absence of **1**, due to the presence of a *tetra*-substituted carbon atom on the epoxide ring. The addition of $Ru(TPP)(NAr)_2$ (**1**) did not promote the formation of the desired compound in an acceptable amount. It should be noted that the epoxide conversion was not determined in this case because its low boiling point favoured the complete elimination of the reagent during the work-up, which was executed in order to perform the NMR analysis of the crude. Very modest catalytic results were also observed in the synthesis of cyclic carbonate **11** (Table 1, entry 7) where the epoxide was converted in a very low extent in both cases. In spite of the small amount of the converted epoxide, a 99% of the cyclic carbonate selectivity was obtained by using both the catalytic procedures. Finally, the low yield in which cyclic carbonate **12** was obtained could be due to the pronounced attitude of 7-oxabicyclo[4.1.0]heptane reacting with CO_2 forming poly(cyclohexene carbonate) alongside the corresponding cyclic carbonate.

As reported in the Introduction, $Ru(TPP)(NAr)_2$ (**1**)/TBACl binary system also mediated the CO_2 cycloaddition to aziridines, thus a competitive experiment was performed to assess which, between epoxides and aziridines, can be better activated by this catalytic system. The reaction was performed by reacting equimolar amounts of styrene oxide and 1-butyl-2-phenyl aziridine with CO_2 under the experimental conditions reported in Table 2. The NMR analysis of the crude after 8 hours revealed the lower reactivity of aziridine with respect to that of epoxide. In fact, while epoxide was completely converted into corresponding cyclic carbonate **9**, only 21% of the aziridine conversion occurred to form corresponding *N*-butyl oxazolidinone **13** with 99% of selectivity (Scheme 3).

Insert Scheme 3

In order to better clarify the role of Ru(TPP)$(NAr)_2$ in the catalytic reaction, some experiments were executed. In our previously published paper on the CO_2 cycloaddition to aziridines catalysed by Ru(TPP)$(NAr)_2$ (**1**)/TBACl binary system, we reported the formation of the deactivated Ru(TPP)(NAr)($ArNCOO^-TBA^+$) complex (**14**) at the end of the catalytic reaction. [35] The formation of this latter complex indicated that the imido axial ligand on the ruthenium atom was able to interact with CO_2 thanks to the high electron density on the nitrogen atom, as already indicated by our previous DFT study. [36]

The formation of complex **14** was also detected by ESI-MS at the end of the catalytic reaction forming cyclic carbonate **2**. Analogously to what was observed in the case of the oxazolidinone synthesis, [35] ruthenium complex **14** was catalytically inactive when used in combination with TBACl for promoting the synthesis of **2**, which was formed with the same conversion and selectivity values as achieved in the presence of TBACl alone (see Table 1, entry 1). In view of the formation of **14**, a positive interaction between Ru(TPP)$(NAr)_2$ (**1**) and CO_2 was again supposed and it may be responsible for the formation of the putative CO_2/**1** adduct **A** (Scheme 4). While the formation of intermediate **A** should represent the first step of the cyclic carbonate formation in the presence of the epoxide (*path a*, Scheme 4), it could be responsible for the formation of the inactive compound **14** when the epoxide is not present in the reaction medium (*path b*, Scheme 4). Thus, intermediate **A** can either evolve during the productive catalytic cycle or be transformed into the deactivated catalytic compound **14** by a dead-end reaction.

Unfortunately, any attempt to detect the adduct **A** between CO_2 and complex **1** as well as products containing chlorine atoms, which derive from the TBACl decomposition forming **14**, have failed up to now. Even if the mechanism showed in Scheme 4 is not fully supported by experimental data, the isolation of compound **14** at the end of the catalytic reaction strongly indicated the reactivity of ruthenium imido nitrogen atoms towards carbon dioxide.

Insert Scheme 4

Considering that cyclic carbonates were also formed in the presence of TBACl alone and that all the reactions were carried out by using a **1**/TBACl molar ratio of 1:10, it was difficult to assess the real contribute of complex **1** in catalytic reactions occurring in the presence of a TBACl excess. To shed some light on this aspect, the model reaction forming **2** was performed by using a TBACl defect (**1**/TBACl/epoxide = 2:1:100) in order to favour the catalytic activity of **1** at the expense of the free TBACl. The reaction carried out under these conditions occurred in a higher yield (93%) than that performed in the presence of TBACl alone (57%), suggesting the active role of the ruthenium species in the catalytic cycle. It should be noted, the model reaction forming **2** didn't occur in presence of the sole ruthenium complex **1**.

In the suggested mechanism, while ruthenium complex is responsible for the CO_2 activation, TBACl is necessary for the epoxide ring-opening reaction. This proposal was supported by the lack of interaction between 2-((allyloxy)methyl)oxirane and complex **1**, as pointed out by the absence of any shift of original IR signals when the two compounds were reacted in the absence of CO_2. On the other hand, when 2-((allyloxy)methyl)oxirane was reacted with Ru(TPP)CO, which presents a free coordinating site, the IR spectrum of the resulting solution showed the shift of

the C=O IR signal of Ru(TPP)CO from 1957 cm^{-1} to 1817 cm^{-1}. In addition, the IR signal attributed to epoxide shifted from 1814 cm^{-1} to 1715 cm^{-1} upon its plausible coordination to the penta-coordinated ruthenium atom.

EXPERIMENTAL

General

Unless otherwise specified, all the reactions were carried out under nitrogen atmosphere employing standard Schlenk techniques and vacuum-line manipulations. All the solvents were dried by using standard procedures unless where it is specified. 3,5-*Bis*(trifluoromethyl)phenyl azide, [37] 3,5-*bis*(nitro)phenyl azide, [37] Ru(TPP)CO (TPP = dianion of tetraphenyl porphyrin), [38] $Ru(TPP)(NAr)_2$ (**1**) (Ar = 3,5-$(CF_3)_2C_6H_3$), [39] $Ru(TPP)(NAr')_2$ (**3**) (Ar' = 3,5-$(NO_2)_2C_6H_3$, [40] $Ru(F_{20}TPP)(NAr)_2$ (**4**) ($F_{20}TPP$ = dianion of tetrapentafluorophenyl porphyrin), [35] and $Ru(TMP)(NAr)_2$ (**5**) (TMP = dianion of tetramesityl porphyrin) [35] were synthesised by methods reported in literature or by using minor modifications of them. All the other starting materials were commercial products and used as received. Analytical data of cyclic carbonates **2**, **6-12** [41, 42] and oxazolidinone **13** [35] were in accordance with those reported in literature. NMR spectra were recorded at room temperature either on a Bruker Avance 300-DRX, operating at 300 MHz for ^1H and at 75 MHz for ^{13}C , or on a Bruker Avance 400-DRX spectrometers, operating at 400 MHz for ^1H and at 100 MHz for ^{13}C. Chemical shifts (ppm) are reported relative to TMS. The ^1H NMR signals of the compounds described in the following were attributed by 2D NMR techniques. Assignments of the resonance in ^{13}C NMR were made by using the APT pulse sequence, HSQC and HMBC techniques. Infrared spectra were recorded on a Varian Scimitar FTS 1000 spectrophotometer. UV/Vis spectra were recorded on an Agilent 8453E instrument. Mass spectra were recorded in the analytical laboratories of Milan University.

General catalytic procedures

Method A*:* In a 100 mL glass liner equipped with a screw cap and glass wool, TBACl (9.71 x 10^{-5} mol) and the epoxide (9.71 x 10^{-4} mol) in a molar ratio = 10/100 were dissolved in THF (3.3 mL). The reaction mixture was cooled with liquid nitrogen and the flask was transferred into a stainless-steel autoclave, three vacuum-nitrogen cycles were performed and 0.6 MPa of CO_2 was charged at room temperature. The autoclave was placed in a preheated oil bath at 100 °C and stirred for 8 h, then it was cooled at room temperature and slowly vented. The solvent was evaporated to dryness and the crude was analysed by ^1H NMR with 2,4-dinitrotoluene as the internal standard.

Method B*:* the procedure illustrated for method A was employed by using the ruthenium catalyst (5.14 x 10^{-6} mol), TBACl (5.14 x 10^{-5} mol) and the epoxide (5.14 x 10^{-4} mol) in the molar ratio = 1/10/100 and benzene (3.3 mL) as the reaction solvent.

Synthesis of 4-((allyloxy)methyl)-1,3-dioxolan-2-one (2): The epoxide 2-((allyloxy)methyl)oxirane was employed. Collected data were in accordance with those reported in literature. [41] ^1H NMR (300 MHz, $CDCl_3$): δ_H, ppm 6.00–5.86 (1H, m), 5.31–5.21 (2H, m), 4.86–4.75 (1H, m), 4.50 (1H, t, *J*=8.3 Hz), 4.43–4.36 (1H, m), 4.07 (2H, d, *J*=4.6 Hz), 3.71–3.59 (2H, m).

Synthesis of 4-(phenoxymethyl)-1,3-dioxolan-2-one (6): The epoxide 2-(phenoxymethyl)oxirane was employed. Collected data were in accordance with those reported in literature. [42] ^1H NMR (300 MHz, $CDCl_3$): δ_H, ppm 7.30 (2H, t, *J*=8.3 Hz), 7.01 (1H, t, *J*=7.3 Hz), 6.92 (2H, d, *J*=7.9 Hz), 5.06–4.99 (1H, m), 4.64–4.58 (1H, m), 4.54–4.50

(1H, m), 4.28–4.09 (2H, m).

Synthesis of 4-(chloromethyl)-1,3-dioxolan-2-one (7): The epoxide 2-(chloromethyl)oxirane was employed. Collected data were in accordance with those reported in literature. [42] ^{1}H NMR (400 MHz, $CDCl_3$): δ, ppm 5.09–4.89 (1H, m), 4.61 (1H, t, *J*=8.5 Hz), 4.45–4.38 (1H, m), 3.75 (2H,d, *J*=5.1).

Synthesis of 4-ethyl-1,3-dioxolan-2-one (8): The epoxide 2-ethyloxirane was employed. Collected data were in accordance with those reported in literature. [41] ^{1}H NMR (400 MHz, $CDCl_3$): δ, ppm 4.66–4.60 (1H, m), 4.46 (1H, t, *J*=8.2 Hz), 3.98 (1H, t, *J*=8.0 Hz), 1.60–1.66 (2H, m), 0.97 (3H, t, *J*=7.4 Hz).

Synthesis of 4-phenyl-1,3-dioxolan-2-one (9): The epoxide 2-phenyloxirane was employed. Collected data were in accordance with those reported in literature. [42] ^{1}H NMR (300 MHz, $CDCl_3$): δ, ppm 7.47–7.34 (5H, m), 5.67 (1H, t, *J*=8.0 Hz), 4.79 (1H, t, *J*=8.4 Hz), 4.33 (1H, t, *J*=8.0 Hz).

Synthesis of 4,4-dimethyl-1,3-dioxolan-2-one (10): The epoxide 2,2-dimethyloxirane was employed. Collected data were in accordance with those reported in literature. [41] ^{1}H NMR (400 MHz, $CDCl_3$): δ, ppm 4.13 (2H, s), 1.91 (6H, s).

Synthesis of 4,5-diphenyl-1,3-dioxolan-2-one (11): The epoxide 2,3-diphenyloxirane was employed. Collected data were in accordance with those reported in literature. [41] ^{1}H NMR (300 MHz, $CDCl_3$): δ, ppm 7.51–7.45 (6H, m), 7.35–7.36 (4H, m), 5.44 (2H, s).

Synthesis of hexahydrobenzo[*d*][1,3]dioxol-2-one (12): The epoxide 7-oxabicyclo[4.1.0]heptane was employed. Collected data were in accordance with those reported in literature. [41] ^{1}H NMR (400 MHz, $CDCl_3$): δ, ppm 4.69–4.64 (2H, m), 1.91–1.79 (2H, m), 1.72–1.50 (4H, m), 1.48–1.33 (2H, m).

Recycle of Ru(TPP)(NAr)$_2$ (1)/TBACl. Method B was followed by using 2-((allyloxy)methyl)oxirane as the reagent. After the consumption of epoxide, which was monitored by TLC analysis (*n*-hexane/AcOEt = 8:2), 2-((allyloxy)methyl)oxirane was added again to the catalytic mixture for two more consecutive times. The ^{1}H NMR analysis of the crude revealed 99% of global yield of compound **2**.

Scale-up of the cyclic carbonate 2 synthesis. The catalytic procedure was followed by using Ru(TPP)(NAr)$_2$ (**1**) (1.72 x 10^{-6} mol), TBACl (8.76 x 10^{-4} mol) and 2-((allyloxy)methyl)oxirane as the epoxide reagent (1.0 g, 8.76 x 10^{-3} mol) in the molar ratio **1**/TBACl/epoxide= 1/10/100 and benzene (25.0 mL) as the reaction solvent. Compound **2** was obtained with 99% yield.

Comparison of the reactivity of 2-((allyloxy)methyl)oxirane and 1-butyl-2-phenilaziridine towards CO_2 in the presence of 1/TBACl system.

The catalytic procedure was followed by using Ru(TPP)(NAr)$_2$ (**1**) (1.72 x 10^{-6} mol), TBACl (1.72 x 10^{-5} mol) and an equimolar amount of 1-butyl-phenyl aziridine (1.72 x 10^{-4} mol) and 2-phenyloxirane (1.72 x 10^{-4} mol) as the reagents in 1.1 mL of benzene. The NMR analysis of the crude revealed the formation of **9** (99% yield) and **13** (21% yield) and collected analytical data of **9** [42] and **13** [35] were in accordance with those reported in literature.

Synthesis of 3-butyl-5-pheniloxazalidin-2-one (13): Collected data are in accordance with those reported in literature.[35] ^{1}H NMR (300 MHz, $CDCl_3$): δ, ppm 0.94 (t, *J*=7.2 Hz, 3H), 1.31-140 (2H, m), 1.51-1.58 (2H, m), 3.23-3.38 (2H, m) 3.43 (1H, t, *J*=8.0 Hz), 3.92 (1H, t, *J*=8.8 Hz), 5.49 (1H, t, *J*=8.0 Hz), 7.28-7.42 (5H, m).

Study of the interaction between 2-((allyloxy)methyl)oxirane and Ru(TPP)CO by IR spectroscopy. 24 μL of

2-((allyloxy)methyl)oxirane (2.03 x 10^{-4} mol) in benzene, showing the characteristic IR signal at 1814 cm^{-1}, was added to a benzene (0.3 mL) solution of Ru(TPP)(CO) (15.0 mg, 2.03 x 10^{-5} mol), showing the characteristic IR signal at 1957 cm^{-1}. The IR spectrum of the resulting solution displayed two new signals at 1715 cm^{-1} and 1817 cm^{-1} as well as the absence of signals at 1814 cm^{-1} and 1957 cm^{-1}.

Study of the interaction between 2-((allyloxy)methyl)oxirane and Ru(TPP)$(NAr)_2$ (1) by IR spectroscopy. The analogous reaction was performed by using Ru(TPP)$(NAr)_2$ (**1**) (IR signal at 1485 cm^{-1}). No shifts were observed upon the epoxide addition.

CONCLUSIONS

In conclusion, we described the activity of the ruthenium(VI) *bis*-imido porphyrin complex/TBACl binary system in catalysing the synthesis of cyclic carbonates by the insertion of CO_2 into the epoxide ring. Under the optimised experimental conditions of 0.6 CO_2 MPa and 100 °C, the activity of TBACl was enhanced by the addition of the ruthenium species, which was fundamental for maximising both the epoxide conversion and the cyclic carbonate selectivity. The catalytic system was effective for the CO_2 cycloaddition to differently substituted epoxides, which were completely transformed into corresponding cyclic carbonates displaying a low steric hindrance on the ring. The chemical stability of the catalytic system allowed its efficient recyclability, as proven by the reuse of the binary system for three consecutive times. In addition, the reaction scale-up was also carried out by transforming 1.00 g of starting 2-((allyloxy)methyl)oxirane into cyclic carbonate **2** (99% yield). Obtained data indicated that the presence of a Lewis acidic transition metal catalyst is not always required and that the coordinatively saturated and '*non-acid*' ruthenium(VI) *bis*-imido porphyrin species probably activates CO_2 instead of epoxide, conversely to what is usually proposed for transition metal-catalysed cyclic carbonate syntheses. This hypothesis can open the door to several applications of Ru(porphyrin)$(NAr)_2$-based catalytic systems where CO_2 can be activated in other carbon dioxide valorisation processes.

Finally, the good performances of TBACl alone indicated that, in order to really evaluate the catalytic activity of a transition metal catalyst, the blank reaction must always be carried out for all the tested substrates by using the same experimental conditions applied for the catalytic species under investigation.

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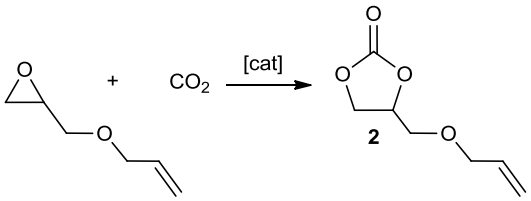
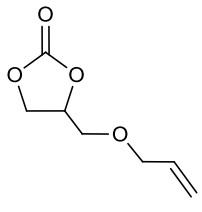
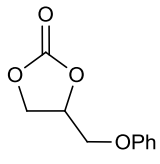
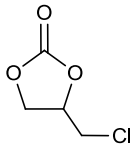
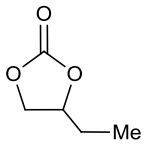
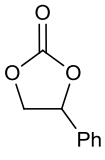
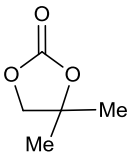
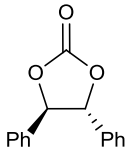
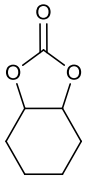
Table 1. Synthesis of 4-((allyloxy)methyl)-1,3-dioxolan-2-one (**2**)[a]



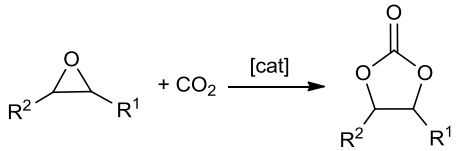
entry	catalytic system	conv. (%)[b]	select. (%)[b]
1[c]	TBACl	74	62
2[d]	Ru(TPP)CO/TBACl	77	99
3[d]	Ru(TPP)$(NAr)_2$ (**1**)/TBACl	100	99
4[d]	Ru(TPP)$(NAr)_2$ (**1**)/TBACl	100[e]	99[e]
5[f]	Ru(TPP)$(NAr)_2$ (**1**)/TBACl	100	99
6[d,g]	Ru(TPP)$(NAr')_2$ (**3**)/TBACl	100	99
5[d]	Ru(F_{20}TPP)$(NAr)_2$ (**4**)/TBACl	93	99
6[d]	Ru(TMP)$(NAr)_2$ (**5**)/TBACl	95	99

[a]Reactions were performed in a steel autoclave for 8.0 h at 100 °C and 0.6 MPa of CO_2. [b]Determined by ^{1}H NMR spectroscopy using 2,4-dinitrotoluene as the internal standard (uncertainty calculation: ±1%). [c]Method A was used, except benzene was the reaction solvent. [d]Method B was used. [e]After three consecutive reactions. [f]Performed by using 1.0 g of starting epoxide and **1**/TBACl/epoxide = 1:10:100 in 25.0 mL of benzene. [g]Ar' = 3,5-$(NO_2)_2C_6H_3$.

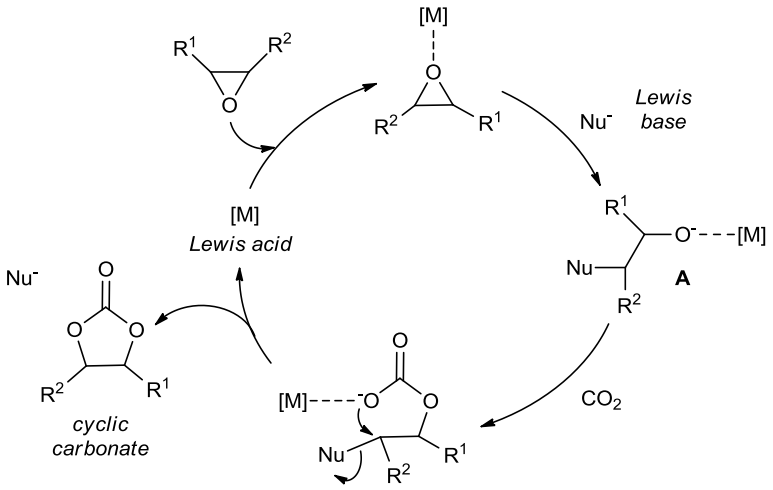
Table 2. Synthesis of cyclic carbonates **2**, **6-12**[a]

entry	cyclic carbonate	TBACl[b]		Ru(TPP)(NAr)$_2$ (**1**)/TBACl[c]	
		conv. (%)[d]	sel. (%)[d]	conv. (%)[d]	sel. (%)[d]
1	 (**2**)	91	63	100	99
2	 (**6**)	100	84	100	94
3	 (**7**)	100	99	100	99
4	 (**8**)	100	27	100	65
5	 (**9**)	81	95	100	99
6	 (**10**)	-[e]	14[f]	-[e]	15[f]
7	 (**11**)	10	99	15	99
8	 (**12**)	100	9	100	17

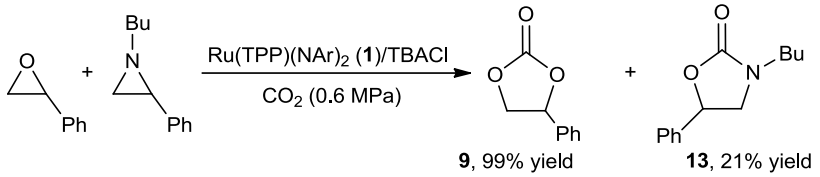
[a]Reactions were performed in a steel autoclave for 8.0 h at 100 °C and 0.6 MPa of CO_2. [b]TBACl/epoxide = 10:100 in THF. [c]**1**/TBACl/epoxide = 1:10:100 in benzene. [d]Determined by ^{1}H NMR spectroscopy by using 2,4-dinitrotoluene as the internal standard (uncertainty calculation: ±1%). [e]The selectivity was not determined because the unreacted epoxide was eliminated during the work-up due to its low boiling point. [f]Yields



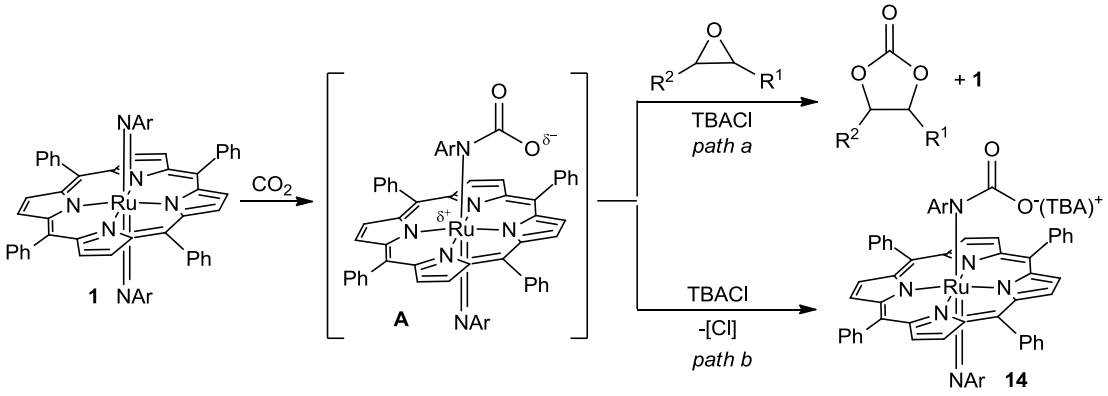
Scheme 1. General route of the cycloaddition of CO_2 to epoxides forming cyclic carbonates



Scheme 2. Mechanistic proposal of the cyclic carbonate formation



Scheme 3. Competitive cycloaddition of CO_2 to an equimolar mixture of epoxide and aziridine



Scheme 4. Formation of complex **14**