

# Metal *N,N*-dialkylcarbamates as Easily Available Catalytic Precursors for the Carbon Dioxide/Propylene Oxide Coupling Under Ambient Conditions

*Giulio Bresciani,<sup>a,b</sup> Fabio Marchetti,<sup>a,b</sup> Giorgia Rizzi,<sup>a</sup> Alessio Gabbani,<sup>a</sup> Francesco Pineider,<sup>a,b</sup>*

*Guido Pampaloni <sup>\*,a,b</sup>*

<sup>a</sup> *Università di Pisa, Dipartimento di Chimica e Chimica Industriale, Via Moruzzi 13, I-56124 Pisa.*

<sup>b</sup> *CIRCC, via Celso Ulpiani 27, I-70126 Bari, Italy.*

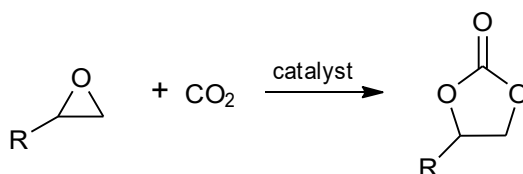
\* To whom correspondence should be addressed.

E-mail: [guido.pampaloni@unipi.it](mailto:guido.pampaloni@unipi.it)

**Abstract.** A series of previously reported homoleptic and non-homoleptic *N,N*-dialkylcarbamates of a range of non precious metals and *N,N*-dialkylcarbamate of Al(III) were investigated as easily available and inexpensive catalysts in the solventless synthesis of propylene carbonate (PC) from CO<sub>2</sub>/propylene oxide (PO). **By operating at atmospheric CO<sub>2</sub> pressure at ambient temperature,** high conversion and nearly quantitative selectivity were achieved using Ti(O<sub>2</sub>CNEt<sub>2</sub>)<sub>4</sub>, Al(O<sub>2</sub>CNR<sub>2</sub>)<sub>3</sub> (R = Et, <sup>i</sup>Pr), Cu(O<sub>2</sub>CNEt<sub>2</sub>)<sub>2</sub> and Sn(O<sub>2</sub>CNEt<sub>2</sub>)<sub>4</sub>, in combination with NBu<sub>4</sub>X (X = Br or Cl) as a co-catalyst. The reactions of MCl<sub>2</sub>(O<sub>2</sub>CNEt<sub>2</sub>)<sub>2</sub> (M = Ti, Zr) with amorphous silica were straightforward through partial release of both chlorido and carbamato ligands, and readily afforded solid materials which were characterized by ICP-OES and EDS analyses, coupled to SEM. These heterogeneous catalytic systems revealed less efficient than the homogeneous counterparts.

## Introduction

Carbon dioxide is a largely available, non toxic and economic chemical feedstock that, in principle, could be conveniently used to synthesize valuable organic compounds.<sup>1</sup> Indeed, diverse reactions aimed to convert CO<sub>2</sub> into a range of chemicals have seen a significant recent advance, and in this regard the carbonation of epoxides to produce cyclic carbonates represents one of the most investigated routes.<sup>2</sup> This transformation provides an attractive and environmentally friendly access to compounds which find applications in many fields, for instance they have been employed as non classical solvents with a high boiling point,<sup>3</sup> electrolytes for lithium-ion batteries,<sup>4</sup> intermediates to access high value-added products,<sup>5</sup> and monomers for constructing polycarbonates.<sup>2,6</sup>

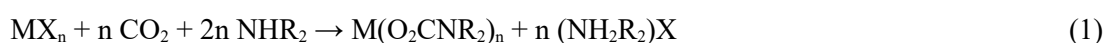


**Scheme 1.** Catalyzed CO<sub>2</sub>/epoxide coupling reaction to cyclic carbonate

A variety of catalysts which proved to be efficient in combining epoxides and CO<sub>2</sub> to obtain cyclic carbonates have been developed: they include metal organic frameworks (MOF),<sup>7</sup> metal complexes usually comprising porphyrin and Schiff bases as ligands,<sup>8</sup> ammonium<sup>9</sup> or phosphonium salts,<sup>10</sup> ionic liquids,<sup>11</sup> organocatalysts.<sup>12</sup>

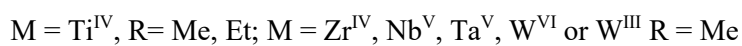
In alignment with the Green Chemistry approach,<sup>13</sup> the catalyst is expected to be simple and obtainable from non expensive precursors,<sup>14</sup> and, when dealing with a metal-based catalyst, earth abundant and non-toxic metal elements are highly desired.<sup>15</sup> In alignment with these ideas, various compounds have been investigated as catalysts in the CO<sub>2</sub>/epoxides coupling,<sup>16</sup> including titanium,<sup>17</sup> niobium,<sup>9a,18</sup> iron,<sup>19</sup> zinc,<sup>19b,20</sup> aluminum,<sup>21</sup> tin,<sup>22</sup> and gold<sup>23</sup> derivatives. However, high temperatures (70-140 °C) and compressed CO<sub>2</sub> (p = 5-50 bar) are usually required to achieve satisfying conversions; otherwise, catalysts working under mild conditions (p<sub>CO<sub>2</sub></sub> = 1 bar, T < 70°C) are relatively rare.<sup>20d,22b,24</sup>

Metal *N,N*-dialkylcarbamates have the general formula  $M(O_2CNR_2)_n$  ( $R = \text{alkyl group}$ ), and can be synthesized by the one pot reaction of metal halides (usually chlorides) with dialkylamines in the presence of  $CO_2$  at atmospheric pressure (Eq. 1).<sup>25</sup> The metal product is typically soluble in the reaction solution (toluene is conveniently used as the solvent), allowing its separation from the ammonium halide co-product. Remarkably, compounds  $M(O_2CNR_2)_n$  have been obtained with reference to a wide number of metal elements across the periodic table.<sup>25</sup>



Some metal carbamates have been proved to promote different organic reactions such as the hydrogenation<sup>26</sup> and the polymerization of alkenes,<sup>27</sup> and also the polymerization of cyclic esters.<sup>28</sup>

In spite of this versatility, the employment of metal carbamates in catalysis has been limitedly explored and, for instance, the possible activity in  $CO_2$  activation reactions has not been documented hitherto. In this respect, the observation by Chisholm and coworkers that carbamates of metals belonging to groups 4-6 are labile towards  $CO_2$  exchange with external  $CO_2$  (Eq. 2) is rather intriguing,<sup>29</sup> in that this property could favor in principle the catalytic activity of the complexes. The same exchange process was then demonstrated to occur also with carbamates based on other transition or main group elements.<sup>25</sup>



We decided to screen a series of metal carbamate complexes, based on various, non-precious metal (or semi-metal) elements, as homogeneous catalysts in the solventless formation of propylene carbonate (PC) from  $CO_2$  and propylene oxide (PO), which was selected as a model reaction

(Scheme 2). This study was extended to the heterogeneous version of the recently reported mixed chlorido-carbamates  $MCl_2(O_2CNEt_2)_2$  ( $M = Ti, Zr$ ),<sup>30</sup> which were supported on silica.

**Scheme 2.** Formation of propylene carbonate from  $CO_2$  and propylene oxide.

## Results and discussion

Homoleptic carbamates of group 4 metals ( $Ti^{IV}$ ,  $Zr^{IV}$ ,  $Hf^{IV}$ ), group 5 metals ( $Nb^V$ ,  $Ta^V$ ),  $Cu^{II}$ ,  $Ag^I$ ,  $Al^{III}$ ,  $Si^{IV}$  and  $Sn^{IV}$ , and mixed chlorido-carbamates of  $Ti^{IV}$  and  $Zr^{IV}$  and an oxido-carbamate of  $Nb^V$  were selected as possible homogeneous catalysts for the present study. The synthesis of all compounds was previously reported,<sup>31</sup> except that of the unprecedented  $Al(O_2CNEt_2)_3$ .

The preparation of  $Al(O_2CNEt_2)_3$  was attempted according to the general method (Eq. 1), but the expected product was isolated in very low yield from a mixture of  $AlBr_3/NHEt_2/CO_2$  in toluene (see Figure S1 in the Supporting Information). Conversely, the dimeric aluminum species  $[Al(O_2CN^iPr_2)]_2$  is efficiently obtained from  $AlBr_3/NH^iPr_2/CO_2$  following the same procedure.<sup>32</sup> It is presumable that  $Al(O_2CNEt_2)_3$  has a polymeric structure, which makes it poorly soluble in toluene, thus complicating its separation from the ammonium bromide co-product (see Introduction and Eq. 3).<sup>33</sup>



Therefore,  $[Al(O_2CNEt_2)_3]_n$  was synthesized through a metathesis reaction, consisting in the treatment of  $[Al(O_2CN^iPr_2)_3]_2$  with  $NHEt_2$  in toluene under  $CO_2$  atmosphere (Eq. 4).<sup>25</sup>



The novel aluminum diethylcarbamate was characterized by elemental analysis and IR spectroscopy. **The IR solid state spectrum** displays diagnostic, strong absorptions in the 1620-1500  $\text{cm}^{-1}$  region, ascribable to the C=O stretching vibrations of both bidentate and bridging carbamate ligands.<sup>25</sup>

In order to extend the series of investigated catalysts, we tried to synthesize phosphorus(V) *N,N*-dialkylcarbamates. These complexes were never reported in the literature, while analogous P(III) systems are known.<sup>34</sup> However, our attempts did not allow the clean isolation of products. In general, the reactions of  $\text{PCl}_5$  or  $\text{POCl}_3$  with secondary amines, in the presence of  $\text{CO}_2$ , proceeded with  $\text{P}^{\text{V}}$  to  $\text{P}^{\text{III}}$  reduction affording inseparable, highly hygroscopic mixtures of  $[\text{PO}_2\text{Cl}_2]^-$  ammonium salts and, presumably, P-carbamato species (see Supporting Information for details).

The preliminary catalytic tests were conducted at 25 °C and 1 atm  $\text{CO}_2$  pressure, during 24 h and using tetrabutylammonium bromide (TBAB) as co-catalyst (Table 1, entries 1-15).

**Table 1.** Conversion and selectivity values of propylene carbonate formation (Scheme 2) by means of metal *N,N*-dialkylcarbamates.

| Entry | Catalyst   | Conversion [%] <sup>[a]</sup> | Selectivity [%] <sup>[b]</sup> |
|-------|--|-------------------------------|--------------------------------|
| 1     | $\text{Ti}(\text{O}_2\text{CNEt}_2)_4$   | 37                            | 73                             |
| 2     | $\text{TiCl}_2(\text{O}_2\text{CNEt}_2)_2$   | 69                            | 75                             |
| 3     | $\text{Zr}(\text{O}_2\text{CNEt}_2)_4$   | 35                            | 71                             |
| 4     | $\text{ZrCl}_2(\text{O}_2\text{CNEt}_2)_2$   | 46                            | 68                             |
| 5     | $\text{Hf}(\text{O}_2\text{CNEt}_2)_4$   | 42                            | 67                             |
| 6     | $\text{Nb}(\text{O}_2\text{CNMe}_2)_5$   | 37                            | 38                             |
| 7     | $\text{Nb}(\text{O}_2\text{CNEt}_2)_5$   | 10                            | 30                             |
| 8     | $\text{NbO}(\text{O}_2\text{CNEt}_2)_3$  | 26                            | 58                             |
| 9     | $\text{Ta}(\text{O}_2\text{CNMe}_2)_5$   | 22                            | 64                             |
| 10    | $\text{Ta}(\text{O}_2\text{CNEt}_2)_5$   | 30                            | 40                             |
| 11    | $\text{Cu}(\text{O}_2\text{CNEt}_2)_2$   | 18                            | >99                            |
| 12    | $\text{Ag}(\text{O}_2\text{CNMe}_2)$   | 30                            | <5                             |
| 13    | $\text{Al}(\text{O}_2\text{CNEt}_2)_3$ <sup>[c]</sup>  | 31                            | 77                             |
| 14    | $\text{Si}(\text{O}_2\text{CNEt}_2)_4$   | 50                            | 16                             |
| 15    | $\text{Sn}(\text{O}_2\text{CNEt}_2)_4$   | 46                            | >99                            |
| 16    | $\text{TiCl}_2(\text{O}_2\text{CNEt}_2)_2 \equiv \text{SiO}_2$ , <b>Si-Ti</b> <sup>[d]</sup> | 27                            | 56                             |

| 17  | ZrCl <sub>2</sub> (O <sub>2</sub> CNEt <sub>2</sub> ) <sub>2</sub> ≡SiO <sub>2</sub> , <b>Si-Zr</b> <sup>[d]</sup> | 40 | 63 |
|---|--|----|----|
| Reaction conditions: propylene oxide (PO) (1 mL, 14.3 mmol), catalyst 1 mol%, TBAB 1 mol%, T = 25 °C, pCO <sub>2</sub> = 1 atm, t = 24 h. <sup>[a]</sup> Determined by <sup>1</sup> H NMR <sup>35</sup> using mesitylene as standard. <sup>[b]</sup> Calculated respect to PC; selectivity towards polypropylene carbonate in parenthesis. <sup>[c]</sup> [ <sup>36</sup> ]. <sup>[d]</sup> Complex supported on silica, M = 0.5 mol %. |  |    |    |

All the catalytic systems afforded PC with low to moderate conversion of PO and variable selectivity values. The by-products generated from those reactions occurring with low selectivity could not be unambiguously identified, since these species give rise to very broad signals in the NMR spectra. However, the formation of poly/oligoethers<sup>37</sup> and of cyclic carbamates might be hypothesized; in principle, the latter species may be generated due to released amine from some degradation of carbamato ligands. Otherwise, the formation of polycarbonates has been ruled out on the basis of a careful analysis of NMR data. Non homoleptic compounds performed slightly better respect to the homoleptic counterparts (compare entries 2, 4 and 8 with 1, 3 and 7, respectively). As outliers, copper and tin diethylcarbamates exhibited almost quantitative selectivity (Table 1, entries 11 and 15).

With the aim of exploring the catalytic potential of relevant heterogeneous systems, we grafted the mixed chlorido-carbamato complexes MCl<sub>2</sub>(O<sub>2</sub>CNEt<sub>2</sub>)<sub>2</sub> (M = Ti, Zr) on amorphous silica. The silica implantation of early transition metal carbamates takes advantage from the oxophilicity of the metal centre<sup>38</sup> and the favorable reaction of the carbamato moieties with the acidic silanol groups on the solid surface.<sup>25, 39</sup> The grafting process is quantitatively shifted to the products due to the dissociation of carbon dioxide from the carbamato group, and is represented in Eq. 5 with reference to a generic homoleptic reactant.



The functionalized silica powders (**Si-Ti** and **Si-Zr**) were characterized<sup>40</sup> by Inductively Coupled Plasma – Optical Emission Spectroscopy (ICP-OES) and Energy Dispersive X-ray Spectroscopy

(EDS), coupled to Scanning Electron Microscopy (SEM). The two techniques provide complementary information: the former supplied us the average metal-to-silicon ratio, while SEM/EDS allows for a semiquantitative determination of the elemental composition in selected areas of the sample, including the evaluation of the chlorine content, otherwise not possible through ICP-OES.

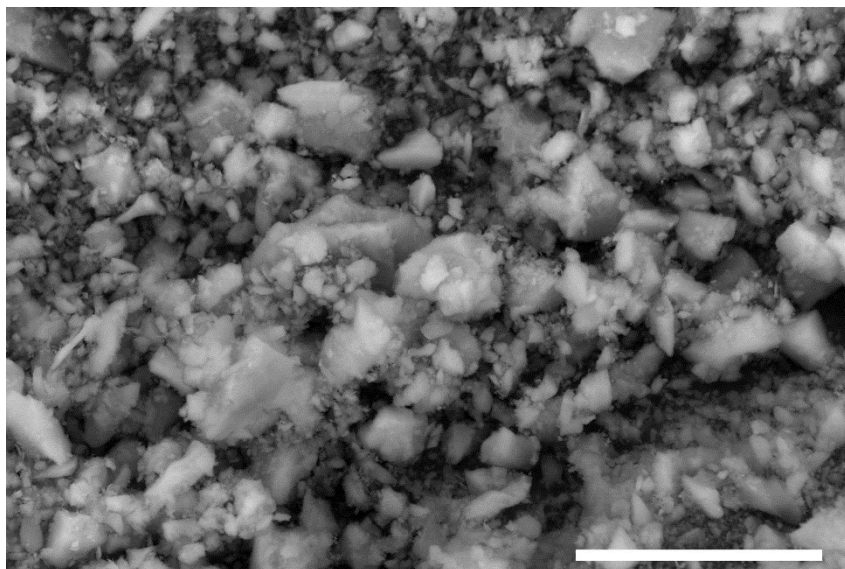
As far as **Si-Ti** is concerned, the **metal/silicon** atomic ratio obtained through EDS analysis on a relatively large area of the sample (magnification of 3000x) and the bulk metal-to-silicon atomic ratio determined through ICP-OES are comparable; on the other hand, slightly different ratios were detected for **Si-Zr** by the two methods (see Table 2). The **metal/silicon** atomic ratios were similar in **Si-Ti** and **Si-Zr**, indicating the grafting of comparable amounts of metal on the silica surface.

SEM images of the functionalized silica powders (see Figures 1 and S3) show brighter aggregates on both samples. EDS elemental analysis on these brighter areas of the samples revealed a higher metal content, **which may be associated** to a small amount of **intact** metal complex. Since the metal-to-silicon ratios obtained with EDS on a large area of the sample is consistent with the corresponding ICP-OES value, we can reasonably conclude that the bright regions **are negligible over the entire samples, from a statistical point of view**. A measurable amount of chlorine was also detected through EDS characterization. The decrease of the metal-to-chlorine ratio in **Si-Ti** and **Si-Zr** with respect to that in the precursors  $MCl_2(O_2CNEt_2)_2$  ( $M = Ti, Zr$ ), suggests that the loss of both carbamato and chlorido ligands may be involved in the grafting process, as we already found in similar systems.<sup>39</sup> **The absence of chlorine in the untreated silica powders was confirmed by blank experiments.**

**Table 2.** Metal-to-silicon and metal-to-chlorine atomic ratios in **Si-Ti** and **Si-Zr**, from ICP-OES and EDS.

|              | M/Si (ICP) | M/Si (EDS) | M/Cl(EDS) |
|--------------|------------|------------|-----------|
| <b>Si-Ti</b> | 0.039      | 0.036      | 0.80      |
| <b>Si-Zr</b> | 0.039      | 0.028      | 0.61      |

**Figure 1:** A representative SEM image of **Si-Ti**. Scale bar is 40  $\mu\text{m}$ .



The lower sensibility to moisture and the more eco-compatibility of **Si-Ti** and **Si-Zr**, compared to the Si-V(V) and Si-W(VI) systems already reported,<sup>39</sup> made the Ti and Zr derivatives good candidates to be used as heterogeneous catalysts. **Si-Ti** and **Si-Zr** were employed in the PO/CO<sub>2</sub> coupling reaction<sup>41</sup> providing worsened catalytic performances respect to those obtained using the non-grafted parent complexes (Table 1, compare entries 2 and 4 with 16 and 17, respectively). This fact might be the consequence of a scarce contact between surface active sites and reactants or related to the decreased chlorine content in the silica materials **Si-Ti** and **Si-Zr** (Cl/M molar ratios are 1.25 and 1.64 respectively), with respect to  $\text{MCl}_2(\text{O}_2\text{CNEt}_2)_2$  (M = Ti, Zr; Cl/M = 2). As a matter of fact, literature reports indicate that solid surfaces decorated with early transition metal complexes may exhibit enhanced catalytic activity when enriched in the chlorine content.<sup>27b,42</sup>

Following the preliminary screening (Table 1), a series of metal carbamates was selected to study the influence of the co-catalyst in the PO/CO<sub>2</sub> coupling (Table 3).

**Table 3.** PO/CO<sub>2</sub> to PC conversion: dependence of conversion and selectivity on the nature and amount of co-catalyst.

| Entry | Catalyst | Co-catalyst | Conversion | Selectivity |
|-------|----------|-------------|------------|-------------|
|-------|----------|-------------|------------|-------------|



|                   |  | (%)                          | [%] <sup>[a]</sup> | [%] <sup>[b]</sup> |
|-------------------|--|------------------------------|--------------------|--------------------|
| 1                 | Ti(O <sub>2</sub> CNEt <sub>2</sub> ) <sub>4</sub> | none                         | 39                 | 0                  |
| 2                 | Ti(O <sub>2</sub> CNEt <sub>2</sub> ) <sub>4</sub> | [NBu <sub>4</sub> ]Cl (0.1%) | 46                 | 2                  |
| 3                 | Ti(O <sub>2</sub> CNEt <sub>2</sub> ) <sub>4</sub> | [NBu <sub>4</sub> ]Cl (1%)   | 46                 | 61                 |
| 4                 | Ti(O <sub>2</sub> CNEt <sub>2</sub> ) <sub>4</sub> | [NBu <sub>4</sub> ]Br (0.1%) | 40                 | 5                  |
| 5                 | Ti(O <sub>2</sub> CNEt <sub>2</sub> ) <sub>4</sub> | [NBu <sub>4</sub> ]Br (1%)   | 40                 | 73                 |
| 6                 | Ti(O <sub>2</sub> CNEt <sub>2</sub> ) <sub>4</sub> | [NBu <sub>4</sub> ]Br (2%)   | 60                 | 67                 |
| 7                 | Ti(O <sub>2</sub> CNEt <sub>2</sub> ) <sub>4</sub> | [NBu <sub>4</sub> ]I (0.1%)  | 34                 | 59                 |
| 8                 | Ti(O <sub>2</sub> CNEt <sub>2</sub> ) <sub>4</sub> | [NBu <sub>4</sub> ]I (1%)    | 38                 | 74                 |
| 9                 | Ti(O <sub>2</sub> CNEt <sub>2</sub> ) <sub>4</sub> | DMAP (0.1%)                  | 20                 | 0                  |
| 10                | Ti(O <sub>2</sub> CNEt <sub>2</sub> ) <sub>4</sub> | DMAP (1%)                    | 24                 | 0                  |
| 11                | Ti(O <sub>2</sub> CNEt <sub>2</sub> ) <sub>4</sub> | [PPN]Cl (0.1%)               | 36                 | 11                 |
| 12                | Ti(O <sub>2</sub> CNEt <sub>2</sub> ) <sub>4</sub> | [PPN]Cl (1%)                 | 60                 | 22                 |
| 13                | Al(O <sub>2</sub> CNEt <sub>2</sub> ) <sub>3</sub> | [NBu <sub>4</sub> ]Cl (1%)   | 28                 | >99                |
| 14                | Al(O <sub>2</sub> CNEt <sub>2</sub> ) <sub>3</sub> | [NBu <sub>4</sub> ]Br (1%)   | 31                 | 77                 |
| 15                | Al(O <sub>2</sub> CNEt <sub>2</sub> ) <sub>3</sub> | [NBu <sub>4</sub> ]I (1%)    | 41                 | 59                 |
| 16                | Al(O <sub>2</sub> CNEt <sub>2</sub> ) <sub>3</sub> | DMAP (1%)                    | 22                 | 32                 |
| 17                | Cu(O <sub>2</sub> CNEt <sub>2</sub> ) <sub>2</sub> | [NBu <sub>4</sub> ]Br (1%)   | 18                 | >99                |
| 18 <sup>[c]</sup> | Cu(O <sub>2</sub> CNEt <sub>2</sub> ) <sub>2</sub> | [NBu <sub>4</sub> ]Br (2%)   | 71                 | >99                |
| 19                | Sn(O <sub>2</sub> CNEt <sub>2</sub> ) <sub>4</sub> | [NBu <sub>4</sub> ]Br (1%)   | 46                 | >99                |
| 20 <sup>[d]</sup> | Sn(O <sub>2</sub> CNEt <sub>2</sub> ) <sub>4</sub> | [NBu <sub>4</sub> ]Br (2%)   | 66                 | 90                 |

Reaction conditions: propylene oxide (PO) (1 mL, 14.3 mmol), catalyst = 1 mol%, T = 25 °C, pCO<sub>2</sub> = 1 atm, t = 24 h. <sup>[a]</sup> Determined by <sup>1</sup>H NMR <sup>35</sup> using mesitylene as standard. <sup>[b]</sup> Calculated respect to PC. <sup>[c]</sup> t = 72 h <sup>[d]</sup> t = 48h. DMAP = dimethylaminopyridine; [PPN]<sup>+</sup> = bis(triphenylphosphine)iminium.

Data referring to Ti(O<sub>2</sub>CNEt<sub>2</sub>)<sub>4</sub> as catalytic precursor point out that a co-catalyst is essential to the formation of PC (Table 3, entries 1-12). Moreover, tetrabutylammonium halides appear as the most convenient choice, wherein different halides do not determine dramatic changes in the catalytic performance (see entries 3, 5 and 8). The selectivity increases in the order Cl < Br < I. This is in alignment with the leaving ability of the halides (see entries 3, 5 and 8). On the other hand, the lower nucleophilicity of DMAP with respect to X<sup>-</sup> (with X = Cl, Br, I) probably makes the ring opening reaction slower, favoring side-reactions due to epoxide activation by the metal center.<sup>43, 44</sup> The promising result obtained with Cu(O<sub>2</sub>CNEt<sub>2</sub>)<sub>2</sub> (Table 1) was significantly improved in terms of conversion by increasing the [NBu<sub>4</sub>]Br amount (entries 17-18). It is noteworthy that almost

quantitative selectivity towards the formation of PC was achieved by associating the use of  $[\text{NBu}_4]\text{Cl}$  to  $\text{Al}(\text{O}_2\text{CNEt}_2)_3$  (entry 13).

Additional experiments were carried out using selected catalysts, in order to find a correlation between the amount of catalyst and related conversion and selectivity values (Table 4);  $\text{Al}(\text{O}_2\text{CN}^i\text{Pr}_2)_3$  was included in these trials.

**Table 4.** PO/CO<sub>2</sub> to PC conversion. Correlation between catalyst amount and conversion/selectivity.

| Entry             | Catalyst  | mol % | Conversion [%] <sup>[a]</sup> | Selectivity [%] <sup>[b]</sup> |
|-------------------|---|-------|-------------------------------|--------------------------------|
| 1                 | $\text{Ti}(\text{O}_2\text{CNEt}_2)_4$          | 0.1   | 27                            | 48                             |
| 2                 | $\text{Ti}(\text{O}_2\text{CNEt}_2)_4$          | 1     | 37                            | 73                             |
| 3                 | $\text{Ti}(\text{O}_2\text{CNEt}_2)_4$          | 2     | 57                            | 81                             |
| 4                 | $\text{Ti}(\text{O}_2\text{CNEt}_2)_4$          | 3     | 74                            | 65                             |
| 5 <sup>[c]</sup>  | $\text{Al}(\text{O}_2\text{CNEt}_2)_3$          | 0.1   | 25                            | 24                             |
| 6 <sup>[c]</sup>  | $\text{Al}(\text{O}_2\text{CNEt}_2)_3$          | 1     | 26                            | >99                            |
| 7 <sup>[d]</sup>  | $\text{Al}(\text{O}_2\text{CNEt}_2)_3$          | 1     | 55                            | >99                            |
| 8 <sup>[c]</sup>  | $\text{Al}(\text{O}_2\text{CNEt}_2)_3$          | 2     | 35                            | 51                             |
| 9 <sup>[d]</sup>  | $\text{Al}(\text{O}_2\text{CN}^i\text{Pr}_2)_3$ | 0.5   | 62                            | >99                            |
| 10                | $\text{Cu}(\text{O}_2\text{CNEt}_2)_2$          | 1     | 18                            | >99                            |
| 11 <sup>[e]</sup> | $\text{Cu}(\text{O}_2\text{CNEt}_2)_2$          | 1     | 71                            | >99                            |
| 12 <sup>[f]</sup> | $\text{Cu}(\text{O}_2\text{CNEt}_2)_2$          | 2     | 38                            | 66                             |

General reaction conditions: propylene oxide (PO) (1 mL, 14.3 mmol), TBAB 1 mol%, T = 25 °C, pCO<sub>2</sub> = 1 atm, t = 24 h. <sup>[a]</sup> Determined by <sup>1</sup>H NMR <sup>35</sup> using mesitylene as standard. <sup>[b]</sup> Calculated respect to PC. <sup>[c]</sup> TBAC 1 mol%. <sup>[d]</sup> TBAC 1 mol%, t = 72 h. <sup>[e]</sup> TBAB 2 mol%, t = 72 h. <sup>[f]</sup> t = 48 h

The optimal quantity of catalyst does not generally exceed 1 mol%, higher amounts being ineffective or even detrimental to both conversion and selectivity. Working with optimized reaction parameters, aluminum and copper carbamates led to the formation of PC from PO and CO<sub>2</sub> with quantitative selectivity and good conversion, maintaining ambient conditions.

This result is remarkable since many other aluminum compounds have been investigated as catalysts for the same process, but they usually require elevated temperatures and super-atmospheric pressure of CO<sub>2</sub>.<sup>21</sup> Indeed, examples of effective aluminum compounds working at RT

and 1 atm CO<sub>2</sub> are rare.<sup>21d,45</sup> On the other hand, copper complexes have been limitedly explored in epoxide carbonation, and those proposed so far comprise elaborated ligands.<sup>46</sup>

Regarding the reaction mechanism, the PC formation by metal carbamates may proceed through to the generally accepted catalytic cycle, involving initial coordination of the epoxide to the metal centre, ring opening by nucleophilic attack and subsequent CO<sub>2</sub> insertion (Figure 2).<sup>47</sup> However, herein some variability might be offered by the viable CO<sub>2</sub> dynamic exchange between the carbamato ligand and free carbon dioxide (see Introduction). This “CO<sub>2</sub> pre-activation” mechanism could be involved and possibly favor the insertion step. According to the pathway in Figure 2, it is presumable that the relatively low selectivity values observed with early transition metal compounds (see Table 1, entries 1-10) is related to the strong oxophilicity of the metal centers, enhancing undesired activation of coordinated propylene oxide<sup>44</sup> and thus leading to the formation of side products, which could not be identified.

**Figure 2.** Generally accepted pathway for the cycloaddition of CO<sub>2</sub> to propylene oxide by means of a metal-based catalyst in the presence of a nucleophile (Nu<sup>-</sup>) as a co-catalyst.

## Conclusions

Metal carbamates constitute an extended family of simple compounds easily available from economic precursors, but sparsely investigated for their catalytic potential so far. Herein, we have described a systematic study on the ability of various metal carbamates, being an intrinsic form of activated CO<sub>2</sub>, to catalyze the synthesis of propylene carbonate from the appropriate epoxide and CO<sub>2</sub> under ambient conditions, as a model reaction. Also, the heterogeneous version of two chlorido-carbamates was evaluated, after implantation of the precursors on silica and characterization of the resulting solid materials. In general, the compounds resulted active in the presence of a tetrabutylammonium halide as a suitable co-catalyst, and promising results were achieved with homoleptic carbamates based on earth abundant metals such as tin, aluminum and

copper. These results compare to the challenge usually encountered in the development of simple catalytic systems based on non-precious metals operating effectively under mild conditions. We are currently working to further explore the capability of metal carbamates to exploit CO<sub>2</sub> as a synthon for organic synthesis, which might be facilitated by the previously documented dynamic exchange process between gaseous and carbamate-entrapped CO<sub>2</sub>. In this regard, mechanistic studies are also in progress.

## Experimental section

**General experimental details.** Unless otherwise stated, all operations were carried out under an atmosphere of prepurified nitrogen. The reaction vessels were oven dried at 140 °C prior to use, evacuated (10<sup>-2</sup> mmHg) and then filled with nitrogen. CO<sub>2</sub> (99.99%) was purchased from Rivoira, while organic reactants, of the highest purity available, were obtained from Sigma Aldrich or TCI Europe, and stored under nitrogen atmosphere as received.

M(O<sub>2</sub>CNEt<sub>2</sub>)<sub>4</sub> (M = Ti, Zr, Hf),<sup>48</sup> MCl<sub>2</sub>(O<sub>2</sub>CNEt<sub>2</sub>)<sub>2</sub> (M = Ti, Zr),<sup>30</sup> M(O<sub>2</sub>CNR<sub>2</sub>)<sub>5</sub> (M = Nb or Ta, R = Me, Et),<sup>49</sup> NbO(O<sub>2</sub>CNEt<sub>2</sub>)<sub>3</sub>,<sup>50</sup> Cu(O<sub>2</sub>CNEt<sub>2</sub>)<sub>2</sub>,<sup>51</sup> Ag(O<sub>2</sub>CNMe<sub>2</sub>),<sup>52</sup> Al(O<sub>2</sub>CN<sup>i</sup>Pr<sub>2</sub>)<sub>3</sub>,<sup>32</sup> Si(O<sub>2</sub>CNEt<sub>2</sub>)<sub>4</sub><sup>32</sup> and Sn(O<sub>2</sub>CNEt<sub>2</sub>)<sub>4</sub><sup>53</sup> were prepared according to literature procedures. Commercial silica (Grace, SD 3217/50; surface area = 318 m<sup>2</sup> g<sup>-1</sup>, pore volume = 2.22 cm<sup>3</sup> g<sup>-1</sup>) was treated at 160 °C for 12 h under vacuum (ca. 0.01 mmHg) to eliminate the physisorbed water and then stored in flame-sealed vials under argon atmosphere. The total silanol content (3.4 mmol g<sup>-1</sup>) was assumed to correspond to the weight loss (as water) by calcination at 850 °C. Solvents (Sigma Aldrich), diethylamine and mesitylene were distilled before use over appropriate drying agents.

Infrared spectra were recorded at room temperature on a FTIR-Perkin Elmer Spectrometer, equipped with a UATR sampling accessory. NMR spectra were recorded at 298 K on a Bruker Avance II DRX400 instrument equipped with a BBFO broadband probe; values of selectivity and conversion were evaluated on <sup>1</sup>H NMR spectra using mesitylene as internal standard. Carbon, hydrogen and nitrogen analysis was performed on a Vario MICRO cube instrument (Elementar).

SEM/EDS analysis was performed on a SEM-FEG Quanta 450, with an accelerating voltage of 15 kV. The images were collected using a backscattered electron detector. The sample powders were deposited on a conductive tape before the introduction in the high vacuum chamber. EDS analysis was performed with a Quanta XFlash EDS detector to obtain local metal-to-silicon and metal-to-chloride atomic ratios for the two samples. ICP-OES analysis of the Silicon, Titanium and Zirconium content in the samples was performed with an Ar plasma spectrometer ICP Perkin Elmer Optima 2000 OES DV.

### **Synthesis and characterization of $[\text{Al}(\text{O}_2\text{CNEt}_2)_3]_n$ .**

A solution of  $\text{Al}(\text{O}_2\text{CN}^i\text{Pr}_2)_3$ <sup>32</sup> (0.85 g, 0.92 mmol) in toluene (50 mL) in a round-bottom flask was treated with  $\text{NHEt}_2$  (1.91 mL, 18.5 mmol). The flask was evacuated and filled with  $\text{CO}_2$  at atmospheric pressure. The mixture was stirred at room temperature for 72 h. Afterwards, the volatiles were removed, and the resulting residue was washed with pentane (2 x 20 mL) and then dried under vacuum at room temperature. A colorless solid (0.61 g, 87%) was obtained, sensitive to moisture and almost insoluble in hydrocarbons and in halogenated solvents. Anal. Calc. for  $\text{C}_{15}\text{H}_{30}\text{AlN}_3\text{O}_6$ : C, 48.0; H, 8.1; N, 11.2. Found: C, 48.1; H, 8.0; N, 10.8. IR (solid state):  $\nu = 2960\text{w}$ ,  $2932\text{w}$ ,  $2870\text{vw}$ ,  $1553\text{m-s}$ ,  $1504\text{vs}$ ,  $1457\text{w-m}$ ,  $1433\text{m-s}$ ,  $1375\text{wm}$ ,  $1321\text{s}$ ,  $1227\text{w}$ ,  $1073\text{m-sh}$ ,  $977\text{w-m}$ ,  $939\text{w}$ ,  $799\text{s cm}^{-1}$ .

### **Reactions of $\text{TiCl}_2(\text{O}_2\text{CNEt}_2)_2$ and $\text{ZrCl}_2(\text{O}_2\text{CNEt}_2)_2$ with amorphous silica.**

**a) Preparation of Si-Ti.** Silica (0.869 g) was suspended in 40 mL of toluene and added of  $\text{TiCl}_2(\text{O}_2\text{CNEt}_2)_2$  (0.127 g, 0.36 mmol, OH/M molar ratio = 8.2). The mixture was stirred at 25 °C for 20 h and then filtered. The recovered pale-yellow solid was washed with toluene (2 x 10 mL) and dried under vacuum for 3h at room temperature. Final titanium content (from ICP analysis) = 2.18%.

**b) Preparation of Si-Zr.**  $\text{ZrCl}_2(\text{O}_2\text{CNEt}_2)_2$  (0.090 mg, 0.23 mmol) was added to a suspension of silica (0.590 g, OH/M molar ratio = 8.8) in toluene (30 mL). The mixture was stirred at 25°C for 10 h and then filtered. The recovered pale grey solid was washed with toluene (2 x 5 mL) and dried under vacuum at room temperature. Final zirconium content (from ICP analysis) = 3.29%.

### **Reaction between propylene oxide and carbon dioxide.**

The appropriate amounts of catalyst and co-catalyst were introduced into a Schlenk tube, which was evacuated by a vacuum pump and then filled with  $\text{CO}_2$ . The vacuum/ $\text{CO}_2$  sequence was repeated twice. Propylene oxide (1 mL) was added under a stream of carbon dioxide, and the resulting mixture was stirred for 24 hours at room temperature and atmospheric pressure. A carefully measured amount of mesitylene as internal standard (ca. 0.3 mL) was added, and an aliquot (ca 0.1 mL) of the mixture was mixed with  $\text{CDCl}_3$  (0.5 mL) in a NMR tube under nitrogen atmosphere. Selectivity and conversion values were determined by  $^1\text{H}$  NMR spectroscopy and are referred to mesitylene.

### **Supporting Information**

Attempted procedures to synthesize phosphorus carbamates, IR spectrum of the precipitate obtained from the reaction of  $\text{AlBr}_3$  with diethylamine and  $\text{CO}_2$  in toluene (Figure S1),  $^1\text{H}$  NMR spectrum of the mixture  $\text{PO}/\text{CO}_2/\text{Al}(\text{O}_2\text{CNEt}_2)_3/\text{TBAC}$  (Figure S2), and SEM image of **Si-Zr** (Figure S3).

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