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Metal *N,N*-dialkylcarbamates as easily available catalytic precursors for the carbon dioxide/propylene oxide coupling under ambient conditions

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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 propylene oxide (PO) and CO$_2$. By operating at atmospheric CO$_2$ pressure at ambient temperature, excellent results were achieved using Ti(O$_2$CNEt$_2$)$_4$, Al (O$_2$CNR$_2$)$_3$ (R = Et, [i]Pr), Cu(O$_2$CNEt$_2$)$_2$ and Sn(O$_2$CNEt$_2$)$_4$, in combination with NBu$_4$X (X = Br or Cl) as a co-catalyst. The reactions of MCl$_2$(O$_2$CNEt$_2$)$_2$ (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.

1. Introduction

Carbon dioxide is a largely available and economic chemical feedstock that, in principle, could be conveniently used to synthesize valuable organic compounds [1]. Indeed, diverse reactions conceived to convert carbon dioxide into diverse 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 [2] (Scheme 1). 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 [3], electrolytes for lithium-ion batteries [4], intermediates to access high value-added products [5], and monomers for constructing polycarbonates [2,6].

A variety of catalysts which proved to be efficient in combining epoxides and CO$_2$ to obtain cyclic carbonates have been developed: they include metal organic frameworks (MOF) [7], metal complexes usually comprising porphyrin and Schiff bases as ligands [8], ammonium [9] or phosphonium salts [10], ionic liquids [11], organocatalysts [12].

In alignment with the Green Chemistry approach [13], the catalyst is expected to be simple and obtainable from non expensive precursors [14], and, when dealing with a metal-based catalyst, earth abundant and non-toxic metal elements are highly desired [15]. In alignment with these ideas, various compounds have been investigated as catalysts in the CO$_2$/epoxides coupling, [16] including titanium [17], niobium [9a,18] iron [19], zinc [19b,20], aluminum, [21] tin [22], and gold [23] derivatives. However, high temperatures (70–140 °C) and compressed CO$_2$ (p = 5–50 bar) are usually required to achieve satisfying conversions; otherwise, catalysts working under mild conditions (pCO$_2$ = 1 bar, T < 70 °C) are relatively rare [20d,22b,24].

Metal *N,N*-dialkylcarbamates have the general formula M(O$_2$CNR$_2$)$_n$ (R = alkyl group), and can be synthesized by the one pot reaction of metal halides (usually chlorides) with dialkylamines and CO$_2$ at atmospheric pressure (Eq. 1) [25]. 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$_2$CNR$_2$)$_n$ have been obtained with reference to a wide number of metal elements across the periodic table [25].

$$MX_n + n\,CO_2 + 2n\,NHR_2 \rightarrow M(O_2CNR_2)_n + n\,(NH_2R_2)X \qquad (1)$$
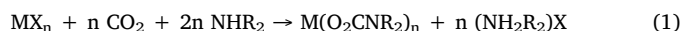
Some metal carbamates have been proved to promote different organic reactions such as the hydrogenation [26] and the polymerization of alkenes, [27] and the polymerization of cyclic esters. [28] In spite of this versatility, the employment of metal carbamates in catalysis has been limitedly explored and, for instance, the possible activity in CO$_2$
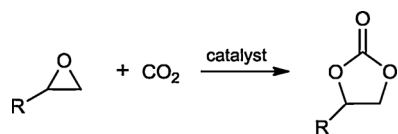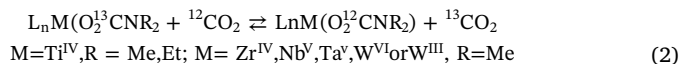
Scheme 1. Synthesis of cyclic carbonate using CO_2 and epoxide as starting materials.
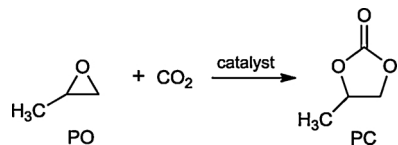
Scheme 2. Solventless formation of propylene carbonate from CO_2 and propylene oxide.

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 [29], 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 [25].

$$L_nM(O_2^{13}CNR_2 + {}^{12}CO_2 \rightleftarrows LnM(O_2^{12}CNR_2) + {}^{13}CO_2$$
$$M=Ti^{IV}, R = Me,Et; M= Zr^{IV}, Nb^V, Ta^v, W^{VI} orW^{III}, R=Me \quad (2)$$

We decided to screen a series of metal carbamato complexes, based on various, non-precious metal (or semi-metal) elements, to test them as homogeneous catalysts for 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) [30], which were supported on silica.

2. 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 [31], 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 produced in very low yield from $AlBr_3/NHEt_2/CO_2$ in toluene (see Fig. 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 [32]. 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) [33].

$$n \, AlBr_3 + 3n \, CO_2 + 6n \, NHEt_2 \rightarrow [Al(O_2CNEt_2)_3]_n + 3n \, (NH_2Et_2)Br \quad (3)$$
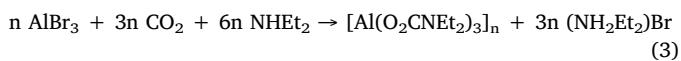
Therefore, $[Al(O_2CNEt_2)_3]_n$ was synthesized through a metathesis reaction, consisting in the treatment of $Al_2(O_2CN^iPr_2)_6$ with $NHEt_2$ in toluene under CO_2 atmosphere Eq. (4) [25].

$$n \, Al_2(O_2CN^iPr_2)_6 + 6n \, NHEt_2 \xrightarrow{CO_2} 2[Al(O_2CNEt_2)_3]_n + 6n \, NH^iPr_2 \quad (4)$$

The IR solid state spectrum of the novel aluminum diethylcarbamate displays diagnostic, strong absorptions ascribable to the C=O stretching vibrations of both bidentate and bridging carbamato ligands [25].

In order to extend the series of investigated catalysts, we tried to synthesize phosphorus(V) *N,N*-dialkylcarbamates. These complexes

Table 1

Propylene carbonate formation (Scheme 2) via metal *N,N*-dialkylcarbamates.

	Catalytic precursor	Conversion [%][a]	Selectivity [%][b]
1	$Ti(O_2CNEt_2)_4$	37	73
2	$TiCl_2(O_2CNEt_2)_2$	69	75
3	$Zr(O_2CNEt_2)_4$	35	71
4	$ZrCl_2(O_2CNEt_2)_2$	46	68
5	$Hf(O_2CNEt_2)_4$	42	67
6	$Nb(O_2CNMe_2)_5$	37	38
7	$Nb(O_2CNEt_2)_5$	10	30
8	$NbO(O_2CNEt_2)_3$	26	58
9	$Ta(O_2CNMe_2)_5$	22	64
10	$Ta(O_2CNEt_2)_5$	30	40
11	$Cu(O_2CNEt_2)_2$	18	> 99
12	$Ag(O_2CNMe_2)$	30	< 5
13	$Al(O_2CNEt_2)_3$[c]	31	77
14	$Si(O_2CNEt_2)_4$	50	16
15	$Sn(O_2CNEt_2)_4$	46	> 99
16	$TiCl_2(O_2CNEt_2)_2\equiv SiO_2$, **Si-Ti**[d]	27	56
17	$ZrCl_2(O_2CNEt_2)_2\equiv SiO_2$, **Si-Zr**[d]	40	63

Propylene oxide (1 mL, 14.3 mmol), catalyst 1 mol%, TBAB 1 mol%, T = 25 °C, pCO_2 = 1 atm, t = 24 h.
[a] By ^{1}H NMR [35].
[b] vs. PC; selectivity towards polypropylene carbonate in parenthesis.
[c] Ref. [36].
[d] Complex supported on silica, M = 0.5 mol %.

were never reported in the literature, while analogous P(III) systems are known [34]. However, our attempts did not allow the clean isolation of products. In general, the reactions of PCl_5 or $POCl_3$ with secondary amines, in the presence of CO_2, proceeded with P^V to P^{III} reduction affording inseparable, highly hygroscopic mixtures of $[PO_2Cl_2]^-$ ammonium salts and, presumably, *P*-carbamato species (see Supporting Information for details).

The preliminary catalytic tests were conducted at 25 °C and 1 atm CO_2 pressure, during 24 h and using the bromide of tetrabutylammonium as co-catalyst (Table 1, entries 1–15).

All the catalytic systems afforded PC with low to moderate conversion of PO and variable selectivity values. The by-products occurring with low selectivity could not be unambiguously identified, since these species give raise to very broad signals in the NMR spectra. However, the formation of polyethers [37] and of cyclic carbamates might be hypothesized; in principle, the latter species may be generated due to released amine from some decomposition of carbamato fragments. 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 $MCl_2(O_2CNEt_2)_2$ (M = Ti, Zr) on amorphous silica [25,38,39]. The implantation process is shifted to products because of the dissociation of carbon dioxide from the carbamato group, and is represented in Eq. (5) with reference to a generic homoleptic reactant.

$$M(O_2CNR_2)_n + \equiv Si(OH) \rightarrow \equiv SiO-M(O_2CNR_2)_{n-1} + CO_2 + NHR_2 \quad (5)$$
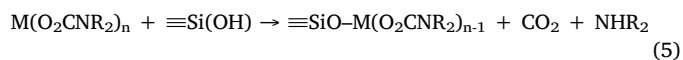
The functionalized silica powders (**Si-Ti** and **Si-Zr**) were characterized [40] by ICP-OES and EDS, joint to SEM. The two techniques provide complementary information: the former supplied us the average metal-to-silicon ratio, while SEM/EDS allows for a semi-quantitative determination of the elemental composition in selected areas of the sample, including the evaluation of the chlorine content, otherwise not possible through ICP-OES.