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(n-Bu$_2$Sn)$_2$O(CO$_3$): An active, robust and recyclable organotin(IV) for the direct synthesis of linear organic carbonates from carbon dioxide and alcohols

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Organotin(IV) compounds are known to promote the direct synthesis of organic carbonates from carbon dioxide and alcohols. In the past, structural studies have highlighted that the carbonato moiety is a recurring ligand of tin species collected during CO_2 pressurized reactions. In a mimetic approach and in order to achieve an available and recyclable precursor, the title compound (n-Bu$_2$Sn)$_2$O(CO$_3$) (**1**) was prepared in a single step by reacting commercial di-n-butyltin dichloride with an aqueous solution of sodium carbonate. Compound **1** was characterized using infrared spectroscopy and thermogravimetric and elemental analyses. Multinuclear NMR investigations in solution were also conducted. Compound **1** was then evaluated for the direct carbonation of alcohols (methanol, ethanol, n-butanol and isopropanol) under CO_2 pressure. Recycling experiments were performed showing the efficient reuse of **1** without loss of activity. Furthermore, the infrared fingerprint of **1** was preserved even after several runs demonstrating a good stability. The effects of pressure and of reaction time on dimethyl carbonate formation were also studied.

KEYWORDS
alcohol conversion, carbon dioxide utilization, carbonato complex, diorganotin(IV), linear organic carbonates
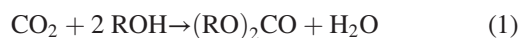
1 | INTRODUCTION

The past two decades have witnessed a steadily growing interest in the chemical transformation of carbon dioxide (CO_2) into chemicals with higher added value. The large number of review articles published on this field in recent years[1] as well as the periodic organization of several international events[2] reflect the strong attention and involvement of the scientific community worldwide. Considered initially as a waste, in particular partially responsible for the greenhouse effect, CO_2 is increasingly seen as a potential valuable raw material. Thus, with the depletion of fossil fuels, CO_2 can be considered as a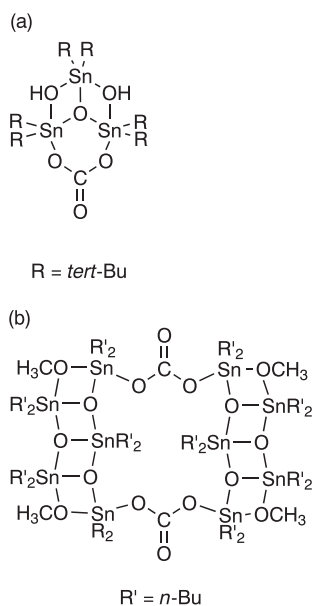n alternative and abundant source of carbon, acting as C1 building blocks. To date a wide range of CO_2-based syntheses have been identified leading to several classes of commodity chemicals, some of which have been produced at an industrial scale for a long time.

Organic carbonates, (RO)$_2$CO, also called carbonic esters, represent historical target molecules of the concept of CO_2 utilization, often considered as a case study. They are classified in three groups. Depending on the nature of R, they can be linear, cyclic or polymeric. Highly oxygenated and polar, organic carbonates are considered as environmentally friendly and used for various types of applications. Dialkyl carbonates are increasingly used as solvents in organic synthesis and homogeneous catalysis, taking advantage of their green

character.[3] Conventionally organic carbonates are prepared from hazardous reactants such as phosgene and carbon monoxide. The alternative routes involving CO_2 are particularly attractive in terms of green chemistry and atom economy. While the synthesis of cyclic carbonates by reacting oxiranes with CO_2 has been widely studied and is now well documented,[4] the direct synthesis of linear organic carbonates from alcohols and CO_2 still arouses a strong interest from academic groups and continues to be a real challenge. In this context and from an organometallic chemistry point of view, organotin(IV) compounds have been recognized for a long time as efficient precursors for the transformation of CO_2 into linear alkyl carbonates (equation (1)).

$$CO_2 + 2\,ROH \rightarrow (RO)_2CO + H_2O \qquad (1)$$

Since the preliminary work of Kizlink during the 1990s,[5] several groups have reported the beneficial use of tin complexes for carbonate synthesis, directly in solution[6] or grafted on various supports.[7] Furthermore, organotin(IV) compounds are also known to be effective for the CO_2-based synthesis of 2-oxazolidones[8] and carbamates.[9] In our group, we especially focused on diorganotin(IV) alkoxides $R_2Sn(OR')_2$ (R = n-Bu, tert-Bu, Bz; R′ = Me, Et, iPr). We studied in particular the CO_2 insertion into the Sn—OR bond and the assisting role of these complexes in the direct carbonation of alcohols (equation 1).[10] Recently we supported mechanistic insights by high-pressure NMR spectroscopy studies in a sapphire tube.[11]
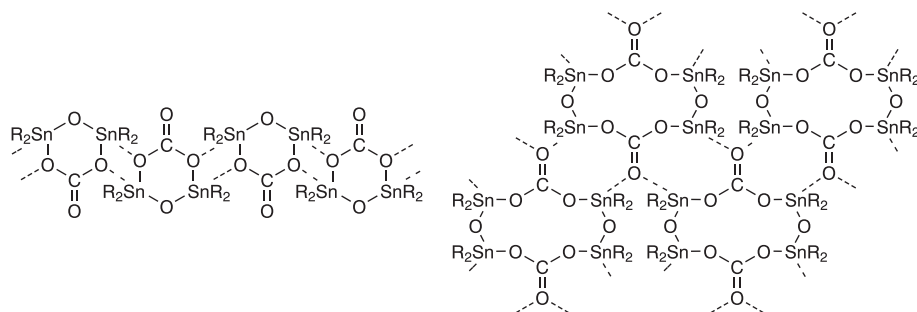
Interestingly, when dialkoxide diorganotin(IV) compounds are used as precursors, we characterized using X-ray diffraction analysis and during recycling experiments unexpected structures of polynuclear oxodiorganotin(IV) complexes bearing carbonato ligands.[12] Two of them obtained for the di-tert-butyl and di-n-butyl derivatives, respectively, are depicted in Scheme 1. Moreover, solid-state ^{119}Sn NMR investigations conducted on insoluble organotin residues collected from high-pressure reactions have led to the suggestion of the formation of cross-linked networks based on a central contribution of the carbonato ligands (Scheme 2).[13] Thus, organotin carbonates occupy a preponderant place in tin-catalysed organic carbonate synthesis.

Based on these previous experimental results and with the aim of a mimetic approach, we seek to develop a simple, robust and recyclable precursor for the direct synthesis of linear dialkyl carbonates from alcohols and CO_2. We report in this paper the preparation, the characterization and the evaluation of the activity of $(n\text{-}Bu_2Sn)_2O(CO_3)$ (1) for the direct carbonation of various primary alcohols.
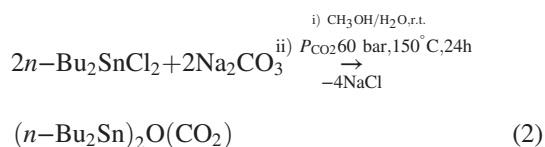
2 | RESULTS AND DISCUSSION

2.1 | Synthesis and characterization of 1

The preparation and characterization of carbonate derivatives of organotin complexes were initially studied from the 1960s to 1980s.[14] Since then, and due to the growing interest in CO_2 activation, several compounds have been isolated as single crystals and their structures have been fully resolved. In general the carbonato ligand exhibits μ_2-O,O′[15] and μ_3-O,

SCHEME 1 Molecular representations of (a) [OC(OSn-tert-Bu$_2$)$_2$O·tert-Bu$_2$Sn(OH)$_2$][12] and (b) (n-Bu$_2$SnO)$_6$[(n-Bu$_2$SnOCH$_3$)$_2$(CO$_3$)]$_2$[12] which were obtained during recycling experiments and isolated at room temperature as single crystals from methanolic solutions

SCHEME 2 Possible arrangements of oxycarbonate-based networks (R = n-Bu)[13]

O', O''[16] coordination modes, linking distinct tin atoms and leading to the formation of polynuclear and polymeric structures. Rare examples of organotin carbonates with terminal CO_3 moiety have been recently reported by Jambor and coworkers for mononuclear tin complexes.[17] In 1976, Goel and co-workers reported the synthesis and the characterization of $(Me_2Sn)_2O(CO_3)$, which was obtained by reacting an aqueous solution of potassium carbonate with an acetone solution of dimethyltin dichloride.[14] Interestingly, previously we concluded on the basis of solid-state NMR experiments that the tin residue collected from the direct carbonation of alcohols was related to the oxycarbonate structure advanced by Goel.[13] Therefore, we decided to prepare the *n*-butyl analogue of $(Me_2Sn)_2O(CO_3)$ by adding an aqueous solution of sodium carbonate to a methanolic solution of di-*n*-butyltin dichloride (equation 2).

$$2n-Bu_2SnCl_2 + 2Na_2CO_3 \xrightarrow[-4NaCl]{\substack{\text{i) } CH_3OH/H_2O, \text{r.t.} \\ \text{ii) } P_{CO_2} 60 \text{ bar}, 150°C, 24h}}$$

$$(n-Bu_2Sn)_2O(CO_2) \qquad (2)$$

The initial procedure of Goel was modified by keeping the reaction mixture under CO_2 pressure for 24 h (see Section 2). Indeed, we observed experimentally that the conditions used for the synthesis of $(Me_2Sn)_2O(CO_3)$ (CO_2-saturated acetone solution) were insufficient for the preparation of **1**.

TABLE 1 Elemental analyses of several batches of **1**

	Batch 1	Batch 2	Batch 3	Theoretical values[a]
Carbon (%)	37.69	37.68	37.61	37.68
Hydrogen (%)	7.02	6.70	7.50	6.70

[a]Calculated for $C_{17}H_{36}O_4Sn_2$.

Thus, the infrared (IR) spectra recorded from the material synthesized according to Goel's conditions showed that the carbonate bands ($\nu_{as}CO_3$ and ν_sCO_3) exhibited much lower intensities than expected (Figure S1a). In addition, decarbonation occurs rapidly from 100 °C (Figure S1b). A CO_2 pressure treatment was found to be beneficial leading to IR data consistent with Goel's description. Finally, **1** was obtained as a white solid which turns out to be insoluble in most common organic solvents. Several batches were synthesized with yields in the range of 35–45%. Elemental analyses confirm the reproducibility of **1** and are in agreement with the expected theoretical formula (Table 1). The tin content of one of the batches was also determined using inductively coupled plasma atomic emission spectrometry (ICP-AES) and matches satisfactorily with $C_{17}H_{36}O_4Sn_2$ (found: Sn = 45.95%; calculated: Sn = 43.82%).

The IR spectrum of a fresh sample of **1** (ATR mode), dried under vacuum at room temperature (Figure S2a), also corroborates the organotin oxycarbonate structure. The *n*-butyl chains are distinctly identified by the vibration bands located in the range 2900–3000 cm^{-1} (ν_{C-H}). The carbonate function is recognizable by the two large bands at 1507 and 1371 cm^{-1}, and corresponding to asymmetric and symmetric ν_{CO3} stretching elongations, respectively. In the past, comparable values which characterize bridging carbonate groups were reported by Goel for $(Me_2Sn)_2O(CO_3)$.[14] The bands in the 500–650 cm^{-1} region reflect Sn—O bonds. Increasing the temperature during the drying stage does not induce significant changes in the structure of **1**, the infrared fingerprints remaining strictly comparable (Figures S2b and S2c). However, at 150 °C the spectrum undergoes substantial transformations. The characteristic absorptions of the carbonate function disappeared leading unambiguously to the formation of di-*n*-butyltin oxide (Figure S2d).

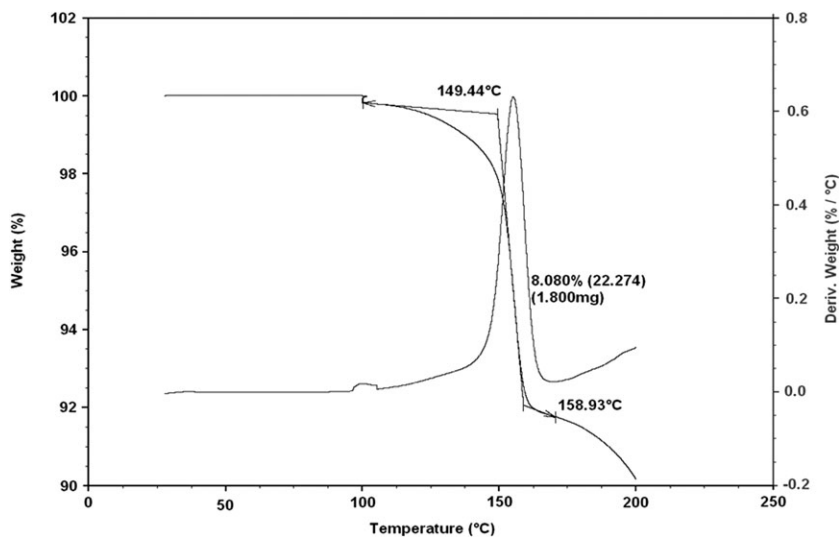The thermogravimetric analysis (TGA) of **1** was carried out under nitrogen atmosphere at a heating rate of 5 °C min^{-1}

FIGURE 1 TGA and differential TGA of **1** focusing on the loss of CO_2

(Figure 1). A major weight loss of 8% is recorded in the range 149–160 °C, which can be attributed to the release of CO_2. The loss of CO_2 calculated for **1** is 8.12 wt% which is very close to the loss observed experimentally. This analysis supports also the formula of **1**.

The characterization of **1** was also undertaken using multinuclear NMR measurements in solution. Despite a very low solubility, ^1H NMR, $^{13}C\{^1H\}$ NMR and $^{119}Sn\{^1H\}$ NMR data could be collected from a solution of **1** in CD_3OD (in the presence of CO_2). The ^1H NMR and $^{13}C\{^1H\}$ NMR spectra depicted in Figures S3 and S4, respectively, show the characteristic signals of the *n*-butyl chains linked to Sn. Two sets of signals are observed in the $^{13}C\{^1H\}$ NMR spectrum. A $^1J_{CSn}$ coupling of the order of 600 Hz could also be measured. In addition, a weak signal visible at 160.1 ppm can be assigned to the carbonyl group of the carbonate moiety. In the $^{119}Sn\{^1H\}$ NMR spectrum (Figure S5), two resonances (broad signals) located at −173.5 and −205.6 ppm are detected, exhibiting a 1:1 relative integration. Such chemical shifts suggest the presence of tin atoms in a pentacoordinate environment. The involvement of the carbonato ligands in intermolecular interactions is assumed, which probably leads to the formation of polymeric structures (explaining the difficulties encountered for the solubilization of **1**).

2.2 | Synthesis of linear organic carbonates

Firstly, **1** was employed as precursor for the synthesis of dimethyl carbonate (DMC) from methanol and CO_2 (equation 1, R = Me). The reaction was carried out at 150 °C, under a pressure of 200 bar for 24 h. As expected, **1** is active for DMC synthesis showing an almost complete selectivity (Figure 2, run 1). After separating the volatiles by a trap-to-trap distillation (MeOH, DMC), the tin-based residue can be reused efficiently for several runs in the presence of new charges of methanol (20 ml) and CO_2 (Figure 2, runs 2–7). The amount of DMC increases even slightly compared to the first run. However, no conversion of DMC was noted in the absence of tin residue. The same observation was made using only Na_2CO_3 as precursor. The activity of di-*n*-butyltin carbonate was also tested in the presence of 2,2-dimethoxypropane (DMP), used as a dehydrating agent. DMP, which is an acetal, is known to react *in situ* with the water formed, thus promoting the displacement of the carbonation reaction to the right.[18] Acetone, resulting from the hydrolysis of DMP, proves to be inert to the carbonation reaction. However, a significant effect was observed on the amount of DMC (Figure 2, run 5) which is growing even more with a longer reaction time (Figure 2, run 6).

At the end of each run, the IR fingerprint of the tin-based residues was recorded and compared to **1**. Interestingly, as demonstrated in Figure S6, the spectra are very similar. Thus, **1** does not undergo significant changes during the successive runs and is recovered without alteration. Elemental analyses also support the preservation and the stability of **1** (Table 2).

In the presence of DMP, IR spectra of the residues highlight a noteworthy evolution (Figures S7a and S7b). In addition to the spectrum of **1**, three additional bands appear at 2804, 1539 and 1062 cm^{-1} and can be attributed to ν_{OC-H},

TABLE 2 Elemental analyses of tin residues

	Run 2	Run 3	Theoretical values[a]
Carbon (%)	37.61	37.48	37.68
Hydrogen (%)	6.63	7.53	6.70

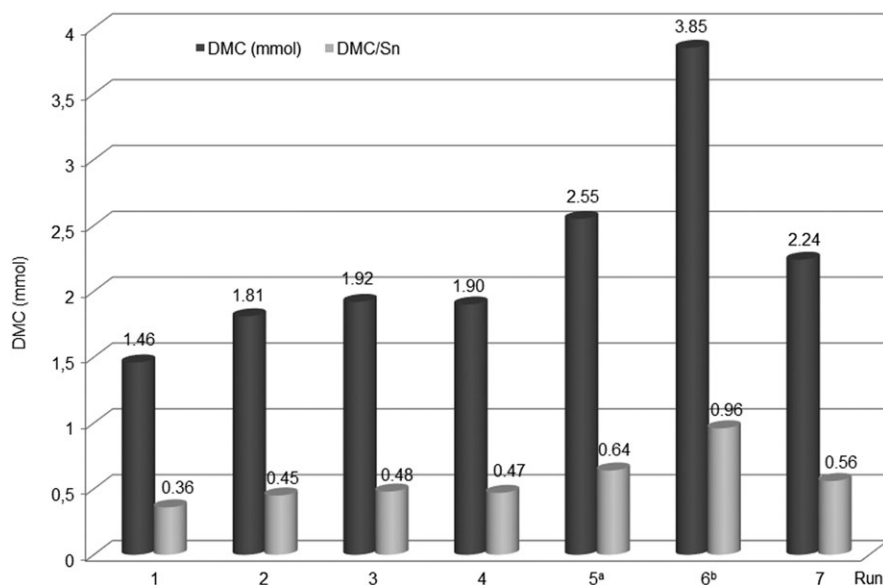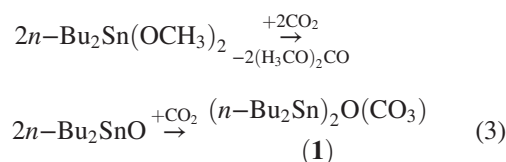[a]Calculated for $C_{17}H_{36}O_4Sn_2$.

FIGURE 2 Recycling experiments. Reaction conditions: 20 ml of MeOH, 4 mmol of **1** (run 1), reaction temperature of 150 °C, pressure of 200 bar, reaction time of 24 h. [a]Addition of 10 mmol of DMP. [b]Addition of 10 mmol of DMP, reaction time 48 h

ν_{CO3} and ν_{O-C} absorptions, respectively. They remarkably match with the signature of the deca-tin compound, $(n\text{-}Bu_2SnO)_6[(n\text{-}Bu_2SnOCH_3)_2(CO_3)]_2$, depicted in Scheme 1 and fully characterized in the past.[13,12] $(n\text{-}Bu_2SnO)_6[(n\text{-}Bu_2SnOCH_3)_2(CO_3)]_2$ consists of two pentameric ladders, $(n\text{-}Bu_2Sn)_5O_5$, bridged by two carbonato ligands. Four bridging methoxy groups are located at each corner of the framework and the alkyl chains are located on either side of the inorganic plane. Tin residues collected in runs 5 and 6 contain both species, **1** and $(n\text{-}Bu_2SnO)_6[(n\text{-}Bu_2SnOCH_3)_2(CO_3)]_2$. In terms of DMC produced, the mixture leads to a concomitant benefit. A better activity is observed (Figure 2, runs 5 and 6). In addition to the dehydration action of DMP, this can be explained by the *in situ* formation of Sn—OCH$_3$ bonds which are known to exhibit a great reactivity towards CO_2 and leading to hemicarbonate moieties (Sn—OC(O)OCH$_3$).[10] Such reminiscent methoxy groups are observable in bridging positions in the structure of $(n\text{-}Bu_2SnO)_6[(n\text{-}Bu_2SnOCH_3)_2(CO_3)]_2$. Moreover, in the absence of dehydrating agent, the initial spectrum of **1** is fully recovered (Figure S7c). The characteristic IR bands of the decanuclear tin species disappear. Thus, these observations point to a direct link existing between **1** and $(n\text{-}Bu_2SnO)_6[(n\text{-}Bu_2SnOCH_3)_2(CO_3)]_2$, which implies a reversible process.

The stannane complex $n\text{-}Bu_2Sn(OCH_3)_2$ is recognized as one of the most active and selective molecular organometallic species for DMC synthesis.[19] Often considered as a reference, its reactivity towards CO_2 has been widely studied, experimentally and by modelling.[20] To assess the activity of **1**, $n\text{-}Bu_2Sn(OCH_3)_2$ was used as precursor under the same reaction conditions (150 °C, 200 bar). Using 4 mmol of $n\text{-}Bu_2Sn(OCH_3)_2$, a DMC/Sn ratio of 0.85 was found after a reaction time of 24 h. The activity of **1** is thus lower (almost half), but it has the advantage to being easily manipulated in ambient air, which is not the case with $n\text{-}Bu_2Sn(OCH_3)_2$, easily hydrolysable. Moreover, examination using IR of the collected residual material (white powder) at the end of the experiment conducted with $n\text{-}Bu_2Sn(OCH_3)_2$ exhibits very strong similarities with the fingerprint of **1** (Figure S8). The two spectra are very close, demonstrating a strong relationship between the two compounds. A possible pathway of transformation of $n\text{-}Bu_2Sn(OCH_3)_2$ into **1** is reported in equation 3, involving the *in situ* formation of $n\text{-}Bu_2SnO$.

$$2n\text{-}Bu_2Sn(OCH_3)_2 \xrightarrow[-2(H_3CO)_2CO]{+2CO_2}$$

$$2n\text{-}Bu_2SnO \xrightarrow{+CO_2} \underset{(\mathbf{1})}{(n\text{-}Bu_2Sn)_2O(CO_3)} \quad (3)$$

In parallel with these experiments, the optimization of reaction conditions was conducted. The influences of pressure and reaction time on DMC formation were successively investigated. As shown in Figure 3, the DMC yield was found to increase linearly with the pressure. Previously, this strong effect of the pressure on the reaction was also observed by Sakakura and co-workers when using $Bu_2Sn(OCH_3)_2$ as tin precursor. Pressures above 1000 bar were then tested.[19] In our case and because of the limitations of our equipment it was not possible to continue beyond 200 bar. However, the impact is already significant. The influence of reaction time on the amount of DMC was also studied (Figure 4). From 15 h, the activity slows and reaches a plateau beyond 20 h of reaction. Thus, a duration of 24 h has been selected as the optimum reaction time.

The initial aim of this work was also to design a versatile tin precursor for the synthesis of linear dialkyl organic carbonates. Therefore the activity of **1** was extended to the direct carbonation of higher alcohols: (i) ethanol, (ii) *n*-butanol and
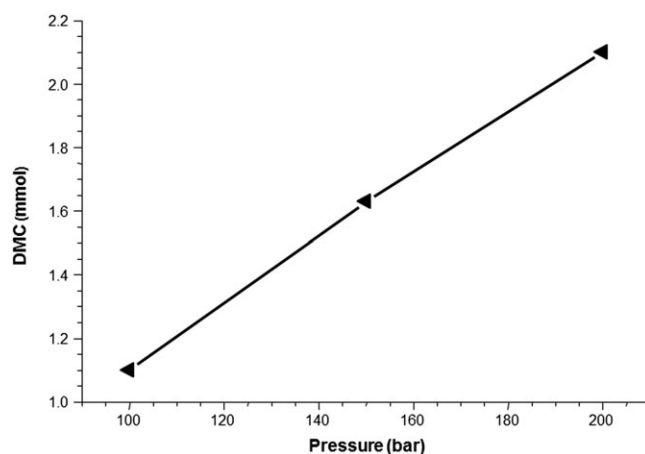
FIGURE 3 Effect of pressure on amount of DMC. Reaction conditions: 20 ml of MeOH, 4 mmol of **1**, reaction temperature of 150 °C, reaction time of 24 h
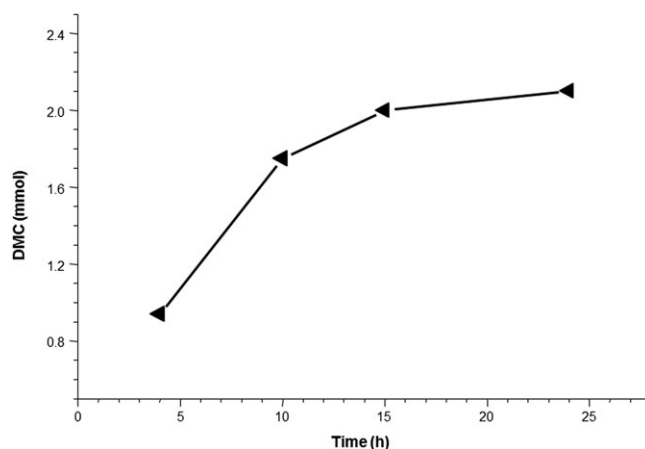
FIGURE 4 Effect of reaction time on amount of DMC. Reaction conditions: 20 ml of MeOH, 4 mmol of **1**, reaction temperature of 150 °C, pressure of 200 bar

(iii) isopropanol. The corresponding amounts of diethyl carbonate (DEC), di-*n*-butyl carbonate (DBC) and di-isopropyl carbonate (DIPC) are shown in Figure 5 and compared to that of DMC. Compound **1** is active for the conversion of ethanol into DEC but it is less effective than for the synthesis of DMC. Similarly, **1** can be efficiently recycled several times for the synthesis of DEC (Figure 6). However, the activity decreases markedly for the synthesis of DBC and is almost nil for the synthesis of DIPC. In previous studies of the synthesis of DMC,[12] we showed that the yield of carbonates was closely related to the phase diagram of the CO_2/methanol binary mixture and was closely linked to the supercritical properties of the reaction medium. Indeed, we determined experimentally and by simulation that the optimal conditions were obtained when the pressure–temperature parameters are above the critical point of the mixture (monophasic medium). One hypothesis to explain the fall in activity of **1** could be
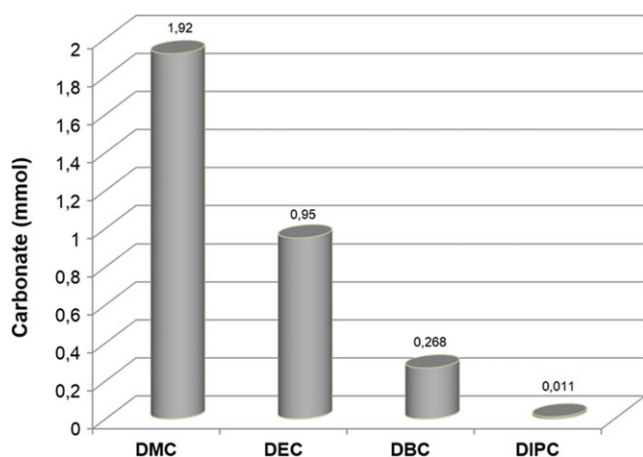
that the *P–T* conditions are not sufficient in the cases of *n*-butanol and isopropanol. These parameters should be optimized to approach the expected supercritical conditions of the mixtures. Work in this direction is currently in progress.

3 | CONCLUSIONS

We have shown that complex **1**, $(n\text{-}Bu_2Sn)_2O(CO_3)$, prepared in one step from a commercial precursor, is active under CO_2 pressure for the conversion of methanol into DMC. Recyclable several times without loss of activity, **1** has the advantage of being robust, undergoing little deterioration even after high-pressure runs. Compared to the diorganotin dialkoxide complexes, which are recognized as being the most effective promoters for the direct carbonation of alcohols, **1** is air-stable and can be stored for several months without notable modifications. Moreover, **1** is a versatile precursor and can also be used in the presence of ethanol and *n*-butanol leading to the synthesis of diethyl carbonate and di-*n*-butyl carbonate, respectively. However, **1** is not active in the presence of isopropanol. From a mechanistic point of view, the use of 2,2-dimethoxypropane has highlighted an interconnection between **1** and the decameric oxocluster $(n\text{-}Bu_2SnO)_6[(n\text{-}Bu_2SnOCH_3)_2(CO_3)]_2$. The formation of **1** was also clearly observed when $n\text{-}Bu_2Sn(OCH_3)_2$ was used as precursor. Thus, **1** can be viewed as a key intermediate. Further work is currently underway to deepen the understanding of the links existing between these species.

4 | EXPERIMENTAL

4.1 | General aspects

All manipulations were carried out using standard Schlenk techniques or a stainless steel reactor. Methanol, ethanol, *n*-butanol and isopropanol (Carlo Erba, RPE grade) were dried with suitable drying agents and distilled under argon. Carbon dioxide N45 TP purchased from Air Liquide was used without further purification. $n\text{-}Bu_2SnCl_2$ (purity ≥98%), dimethyl carbonate (purity ≥99%), diethyl carbonate (purity ≥99%) and 2,2-dimethoxypropane (purity ≥98%) were purchased from Sigma-Aldrich, and were used without further purification. IR spectra were recorded using a Bruker Vector 22 equipped with a Specac Golden Gate™ ATR device. ^{1}H, NMR ^{13}C{^{1}H} NMR and ^{119}Sn{^{1}H} NMR spectra were recorded at 300 K in CH_3OD with Bruker Avance 300 MHz and 500 MHz spectrometers. [119]Sn{[1]H} chemical shifts were reported downfield from $(CH_3)_4Sn$ used as external standard. TGA was performed with a TA Instruments TGA Q500 thermoanalyser using aluminium pans. Samples were heated at a rate of 5 °C min^{-1} under flowing nitrogen gas. The gas flow rate at the sample was 60 ml min^{-1}, while

FIGURE 5 Comparison of activity of **1** for the synthesis of higher dialkyl carbonates
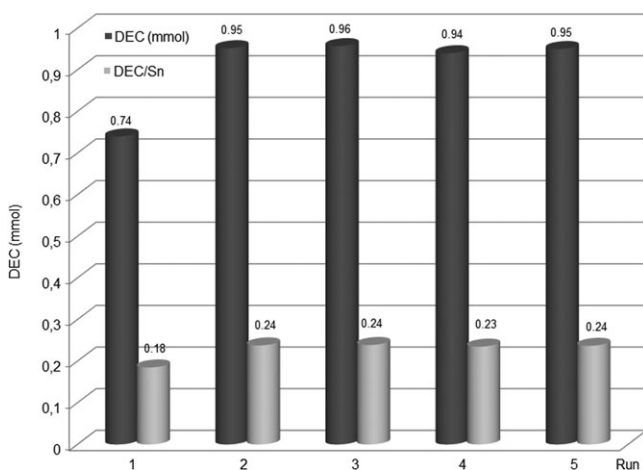

FIGURE 6 Recycling experiments. Reaction conditions: EtOH (20 ml), 4 mmol of **1** (run 1), reaction temperature of 150 °C, pressure of 200 bar, reaction time of 24 h

the balance flow rate was 40 ml min^{-1}. Weight loss percentages and onset temperatures were determined using the TA Universal Analysis 2000 software dedicated to the instrument. Elemental analyses and ICP-AES measurements were performed at the Plateforme d'Analyse Chimique et de Synthèse Moléculaire de l'Université de Bourgogne (PACSMUB) with a Fisons EA 1108 CHNS-O apparatus and a Thermo Scientific iCAP 7400 Series analyser, respectively.

4.2 | Preparation of 1

A methanolic solution of di-n-butyltin dichloride (3.09 g, 0.01 mol, 15 ml of CH_3OH) was mixed slowly with 15 ml of an aqueous solution of sodium carbonate (1.06 g, 0.01 mol). The white solid, which precipitated immediately, was then transferred to a 125 ml stainless steel reactor and the mixture was heated under CO_2 atmosphere at 150 °C for 24 h (P_{total} = 60 bar). After the reaction, the excess CO_2 was removed slowly and the resultant solid was filtered and washed several times with deionized water, then dried under vacuum at 100 °C for 3 h. The dry material was finally stored under argon atmosphere for future use.

^{1}H NMR (CD$_3$OD, 300 K, δ, ppm): 0.96 (t, $^3J_{H-H}$ = 6.7 Hz, 12H), 1.49 (m, 16H), 1.71 (m, 8H). ^{13}C{^{1}H} NMR (CD$_3$OD, 300 K, δ, ppm): 14.02, 14.07, 24.03 ($^1J_{CSn}$ = 600 Hz), 28.09, 28.29, 28.49, 28.58, 28.72, 160.12. ^{119}Sn{^{1}H} NMR (CD$_3$OD, 300 K, δ, ppm): −173.5, −205.8. IR (cm^{-1}): 2956, 2924, 2871, 2857, 1507, 1464, 1371, 1287, 1156, 1078, 869, 826, 675, 617. Anal. Calcd for $C_{17}H_{36}O_4Sn_2$ (541.88) (%): C, 37.68; H, 6.70. Found (%): C, 37.69; H, 7.02.

4.3 | High-pressure organic carbonate synthesis

4.3.1 | Safety warning

Experiments involving pressurized gases can be hazardous and must only be conducted with suitable equipment and following appropriate safety considerations.[21]

The reaction was carried out in a 125 ml stainless steel reactor equipped with a magnetic stirrer. The reactor was purged with argon and a 20 ml suspension of 1 in the required alcohols (methanol, ethanol, n-butanol or isopropanol) was introduced by syringe. Then, CO_2 was admitted to the desired amount (32 g). The reaction temperature was controlled by an internal thermocouple. After a reaction time of 24 h, the reactor was cooled to 0 °C, the pressure was gently released and the liquid phase was transferred to a Schlenk tube. Trap-to-trap distillation under vacuum at ambient temperature allowed separation of volatile compounds that were quantitatively analysed using GC (DEC external standard, Thermo Scientific FOCUS GC, TR-Wax 30 m capillary column, FID detector). The tin-based residue was characterized using IR spectroscopy and elemental analyses.

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