# Nucleophile-directed selectivity towards linear carbonates in the niobium pentaethoxide -catalysed cycloaddition of CO<sub>2</sub> and propylene oxide

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#### **1** General information

All experiments requiring inert conditions were performed under argon atmosphere using standard vacuum line and Schlenk techniques or within a glovebox containing less than 1 ppm of oxygen and water. All solvents used were obtained from a standard solvent purification system. Solvents for NMR measurements were purchased from Sigma Aldrich, dried over activated molecular sieves and degassed via freeze-pump cycles.

Commercially available compounds, NbCl<sub>5</sub> (Sigma Aldrich,  $\ge 99.9$  %), NbBr<sub>5</sub> (Strem Chemicals, 99.5 %), NbF<sub>5</sub> (Strem Chemicals, 99.5 %), [Nb(OEt)<sub>5</sub>] (Sigma Aldrich, 99.95 %), TCAP (9-Azajulolidine, Tokyo Chemical Industry, > 97.0 %), DMAP (Acros, 99 %), [Nb(NMe<sub>2</sub>)<sub>5</sub>] (Strem chemicals, 99 %) were used as received and stored in a glovebox. NBu<sub>4</sub>Br (Tetra-n-butylammonium bromide, Sigma Aldrich,  $\ge 99$  %) was molten at 100-150 °C in a Schlenk tube, stirred under vacuum for 6 h and stored in a glovebox. [NbOCl<sub>3</sub>] was prepared according to published procedure.<sup>5-1</sup> NMR spectra were recorded using Bruker DPX-400 and Bruker Avance III 400 9.4 T spectrometer (<sup>1</sup>H NMR 400.13 MHz, <sup>13</sup>C NMR 100.53 MHz) at 300 K unless otherwise stated. Chemical shifts are reported in ppm ( $\delta$ , relative to TMS) using the solvent residual peak as an internal standard. Signal multiplicities are abbreviated as: s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet). FT-IR spectra were recorded on a Varian 670 FT-IR spectrometer. *In situ* infrared spectroscopy was performed on a Mettler Toledo ReactIR 45/Multimax RB 04-50 station equipped with 50 mL stainless steel autoclaves geared with *DiComp* diamond probes at the bottom as multiple reflection ATR elements. The autoclaves were connected to a CO<sub>2</sub> cylinder through a Mettler Toledo LMPress60 pressure controller to provide gas dosage and constant pressure throughout the reaction. ESI-MS data were collected on a ThermoScientific LTQ-Velos Orbitrap mass spectrometer.

#### 2 Experimental set-up and procedures

The set-up in figure S-1 was used for the catalytic tests in Table 1, for the determination of the initial rate of PC formation and for the mechanistic investigation. The stainless steel "IR autoclave" was heated for at least 4 h at 130 °C under vacuum before each experiment.

For each experiment, 1 mmol of Nb-complex and the suitable amounts of the nucleophile were added to the reaction autoclave under a stream of argon. Subsequently, PO (7 mL, 100 mmol) was added through a syringe and the mixture stirred at 500 r.p.m. through a mechanical stirrer. CO<sub>2</sub> was dosed and kept at the desired pressure during the whole course of the experiment by the automated pressure controller. The ATR-IR spectrum of the reaction was collected every 60 s through the window at the bottom of the reaction vessel. For all reactions in this study the temperature was kept constant at 25 °C through a thermostat.



Fig. S-1 Experimental set up for the *in situ* IR measurement under constant CO<sub>2</sub> pressure.

#### **3** Optimized conditions for the synthesis of carbonate ester **1**

A Fisher Porter tube was charged with 1 mmol (318.2 mg, 0.25 mL)  $[Nb(OEt)_5]$  inside an argon filled glove box. In a separate Schlenk tube a solution of DMAP (1 mmol, 122.2 mg) and propylene oxide (50 mmol, 3.5 mL) was stirred for around 30 min to obtain a homogeneous solution. This solution was added to  $[Nb(OEt)_5]$  in the Fisher Porter tube at room temperature. The tube was quickly evacuated and CO<sub>2</sub> (2 bar) was introduced into the tube. The reaction was stirred for 5h. Thereafter, the reaction was quenched by addition of 25 mL of 1 N HCl solution and the organic material was extracted using 30 mL methylene chloride (DCM). The organic layer was washed with 25 mL of saturated NaHCO<sub>3</sub> solution. The DCM solution was dried over dry Na<sub>2</sub>SO<sub>4</sub> and filtered. The linear carbonate could be obtained after evaporation of DCM in a rotary evaporator affording of **1** 144.7 mg (0.98 mmol, 98%).

**Ethyl (1-hydroxypropan-2-yl) carbonate (1)**, <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz) δ (ppm): 4.21 (q, OCOCH<sub>2</sub>CH<sub>3</sub>, J = 7.0 Hz, 2H), 4.10, 3.99 (m, CH<sub>2</sub>OH, 2H), 4.05 (m, CH, J = 8.0, 1H), 2.30 (app s, CH<sub>2</sub>OH, 1H), 1.30 (t, OCOCH<sub>2</sub>CH<sub>3</sub>, J = 7.0, 3H), 1.19 (d, CHCH<sub>3</sub>, J = 6.25, 3H); <sup>13</sup>C{<sup>1</sup>H} (CDCl<sub>3</sub>, 100 MHz) δ (ppm): 155.30 (CO), 72.71 (CH<sub>2</sub>OH), 65.83 (CH), 64.29 (OCOCH<sub>2</sub>CH<sub>3</sub>, 18.85 (CHCH<sub>3</sub>), 14.26 (OCOCH<sub>2</sub>CH<sub>3</sub>). FT-IR (v, cm<sup>-1</sup>): 3650-3200 (v<sub>O-H</sub>), 1747 (v<sub>C=O</sub> (asymmetric)), 1250 (v<sub>C=O</sub> (symmetric)); HR-MS (ESI-MS), for C<sub>6</sub>H<sub>12</sub>O<sub>4</sub>, [M-H]<sup>+</sup>= 149.08018 was found (δ = 4 ppm).

**Byproducts:** The presence of minor amounts of side products in **1** has been noticed via NMR and ESI-MS. Products such as **S-1** and **S-2** (Fig. S-2) have been individuated as impurities by <sup>1</sup>H NMR and LC-ESI mass spectroscopy. By-product **S-1** presents the characteristic <sup>1</sup>H NMR shift of a "ether linkage" in poly(propylene carbonate) at 3.5-3.7 ppm;<sup>S-2</sup> for this compound (C<sub>9</sub>H<sub>18</sub>O<sub>5</sub>), [M-Na]<sup>+</sup> = 229.10447 ( $\delta$  = 3 ppm) was found in HR-MS (ESI-MS). By-product **S-2** represents the "dimeric form" of carbonate **1** and resembles the structure of a polymeric linear carbonate. A small signal at 4.8 ppm in the <sup>1</sup>H NMR of **1** can be correlated with this product;<sup>S-2</sup> For this compound (C<sub>10</sub>H<sub>18</sub>O<sub>7</sub>), [M-Na]<sup>+</sup> = 273.09320 ( $\delta$  = 4 ppm) was found in HR-MS (ESI-MS).



Fig. S-2 by-products formed along with linear carbonate 1, the characteristic <sup>1</sup>H NMR signals are shown.

#### 4 NMR analysis of carbonate ester 1



Fig. S-3 Structure of compound 1

The <sup>1</sup>H NMR spectrum (Fig. S-4) of **1** (See Fig. S-3 for nuclei numbering) shows a characteristic ABX<sub>3</sub> splitting for the H2 protons at 4.20 ppm. This splitting is common for ethyl groups in chiral organic molecules as these protons are diastereotopic (C4 is chiral). H5 and H5' are also non-equivalent and since they are each adjacent to 2 sets of non-equivalent protons (its partner and proton 4), they appear as a doublet of doublets at 3.99 and 4.11 ppm. The DEPT135 spectrum (Fig. S-5) shows 3 peaks in the positive region and 2 in the negative, which allows for the separation of CH, CH<sub>3</sub> (positive peaks at 65.83, 18.85, 14.25 ppm) and CH<sub>2</sub> (negative peaks at 72.71, 64.29 ppm). The HSQC experiment enabled the assignment of the proton-carbon pairs from the correlation peaks (Fig. S-6). Integration of the proton spectrum at 1.30 and 1.19 ppm accounted for 3 protons each and the splitting pattern allowed for the assignment of H1 (triplet, 1.30 ppm) and H6 (doublet, 1.19 ppm) protons. The remaining positive carbon peak in DEPT135 at 65.98 ppm was then assigned to C4, with its proton resonance appearing at 4.05 ppm (multiplet). Having paired the proton and carbon peaks from HSQC, the compound is fully elucidated. The

2D NMR (HMBC) also supports the assignment of all peaks (Fig. S-7). The NMR data are collected in table S-1.

Entry	δΗ	δC	HMBC ( <sup>1</sup> H- <sup>13</sup> C)
1	1.30	14.26	2
2	4.21	64.29	1, 3
3	-	155.30	-
4	4.05	65.83	3, 6
5	3.99	72.71	3, 4, 6
5'	4.10	72.71	3, 4, 6
6	1.19	18.85	4, 5
7	2.30	-	4, 5, 6

Table S-1. Summary of NMR data for compound 1

#### 5 Copies of NMR and IR spectra



Fig. S-4 <sup>1</sup>H NMR spectrum of 1 (CDCl<sub>3</sub>)



Fig. S-6 HSQC spectrum of 1 (CDCl<sub>3</sub>)



Fig. S-7 HMBC spectrum of 1 (CDCl<sub>3</sub>)

#### Agilent Resolutions Pro



Fig. S-8 FT-IR spectrum of 1 (DCM, r.t.)

#### 6 In situ IR experiments

The *in situ* IR experiments were carried out using the set-up in Fig. S-1; the following experiments were carried out:

## 6.1 Catalytic tests, profiles of PC formation, and determination of the initial reaction rate $(k_{obs})$ , (Table 1; Fig. 1)

In a standard experiment,  $[Nb(OEt)_{S}]$  (318.2 mg, 1 mmol) was placed in a vial inside a glovebox and PO (7 mL, 100 mmol) was added via syringe through a rubber septum. This solution and NBu<sub>4</sub>Br (644.7 mg, 2 mmol) were added to the reaction vessel in Fig. S-1 under a stream of argon at 25 °C. 1 bar CO<sub>2</sub> was introduced into the reaction autoclave and the mixture was stirred mechanically at 500 r.p.m for 4 h. The CO<sub>2</sub> pressure was kept constant during the whole course of the experiment with the losses in CO<sub>2</sub> pressure, due to conversion to PC, immediately compensated by the automated pressure regulator. The ATR-IR spectrum of the reaction was collected every 60 s through the window at the bottom of the reaction showed in all cases a linear behavior at the beginning of the process for all catalytic tests in Table 1. The slope of these lines, calculated for the first 10 minutes of the reaction, was taken as the apparent initial reaction rate ( $k_{obs}$ ). The complete profiles of PC formation for NbCl<sub>5</sub>/TBAB and for [Nb(OEt)<sub>5</sub>]/TBAB are reported in Fig. 1. After 4 h, the reactor was slowly depressurized and an aliquot of the solution was placed into a NMR tube and diluted with CDCl<sub>3</sub> in order to determine PO conversion. The conversion was determined by comparison between the integrals of the corresponding protons of PO and PC in the <sup>1</sup>H NMR of the reaction mixture as previously described.<sup>6</sup>

## 6.2 In situ IR study on the reaction between $CO_2$ and PO in the presence of $[Nb(OEt)_5]$ and DMAP (Fig. 2, Scheme 2)

[Nb(OEt)<sub>5</sub>] (318.2 mg, 1 mmol) was placed in a vial inside a glovebox and PO (7 mL, 100 mmol) was added via syringe through a rubber septum. Under a flow of argon, this solution and DMAP (122.2 mg, 1 mmol) were added at 25 °C to the reaction vessel shown in Fig. S-1. The mixture was stirred mechanically at 500 r.p.m.  $CO_2$  (1 bar) was introduced into the reactor immediately after formation of the solution of DMAP and [Nb(OEt)<sub>5</sub>] in PO or after 2 h to obtain an induction-free profile (Fig. 2). The  $CO_2$  pressure was kept constant during the whole course of the experiment at the desired value with the losses in  $CO_2$  pressure, due to conversion to PC, immediately compensated by the automated pressure regulator. The ATR-IR spectrum of the reaction was collected every 60 s through the window at the bottom of the reaction

vessel and the time-evolution of the relevant IR absorption bands in the ARS and carbonyl stretching region was monitored to afford the graphics in Fig. 2.

#### 6.3 In situ studies on the hemicarbonate species and on the effect of the CO<sub>2</sub> pressure

The same solution of  $[Nb(OEt)_5]$  and DMAP in PO and the same reaction conditions as in section 6.2 of this ESI were used. 2 h after the preparation of the solution, 0.5 bar CO<sub>2</sub> were added to the reaction autoclave and the CO<sub>2</sub> pressure in the reactor was increased stepwise up to 2.5 bar by equally spaced (20 min) increments of 0.5 bar each. Each step of increase of the CO<sub>2</sub> pressure was carried out within 1 min. By taking the spectrum of the solution measured just before the first stage of CO<sub>2</sub> addition as a background, the signals belonging to CO<sub>2</sub>, to linear carbonate **2** and to the products of CO<sub>2</sub> insertion emerge (Fig. S-9).



**Figure S-9**. IR spectrum of a PO solution of Nb(OEt)<sub>5</sub> and DMAP (both 0.14 M) at different  $P_{CO2}$  values (0.5-2.5 bar). The spectrum of the solution taken just before the addition of  $CO_2$  is used as a background.

Along the band assigned to linear carbonate **2** at 1747 cm<sup>-1</sup> and the CO<sub>2</sub> signal at 650 cm<sup>-1</sup>, new signals appear at 1675 cm<sup>-1</sup>, 1290 cm<sup>-1</sup> and in the 1000-1200 cm<sup>-1</sup> region. These bands, (1675 cm<sup>-1</sup>, 1290 cm<sup>-1</sup>, 1096 cm<sup>-1</sup>, 990 cm<sup>-1</sup>) are strongly correlated with each other as they all respond immediately to any increase of the CO<sub>2</sub> pressure (Fig. S-10) and their intensity decreases by removing CO<sub>2</sub> from the reactor (Fig.S-11), hinting at a reversible CO<sub>2</sub> insertion. This is in agreement with literature reports that have described the insertion of CO<sub>2</sub> in Nb-alkoxy bonds to yield hemicarbonates to be reversible.<sup>11</sup> According to these reports, the expected frequencies for the asymmetric and symmetric C=O stretching modes of the hemicarbonate formed following the insertion of CO<sub>2</sub> in the Nb-alkoxy bond appear at 1600 cm<sup>-1</sup>

the two bands,<sup>S-3</sup> a chelating (bidentate) binding mode of the –COO moiety on the metal center has been proposed.<sup>11a</sup> According to the previous considerations, the bands at 1675 cm<sup>-1</sup> and at 1290 cm<sup>-1</sup> can be assigned, respectively, to the asymmetric and symmetric C=O stretching in hemicarbonate **7**, while the bands at 990 cm<sup>-1</sup> and at 1096 cm<sup>-1</sup> fall in the single bond C-O stretching region. In this case, the large difference of 385 cm<sup>-1</sup> between  $v_{c=0}$ (asymm) and  $v_{c=0}$ (symm), the high IR frequency value of 1675 cm<sup>-1</sup> for  $v_{c=0}$ (asymm) and the stronger absorption intensity of  $v_{c=0}$ (symm) versus  $v_{c=0}$ (asymm) can be taken as evidences of a non-chelating (monodentate) binding mode of the –COO moiety on the metal center.<sup>S-3</sup> The calculated IR spectrum for a model hemicarbonate compound is in good agreement with the spectrum in Fig. S-9 (See section 7 of this ESI file).



**Figure S-10**. Time-evolution of the IR bands in Fig. S-9 by stepwise increases of  $P_{co2}$  (for time < 120 min,  $P_{co2} = 0$ ). The bands at 1675 cm<sup>-1</sup>, 1290 cm<sup>-1</sup>, 1096 cm<sup>-1</sup>, 990 cm<sup>-1</sup> show a comparable behavior with a marked increase in intensity following  $P_{co2}$  variations. The bands at 1747 cm<sup>-1</sup> (linear carbonate **2**) and at 830 cm<sup>-1</sup> show a linear increase in intensity, independent of the pressure applied.

We have attempted to locate the possible Nb-oxo intermediate, formed following the formation of linear carbonate **2** from hemicarbonate **7**, in the IR spectrum of Fig. S-9. According to literature reports, the IR signal relative to the Nb=O bond stretching should appear in the 800-1000 cm<sup>-1</sup> region.<sup>S-4</sup> Two main bands appear in this region at 990 cm<sup>-1</sup> and at 830 cm<sup>-1</sup>. As observed in Fig. S-10 the band at 990 cm<sup>-1</sup> shows a pressure dependent behavior that we have previously associated to the bands of hemicarbonate **7** and therefore it cannot be assigned to the Nb=O stretching (but might be covering the Nb=O stretching

signal). The weaker band at 830 cm<sup>-1</sup> forms progressively with the increase of  $P_{co2}$  but could not be unequivocally assigned to the Nb=O stretching at this stage.



**Figure S-11**. Time-evolution of some of the IR bands in Fig. S-9 by lowering the  $P_{CO2}$  in the reaction vessel. The bands at 1675 cm<sup>-1</sup>, 1290 cm<sup>-1</sup> and, 990 cm<sup>-1</sup> decrease in intensity following the release of CO<sub>2</sub>, hinting at a reversible CO<sub>2</sub> insertion. The band at 1747 cm<sup>-1</sup> (linear carbonate **2**) remains unchanged.

Finally, the evolution of the intensity of the bands at 1675 cm<sup>-1</sup> ( $v_{C=O}$  of hemicarbonate 7), 2340 cm<sup>-1</sup> ( $v_{C=O}$  of CO<sub>2</sub>) and at 1747 ( $v_{C=O}$  of linear carbonate 2) at increasing P<sub>CO2</sub> values was analyzed in order to study the correlation between the CO<sub>2</sub> pressure and the rate of formation of 2. Although the signals relative to the concentration of CO<sub>2</sub> and 7 in solution increased immediately following any increase in CO<sub>2</sub> pressure (Fig. S-12), the rate of formation of 2 did not change significantly upon variation of the CO<sub>2</sub> pressure (or concentration in solution) as observed from the slope of the profile of PC formation in each given time segment (Table S-2). This shows that the rate of formation of 2 does not depend on the CO<sub>2</sub> pressure.



Fig. S-12 In situ IR study on the relationship between CO<sub>2</sub> pressure and rate of formation of 2.

Table S-2.				
<b>Fisher</b>	Time frame	CO <sub>2</sub> pressure	slope <sup>a</sup>	
Entry	(min)	(bar)		
1	120-140	0.5	0.0008	
2	140-160	1	0.0009	
3	160-180	1.5	0.0009	
4	180-200	2	0.0009	
5	200-220	2.5	0.0009	

<sup>*a*</sup> Slope of the profile of formation of **2** in Fig. S-12 in the given time interval corresponding to a set  $CO_2$  pressure value.

#### 7 DFT calculations

Gas phase DFT calculations have been carried out to support the assignment of the IR frequencies at 1675 cm<sup>-1</sup> and at 1290 cm<sup>-1</sup> to the asymmetric and symmetric C=O stretching of hemicarbonate **7** respectively (See section 6.3). The gas-phase DFT calculations have been performed on model hemicarbonate **S-3**. The calculated coordinates and energies for **S-3** are listed in table S-3. The calculated frequencies for the asymmetric (v = 1703 cm<sup>-1</sup>) and symmetric (v = 1259 cm<sup>-1</sup>) C=O stretching of **S-3** are in good agreement with the frequencies assigned to **7** in the NMR spectrum in Fig. S-9 (Fig. S-13).



**Figure S-13.** Comparison between the calculated frequency values for the symmetric and asymmetric C=O stretching frequencies in S-3 and the corresponding frequencies (taken from the spectrum in Fig. S-9 ( $P_{CO2} = 1$  bar)) assigned to hemicarbonate **7**.

Center	Atomic	Atomic	(	Coordinates	(Angstroms)
		туре	X	1 	ــــــــــــــــــــــــــــــــــــــ
1	8	0	-2.801117	0.126507	1.684238
2	8	0	-0.652811	-1.374957	0.886753
3	8	0	-0.929300	-0.446230	-1.785121
4	8	0	-2.860425	1.378329	-0.768326
5	8	0	-3.229408	-1.448254	-0.623061
6	6	0	-0.310634	-1.568888	2.242478
7	1	0	-0.055332	-2.628097	2.402394
8	1	0	-1.161519	-1.310663	2.886676
9	6	0	-1.462984	-0.347627	-3.081401
10	Ţ	0	-1.908070	0.644134	-3.250252
	L C	0	-2.250617	-1.101145	-3.234452
12	0	0	-2.824600	2.1/5130	-0.882964
14	1	0	-1.049203	3.104493	-0.265559
15	1 6	0	-4 614434	-1 493723	-0.378360
16	1	0	-5 116809	-0 630052	-0.838196
17	1	0	-4.819218	-1.481223	0.701548
18	6	0	-3.594619	1.110163	2.287145
19	1	0	-4.267202	1.579760	1.554786
20	1	0	-2.963495	1.895506	2.728882
21	1	0	-0.674286	-0.509451	-3.832534
22	1	0	0.541862	-0.937531	2.515619
23	1	0	-4.202386	0.667334	3.088934
24	1	0	-5.028950	-2.414106	-0.809961
25	1	0	-3.003312	3.067148	-1.928117
26	41	0	-1.892662	-0.162367	-0.040409
27	8	0	1.360576	2.666136	0.043849
28	6	0	2.731609	2.951855	0.296144
29	1	0	2.986796	2.597709	1.300273
30	6	0	3.58/885	2.194546	-0.741125
31	1	0	3.326078	2.526130	-1./49698
32	1 6	0	4.652027	2.38/621	-0.580261
34	1	0	2.949140	4.45/440	-0 814509
35	1	0	2 333980	4 973601	0.014000
36	1	0	3.997937	4.720608	0.356626
37	7	0	3.376976	0.734964	-0.681359
38	6	0	4.154145	-0.048183	0.111038
39	6	0	2.278777	0.183185	-1.276516
40	6	0	3.878651	-1.373640	0.323614
41	1	0	5.001020	0.438511	0.579698
42	6	0	1.933068	-1.126559	-1.095445
43	1	0	1.654810	0.848875	-1.857956
44	6	0	2.715764	-1.968170	-0.255412
45	1	0	4.537633	-1.929510	0.976069
46	1	0	0.995697	-1.438140	-1.539231
47	7	0	2.366811	-3.248847	-0.019600
48	6	0	1.095927	-3.//4/50	-0.545336
49 50	⊥ 1	0	0.333/91 0.263171	-4.//3U31 -3 130155	-0.130200 -0.244209
51	⊥ 1	0	1 128120	-3 847460	-1 638620
52	- 6	0	3 184744	-4 091350	0 849325
53	1	0	4.221710	-4.133573	0.497219
54	- 1	Ũ	3.176174	-3.730001	1.885490
55	1	0	2.785493	-5.104510	0.836731
56	8	0	-0.445498	1.471502	0.441666
57	6	0	0.733065	1.678089	0.854764
58	8	0	1.368853	1.181999	1.783300

Table	e S-3. Coordinates &	& energies of	hemicarbonate S	-3.

Sum	of	electronic	and	thermal	Enthalpies=	-1396.419113
Sum	of	electronic	and	thermal	Free Energies=	-1396.526379
HF=-1396.9325985						

DFT calculations have been performed by Gaussian 09.  $D.01^{\{1\}}$  optimizations and frequency/thermochemistry determinations have been conducted using the density functional B3LYP<sup>{2-4}</sup> together with the basis set 6-31+G<sup>\*\*{5-6}</sup> (as implemented in Gaussian 09) for all atoms excluding Nb and the Stuttgart 1997 ECP for niobium,<sup>{7}</sup> downloaded from the Basis Set Exchange.<sup>{8}</sup> All reported energies are unscaled and reported in kcal/mol relatively to a defined zero point. IR frequencies derived from frequency calculations have been scaled using reported frequency scale factors.<sup>{9</sup>}

#### References related to the DFT calculations:

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