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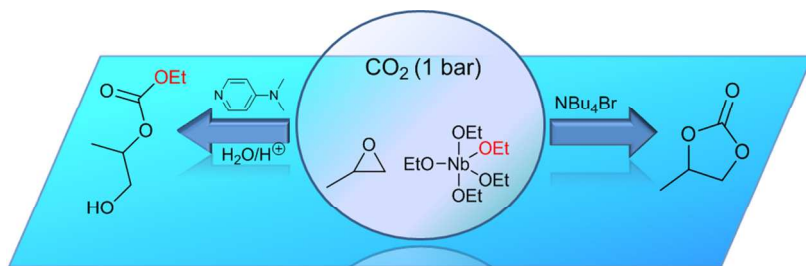
COMMUNICATION

Nucleophile-directed selectivity towards linear carbonates in the niobium pentaethoxide-catalysed cycloaddition of CO$_2$ and propylene oxide

Barnali Dutta,[a] Julien Sofack-Kreutzer,[b] Amylia A. Ghani,[a,b] Valerio D'Elia,[b,*] Jérémie D. A. Pelletier,[b] Mirza Cokoja,[a] Fritz E. Kühn[a,*] and Jean-Marie Basset[b]

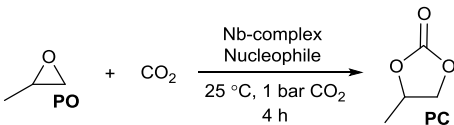**Homoleptic Nb-complexes combined with selected organic nucleophiles generate very active catalytic systems for the cycloaddition of propylene oxide and CO$_2$ under ambient conditions. An unprecedented reaction pathway towards an acyclic organic carbonate is observed when extending the study to [Nb(OEt)$_5$] in combination with 4-dimethylamino-pyridine (DMAP) or tetra-n-butylammonium bromide (TBAB). Mechanistic insights of the reaction are provided based on experimental and spectroscopic evidences.**

Efficient strategies for the valorisation of CO$_2$ as a C-1 feedstock for the synthesis of bulk commodity chemicals are urgently sought in the light of dwindling fossil fuels reserves and of increasing concerns over the sustainability of the current levels of greenhouse gases emissions and concentrations in the atmosphere.[1] Industrial processes employing CO$_2$ on a relatively large scale for the preparation of chemicals are available; though, at the moment, just about 0.5 % of the anthropogenic CO$_2$ is being recycled in this way.[2,3] Notwithstanding, the cycloaddition of CO$_2$ and epoxides to industrially relevant cyclic carbonates has shown some potential as a carbon footprint-free process by applying catalytic systems able to operate under ambient conditions.[4,5] In this case, the driving force of the process is provided by the release of the ring strain energy contained in the 3-membered ring of the epoxide to afford the more stable 5-membered cyclic carbonate. We have recently demonstrated that simple and readily available early transition metal complexes can catalyse the cycloaddition of CO$_2$ and epoxides under mild temperature and low pressure.[6] The addition of suitable nucleophiles as co-catalysts is required. In particular, the NbCl$_5$-DMAP and NbCl$_5$-TBAB pairs form very efficient catalytic systems for the title reaction even at sub-atmospheric pressure, making them suitable candidates for their future implementation in the direct conversion of CO$_2$ from flue gas. A general mechanism for this reaction is accepted: the nucleophile attacks the metal-coordinated epoxide ring at the less substituted carbon atom. This is followed by insertion of CO$_2$ in the metal-oxygen bond generated after ring opening. The final cyclisation step occurs via backbiting, thereby releasing the carbonate product.[7] Modulation of the relative acidity of the nucleophilic and of the Lewis acidic components of the catalytic pair has generally a large impact on the efficiency of this cooperative

catalysis as strongly interacting Lewis acid-Lewis base pairs will result in catalyst deactivation. Moreover, high oxophilicity of the metal centre could hinder the release of the carbonate in the last step of cyclisation. A series of niobium-based complexes were investigated in combination with different nucleophilic co-catalysts for the cycloaddition of propylene oxide (PO) and CO$_2$ to afford propylene carbonate (PC). The results obtained during the catalyst screening are presented in Table 1.

Table 1. Screening of various Nb-based complexes and organic nucleophiles for the synthesis of PC from CO$_2$ and PO.[a]

Entry	Nb-complex/ Nucleophile	Conv. (%)[b]	TON[c]/ (TOF, h^{-1})[d]	k$_{obs}$ (mol L^{-1} min^{-1})[e]
1	NbCl$_5$/TBAB	74[f]	74/(18.5)	0.0138
2	NbCl$_5$/NBu$_4$Cl	51	51/(12.7)	0.011
3	NbCl$_5$/NBu$_4$I	32	32/(8)	0.007
4	NbCl$_5$/DMAP	20[g]	20/(5)	0.0027
5	NbCl$_5$/TCAP[h]	10[g]	10/(2.5)	0.0016
6	NbBr$_5$/TBAB	65	65/(16.2)	0.0124
7	NbF$_5$/TBAB	11	11/(2.7)	0.0018
8	[Nb(OEt)$_5$]/TBAB	43	43/(10.7)	0.0301
9	[Nb(OEt)$_5$]/DMAP	0[i]	0	0
10	[Nb(NMe$_2$)$_5$]/TBAB	7	7/(1.7)	0.0009
11	[NbOCl$_3$]/TBAB	18	13/(3.2)	0.0038

[a] Propylene oxide (100 mmol), Nb-complex (1 mmol), nucleophile (2 mmol) at 25 °C, 1 bar CO$_2$ for 4 h. [b] Conversion determined by the integration of PO and PC peaks in the ^{1}H NMR of the reaction mixture. [c] mol of PC/mol of Nb. [d] TOF = TON/4 h. [e] Apparent initial rate of PC formation as determined by *in situ* IR (see the ESI). [f] Taken from ref. 6. [g] CO$_2$ was added 90 min after the mixing of PO, NbCl$_5$ and DMAP or TCAP in order to take the induction period into account (See ref. 6). [h] TCAP: 9-azajulolidine. [i] The formation of a different product was observed (*vide infra*).

Under the reaction conditions applied, NbCl$_5$/TBAB revealed the highest conversion; all other combinations of Nb halides and

quaternary ammonium salts performed less well. The efficiency of the nucleophilic anion decreased in the order Br > Cl > I (Table 1, entries 1-3) and the catalytic activity of the Nb halides decreased in the order $NbCl_5$ > $NbBr_5$ >> NbF_5 (Table 1, entries 1, 6, 7). Increasing the nucleophilicity of the co-catalyst had a detrimental effect on the efficiency of the reaction promoted by $NbCl_5$ as the conversion strongly decreased when TBAB was substituted by DMAP (Table 1, entry 4) or by an even stronger nucleophile such as TCAP (9-azajulolidine, Table 1, entry 5).[8] Differently substituted Nb complexes where also used in combination with TBAB; once again $NbCl_5$ proved to be the most active catalyst with the catalytic performance decreasing in the order $NbCl_5$ > [$Nb(OEt)_5$] >> $NbOCl_3$ > [$Nb(NMe_2)_5$] (entries 1, 8, 10, 11). Yet, an examination of the apparent initial rates of PC formation (k_{obs}) by in situ IR spectroscopy, revealed that the reaction catalysed by [$Nb(OEt)_5$]/TBAB is initially more than twice as fast as that by $NbCl_5$/TBAB (Table 1, entries 1, 8). By comparing the in situ IR profile of PC formation for the two different catalytic pairs, in the case of [$Nb(OEt)_5$]/TBAB the reaction rate decreases very rapidly and the amount of PC formed in solution reaches a plateau within about 100 min from the beginning of the reaction (Fig. 1). This loss of catalytic activity can be attributed to a progressive decomposition of the catalyst or to a lower efficiency of the catalytic system in the increasingly polar reaction medium generated following the formation of considerable amounts of PC. It was also observed that for the reaction catalysed by [$Nb(OEt)_5$]/TBAB, an additional product forms over time which shows an IR absorption band centred at 1747 cm^{-1}. Interestingly, in the case of [$Nb(OEt)_5$]/DMAP no PC appeared during the first 7 h of reaction. The only product observed presented as well an IR absorption band at 1747 cm^{-1}. This signal falls in the range of frequencies characteristic of linear carbonates such as acyclic linear carbonate or poly(propylene) carbonate.
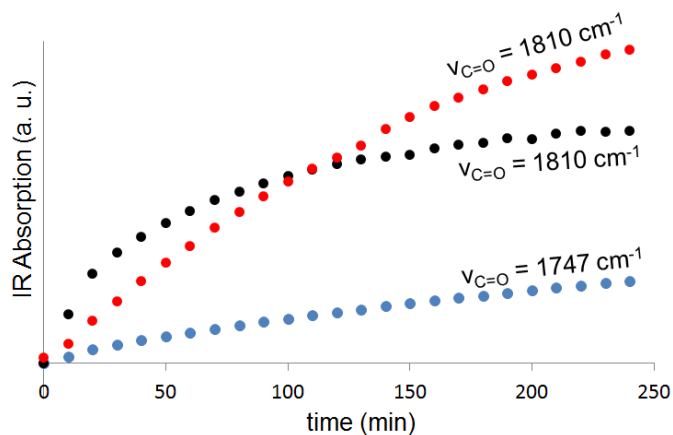

Fig. 1 Time evolution of the characteristic IR absorption band of PC ($v_{C=O}$ = 1810 cm^{-1}) in the cycloaddition of CO_2 and PO catalysed by $NbCl_5$/TBAB (●) and by [$Nb(OEt)_5$]/TBAB (●); In the case of [$Nb(OEt)_5$]/TBAB a second product forms with an IR absorption at 1747 cm^{-1} (●).

The isolation and characterisation of this species was attempted in order to investigate the mechanistic and synthetic implications of the catalytic behaviour of [$Nb(OEt)_5$]. Chromatography purification of the mixture obtained in the case of [$Nb(OEt)_5$]/TBAB or of the unknown carbonate species obtained in the case of [$Nb(OEt)_5$]/DMAP, resulted exclusively in PC, hinting at the decomposition/back-biting of a linear carbonate species in to cyclic carbonate.

Carrying out an acidic workup of the reaction mixture obtained from the reaction catalysed by [$Nb(OEt)_5$]/DMAP yielded linear carbonate **1** (ethyl (1-hydroxypropan-2-yl) carbonate, Scheme 1) following chromatographic purification. It contains traces of oligomeric polyether and polycarbonate also bearing terminal ethyl ester moieties (see the ESI). This compound represents the first non-polymeric linear carbonate prepared directly from CO_2 under ambient conditions.[9] Under optimised reaction conditions it was possible to prepare **1** in stoichiometric yield from [$Nb(OEt)_5$], PO and CO_2 although the reaction is not catalytic at this stage (see the ESI).

A proposed mechanism for the formation of **1** is suggested in Scheme 1. The ethyl ester moiety is formed following the intramolecular nucleophilic attack of the ethoxide anion of hemicarbonate **3** to yield **2**. The nucleophilic moiety of **2** is cleaved during the acidic workup to yield **1**. The formation of **1** via this pathway would explain the fast drop in activity observed for the synthesis of PC in the case of [$Nb(OEt)_5$]/TBAB, as the Nb complex is progressively decomposed by the stoichiometric formation of the linear species in competition with the synthesis of PC. In the process, an anionic Nb-complex (**4**) should form, most likely bearing a metal-oxo functionality. Identification of the exact structure of **4** by in situ IR studies has proved challenging (See the ESI, section 6.3).
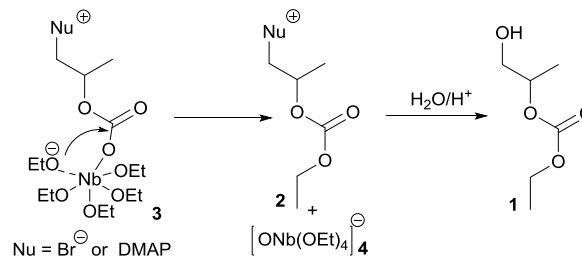
Scheme 1 Proposed mechanism for the formation of **1** from hemicarbonate **3** in the presence of a nucleophile, [$Nb(OEt)_5$], PO, CO_2 and following an acidic workup.

In order to confirm this hypothesis, in situ IR studies were carried out to identify the reaction intermediates involved in the formation of **1** by monitoring the evolution of the signals present in the 1600-1850 cm^{-1} spectral region for the [$Nb(OEt)_5$]/DMAP promoted reaction (Fig. 2). One of the most evident changes in the IR spectrum during the reaction is the progressive appearance of a new signal at 1655 cm^{-1} and the concomitant disappearance of a band at 1620 cm^{-1}. These signals fall in the asymmetric ring stretching region (ARS) of the pyridine ring of DMAP and their behavior can be explained in terms of a change in the coordination at the nucleophilic nitrogen.[10] Similar to our previous study on the synthesis of cyclic carbonates promoted by $NbCl_5$/DMAP, this observation can be related to the formation of ring-opened intermediate **6** from DMAP-$Nb(OEt)_5$ adduct **5** (Scheme 2).[6] The role of **6** as a key reaction intermediate is confirmed by the fact that by adding CO_2 to the reaction vessel directly at the beginning of the reaction, when the concentration of **6** is low, an induction period of about 2 h is observed before the rate of formation of **2** stabilises. On the other hand, by adding CO_2 2 h after the initial mixing of PO, [$Nb(OEt)_5$] and DMAP, no induction period is observed, as during this time interval a sufficient amount of **6** is formed in solution. The addition of CO_2 leads as well to the appearance of new signals, in particular at 1675 cm^{-1} and at 1290 cm^{-1}; the IR intensity of such bands shows a pressure dependant profile and decreases by removing CO_2 from the reaction mixture (See the ESI, section 6.3). The position of such signals and
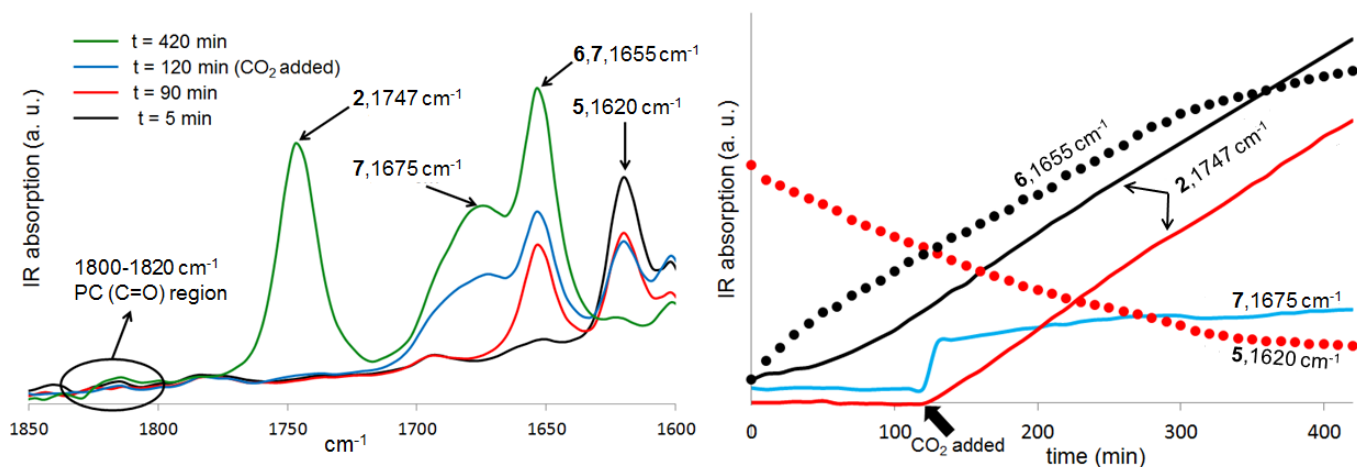
Fig. 2 (Left) *In situ* IR spectra taken at different times for a PO solution of [Nb(OEt)$_5$] (0.1425 M) and DMAP (0.1425 M) in the 1600-1850 cm^{-1} region. (Right) Time evolution of the IR signals observed in the left side of the graphic. Initially, only a signal at 1620 cm^{-1} is visible. This band disappears progressively in ca. 7 h to form a new signal at 1655 cm^{-1}, independent of the presence of CO$_2$ into the system. Following CO$_2$ addition, a new broad signal centred at 1675 cm^{-1} appears immediately and the formation of linear carbonate **2** begins ($v_{C=O}$ = 1747 cm^{-1}). No signal relative to PC is detected during the experiment in the 1800-1820 cm^{-1} region. On the right side of the figure, it is possible to observe that if CO$_2$ is added at the beginning of the process (black line) an induction period for the formation of **2** exist which is not observed when CO$_2$ is added 120 min after the mixing of the catalytic components with PO (red line). For the assignment of the IR signals see the text and Scheme 2.
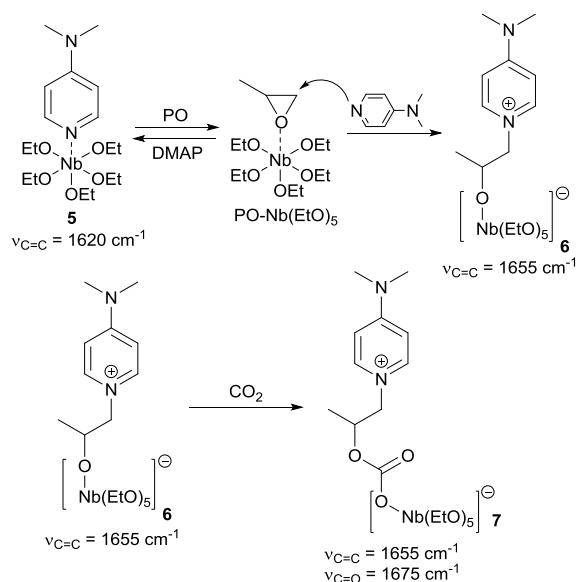

Scheme 2 Intermediates in the reaction of [Nb(OEt)$_5$], DMAP, PO and CO$_2$. The characteristic IR frequencies observed by real time *in situ* monitoring are listed.

their pressure-dependent and reversible behaviour are consistent with the formation of hemicarbonate species **7** generated by the insertion of CO$_2$ in the Nb-oxo bond of intermediate **6**.[11] Moreover, there is a good agreement between the IR frequencies calculated for the symmetric and asymmetric C=O stretching of a model hemicarbonate compound and the frequencies attributed to hemicarbonate **7** in the *in situ* IR of the reaction mixture (See the ESI). This provides good evidence that a hemicarbonate species comparable to intermediate **3** of Scheme 1 is present in solution during the formation of **2**. The rate of formation of **2** measured through *in situ* IR does not depend on the kind of nucleophile employed, as by substituting DMAP with more nucleophilic

pyridines such as TCAP no difference in the rate of formation of **2** was observed. Similarly no influence of the CO$_2$ pressure (P$_{CO2}$) was observed in an *in situ* IR experiment when P$_{CO2}$ was varied in the 0.5-2.5 bar range (see the ESI).

A parallel with a recent study carried out on the mechanism of the NbCl$_5$-catalysed cycloaddition of PO and CO$_2$ can be used to provide deeper insight into the mechanism of formation of **2** versus PC for the different [Nb(OEt)$_5$]/co-catalyst combinations; kinetic and theoretical studies have shown that in the case of NbCl$_5$/DMAP a second molecule of DMAP is necessary for the liberation of PC from the parent hemicarbonate (**8**, scheme 3) as the barrier for the unassisted ring closure would be too high for the reaction to proceed under mild conditions. This step requires the dissociation of a chloride ligand from the Nb centre to allow for the coordination of a second molecule of DMAP on hemicarbonate **8'**.[12] In the case of [Nb(OEt)$_5$]/DMAP, although hemicarbonate **7** is observed in solution, the DMAP-assisted liberation of PC evidently does not take place. This is possibly due to the fact that the dissociation of an ethoxide ligand from the Nb centre is less favourable compared to the dissociation of Cl or to steric reasons, as when [Nb(OMe)$_5$]/DMAP is used as a catalyst for the cycloaddition of CO$_2$ and PO, PC is observed again as the main product of the reaction. Therefore, the intramolecular attack of an ethoxide anion or ligand of **7'** is the only productive pathway for [Nb(OEt)$_5$]/DMAP. In this case, the dual role of [Nb(OEt)$_5$] as a Lewis acid and as a source of a nucleophilic anion is comparable to the role of TMSCN in the DMAP/TMSCN promoted silylcyanation of aldehydes.[13] In the case of NbCl$_5$/TBAB, the energy barrier for the unassisted ring closure of the hemicarbonate intermediate analogous to intermediate **7** is lower than in the case of NbCl$_5$/DMAP because of the inferior strength of the C–Br bond and of the better leaving ability of the bromide anion. Therefore, competition exists between the pathways of cyclisation through backbiting and the intramolecular attack of a ethoxide ligand on the C=O bond of the hemicarbonate, leading to the concomitant formation of PC and of the linear carbonate, respectively. This is corroborated by our experimental observations. We are currently investigating

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this mechanism through DFT calculations to elucidate the effects arising from alkoxy ligand and nucleophile. In addition, attempts to isolate and characterise the so far unknown Nb-complex (**4**, Scheme 3) formed after the release of the linear carbonate **2** are ongoing.
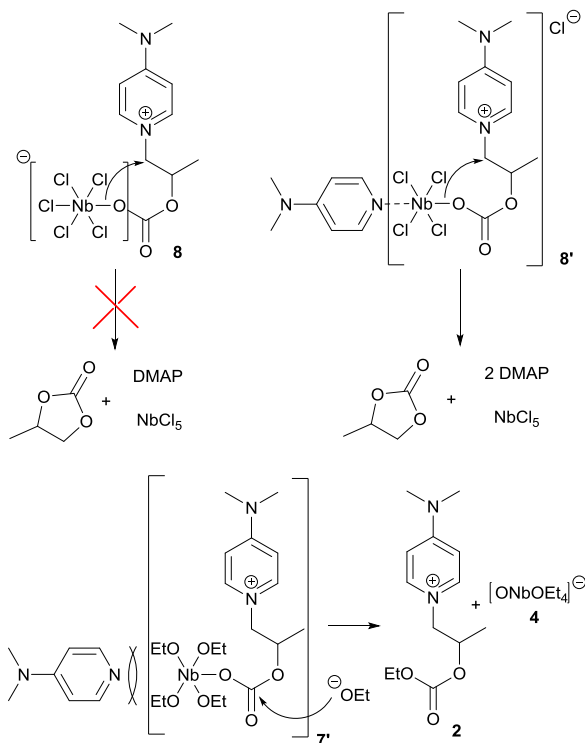
Scheme 3 Top: a second molecule of DMAP is required for the ring-closure step of hemicarbonate **8'** to proceed. Bottom: suggested mechanism for the selective formation of **2** (Nu = DMAP, see Scheme 1) from the hemicarbonate precursor **7'**.

Conclusions

In this study, the catalytic activities of a number of Nb-complexes along with various nucleophiles are compared as dual catalyst systems for the synthesis of PC from CO_2 and PO under ambient conditions. The relative Lewis acidity and basicity of the catalytic partners was found to have a strong impact on the reaction rate. The catalyst system [Nb(OEt)$_5$]/TBAB represents by far the most active catalytic combination based on the reaction rates measured by *in situ* IR. Nevertheless, the catalyst decomposes during the process because of the formation of linear carbonate **2**. Compound **1** can be obtained selectively after work-up when DMAP is used as a nucleophile along with [Nb(OEt)$_5$]. A mechanistic route for the formation of **2** is proposed; the final step in this route is the intramolecular attack of an ethoxide ligand in the hemicarbonate intermediate leading to a transfer of the alkoxide group to the carbonate. This diverts the process into a stoichiometric pathway rather than a catalytic cycle.

The preparation of **1** in the presence of [Nb(OEt)$_5$] and DMAP represents the first synthesis of acyclic (non-polymeric) organic carbonates directly from CO_2 under ambient conditions. **1** can be seen as the intermediate step for the synthesis of industrially relevant diethyl carbonate from the ring opening of PC, which generally requires high temperatures and a large excess of alcohol.[14] Therefore, establishing this process in a catalytic

fashion would be of high importance. In order for this to happen the Nb complex formed after the release of the linear carbonate is to be identified and a strategy for the regeneration of a catalytically active Nb complex is currently developed in our laboratories.

Notes and references

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