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ARTICLE

Niobium(V)chloride and imidazolium bromides as efficient dual catalyst system for the cycloaddition of carbon dioxide and propylene oxide

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The application of niobium(V) chloride with several imidazolium bromides as catalyst system for the cycloaddition of propylene oxide (PO) with carbon dioxide to propylene carbonate (PC) is reported. A set of 31 different imidazolium bromides has been synthesized, with varying substituents at all five imidazolium ring atoms. 17 of them have not been reported before. The impact of different substitution patterns (steric and electronic changes, solubility in PO) at the imidazolium ring on the catalytic activity was investigated. The optimisation of the catalyst structure allows for the valorisation of carbon dioxide at mild reaction conditions with high reaction rates in very good yield and selectivity of PC.

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Introduction

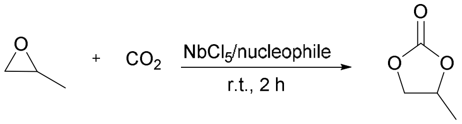
Since fossil fuel deposits are limited and most likely depleted within the next century, the focus of catalysis research is shifting to the utilization of renewable carbon sources as feedstock for chemical processes over the last years.[1-6] The valorisation of carbon dioxide as renewable C_1-feedstock is of particularly high interest, because of the very high capacity and availability, caused by natural emission and the human combustion of fossil fuels (approximately 30 Mt/a).[7] The catalytic conversion of the cheap and non-toxic gas with epoxides to the respective cyclic- or polycarbonates, is one of the most promising routes for the production of industrial relevant compounds.[8-13] Especially the conversion of propylene oxide (PO) to propylene carbonate (PC), which can be used as polar aprotic organic solvent or electrolyte in lithium batteries, is of great industrial interest.[14, 15] A broad variety of catalysts for the synthesis of cyclic carbonates have been developed so far, whereby Zn, Al, Co and Cr complexes with nucleophilic co-catalysts, are the most commonly used metal-based catalytic systems.[16-19] Additionally, tetrabutylammonium salts and imidazolium-based ionic liquids as organocatalysts have emerged as green and metal-free alternative catalysts for the fixation of CO_2 as cyclic carbonates.[20-26] However, these organocatalysts often operate efficiently at high temperatures (> 120 °C) and pressures (>10 bar CO_2), thus rendering the processes unfeasible from the viewpoint of a positive CO_2 balance. In order to improve the reactivity of organocatalysts, which are most often less reactive than metal complexes, the addition of Lewis-acidic metal co-catalysts such as $ZnBr_2$ has shown to have a beneficial effect on the reaction rate.[27-30] Very recently, we showed the possibility to use a simple transition metal salt such as niobium(V) chloride as non-toxic and cost-efficient catalyst for activation of epoxides.[31] The Lewis-acidic niobium centre acts as an electrophile polarizing the C–O ring bond, thus facilitating the ring opening by a nucleophile (pyridine derivatives, halides), resulting in a very reactive system for the formation of PC at mild reaction conditions (r.t., 1 bar CO_2) with high reaction rates.

In this study, the combination of $[(NbCl_5)_2]$ with a series of imidazolium bromides was tested for the catalytic cycloaddition reaction of CO_2 with PO to yield PC. Therefore, the impact of the cation structure on the catalytic activity of the system was investigated through comparison of different substitution patterns at the imidazolium ring. As a result of the subsequent optimisation of the ionic liquid structure, a promising alternative to the common $NbCl_5$ system is provided.

Results and discussion

Synthesis of imidazolium bromides

For a detailed screening of the influence of the imidazolium cation structure, a series of 31 different imidazolium halides was synthesised and characterised. The imidazolium bromides (in the following denoted as ImBr) were obtained by treatment of an imidazole solution in THF with the respective alkyl bromide and heating in a pressure tube for 24 h. The purity of the compounds was determined with ^{1}H-/^{13}C-NMR spectroscopy and elemental analysis (details can be found in the Electronic Supporting Information, ESI). ImBr's bearing aliphatic and/or aromatic side chain substituents were tested on their catalytic behaviour in the cycloaddition of CO_2 with PO to PC in tandem catalysis with $NbCl_5$ (Scheme 1). Additionally, the influence of the substitution at the C2-position of the cation was investigated by varying the chain length of the substituent.



Scheme 1 Tandem catalytic cycloaddition of CO_2 and PO to PC.

Imidazolium bromides bearing aliphatic side chain substituents

Prior to the investigation of imidazolium-based ionic compounds in the tandem catalysis, the impact of the anion on the activity of the system was tested with TBAB and TBAI. Under the given reaction conditions, the time dependent catalytic reactions (for details see ESI) have shown that the usage of TBAB shows a higher yield than detected for TBAI at all investigated reaction times. The lower activity for TBAI can be explained by the more sterically demanding iodide anion. Therefore, the nucleophilic attack towards PO, which is pre-coordinated to $NbCl_5$, is hindered and results in lower yields of PC. For this reason, further investigations were carried out using different ImBr's as nucleophile, due to their higher activity towards the cycloaddition of CO_2 and PO in comparison to the corresponding iodides. ImBr's can also catalyse the formation of PC without any additional Lewis acid like $NbCl_5$. Nevertheless, there are still rather high temperatures and pressures needed, which hinder an ecologically worthwhile use of such organocatalytic systems.[25, 26] The compounds **2** and **24** for example were only able to catalyse the formation of PC in 64 and 86 % yield at 70 °C and 4 bar CO_2 with a catalyst loading of 10 mol-% after 22 h.[25] Therefore, a combination of $NbCl_5$, which binds and activates PO, and an ImBr as nucleophile is investigated and found to be a promising alternative to the common $NbCl_5$/TBAB system. For investigations on the catalytic behaviour in dependency of the substitution pattern a series of ImBr's bearing only aliphatic side chain substituents were synthesized (Fig. 1). For a better understanding of the role of the imidazolium cation structure, the C2-postion of the imidazolium ring was further substituted with different aliphatic chains. The dependency on the catalytic behaviour of **1**–**13** is summarised in Table 1. The results given in Table 1 show good yields of PC for all ImBr's used in the tandem catalysis with $NbCl_5$. However, ImBr's **1** and **6**, which are not substituted in the C2-position of the imidazolium ring, show lower PC yields compared to their substituted analogues. This can be a result of the varying extent of hydrogen-bonding to Br^-, which can be seen in the respective X-ray single crystal structures of **1** and **2**.[32] Thereby, the C2-proton of **1** shows a much stronger interaction to Br^- (2.45 Å) in comparison to the most pronounced contact in **2**, where the C5-backbone proton distance to Br^- is 2.73 Å.[32]

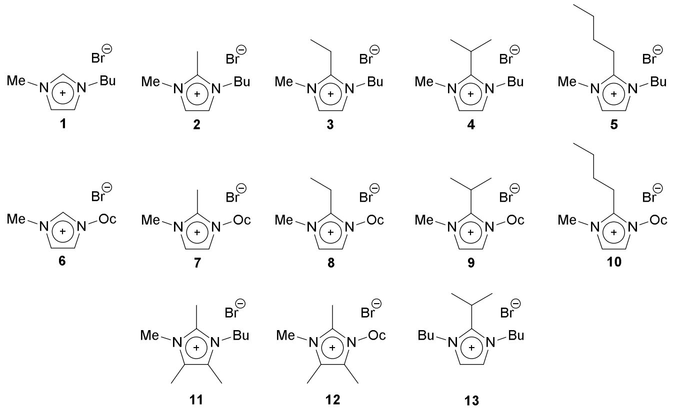


Fig. 1 Structures of imidazolium bromides **1**-**13**.

Table 1 Synthesis of PC from CO_2 and PO using $NbCl_5$ and **1**–**13**.

ImBr	PO [mmol]	$NbCl_5$/Nuc [mmol/mmol]	Yield PC [%]	Sel. PC [%]
1	10.0	0.1/0.2	82	≥ 99
2	10.0	0.1/0.2	87	≥ 99
3	10.0	0.1/0.2	95	≥ 99
4	10.0	0.1/0.2	93	≥ 99
5	10.0	0.1/0.2	80	≥ 99
6	10.0	0.1/0.2	79	≥ 99
7	10.0	0.1/0.2	85	≥ 99
8	10.0	0.1/0.2	86	≥ 99
9	10.0	0.1/0.2	92	≥ 99
10	10.0	0.1/0.2	92	≥ 99
11	10.0	0.1/0.2	91	≥ 99
12	10.0	0.1/0.2	90	≥ 99
13	10.0	0.1/0.2	89	≥ 99

Yield and selectivity were determined using GC analysis; Reaction conditions: r.t., 4 bar CO_2, 120 min.

The stronger hydrogen contact of **1** to the anion leads to a higher stabilization and thus probably to a lower nucleophilicity, which was also shown by Welton et al.[33] and therefore leads to a lower conversion of the epoxide. Additionally, the results indicate a positive effect on the PC yield by introducing at least one *n*-butyl side chain in the imidazolium C1- or C3-position instead of *n*-octyl. Nonetheless, this substitution does not have a significant impact in the catalytic results compared to the other variations of the imidazolium ring (C2, C4 and C5, c.f. the yields of ImBr's **2** and **11**, **6** and **12**). By comparison of **2** and **11** (**12**) it appears that also the backbone protons in the C4- and C5-position of the imidazolium ring reduce the catalytic activity with 82 % for **2** and 91 % PC yield for **11**. Via methylation of the backbone, the stabilisation of the nucleophile through H-contacts, as observed in the crystal structure of **2**,[32] is prevented, so that Br^- in **11** becomes more nucleophilic. By varying the chain length of the substituent in C2-position of the imidazolium ring, a

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dependency of methyl ≤ ethyl ~ *n*-butyl ~ *iso*-propyl on the PC yield was obtained, with the exception of ImBr **5**, which is barely soluble in PO. It can be safely assumed that the increasing steric demand of the substituent at the C2-position leads to a weaker electrostatic interaction of the ion pair, resulting in a higher nucleophilicity of the anion.

ImBr's **3** and **4** were shown to be slightly better nucleophiles than TBAB in combination with $NbCl_5$ with yields of 95 % and 93 % in comparison to 90 % PC yield with TBAB. For further optimization of the nucleophile structure, **13** was synthesized and was found to show a similar activity as **3**, **4** and **11** yielding 89 % PC. Due to the straightforward synthesis (two steps) and their low cost precursors, ImBr's **3**, **4**, **11** and **13** are attractive nucleophiles for the tandem catalysis with $NbCl_5$. For a better insight into the reaction, kinetic curves using **4**, **11** and **13** compared to TBAB were monitored and illustrated in Fig. 2.

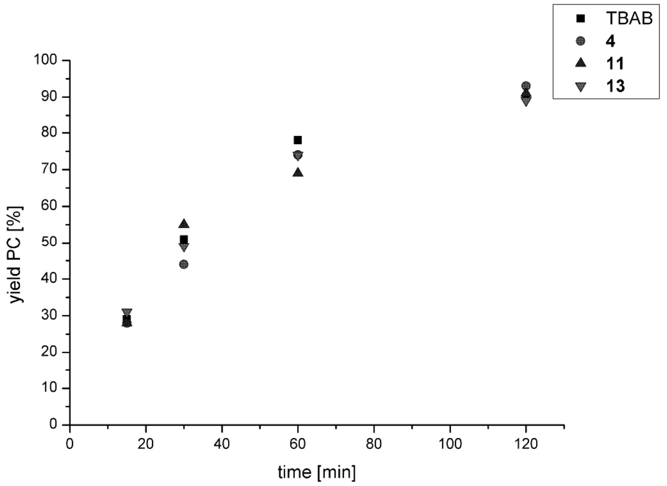

Fig. 2 Kinetic curve of the reaction of PO and CO_2 using $NbCl_5$/**4**, $NbCl_5$/**11**, $NbCl_5$/**13** and $NbCl_5$/TBAB as catalytic system. Reaction conditions: $NbCl_5$:nucleophile:substrate ratio 1:2:100, 120 min, r.t, 4 bar CO_2.

The kinetic data (Fig. 3) show an identical catalytic behaviour for every investigated system. Therefore, no induction period was observed leading to yields of PC at around 90 %. For this reason, every system shows the possibility to be an effective alternative to TBAB.

Variation of the $NbCl_5$/nucleophile ratio

For investigations of the role of the used amount of $NbCl_5$ as well as the corresponding nucleophile, different amounts were tested in the tandem catalytic reaction to yield PC. Since **4** has shown to be a possible alternative to TBAB, these variation reactions were carried out using **4** as nucleophile. The observed results are listed in Table 2. Varying the molar ratio of $NbCl_5$/**4** from 1:2 up to higher or lower ratios has a negative influence on the PC yield. Lowering the ratio to 1:8 (1:4) (Table 2, Entries 1 and 2) results in a decrease of the PC yield (8 % and 50 %, respectively). An analogous trend was observed by increasing the ratio to 2:1 with a reduced PC yield of only 9 % (Table 2, Entry 5). Using only 0.5 mol % $NbCl_5$ and 1.0 mol % **4** with the optimum ratio of 1:2 leads to a PC yield of 59 %, respectively (Table 2, Entry 6).

Table 2 Varying the molar ratio of $NbCl_5$ and **4** for the synthesis of PC from CO_2 and PO.

Entry	PO [mmol]	$NbCl_5$/nuc [mmol/mmol]	molar ratio	yield PC [%]	PC sel [%]
1	10.0	0.025/0.2	1:8	8	≥ 99
2	10.0	0.05/0.2	1:4	50	≥ 99
3	10.0	0.1/0.2	1:2	93	≥ 99
4	10.0	0.1/0.1	1:1	59	≥ 99
5	10.0	0.1/0.05	2:1	9	≥ 99
6	10.0	0.05/0.1	1:2	59	≥ 99

Yield and selectivity were determined using GC analysis; Reaction conditions: r.t., 4 bar CO_2, 120 min.

For this reason, the molar ratio of 1:2 with amounts of 1.0 mol % $NbCl_5$ and 2.0 mol % **4** were found to the most efficient (Table 2, Entry 3).

In-situ IR measurements

Additionally, in-situ IR measurements were performed to get a better insight into the kinetics of the reaction. Therefore, TBAB was compared to ImBr **12** and the used catalyst concentrations were reduced to 0.5 mol % $NbCl_5$ and 1.0 mol % **12**. This leads to a reduction of the reaction rate, which opens the possibility to determine the initial rates of the tandem catalytic reaction. These reactions were performed under 1 and 4 bar CO_2 pressure at room temperature. The observed initial rates are listed in Table 3.

Table 3 Initial reaction rates of TBAB and **12** under 1 and 4 bar CO_2 pressure and observed yields of PC after 6 h reaction time.

Entry	Nucleophile	CO_2 pressure [bar]	Initial rate	Yield^a [%]
1	TBAB	1	0.0067	30
2	**12**	1	0.0174	25
3	TBAB	4	0.0266	68
3	**12**	4	0.0454	94

a: yield determined using NMR after a reaction time of 6 h.

At the beginning of the reaction, it can be shown that the use of **12** as nucleophile results in a dramatically increase of the reaction rate in comparison to TBAB. Nevertheless, after a reaction time of 6 h TBAB is the best co-catalyst under the observed reaction conditions. Imidazolium bromides as nucleophiles for the reaction lead to a higher turnover, but the activity of the nucleophile decreases rapidly while in case of TBAB the reaction rate is lower and the decrease is less strong. This might be an influence of changing the chemical environment from slightly polar (PO) to polar (PC) during the reaction. For this case, aggregation and charge separation apparently affects **12** more than TBAB.

Imidazolium bromides bearing aliphatic and aromatic side chain substituents

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In addition to the study of 1,3-dialkyl substituted ImBr's we investigated the catalytic activity of imidazolium bromides bearing an aliphatic and aromatic side chain substituent (Fig. 4). The influences of substituting the C2 position of the imidazolium moiety, as well as fluorinating the aromatic ring, were investigated and the yields of PC are reported in Table 4. The results indicate that generally lower yields of PC are achieved when compared to **1**-**13**, which originates from the worse solubility in the reaction medium. Since especially **15** and **16** gave yields of only 41 % and 42 %, arising from the poor solubility of this ImBr's, these results have to be excluded from the further discussion. In order to evaluate the impact of the solubility of the benzyl substituted ImBr's, their Bz^{F5} analogues were synthesized and tested in catalysis. With the exception of **23** the fluorination of the compounds indeed results in an enhanced catalytic activity. The substitution of the C2 position follows the same positive trend on the catalytic results, which was detected for **1**-**13**. The increasing steric hindrance of the ion pairing, due to the size of the C2 substituent, leads to a catalytic activity in the order $H \leq Me \leq Et \leq i\text{-}Pr$. As mentioned before, the presence of backbone protons leads to lower PC yields, because of the possible stabilisation of the nucleophile through hydrogen-bonding.[32]

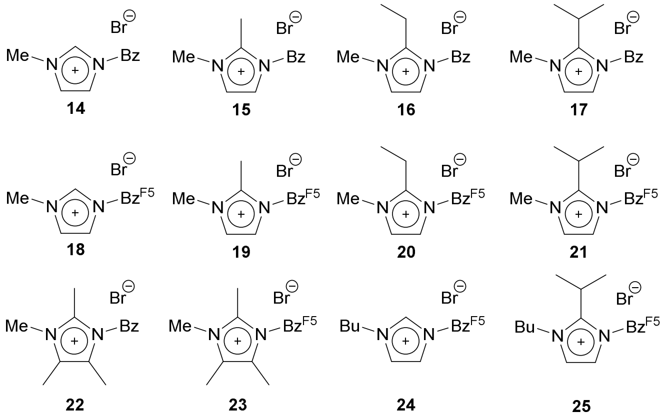

Fig. 3 Structure of imidazolium bromides **14** - **25**.

Table 4 Synthesis of PC from CO_2 and PO using $NbCl_5$ and **14** – **25**.

ImBr	PO [mmol]	$NbCl_5$/nuc [mmol/mmol]	yield PC [%]	PC sel [%]
14	10.0	0.1/0.2	65	≥ 99
15	10.0	0.1/0.2	42	≥ 99
16	10.0	0.1/0.2	41	≥ 99
17	10.0	0.1/0.2	79	≥ 99
18	10.0	0.1/0.2	75	≥ 99
19	10.0	0.1/0.2	77	≥ 99
20	10.0	0.1/0.2	80	≥ 99
21	10.0	0.1/0.2	85	≥ 99
22	10.0	0.1/0.2	89	≥ 99
23	10.0	0.1/0.2	83	≥ 99
24	10.0	0.1/0.2	87	≥ 99
25	10.0	0.1/0.2	85	≥ 99

Yield and selectivity were determined using GC analysis; Reaction conditions: r.t., 4 bar CO_2, 120 min.

Therefore, these protons were replaced by methyl groups (**22**), leading to an increase in yield of PC to 89 % compared to 65 % (**14**). Previously, it was pointed out that *n*-butyl as side chain and *iso*-propyl in the C2 position have a beneficial effect on the catalytic results. Therefore **24** and **25** were synthesized and found to be active with yields of 87 % and 85 % leading to interesting alternatives to TBAB. It can also be seen here that *n*-butyl as wingtip instead of a methyl group increases the reactivity of the ImBr (PC yield: **24** > **18**), most presumably because of the increased steric hindrance, i.e. a relative shielding of the C2-proton, leading to a less pronounced ion-pairing. The substitution of the C2 position, leading to a slightly lower yield, is again caused by the lower solubility of **25**.

Imidazolium bromides bearing aromatic side chain substituents

To complete the screening of imidazolium bromides as nucleophiles for the tandem catalysis with $NbCl_5$ to yield PC, a series of 1,3-bisaromatic compounds were tested (Table 5). Because of the worse solubility also lower yields where obtained in comparison to **1**-**13**. Particularly the low yield of **27** as a nucleophile is a result of the insolubility in PO and the bad solubility in PC during the reaction. The solubility of **27** could derive from the fact that the C2-methylation of imidazolium based ILs results in the formation of a Coulomb network, which stabilizes the system.[34] Due to the substitution pattern of **27** bearing two Bz moieties the stabilization through the network is assumed to be exceptional strong, leading to the observed solubility. The ImBr **26** however is not able to form such network due to the presence of the C2-proton, which forms strong hydrogen bonds to the anion, introducing defects in the network.[34] Through the high steric demand of the iPr group of **28** the formation of a strong Coulombic network is presumably hindered, therefore resulting in enhanced solubility. Substituting the C2 position of the imidazolium moiety here also has a positive influence on the reactivity. However, the steric demand of the C2 substituent ($i\text{-}Pr \leq Me$) shows the opposite behaviour as described before. Through the higher bulkiness of the Bz and Bz^{F5} wingtips, compared to the investigated alkyl-groups, it is likely that the magnitude of ion-pairing to Br^- is no longer affected by the increased size of the C2 substituent. Furthermore, the fluorination of the aromatic side chain here results in higher yields when the ImBr's **26**/**29** and **27**/**30** are considered, whereas the catalytic activity decreased in the case of **28**/**31**, which is caused by the different solubility of the respective ImBr's in PO and PC.

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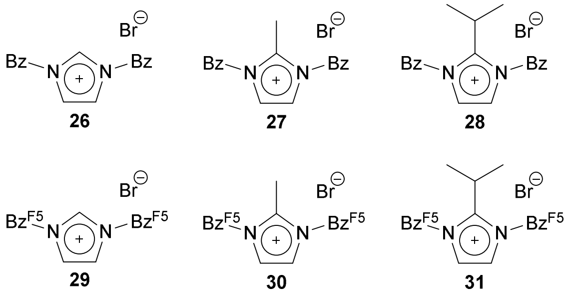


Fig. 4 Structure of imidazolium bromides **26** - **31**.

Table 5 Synthesis of PC from CO_2 and PO using $NbCl_5$ and **25** – **30**.

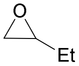
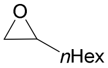
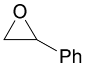
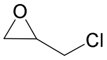
ImBr	PO [mmol]	$NbCl_5$/nuc [mmol/mmol]	yield PC [%]	PC sel [%]
26	10.0	0.1/0.2	65	≥ 99
27	10.0	0.1/0.2	16	≥ 99
28	10.0	0.1/0.2	78	≥ 99
29	10.0	0.1/0.2	69	≥ 99
30	10.0	0.1/0.2	78	≥ 99
31	10.0	0.1/0.2	74	≥ 99

Yield and selectivity were determined using GC analysis; Reaction conditions: r.t., 4 bar CO_2, 120 min.

Transformation of various epoxides with $NbCl_5$/4

Previous studies from D'Elia and Cokoja et al.[31] show the need of different reaction conditions for the efficient transformation of varying epoxides to their cyclic carbonates when $NbCl_5$/TBAB is applied as catalytic system. Therefore, a reaction temperature of 40 °C and a reaction time of 8 h were chosen in this study to show the suitability of $NbCl_5$/**4** for the conversion of other substrates than PO. The yields obtained are illustrated in Table 6.

Table 6 Cycloaddition of CO_2 with different epoxides catalyzed by $NbCl_5$/**4**

Substrate	t [h]	$NbCl_5$/**4** [mmol/mmol]	yield carbonate [%]	Sel carbonate [%]
	8	0.1/0.2	100	≥ 99
	8	0.1/0.2	100	≥ 99
	8	0.1/0.2	91	≥ 99
	8	0.1/0.2	44	≥ 99

ield and selectivity were determined by integration of the epoxide and cyclic carbonate peaks in the ^1H NMR spectrum; Reaction conditions: 40 °C, 4 bar CO_2, 10 mmol substrate.

The results show that the system $NbCl_5$/**4** is able to catalyse the cycloaddition reaction of CO_2 with all tested epoxides in excellent selectivities of ≥ 99 %. The examined aliphatic epoxides could be fully converted to the respective cyclic carbonates, whereas styrene carbonate could be obtained in 91 % yield. The slightly decreased reactivity could derive from a competing interaction of the benzyl ring and the epoxide with $NbCl_5$. However, the conversion of epichlorohydrin is limited under the applied reaction conditions. On the one hand the electron withdrawing effect of the substituent results in lower electron density at the epoxy ring oxygen atom. On the other hand the chloro substituent by itself could also interact with $NbCl_5$, thus competing with the epoxide. Therefore, the interaction with $NbCl_5$ as a Lewis acid is weakened compared to the other tested substrates, leading to a conversion of only 44 %.

Conclusions

In this work is shown that imidazolium bromides, which can be a catalyst on their own for the cycloaddition of CO_2 and epoxides, offer the possibility to yield PC in a tandem catalytic reaction with $NbCl_5$ under very mild reaction conditions (r.t., 4 bar CO_2 pressure). Therefore, $NbCl_5$ acts as an activator of the epoxide and the imidazolium as a nucleophile for the ring opening of the pre-coordinated epoxide. Different imidazolium bromides bearing aliphatic (**1**–**13**), aliphatic/aromatic (**14**–**25**) and aromatic (**26**–**31**) side chain substituents were synthesized, characterized and shown to be active towards the formation of PC with $NbCl_5$. A detailed screening of the nucleophiles lead to **3**, **4**, **9**, **10**, **11**, **12**, **13** and **22** as interesting alternatives to commercially available TBAB. These observations show a positive effect on the catalytic behaviour if the imidazolium bromides have only aliphatic wingtips. Exclusively, **22** is the only example, whereas one side chain has an aromatic moiety. The results help to understand the role of the cation on the catalytic behaviour and showed a positive trend for substitution of the C2-position of the imidazolium moiety. Further research efforts will focus on the development of tailor-made imidazolium cations, which allow the reusability of the $NbCl_5$/imidazolium bromide system e.g. via coordination. Considering these criteria, the system is a very effective and cost-efficient way to yield PC under very mild conditions and thus helping to minimise the carbon footprint for the reaction.

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Notes and references

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