# REALISTIC CATALYSTS FOR THE CYCLOADDITION OF $CO_2$ TO EPOXIDES UNDER AMBIENT CONDITIONS TO GENERATE CYCLIC ORGANIC CARBONATES: THE CASE OF COORDINATION COMPOUNDS AND NATURALLY AVAILABLE HYDROGEN BOND DONORS

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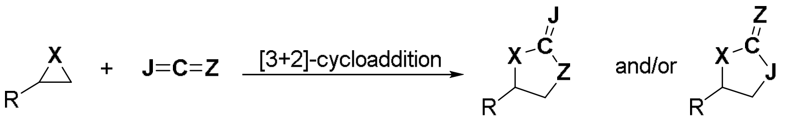
***Abstract.*** *The [3+2]-cycloaddition of heteroallenes to three-membered heterocycles is a convenient way to produce differently substituted five-membered heterocycles such as cyclic carbonates (1,3-dioxolane-2-ones), oxazolidinones, cyclic thiocarbonates, etc. Such cycloaddition processes generally require the use of catalysts that activate and ring-open the three-membered heterocycle in order to favor the insertion of the heteroallene. Among such heterocyclic compounds, cyclic organic carbonates are the most relevant in terms of potential applications and because they provide a potential outlet for the conversion of* $CO_2$ *into value-added chemicals. Herein, we discuss readily available catalytic components and systems for the cycloaddition of* $CO_2$ *to epoxides by considering coordination compounds as Lewis acids and hydroxy compounds as biobased hydrogen bond donors for the activation of the epoxide substrate. The manuscript generally focuses on catalyst design for the generation of cyclic carbonates based on the knowledge of the available mechanistic pathways.*

## Contents

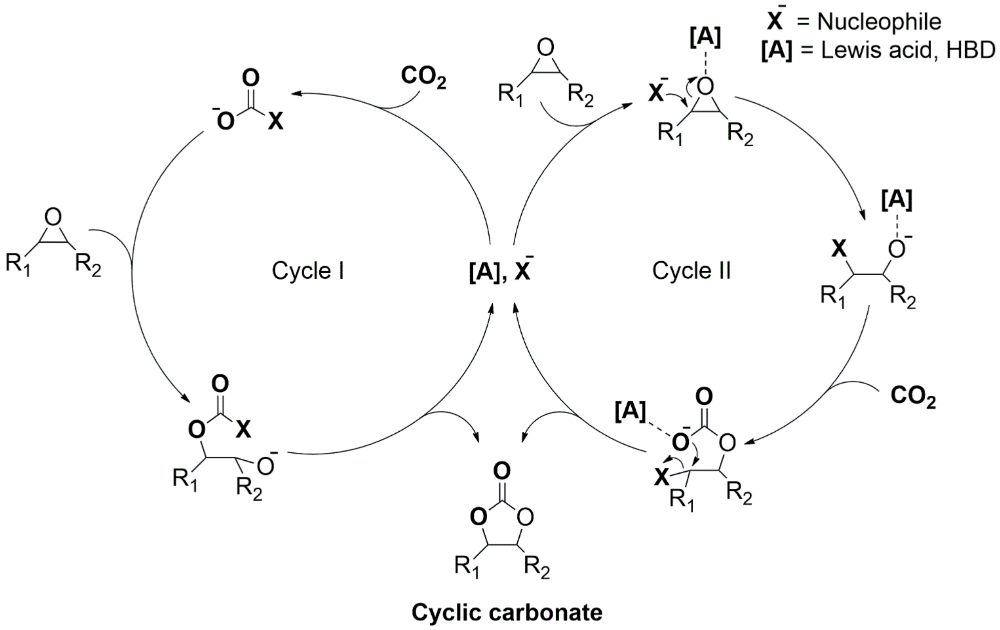
## 1. Introduction

Cyclic organic carbonates are crucially important aliphatic heterocyclic compounds containing differently substituted 2-oxo-1,3-dioxolane scaffolds.[1] There has been an increasing interest in the synthesis and application of cyclic organic carbonates in the last decades because cyclic organic carbonates are widely employed as solvents,[2-4] components of lithium-ion batteries,[5-7] surfactants and demulsifiers,[8,9] intermediates for the synthesis of fine chemicals,[10-12] and as intermediates for the synthesis of polymers.[13-17] As an effect, based on a Sci Finder® search, the number of references (journal articles and patents) involving propylene carbonate (4-methyl-1,3-dioxolan-2-one) has steadily increased in the last 30 years from about 250 to nearly 2000 in the year 2022, testifying the rising importance of this class of compounds. One of the earliest reports on the synthesis of cyclic organic carbonates dates back to 1945 when Kolfenbach *et al.* reported the reaction between 2,3-butanediol and phosgene.[18] To the best of our knowledge, the oldest reference relative to the use of a cyclic organic carbonate in organic synthesis was reported by Delaby *et al.*[19] in 1952, where the authors investigated the reaction of two equivalents of ethylene carbonate (1,3-dioxolan-2-one) with hydrazine to afford the product of aminolysis of the cyclic carbonate moieties with the formation of two urethane groups. Nowadays, such a reaction is widely used to synthesize isocyanate-free polyurethanes.[17,20-22] While the synthesis of cyclic carbonates by the catalytic cycloaddition reaction of $CO_2$ to epoxides is long known,[23] the industrial synthesis of cyclic carbonates has been traditionally carried out from highly toxic phosgene and vicinal diols.[1,24] Nevertheless, as an effect of the increasing focus on sustainability, atom-economic processes and the use of less toxic reagents, the cycloaddition of $CO_2$ to epoxides has steadily increased in relevance and has been marketed as a part of the industrial Asahi-Kasei process for bisphenol A-based polycarbonates.[25] The rise in prominence of the latter reaction is also due to its role as a potential outlet for the highly coveted capture-conversion[26-29] of waste $CO_2$ in the form of value-added compounds thanks to the fact that several catalytic systems can tolerate the use of impure or diluted $CO_2$ as a feedstock have been developed.[30-34] In general, the cycloaddition of $CO_2$ to epoxides is part of a broader family of [3+2]-cycloaddition reactions between three-membered heterocycles and heteroallenes leading to five-membered heterocyclic compounds such as carbonates,[35] 3-aryl-2-oxazolidinones[36-38] (either from the cycloaddition of $CO_2$ to aziridines or isocyanates to epoxides) and various kinds of cyclic thiocarbonates by using OCS or $CS_2$ as the reagents for cycloaddition reactions to epoxides (Scheme 1).[39]



**Scheme 1.** General scheme for the [3+2]-cycloaddition of heteroallenes to 3-membered heterocycles.

Therefore, recent years have seen the development of various classes of catalysts for the cycloaddition of $CO_2$ to different kinds of oil-derived and biobased epoxides.[24,40-45] The design of such catalysts is generally based on a mechanistic understanding of the elementary steps of the cycloaddition process[46-48] that are exemplified in Scheme 2.



**Scheme 2.** Possible general mechanistic pathways for cycloaddition of $CO_2$ to epoxides.

Focusing on the right cycle (cycle II), it is clear that the ring opening of the epoxide by a nucleophile ($X^-$) leads to the formation of an alkoxide anion that can further react with $CO_2$, leading to its fixation in the form of a hemicarbonate. The hemicarbonate intermediate undergoes ring closure to afford the cyclic carbonate product, restoring the nucleophile to a new catalytic cycle. Such a mechanism is typical for halide nucleophiles such as quaternary ammonium salts, quaternary phosphonium salts, and compounds such as PPNCl (bis(triphenylphosphine)iminium chloride) that can be employed as single-component nucleophiles to catalyze the cycloaddition of $CO_2$ to epoxides.[25,49,50] As a limitation, the cycloaddition reaction catalyzed by the single-component halide nucleophiles is generally a sluggish process that requires harsh reaction conditions

($T \geq 100$ °C, $P_{CO2}$: 20-30 atm) and long reaction times, especially in the presence of sterically hindered epoxides.[17,51] For this reason, as shown in cycle II of Scheme 2, compounds ([A]) with the ability to coordinate and activate the epoxide ring by establishing an interaction with the epoxide oxygen atom are generally added to the catalytic reaction besides the nucleophilic catalysts, to accelerate the process. As a consequence, most highly active catalytic systems for the cycloaddition of $CO_2$ to epoxides are binary systems (*i.e.* combinations of two different compounds of type $X^-$ and [A]) or bifunctional catalysts when both moieties ($X^-$ and [A]) are built within the same molecule or material.[24, 40]

It is noteworthy that other mechanistic pathways are possible, such as the one shown in cycle I of Scheme 2, where a nucleophilic moiety initially coordinates $CO_2$. The formed $CO_2$ adduct can act as the nucleophile for the epoxide ring opening, leading to an analogous hemicarbonate intermediate, as shown in cycle II, which generates the carbonate product upon ring closure. Strong nucleophilic bases such as TBD (triazabicyclodecene) follow such a mechanism[52] thanks to their ability to rapidly form the corresponding stable $CO_2$-adducts.[53] A similar mechanism has been reported for $CO_2$ adducts of phosphorus ylides.[54] Other strong nucleophilic bases such as pyridine nucleophiles such as DMAP and its derivatives[55,56] tend to follow the mechanism in Scheme 2, cycle II,[46,52,57] *i.e.* they favor an initial epoxide ring-opening step over the formation of $CO_2$-adduct especially in those cases where catalytic Lewis acids are added to the reaction for epoxide activation.[48,58] This manuscript will mainly focus on catalytic systems following the mechanistic manifold in cycle II of Scheme 2 because they can carry out the target cycloaddition reactions under mild or even ambient conditions.

The catalytic components able to activate the epoxide according to the mechanism in cycle II of Scheme 2 are generally represented by two classes of compounds, *i.e.* Lewis acids based on oxophilic metals[59] able to ligate the epoxide and organocatalytic hydrogen−bond donors (HBDs)[60] that activate the epoxide by establishing an array of H−bonds. The first class of compounds includes homogeneous complexes of various metals such as chromium,[61] cobalt,[62,63] copper,[64] aluminum,[65,66] zinc,[67,68] tin,[69] iron,[70-72] nickel,[73] yttrium,[74] scandium,[75] *etc.* Salen-type ligands,[76] porphyrins rings,[77] and macrocyclic ligands[72] were often employed to harness the metal centers in such complexes. Moreover, Lewis acidic metal atoms[78-80] or the whole complexes[81,82] can be incorporated through different methodologies within heterogeneous materials, matrices, and supports, facilitating their recovery and reuse.

On the other hand, HBDs have been intensively studied as components of catalytic systems for the cycloaddition of $CO_2$ to epoxides.[42,83,84] The main thrust, in this case, is the replacement of traditional metal-based catalysts with organic catalysts (hence the term organocatalysis) that are perceived as less moisture-sensitive and inexpensive and more eco-friendly in terms of toxicity and operational safety according to the increasingly popular paradigms of organocatalysis.[85-88] This is particularly the case when dealing with biobased HBDs that can be sourced from naturally available compounds such as carbohydrates,[89,90] vitamins,[51,91] amino acids,[92,93] peptides[94-96] and other compounds.[44]

Based on the discussion above, there is a great variety of catalytic systems for the cycloaddition of $CO_2$ to epoxides, with new examples being published on a daily basis. Nevertheless, it is worth noting that because cyclic carbonates are expected to serve as commodity chemicals for a wide range of applications, their production needs to be carried out through inexpensive and widely available catalytic systems. This means that catalysts or catalytic components requiring the synthesis of complex organic ligands *via* time-consuming multistep procedures are unlikely to be suitable for commercial development in terms of costs and availability.[97, 98] Additionally, the catalysts should be recyclable (or suitable for dynamic flow synthesis) and safe to operate under mild conditions of temperature and atmospheric pressure, which is a crucial requisite for the utilization of diluted waste $CO_2$ feedstocks and for negating the use of energy-intensive processes.[32,43,99]

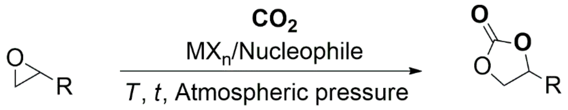
Therefore, in this manuscript, we will review the state-of-the-art readily available catalytic components for the cycloaddition of $CO_2$ under mild conditions with a focus on systems able to operate at room temperature under atmospheric conditions. In this context, Lewis acidic coordination complexes of transition metals stand out as inexpensive molecular species that do not involve sophisticated ligand frameworks. Transition metal coordination compounds are, indeed, widely used as inexpensive Lewis acids in different catalytic transformations.[100-102] Moreover, metal coordination compounds can be easily heterogenized by grafting them on metal oxide supports *via* incipient impregnation methods or by using more accurate techniques such as surface organometallic chemistry (SOMC), which leads to well-defined single-site species.[103-105] The development of the chemistry of coordination compounds as Lewis acids for the cycloaddition of $CO_2$ to epoxides will be analyzed, starting from the discovery of homogeneous compounds followed by the development of heterogeneous systems. As discussed above, a different class of highly available catalytic components for the activation of epoxides is represented by low-molecular-weight homogeneous hydrogen−bond donors, some of which are reported to be active under ambient conditions and will be discussed in this manuscript. For the case of HBDs, there is a paucity of efficient heterogeneous systems able to operate under ambient conditions for the cycloaddition of $CO_2$ to epoxides; however, some examples of biobased heterogeneous HBDs able to operate under mild conditions will be described as well as new methodologies to employ recoverable molecular HBDs in biphasic systems.

## 2. Cycloaddition of $CO_2$ to epoxides catalyzed by coordination compounds

### 2.1. Homogeneous coordination compounds

Earlier attempts to carry out the cycloaddition of $CO_2$ to epoxides to afford cyclic carbonates were done at elevated $CO_2$ pressures (5-200 atm) and temperatures (100-200 °C).[23,106] However, already in 1980, Kisch *et al.* first reported catalytic systems that could produce cyclic carbonates under ambient conditions using a binary catalytic system comprising $MoCl_5$ and triphenylphosphine ($PPh_3$), $MoCl_5/PPh_3$.[107]. However, this catalytic system only provided propylene carbonate (PC) with moderate to good yields after 7 days at 20 °C and 1 atm $CO_2$ (Table 1, entry 1).

**Table 1.** Overview of catalytic performances of metal halide and nucleophile for cycloaddition of epoxide to $CO_2$ under ambient conditions.

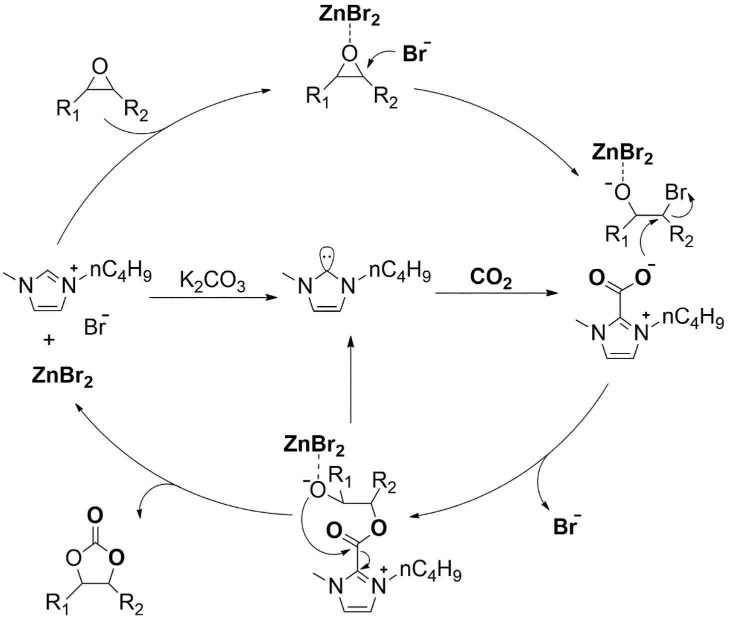


| Entry$^{\mathrm{ref}}$ | R | Coordination compound (mol%) | Nucleophile (mol%) | *T* (°C) | *t* (h) | Yield (%) | TON/TOF ($h^{-1}$) |
|---|---|---|---|---|---|---|---|
| 1[107] | $CH_3$ | $MoCl_5$ (0.7) | PPh3 (3.5) | 20 | 168 (7d) | 78 | 76/0.45 |
| 2[108] | $CH_3$ | $ZnCl_2$ (0.2) | TBAI (0.8) | 25 | 24 | 98 | 490/20 |
| 3[108] | $CH_3$ | $ZnCl_2$ (4) | TBAI (16) | 25 | 3.5 | 90 | 22.50/6.4 |
| 4[109] | $C_6H_5$ | $ZnBr_2/K_2CO_3$ (3) | ImBr (5) | 25 | 20 | 99 | 33/1.65 |
| 5[109] | $C_6H_5$ | $ZnBr_2/K_2CO_3$ (0.5) | ImBr (200) | 25 | 2 | 83 | 166/83 |
| 6[115] | $CH_3$ | $Zn_4(O(C{=}O)CF_3)_6O$ (1) | TBAI (3) | 25 | 6 | 94 | 94/15.7 |
| 7[116] | $CH_3$ | $NbCl_5$ (1) | TBAB (2) | 25 | 4 | 74 | 74/18.5 |
| 8[116] | H | $NbCl_5$ (0.18) | TBAB (0.35) | 23 | 12 | 64 | 365/30.3 |
| 9[118] | $CH_3$ | $Nb(OEt)_5$ (1) | TBAB (2) | 25 | 12 | 43 | 43/10.7 |
| 10[119] | $CH_3$ | $YCl_3$ (1) | TBAB (2) | 25 | 4 | 75 | 75/18.8 |
| 11[a, 120] | $CH_3$ | $YCl_3$ (1) | TBAB (2) | 22 | 5 | 3.5 | 3.5/0.7 |
| 12[121] | $CH_3$ | $InBr_3$ (5) | $PPh_3$ (10) | 25 | 5 | 82 | 16.4/3.3 |
| 13[122] | $OCH_3$ | $InBr_3$ (5) | TBAB (10) | 20 | 2 | 82 | 16.4/8.2 |
| 14[b, 122] | $OCH_3$ | $InBr_3$ (5) | TBAB (10) | 20 | 1 | 11[c] | 2.2/2.2 |
| 15[124] | $CH_3$ | $CaI_2$ (5) | 18-Crown-6 (5) | 23 | 24 | 85 | 17/0.71 |
| 16[124] | $C_4H_9$ | $CaI_2$ (5) | 18-Crown-6 (5) | 23 | 24 | 97 | 17/0.81 |

[a]Using 0.102 atm of $CO_2$ partial pressure. [b]Using 0.125 atm of $CO_2$ partial pressure. [c]Conversion determined by $^1H$-NMR spectroscopy.

Subsequently, the same group published a work that employed zinc halides in the presence of quaternary ammonium iodides as more efficient catalytic systems.[108] As the most active catalyst, $ZnCl_2$/TBAI (TBAI:

tetrabutylammonium iodide) could provide a quantitative synthesis of PC in 24 h under conditions of 1-1.2 atm $CO_2$ at ambient temperature (Table 1, entry 2). When the catalyst loading of $ZnCl_2$/TBAI was increased by a factor of 20, the time required to reach a quantitative yield was reduced to 3.5 h (Table 1, entry 3). In a more recent study using zinc salts, Shi *et al.* applied a ternary catalytic system comprising zinc halides in the presence of $K_2CO_3$ (base) and *N,N*-disubstituted imidazolium salts ($ZnBr_2/K_2CO_3$/ImBr) for the coupling of $CO_2$ to epoxides.[109] The imidazolium salt cation acted as a precursor for the formation of an N-heterocyclic carbene (NHCs) following deprotonation by $K_2CO_3$, as indicated in Scheme 3.[110-113]



**Scheme 3.** Proposed mechanism of $ZnBr_2/K_2CO_3$/ImBr.

At the same time, its nucleophilic bromide anion initiated the ring opening of the Zn-coordinated epoxide. NHCs can activate $CO_2$ and generate nucleophilic adducts[114] that participate in the cycloaddition reaction. The authors observed that the catalytic activity depended mainly on the nucleophilicity of the counterion of the imidazole salt and hardly on the nature of the zinc halide and base applied. Other metal (Al, Fe, and Mg) halides were also used, but their catalytic performance was substantially lower. Styrene carbonate (SC) was quantitatively synthesized from styrene oxide (SO) with 3 mol% of $ZnBr_2/K_2CO_3$ and 5 mol% of imidazolium bromide under ambient conditions within 1 day (20 h) (Table 1, entry 4), slightly faster than the previous zinc halide binary system despite the conversion of a more sterically demanding substrate. The reaction time could be further reduced to 2 h with a reduction of zinc loading to 0.5 mol%, which required increasing the imidazolium bromide loading to over stoichiometric amount (200 mol%) (Table 1, entry 5). Moreover, this ternary catalytic system can quantitatively convert internal epoxides to their targeted cyclic carbonates under ambient conditions in the presence of 2 equiv. of ImBr.

Yang *et al.* reported the first example of a polyatomic metal cluster, a $\mu$-oxo-tetranuclear zinc complex, capable of catalyzing the coupling of $CO_2$ and epoxides into cyclic carbonates under ambient conditions.[115] Initially, various metal trifluoroacetate salts ($M(O(C{=}O)CF_3)_2$, M: Zn, Co, Fe, Mn) were tested under ambient conditions in the presence of TBAI in the $CO_2$ cycloaddition reaction using PO as the substrate. Epoxide conversions from these metal salts with high Lewis acidity ranged from 70 to 80%, with zinc salts showing the best catalytic performance (Table 1, entry 6). The same reaction conditions led to inferior catalytic performance for $Zn(OAc)_2$ with lower Lewis acidity than its trifluoroacetate counterpart. When the number of metal atoms is considered, the tetranuclear zinc cluster (83 % PO conversion) performed slightly better than the mononuclear zinc trifluoroacetate salt (79%) after 6 h. Regarding the ligand types illustrated in Figure 1, the $\mu$-oxo-tetranuclear zinc cluster with the acetate ligand was notably less active than the trifluoroacetate-based cluster. The catalytic performance of $Zn_4(O(C{=}O)CF_3)_6O$ was studied further under $CO_2$ in the presence of additional gases (air, Ar, CO, $NO_2$, $O_2$, $SO_2$) in a 95:5 mixture. A reduction in activity was observed from 83% conversion for pure $CO_2$ to 50-56% for gas mixtures. However, the gas type did not significantly affect the catalytic performance, whether an inert or more reactive gas. As a result, it was suggested that the zinc-based catalyst is resistant to these common flue gas contaminants.

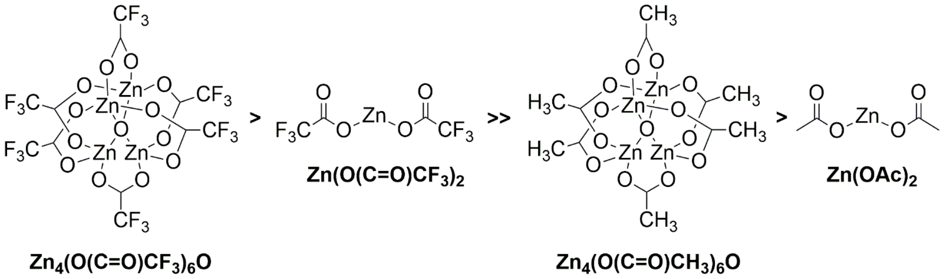
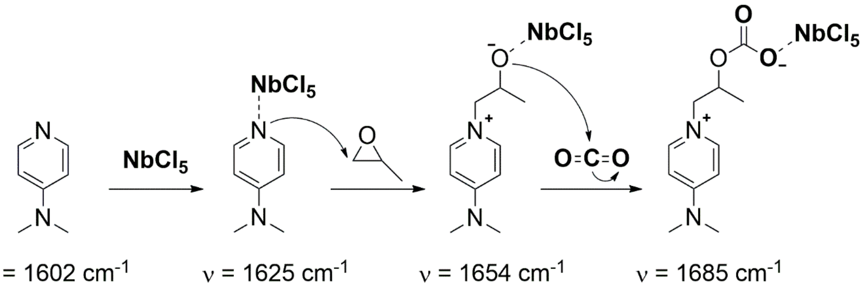


**Figure 1.** The activity order of Zn-based catalysts under the same reaction conditions.

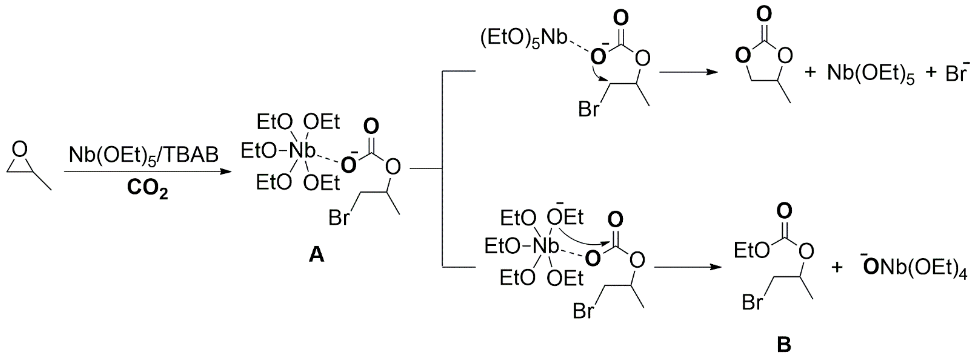
D'Elia *et al.* investigated the catalytic activity under mild conditions (50 °C, 5 atm) of metal halides of early transition metals (groups IV to VI) in combination with 4-dimethylaminopyridine (DMAP) as a nucleophile for the conversion of propylene oxide (PO) to PC.[116] In this series, $NbCl_5$ proved to be the most active homogeneous Lewis acid. When DMAP was replaced by TBAB, the niobium catalytic system could achieve a TOF of over 200 $h^{-1}$ under the same reaction conditions. Inspired by the good catalytic efficiency of the catalysts, $NbCl_5$/DMAP and $NbCl_5$/TBAB were tested under ambient conditions (Table 1, entry 7). The coupling of $CO_2$ with ethylene oxide (EO), an appealing substrate for industry,[25] furnished TOF values as high as 30.3 $h^{-1}$ over $NbCl_5$/TBAB (Table 1, entry 8).

Despite having lower activity, $NbCl_5$/DMAP aided in the *in situ* IR investigation of the reaction mechanism by monitoring the asymmetric ring stretching of the pyridine ring of DMAP and the C=O stretching of the hemicarbonate in the 1600-1700 $cm^{-1}$ region of the spectrum (Scheme 4).[117] This was one of the few cases where the intermediates of the cycloaddition of $CO_2$ to epoxides were actually monitored by *in situ* techniques and clearly identified. Based on the kinetics of the reaction and on the need for a second equivalent of DMAP to induce the final step of cyclization from the hemicarbonate intermediate observed at 1685 $cm^{-1}$ ($\nu_{C=O}$), the authors presented a reaction mechanism involving two molecules of DMAP in the rate-determining ring closure step of the cycloaddition process. One DMAP molecule participates in the formation of the hemicarbonate intermediate, while its free counterpart aids in ring closure by attacking the metal center of the hemicarbonate intermediate. Such a mechanistic view was supported by DFT calculations.



**Scheme 4.** Asymmetric ring stretching region of DMAP and hemicarbonate intermediate.

Numerous niobium complexes in the presence of various nucleophiles were explored by Dutta *et al.* in the pursuit of superior Nb-based catalytic systems for the cycloaddition of $CO_2$ to PO.[118] $NbCl_5$ proved to be the most active catalyst in combination with TBAB as the nucleophile in the following order of activity: $NbCl_5$>$NbBr_5$>$Nb(OEt)_5$≫$NbOCl_3$>$NbF_5$>$Nb(NMe_2)_5$ based on the PC yield attained in 4 h. Regardless of catalytic activity, $Nb(OEt)_5$/TBAB provided the fastest initial reaction rate of all binary catalytic systems tested while exceeding twice the rate for $NbCl_5$/TBAB however, the substrate conversion with this catalyst was only moderate after 12 h (Table 1, entry 9). This contradiction could be explained by the emergence of linear carbonates as by-products observed by *in situ* IR spectroscopy in the reactions catalyzed over $Nb(OEt)_5$/TBAB according to the mechanism displayed in Scheme 5. The hemicarbonate intermediate **A** could access two different mechanistic manifolds leading to different products: the desired PC and an acyclic carbonate **B**, as detected by the C=O stretching at 1747 $cm^{-1}$ in the IR spectra of the reaction mixture (Scheme 5). The latter product would be formed by the release of an ethoxide anion from the niobium center and its subsequent attack on the hemicarbonate carbonyl. The formation of the acyclic carbonate by-product subsequently deactivated the niobium complex, leading to the observed decline in the catalytic activity of $Nb(OEt)_5$/TBAB after the initial turnovers. When considering the activity of the nucleophile, TBAB was the most active out of all the quaternary ammonium halides (TBAC and TBAI). On the other hand, nitrogen nucleophiles were less active than the quaternary ammonium salts, resulting in low carbonate yields. Surprisingly, an acyclic carbonate similar to **B** in Scheme 5 was obtained as the sole product for $Nb(OEt)_5$/DMAP due to the stable nature towards cyclization of the hemicarbonate intermediate formed with DMAP as the nucleophile, as discussed in the previous example, leaving the linear carbonate as the only possible reaction product.



**Scheme 5.** Two plausible pathways of hemicarbonate evolution in the cycloaddition reaction of $CO_2$ to PO catalyzed by $Nb(OEt)_5$ and TBAB.

A rare-earth metal halide exhibiting comparable or greater catalytic activity than $NbCl_5$ when paired with TBAB is $YCl_3$ (Table 1, entry 10); the latter discovery inspired the use of yttrium as a metal center for the preparation of innovative metalorganic frameworks that displayed remarkable performance in the cycloaddition of $CO_2$ to epoxide, although under relatively harsh reaction conditions.[119] Exceeding its capability to work under ambient conditions, $YCl_3$/TBAB was also found to be the most efficient Lewis acid in a screening of metal halides for the cycloaddition of diluted $CO_2$ to epoxides. Therefore, $YCl_3$/TBAB was used as a catalytic system for the first conversion of actual industrial flue gas, including $CO_2$ (10.2%, *v*/v) into cyclic carbonates (Table 1, entry 11).[120]

Metal halides of post-transition metals such as indium were likewise applied to the cycloaddition of $CO_2$ to epoxides. Shibata *et al.* achieved a TOF of 3.3 $h^{-1}$ using a high loading of $InBr_3$ (5 mol%) and $PPh_3$ (10 mol%) in the reaction under ambient conditions (Table 1, entry 12).[121] More recently, Mehrkhodavandi *et al.* reported $InBr_3$/TBAB as another In-based catalytic system.[122] With the same high catalyst loading as $InBr_3$/$PPh_3$ under similar conditions, this catalytic system afforded a TOF of 8.2 $h^{-1}$ for the conversion of glycidyl methyl ether to the corresponding cyclic carbonate (Table 1, entry 13). Despite such a high loading,

$InBr_3$/TBAB was proposed to be suitable for the conversion of epoxides to cyclic carbonates under sub-atmospheric $CO_2$ pressures (0.125 atm, Table 1, entry 14).[122]

Calcium and other alkali metals are attractive metal centers for application in catalysis as they are highly abundant and environmentally benign.[58,123] Werner *et al.* explored a catalytic system combining calcium halides and 18-crown-6 ether (18C6) for the cycloaddition of $CO_2$ to various epoxides.[124] The combination of $CaI_2$ and 18C6 generated an in-situ bifunctional complex (Figure 2). The *in situ* formed calcium-based complex could catalyze the coupling of $CO_2$ to epoxides under ambient conditions without further addition of nucleophilic halides acting, therefore, as a single-component catalyst. The $CaI_2$-18C6 complex (5 mol%) could be adequately employed in the cycloaddition of $CO_2$ to several terminal epoxides, *e.g.* glycidol, terminal aryl, and alkyl epoxides under ambient conditions. High to quantitative carbonate yields were often obtained within 24 h (Table 1, entries 15, 16). To further emphasize the high efficiency of the Ca complex, the authors applied the catalyst for the conversion of less reactive internal epoxides, with the target carbonates being accessible under very mild conditions (45 °C, 10 atm $CO_2$).

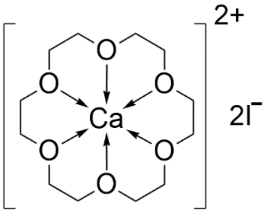


**Figure 2.** *In situ* bifunctional complex of $CaI_2$ and 18-crown-6 ether (18C6).

## 2.2. Surface-supported coordination compounds

While the previous section clearly demonstrates the ability of coordination compounds of transition metals to serve as inexpensive Lewis acids for the cycloaddition of $CO_2$ to epoxides, the main limitation of the molecular catalytic systems comprising coordination compounds and halide nucleophiles is their solubility in the final carbonate products. Although in some cases the halide salts could be precipitated and removed from the products by filtration,[116] or the cyclic carbonates can be purified by distillation under reduced pressure,[125] these tedious and energy-intensive approaches are neither atom-economic nor sustainable. Therefore, our group and other research groups have recently pursued the immobilization of coordination compounds on various materials, mostly readily available metal oxides, to achieve inexpensive heterogeneous Lewis acids and catalysts for the cycloaddition of $CO_2$ to epoxides, which will be discussed in this section.

In principle, metal halides and other coordination compounds can be dispersed on metal oxide supports by simple impregnation techniques.[78,126,127] However, such methodologies generally result in poorly defined catalysts comprising various catalytic sites such as a minority of isolated metal centers, polymeric metal complexes with multiple substitution patterns, and even crystallites of the dispersed metal oxide on the support.[128] The use of the thus prepared system as catalysts does not allow a clear understanding of the catalytic performance of each supported species and may impede the rational utilization of the dispersed metal species. Therefore, recent years have seen a substantial increase in studies focusing on well-defined supported metal centers[129-131] and atomically dispersed catalysts.[132-134] Research on atomically dispersed catalysts aims at the formation of isolated atoms (so-called “single atoms”) on support materials that may favor a more rational utilization of the supported metal centers, leading to very high turnover numbers per metal atom[135-137] or even to specific reactivities and selectivities compared to bulk metals and supported metal nanoparticles.[133,138-140] However, forming single atoms with a tailored coordination environment is challenging as the coordination environment is generally limited to the metal-support interaction.[141] Additionally, in the specific case of the cycloaddition of $CO_2$ to epoxides, single-atom catalysts, whereas highly active as Lewis acid, are generally formed from or included in extended and expensive organic networks that do not conform with the paradigm of high availability for this review.[79,142,143]

A different way to access well-defined surface complexes on metal oxides with an opportunely designed coordination sphere is by the methodology of SOMC.[144,145] The complexes are reacted in well-defined stoichiometric amounts with the hydroxyl groups of the surface of metal oxides. The amount and density of the latter groups can be controlled accurately through simple dehydroxylation treatments under vacuum, leading to mostly isolated hydroxyl groups for temperatures above 500 °C.[146,147] The grafted surface complexes have been successfully used for a large variety of reactions involving C-H activation such as alkane,[144,148] olefin,[145,149] imine metathesis,[150] alkane dehydrogenation,[105,151] as well as $CO_2$ hydrogenation[152,153] and other processes, depending on the design of the coordination environment of the metal.[129,146]

For the cycloaddition of $CO_2$ to epoxides, SOMC studies and comparable techniques have generally employed homoleptic coordination complexes. The latter complexes were grafted on the metal oxide surface by reaction with the surface hydroxyls with one or more ligands acting as leaving groups leading to the immobilization of the molecular fragment as a monopodal (one bond with the support) or bipodal (two bonds with the support) complexes. For an earlier example of the application of SOMC to the synthesis of cyclic carbonates by cycloaddition of $CO_2$ to epoxides, Basset, Pelletier, *et al.* focused on the strong catalytic activity of homogeneous niobium complexes under ambient conditions as discussed above.[116,154,155] Therefore, they immobilized $NbCl_5$ onto silica dehydroxylated at different temperatures ($SiO_{2\text{-}X00}$, where X00 is the temperature of dehydroxylation) by the SOMC method to create active heterogeneous Lewis acids (Figure 3).[156] The different dehydroxylation temperatures of the supports led to a different surface silanol (≡SiOH) density as the anchoring point of the grafted complexes on the surface.[146] Due to the low ≡SiOH density, the grafting of $NbCl_5$ on $SiO_{2\text{-}700}$ led exclusively to monopodal complexes **1a**.[104, 148] Due to the higher silanol density of $SiO_{2\text{-}200}$, two species were observed depending on the amount of $NbCl_5$ applied. As expected, bipodal complex **1b** was obtained by using a stoichiometric amount of $NbCl_5$ compared to the number of silanols,[151,157] while the second species **1c**, made of a pair of adjacent monopodal complexes, was obtained by using an over stoichiometric excess of $NbCl_5$.

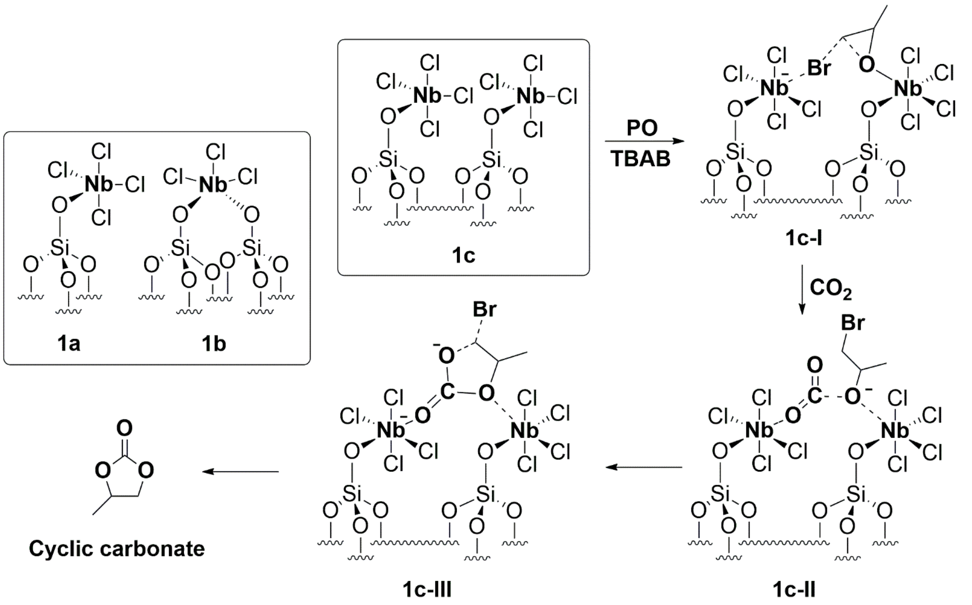
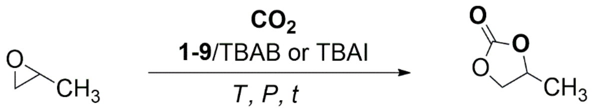


**Figure 3.** Various surface species of $NbCl_5@SiO_2$. Isolated monopodal complex **1a** was prepared on $SiO_{2\text{-}700}$. Bipodal **1b** and neighboring monopodal complexes **1c** were prepared on $SiO_{2\text{-}200}$.

Under the same conditions (60 °C, 10 atm $CO_2$), **1c** had the highest catalytic activity; isolated **1a** was practically inactive, while **1b**, also containing a portion of **1c**, displayed an intermediate activity. (Table 2, entries 1-3). DFT simulations demonstrated that the presence of two neighboring niobium complexes was critical to reducing the energy barrier of the rate-determining step ($CO_2$ activation), as shown in Figure 3 for **1c**. The $CO_2$ insertion was facilitated by a cooperative Nb-Nb mechanism that is certainly not present in **1a,** leading to a much higher $CO_2$ activation barrier (16 kcal/mol higher than for **1c**).

**Table 2.** Overview of catalytic performances of surface complexes **1-9** for cycloaddition of PO to $CO_2$.



| Entry[ref] | Complexes (mol%) | Nucleophile (mol%) | *T* (°C) | *P* (atm) | *t* (h) | Yield (%)[a] |
|---|---|---|---|---|---|---|
| 1[156] | **1a**@$SiO_{2-700}$ (0.33) | TBAB (1) | 60 | 10 | 18 | 25 |
| 2[156] | **1b** (main) + **1c**@$SiO_{2-200}$ (0.33) | TBAB (1) | 60 | 10 | 18 | 61 |
| 3[156] | **1c**@$SiO_{2-200}$ (0.33) | TBAB (1) | 60 | 10 | 18 | 90 |
| 4[158] | **2a**+**2b**(isolated)@$SiO_{2-700}$ (0.33) | TBAB (1) | 60 | 10 | 18 | 96 |
| 5[158] | **2b** (main)+**2c**@$SiO_{2-200}$ (0.33) | TBAB (1) | 60 | 10 | 18 | 90 |
| 6[158] | **2b**+**2c** (≈1:1)@$SiO_{2-200}$ (0.33) | TBAB (1) | 60 | 10 | 18 | 93 |
| 7[162] | **3**@$SiO_{2-700}$ (0.008) | TBAB (1) | 60 | 6.8 | 16 | 29 |
| 8[162] | **3**@$SiO_{2-700}$ (0.012) | TBAB (1) | 60 | 6.8 | 16 | 49 |
| 9[162] | **3**@$SiO_{2-700}$ (0.023) | TBAB (1) | 60 | 6.8 | 16 | 64 |
| 10[166] | **4a**@$SiO_2$ (0.5) | TBAB (1) | 25 | 1 | 24 | 40/63[b] |
| 11[166] | **4b**@$SiO_2$ (0.5) | TBAB (1) | 25 | 1 | 24 | 27/56[b] |
| 12[78] | **5**@$Al_2O_3$ (0.6) | TBAI (1.6) | 60 | 4 | 2 | 100 |
| 13[168] | **6a**@$SiO_2$ (1.27) | - | 25 | 1 | 24 | 92 |
| 14[168] | **6b**@$SiO_2$ (0.29) | - | 25 | 1 | 24 | 93 |
| 15[172] | **7**@$SiO_2$ (0.5) | TBAI (1) | 25 | 1 | 48 | 73 |
| 16[179] | **8a**@SBA-15 (0.5) | TBAB (0.5) | 90 | 10 | 24 | >99 |
| 17[179] | **8b**@SBA-15 (0.5) | TBAB (0.5) | 25 | 1 | 24 | 70 |
| 18[181] | **9** (1.2) | - | 80 | 27.6 | 8 | 99 |

[a] Where isolated yields were not reported in reference data, GC or $^1$H-NMR conversions are provided. [b] Selectivity (%) of propylene cyclic carbonate.

In search of alternative heterogeneous Lewis acids for the cycloaddition of $CO_2$ to epoxides, the same group investigated the grafting of $ZrCl_4$ onto silica.[158] Depending on the kind of dehydroxylated silica support ($SiO_{2-200}$ or $SiO_{2-700}$), different stoichiometric quantities of the $ZrCl_4(OEt)_2$ precursor were used, resulting in the formation of distinct surface complexes **2a-2c** (Figure 4) in varying proportions. A catalyst synthesized with the $SiO_{2-700}$ support featured two separate monopodal surface species: **2a** with two ether ligands, and **2b** with one ether ligand replaced by a coordination bond with a surface siloxane bridge.[159, 160] $SiO_{2-200}$ support was used to synthesize the remaining two catalysts. The first was primarily formed of monopodal **2b** species with a density ratio of zirconium atoms to silanol moieties comparable to niobium-based **1c**, implying a possible cooperation between nearby Zr atoms. In the other case, similar proportions of monopodal **2b** and bipodal **2c** were detected. Surprisingly, when all three catalysts were evaluated for $CO_2$ cycloaddition to epoxides in the presence of TBAB under identical reaction conditions (60 °C, 10 atm $CO_2$), their catalytic activity was comparable despite the apparent differences in surface species compositions (Table 2, entries 4-6). This result is clearly in disagreement with what was observed for the surface niobium complexes in Figure 3; however, for the zirconium complexes, DFT investigation revealed that a bimetallic mechanism had no effect on lowering the energy barrier of the rate-determining step (cyclization).[117,161] Furthermore, the zirconium-based catalysts could give a nearly complete conversion of low levels of $CO_2$ (≈10%v/v) in actual flue gas sourced from the fume stack of a cement factory into cyclic carbonates counting as the first example of the application of heterogeneous catalysts for the conversion of flue gas $CO_2$ to value-added products.

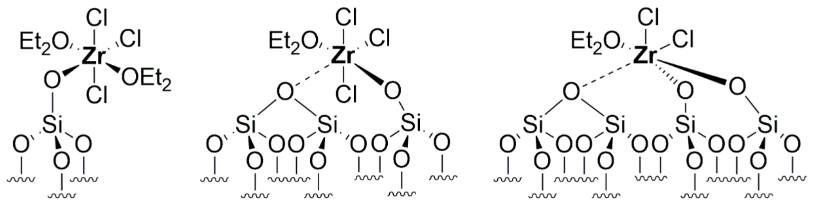

**2a** **2b** **2c**

**Figure 4.** Proposed surface structures of $ZrCl_4(OEt)_2@SiO_2$. Isolated monopodals bearing two ether ligands **2a** and one ether replaced by siloxane bridge **2b** were prepared on $SiO_{2\text{-}700}$. The isolated monopodal **2b** and bipodal **2c** were prepared on $SiO_{2\text{-}200}$.

More recently, Basset *et al.* substituted organometallic $Zr(CH_3)_4(THF)_2$ for metal halides as precursors in the SOMC synthesis of zirconium complexes for the coupling of $CO_2$ with epoxides.[162] The synthesized catalyst **3** (Figure 5), which used $SiO_{2\text{-}700}$ as the support, was made up of two surface species: the minor monopodal complex with three methyl groups **3a** and the major bipodal complex **3b**, which was presumably formed by the rearrangement of a monopodal species and a siloxane bridge of the silica support.[163] Under comparable conditions (60 °C, 7 atm $CO_2$) as in earlier examples, the use of low loadings of **3** for $CO_2$ cycloaddition to PO with high loadings of TBAB (TBAB/Zr≈40-130) resulted in moderate PO conversions with high turnover numbers (TON) up to 4200 (Table 2, entry 7-9). Disregarding the possibility of $CO_2$ activation *via* insertion into the metal–alkyl bond,[164] which might result in high catalytic performance, DFT analyses verified that the cycloaddition reaction catalyzed by **3** followed the conventional Lewis-acid catalyzed cycloaddition mechanism.[165]

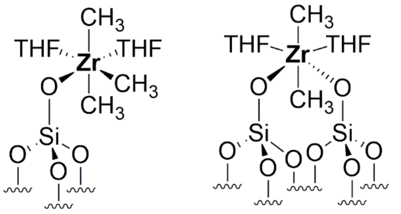
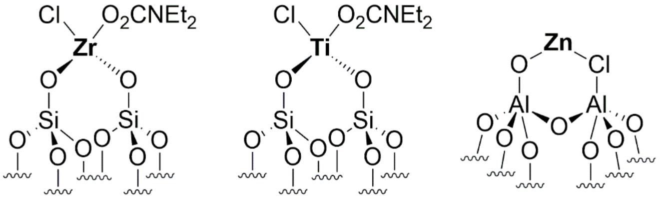

**3a**
(Minor)
**3b**
(Major)

**Figure 5.** Zirconium precursor grafted onto dehydroxylated silica at 700 °C, $Zr(CH_3)_4(THF)_2@SiO_2$ **3**.

Using the SOMC method, Pampaloni *et al.* first developed a heterogeneous Lewis acid catalyst that could transform epoxides into cyclic carbonates under ambient conditions.[166] Initially, a library of homogeneous metal *N,N*-dialkylcarbamates were tested for their catalytic activity in the cycloaddition of $CO_2$ to PO under ambient conditions (25 °C, 1 atm $CO_2$). Besides $Al(O_2CNEt_2)_3$, $Cu(O_2CNEt_2)_2$, and $Sn(O_2CNEt_2)_4$, which yielded PC quantitatively, the other complexes provided overall moderate to adequate epoxide conversions with PC selectivities ranging from 30% to 75%. The authors, on the contrary, utilized partially halogenated metal precursors $ZrCl_2(O_2CNEt_2)_2$ and $TiCl_2(O_2CNEt_2)_2$ for grafting onto pretreated (160 °C) silica substrate to synthesize the heterogeneous Lewis acids. According to the partial dehydroxylation of the support and the experimentally determined atomic ratio of roughly one chlorine atom per metal center, the produced surface species were attributed to the structures of **4a** and **4b** (Figure 6). Under ambient conditions, these heterogeneous catalysts in the presence of TBAB were preliminarily tested and found to lead to moderate PO conversions and relatively poor PC selectivities for $CO_2$ cycloaddition (Table 2, entries 10, 11).

The first homogeneous Lewis acid to catalyze the coupling of $CO_2$ with epoxides under ambient conditions was $ZnCl_2$, a readily available metal halide.[108] Alonso, Beletskaya, *et al.* immobilized $ZnCl_2$ onto metal oxide surfaces motivated by the absence of a heterogeneous analog of Zn-based Lewis acids.[78] Immobilization was accomplished by grinding $ZnCl_2$ (10 wt%) on different oxides ($Al_2O_3$, $CeO_2$, $SiO_2$, $TiO_2$, and so on) to generate metal oxide-supported zinc dichloride. All synthesized catalysts were screened for the cycloaddition of $CO_2$ to styrene oxide (SO) in the presence of TBAI under mild conditions (60 °C, 4 atm $CO_2$). They all proved efficient as Lewis acid catalysts that performed noticeably better than the unfunctionalized metal oxides in the same reaction environment, allowing complete epoxide conversion in 6-16 h. The best catalytic activities were observed for zinc salts on metal oxides; hence, $Al_2O_3$-supported $ZnCl_2$ ($ZnCl_2@Al_2O_3$) was chosen for further exploration. Following IR investigation, the existence of Al-O-Zn-Cl moieties on the alumina surface was proposed **5** (Figure 6). The $ZnCl_2@Al_2O_3$/TBAI system was capable of quantitatively converting various terminal epoxides to their corresponding cyclic carbonates in 2-8 h (Table 2, entry 12 for PO); however, fluoride-containing epoxides were found to be less active, requiring a longer time (24 h) to complete conversion. Conversely, internal epoxides were considered more demanding[45,66] as they only allowed for moderate carbonate production under harsher conditions. It was postulated that two zinc metal centers cooperated in the reaction mechanism, one coordinating $CO_2$ and the other engaging in the epoxide ring opening. This mechanism is comparable to the reaction mechanism of bis-Al salen complexes,[167] although it has not been computationally examined.



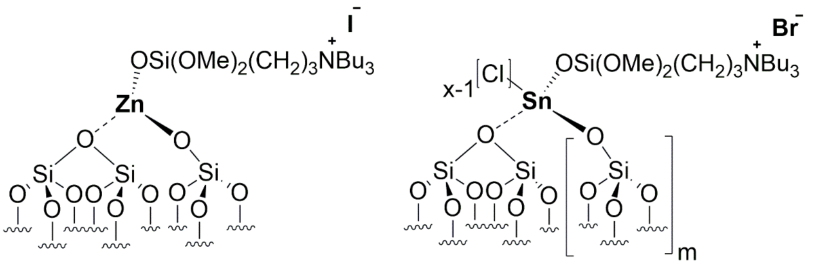
**4a** **4b** **5**

**Figure 6.** Halogenated metal precursors grafted on pretreated silica 160 °C as $ZrCl_2(O_2CNEt_2)_2@SiO_2$ **4a** and $TiCl_2(O_2CNEt_2)_2@SiO_2$ **4b**. $ZnCl_2$ supported on $Al_2O_3$, $ZnCl_2@Al_2O_3$ **5**.

It is important to note that the afore-mentioned catalytic processes are only partially heterogeneous since the addition of soluble quaternary ammonium halides was generally required as sources of homogeneous nucleophiles. D'Elia *et al.* recently reported heterogeneous bifunctional catalysts composed of silica-supported metal complexes (zinc and tin) with anchored quaternary ammonium nucleophiles for the conversion of pure and impure $CO_2$ into cyclic carbonates under (or near) ambient conditions **6a** and **6b** (Figure 7).[168] As part of a rational investigation, under ambient settings, the catalytic activity of various commercial metal (group 12-15) halides was screened for the coupling of $CO_2$ with epichlorohydrin (ECH) in the presence of quaternary ammonium and phosphonium nucleophiles. Based on previous screening, the most practical binary systems were $ZnCl_2$/TBAI and $SnCl_4$/TBAB. This result was exploited to prepare single-component heterogeneous catalysts with high activity. To that aim, different loadings of the metal precursors were first grafted onto the silica support either by mechanical grinding ($ZnCl_2$) or by impregnation ($SnCl_4$, due to its liquid nature). To complete the synthesis of the catalysts, quaternary ammonium halides were immobilized onto the halide-grafted silica surface by using the same quantity of ionic liquids tributyl(3-trimethoxysilylpropyl) ammonium iodide or bromide (IL-X) for $ZnCl_2$ and $SnCl_4$, respectively. Based on the observation that the amount of grafted ionic liquid increased with the amount of metal halide on the support, the authors hypothesized the formation of structures **6a** and **6b** from a $\sigma$–bond metathesis process.[169]

Under mild conditions (40 °C, 1 atm $CO_2$), the prepared bifunctional catalysts with varied metal and IL-X loadings were screened for the ECH conversion to chloropropene carbonate. The best catalytic performance was obtained for catalysts with moderate metal contents. Following preliminary screening, the most active zinc and tin metal catalysts were tested at ambient conditions (25-40 °C, 1 atm $CO_2$) with a variety of epoxides coupled with $CO_2$ into their respective carbonates to achieve high conversions and selectivities

(Table 2, entries 13, 14). Furthermore, under relatively mild conditions, these catalysts could convert impure (including 20% $CH_4$ with/without 1000 ppm $H_2S$) and diluted (50% in $N_2$) $CO_2$ with glycidyl methacrylate to yield the equivalent carbonate quantitatively as a useful compound for polymer synthesis.[22,170,171] This process offers an alternative way to manage low calorific landfill gases with insufficient methane levels for flaring.



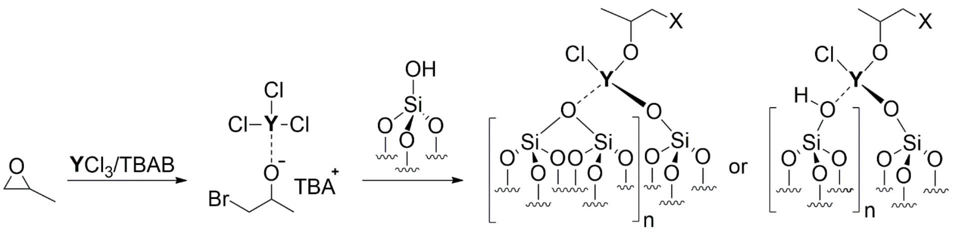
**6a**

**6b**

x = 1-3, m = 3-1

**Figure 7.** Silica-supported zinc **6a** and tin **6b** complex with quaternary ammonium moieties.

Based on the exceptional catalytic performance of $YCl_3$ as a homogeneous catalyst,[120] D'Elia *et al.* sought an analogous yttrium-based heterogeneous catalyst prepared by the SOMC method for the cycloaddition of $CO_2$ to epoxides under ambient conditions.[172] As $YCl_3$ is recognized to be insoluble in common SOMC solvents, the authors proposed an approach to generate a soluble homogeneous adduct between $YCl_3$, quaternary ammonium bromide (TBAB), and the PO substrate as identified in the homogeneous cycloaddition reaction. In homogeneous catalysis, when the bromide anion of TBAB opens the epoxide ring of the yttrium-coordinated epoxide to generate an alkoxide intermediate, a soluble $YCl_3$ complex is formed (Scheme 6). Compound **7** was generated by grafting the soluble alkoxide complex, which used $SiO_{2\text{-}700}$ as support.



**Soluble Yttrium alkoxide intermediate**

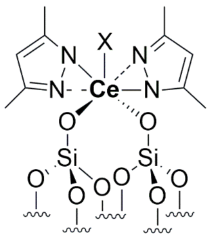
7
X = Cl, Br

7'
X = Cl, Br

**Scheme 6.** Formation of yttrium alkoxide and immobilization on dehydroxylated silica**.** Yttrium alkoxide complex grafted on $SiO_{2\text{-}700}$ ($YCl_3$+PO+TBAB@$SiO_{2\text{-}700}$, **7** and its analog supported on $SiO_{2\text{-}200}$ **7'**.

For comparison, another catalyst **7'** (Scheme 6) was synthesized on silica dehydroxylated at lower temperatures and vacuum. Despite **7** performing slightly better than **7'** when tested on numerous epoxides in the presence of TBAI under mild conditions (60 °C, 1 atm), **7'** was chosen as a more accessible analog to study the catalytic performance of this kind of complexes at ambient settings. A moderate loading of 0.5 mol% of yttrium complex in the presence of 1 mol% TBAI led to moderate to good yields of the target cyclic carbonates in 48 hours (Table 2, entry 15). Despite the long reaction time required with this catalytic system, inorganic heterogeneous catalysts capable of carrying out the $CO_2$ cycloaddition to epoxides under ambient conditions remain highly uncommon. Indeed, the catalytic performance of **7'** is comparable to that of more elaborate catalysts such as MOFs,[173,174] metal-based porous organic polymers,[175, 176] and other metal-organic ligand-based heterogeneous compounds,[177,178] despite the use of significantly lower loading of homogeneous additives.

Anwander *et al.* grafted homoleptic Ce(IV)$^+$ and Ce(III)$^+$, 3,5-dimethylpyrazolate ($Me_2pz$) based complexes $[Ce(Me_2pz)_4]_2$, $Ce(Me_2pz)_4(THF)$ and $Ce_4(Me_2pz)_{12}$ onto high-surface mesoporous silica (SBA-$15_{500}$) supports dehydroxylated at 500 °C under vacuum.[179] Previously, it was discovered that these homogeneous cerium-based complexes could efficiently and reversibly insert $CO_2$ into the metal−pyrazolate bond and catalyze the $CO_2$ cycloaddition to epoxides with TBAB in ambient (or nearly ambient) conditions.[180] Grafting of the complexes was successful using the SOMC approach, as the release of $Me_2pzH$ moieties *via* protonolysis resulted in surface-bound complexes with differing oxidation numbers and metal nuclearity (Ce(IV)$^+$ complexes are shown in Figure 8 as **8a** and **8b**). This technique was also used to synthesize heterogeneous lanthanum analogues. The immobilized complexes were demonstrated to be effective at capturing $CO_2$ through its insertion into metal-pyrazolate moieties, with a weight increase of 10 wt% for Ce(IV)$^+$-based catalysts **8a** and **8b** and 20 wt% (4.54 mmol $CO_2$/g) for their Ce(III)$^+$ counterparts. In the cycloaddition of $CO_2$ to PO in the presence of TBAB (90 °C, 10 atm $CO_2$), all supported species afforded similar catalytic activity. A quantitative production of PC (Table 2, entry 16) and a few other carbonates in high yields could be achieved with low loadings of **8a** (0.1-0.5 mol/mol). Moreover, the **8b**/TBAB catalytic system could achieve catalytic performance comparable to **7'**/TBAI within a shorter reaction time of just 24 h (Table 2, entry 17) for the coupling of $CO_2$ with PO under ambient conditions. These findings suggest that rare earth metal-based heterogeneous catalysts are suitable Lewis acids for catalyzing the conversion of $CO_2$ to cyclic carbonates under relatively mild conditions.

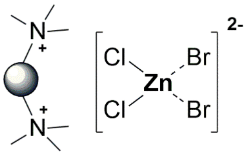


X = $Me_2pzH$ (**8a**), THF (**8b**)

**Figure 8.** Immobilization of cerium pyrazolate complexes, $[Ce(Me_2pz)_4]_2$@SBA-15 are shown as **8a** and **8b**.

Notably, the supports for the generation of efficient, surface-support coordination compounds for the cycloaddition of $CO_2$ to epoxides are not limited to metal oxides. Lee *et al.* supported zinc halides (*i.e.* $ZnBr_2$) on an ion exchange resin featuring quaternary ammonium moieties (Amberlite IRA-900) to construct a unique single-component catalyst for the cycloaddition of $CO_2$ to epoxides.[181] Zinc halides are immobilized by interacting with chloride anions on the resin surface to generate negatively charged zincates $(ZnCl_2)\cdot 2Br^-$ **9** (Figure 9), which resemble homogeneous interactions between zinc salts and quaternary ammonium chlorides.[182] In **9**, a strongly Lewis acidic zinc center for epoxide activation is combined with halide ions as nucleophiles for epoxide ring-opening and leaving groups in the final cyclization step.[108, 117, 121] When the resin-based material was employed for the $CO_2$ cycloaddition to PO and other terminal epoxides in the absence of homogenous nucleophiles, harsh reaction conditions (80 °C, ~28 atm) were required to achieve moderate to good epoxide conversions in 2 h and high PC yield in 8 h (Table 2, entry 18); however, the addition of soluble nucleophiles was not required. Because of its single-component nature, the catalyst could be employed in a plug-flow reactor under flow conditions (100 °C, ~28 atm). Over 96 hours, it exhibited efficient epoxide conversion and relatively stable PC yields without zinc leaching.

For the case of the heterogeneous Lewis acids and single-component catalysts discussed in this work, it is essential to take recyclability into account. In general, SOMC-produced Lewis acids undergo progressive deactivation through various catalytic cycles due to several factors. For instance, the recycling process of **1c**[156] was done in four successive cycles by adding fresh TBAB as a nucleophile at each cycle, demonstrating a significant reduction in propylene carbonate yield from the second cycle onwards. A frequently encountered deactivation factor in the $CO_2$ cycloaddition to epoxides, shared by many heterogeneous catalysts, including this complex, is the material loss during the challenging separation from the viscous carbonate product. In a real case scenario of large-scale production of cyclic carbonates, the latter issue would clearly not appear because the catalysts would be used in a pelletized format within a dynamic reactor rather than undergo recovery by filtration at each cycle. However, the primary determinant for **1c** deactivation lies in the dehalogenation process, wherein larger metal-alkoxide intermediates substitute halide ligands. This substitution reduces both the accessibility and Lewis acidity of the metal center. The secondary factor is attributed to metal leaching, as confirmed by inductively coupled plasma optical emission spectroscopy (ICP-OES) analysis of the carbonate product. Unsurprisingly, the surface complex with the most stable catalytic performance is **5** (Figure 6),[78] affording nearly quantitative PC yield even after five consecutive cycles in the presence of TBAI due to the lack of halogen ligands on the metal and strong metal-support interaction of the bipodal complex.



**9**

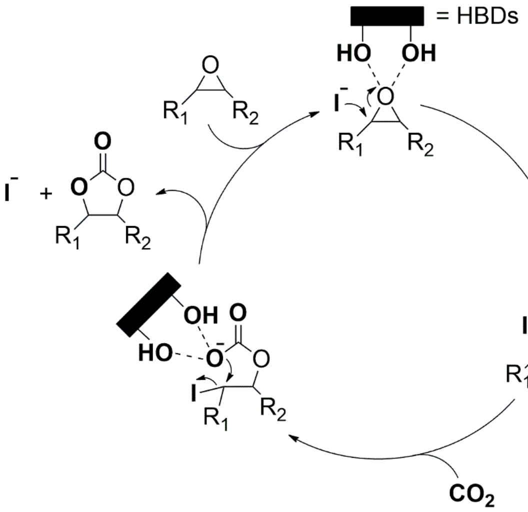
**Figure 9.** Lewis acidic $ZnBr_2$ grafted on ion exchange resin $ZnBr_2$@IER **9**.

## 3. Cycloaddition of $CO_2$ to epoxides catalyzed by biobased H−bond donors

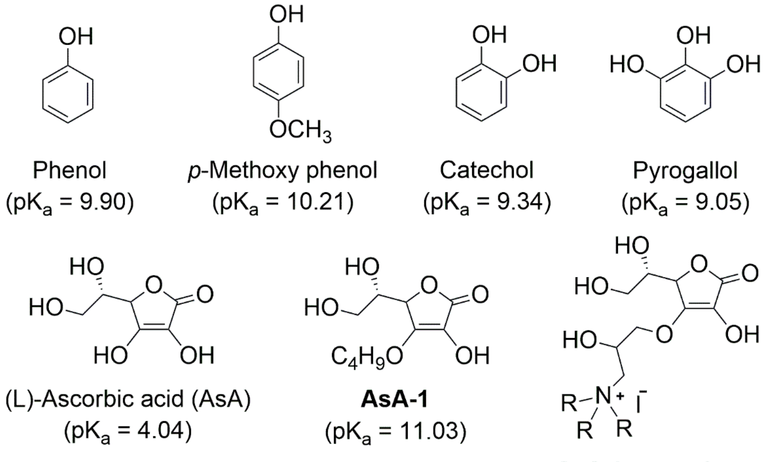
An alternative class of molecules able to serve as catalytic components for the cycloaddition of $CO_2$ to epoxides is represented by HBDs. The HBDs carry out the activation of the epoxide moiety by establishing a network of H−bonds with the oxygen atom of the oxirane ring that, in turn, weakens the C−O bonds, leading to epoxide activation. When combined with quaternary ammonium salts as sources of nucleophilic halide anions, the HBDs can efficiently carry out the cycloaddition of $CO_2$ to a variety of epoxides, albeit with lower turnover numbers under ambient conditions when compared to metal coordination compounds.[43]

Nevertheless, HBDs/quaternary ammonium systems, due to their organocatalytic nature, are regarded as less toxic and expensive and more moisture resilient than metal compounds.[87,97] Overviews of organocatalytic systems, most of them HBD-based, for the cycloaddition of $CO_2$ to epoxides are provided elsewhere,[42,44,84] as well as a comparison of various HBDs applied under ambient conditions;[43] herein, in line with scope of this manuscript, we will only discuss biobased H−bond donors that are active under ambient conditions as well as the related mechanistic aspects. While different kinds of HBDs exist for the cycloaddition of $CO_2$ to epoxides bearing -NH,[183] -OH,[184] -CH[185] moieties as H−bond donors, the HBDs in this section are generally hydroxyl HBDs that activate the H−bond through the mechanism shown in Scheme 7.

(L)-Ascorbic acid (AsA), commonly recognized as vitamin C, a readily available biobased compound (Figure 10), was studied by our group in the cycloaddition of $CO_2$ to epoxides under ambient conditions as an alternative to synthetic and potentially toxic HBDs.[186] In addition to its easy accessibility, ascorbic acid is a renewable, cost-effective, and eco-friendly catalyst. In a catalytic screening involving different kinds of commercially available biobased HBDs in the presence of TBAI, the use of ascorbic acid resulted in the highest epichlorohydrin (ECH) conversion (70%) to the corresponding carbonate under ambient conditions (Table 3, entry 5). A quantitative ECH conversion (94%) was attained by raising the reaction temperature slightly to 40 °C. Several other terminal epoxides could also be converted under ambient reaction conditions, whereas more sterically hindered epoxides required a mild reaction temperature of 60 °C under atmospheric pressure. The authors elucidated the role of the different hydroxyl groups (ethyldiol, enediol) within ascorbic acid through a DFT-based mechanistic investigation of the AsA/TBAI catalytic system. It was found that the cooperation between the enediol and ethyldiol hydroxyl groups of AsA reduced the energy barrier required for inserting $CO_2$, leading to milder reaction barriers. This observation was confirmed by protecting the ethyldiol moiety in the form of an acetal group, leading to an ascorbic acid derivative with lower catalytic efficiency.



**Scheme 7.** Cycloaddition of $CO_2$ to epoxides promoted by hydroxyl H−bond donors.



Phenol ($pK_a = 9.90$)

*p*-Methoxy phenol ($pK_a = 10.21$)

Catechol ($pK_a = 9.34$)

Pyrogallol ($pK_a = 9.05$)

(L)-Ascorbic acid (AsA) ($pK_a = 4.04$)

**AsA-1** ($pK_a = 11.03$)

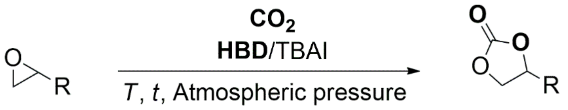
**AsA-2**, (R = $-C_2H_5$)
**AsA-3**, (R = $-C_4H_9$)

**Figure 10.** Biobased homogeneous HBDs and their $pK_a$ values.

In a further development by our group, we looked into the aspects determining the catalytic activity of hydroxyl hydrogen−bond donors, such as the number of hydroxyl moieties, that has a clear role in the ability to establish multipoint H−bond networks, and the $pK_a$ of the HBDs because the strength of the H−bond is closely related to the $pK_a$ of the hydroxyl groups according to the work of Gilli *et al.*[187] Therefore, various compounds with a different number of hydroxyl groups and with a broad spectrum of $pK_a$ values such as phenols, ascorbic acid and its derivatives, carboxylic acids, as well as mono- and aliphatic polyalcohols were investigated in the cycloaddition of $CO_2$ to epichlorohydrin under ambient conditions.[188] In the presence of TBAI as the nucleophile, phenol, *p*-methoxyphenol, and its polyhydroxyphenol counterparts (depicted in Figure 10) emerged as the most active HBDs.

In all cases, the phenolic derivative afforded good epoxide conversions, as indicated in Table 3, entries 1-4. that were higher than for the much more acidic ascorbic acid (Table 3, entry 5, based on the $pK_a$ of the most acidic protons listed in Figure 10). According to the phenolic series, no evident correlation was observed between the number of hydroxyl groups in the HBDs and catalytic activity, as a single hydroxyl group in phenol proved satisfactory in achieving high catalytic performance. Overall, by considering the whole spectrum of hydroxyl HBDs tested, no evident correlation between catalytic activity and the number of hydroxyl groups in the HBD was observed, whereas the $pK_a$ values of the HBDs directly influenced the catalytic activity. Generally, the phenolic compounds aligned with an optimal Brønsted acidity range ($pK_a$=9.0-10.5). When the $pK_a$ exceeded 12 or was lower than 8, there was a strong decline in catalytic performance. Overall, it was concluded that the catalytic activity of the highly acidic HBDs would be limited by the protonation of the crucial alkoxide intermediate while the HBDs with too low acidity would provide only a weak substrate activation, leading to a volcano-type plot with a maximum at about 10 for the $pK_a$. After identification of the suitable $pK_a$ range, a derivative of ascorbic acid (**AsA-1**, Figure 10) was synthesized to access the near-optimal acidity by protecting the hydroxyl proton of the most acidic enediol group ($pK_a \approx 4$), which resulted in the formation of a less acidic yet more active HBD denoted with $pK_a \approx 11.34$. Under identical conditions as the other HBDs, **AsA-1** exhibited a higher conversion of epichlorohydrin than AsA, which was comparable to the activity of phenolic HBDs (Table 3, entries 1-6).

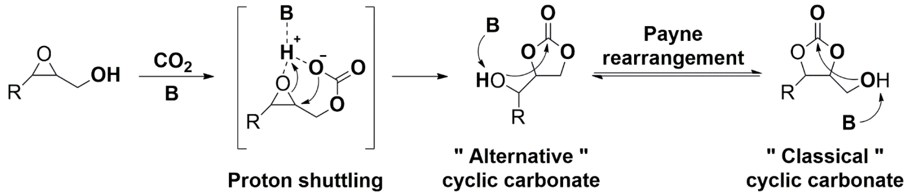
**Table 3.** Catalytic performances of homogeneous HBDs in the cycloaddition of $CO_2$ to epoxides.



| **Entry[ref]** | **R** | **HBD (mol%)** | **TBAI (mol%)** | ***T* (°C)** | ***t* (h)** | **Conversion (%)[a]** | **TON/TOF ($h^{-1}$)** |
|---|---|---|---|---|---|---|---|
| 1[188] | $CH_2Cl$ | Phenol (2) | 4 | 25 | 23 | 87 | 43.50/1.89 |
| 2[188] | $CH_2Cl$ | *p*-methoxyphenol (2) | 4 | 25 | 23 | 84 | 41/1.83 |
| 3[188] | $CH_2Cl$ | Catechol (2) | 4 | 25 | 23 | 82 | 41/1.78 |
| 4[188] | $CH_2Cl$ | Pyrogallol (2) | 4 | 25 | 23 | 82 | 41/1.78 |
| 5[186] | $CH_2Cl$ | (L)-Ascorbic acid (2) | 4 | 25 | 23 | 70 | 35/1.52 |
| 6[188] | $CH_2Cl$ | **AsA-1** (2) | 4 | 25 | 23 | 80 | 40/1.74 |
| 7[196] | $CH_2OH$[b] | $Na_3$-citrate (2) | - | 60 | 24 | 100/99[c] | 45.50/1.90 |
| 8[201] | $C_6H_5$ | **AsA-2** (4) | - | 60 | 24 | 57 | 14.25/0.59 |
| 9[201] | $C_6H_5$ | **AsA-3** (4) | - | 60 | 24 | 97 | 24.25/1.01 |
| 10[d,e,201] | $C_4H_9$ | **AsA-2** (4) | - | 80 | 24 | 99 (90)[f] | 22.50/0.94 |
| 11[e,201] | $C_4H_9$ | **AsA-2** (4)+KI[g] | - | 80 | 24 | 51 | 12.75/0.53 |
| 12[d, 201] | $C_4H_9$ | **AsA-2** (4)+seawater[h] | - | 80 | 12 | 99 (96)[f] | 24/2 |

[a]Conversion determined by $^1$H-NMR spectroscopy. [b]Using dry glycidol. [c]Selectivity (%) of glycerol carbonate. [d]Using 10 atm of $CO_2$. [e]Using 0.5 mL of water in the reaction mixture. [f]Isolated yield from phase separation. [g]Using 4 mol% of KI. [h]Using 0.5 mL of seawater (2.5 mol% NaCl relative to epoxide).

Glycerol carbonate (GC) is a crucially important cyclic carbonate with promising applications in multiple areas.[189,190] There are various ways to produce GC, such as the transesterification of dimethyl carbonate with glycerol[191,192] and the thermodynamically unfavorable reaction between glycerol and $CO_2$.[193] However, the cycloaddition of $CO_2$ to glycidol remains the only atom-economic approach. Besides the typical mechanistic manifold in Scheme 7, the cycloaddition of $CO_2$ to epoxyalcohols, such as glycidol, is known to proceed *via* a proton shuttling mechanism leading to a different cyclic carbonate species compared to the product of the "classical" cycloaddition reaction (Scheme 8).[194,195] The product of the proton shuttling pathway can convert into the "classical" cyclic carbonate product *via* a Payne-type rearrangement (however the two products are undistinguishable for the case of glycidol). Previous investigations on the conversion of epoxyalcohols to cyclic carbonates had focused on using organometallic complexes,[194] or on strong oil-based organic bases.[195] Therefore, the catalytic performance of various readily-available, halogen-free, biobased organic salts was tested for the transformation of glycidol into GC under atmospheric conditions (60 °C, 1 atm $CO_2$).[196]

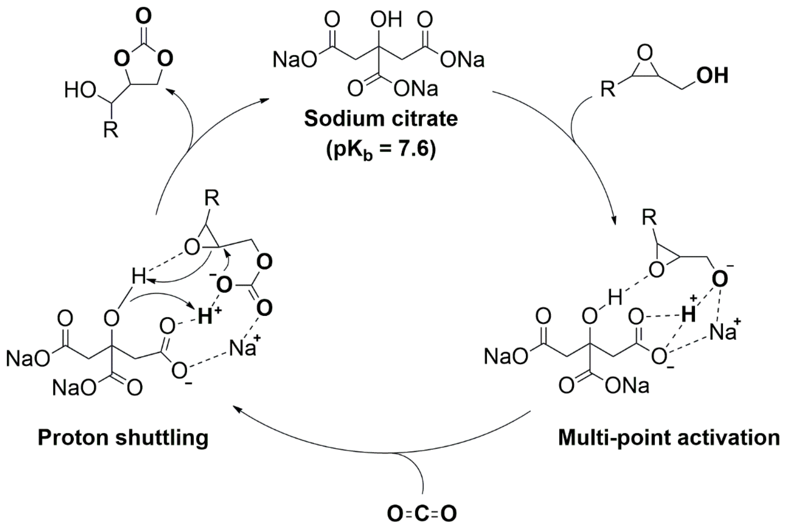


**Scheme 8.** Halogen-free cycloaddition of $CO_2$ to epoxy alcohol *via* a proton-shuttling mechanism to achieve alternative and classical products (Payne rearrangement).

While HBDs such as ascorbic acid was not active for this transformation in the absence of halide-based additives, organic salts of alkali metals displayed remarkable catalytic activity in the absence of halides. Despite its partially heterogeneous nature in the reaction mixture, under atmospheric conditions at 60 °C, sodium citrate ($Na_3$-citrate) was found to be the most efficient biobased catalyst, achieving complete glycidol conversion and high selectivity (Table 3, entry 7) towards GC in place of other undesired products such as glycerol or polyether (product of glycidol homopolymerization). However, because moisture promoted the formation of the glycerol by-product, the selectivity for dry glycidol (99%) was notably greater compared to its commercial form (87%).

Additionally, $Na_3$-citrate could not catalyze the cycloaddition of $CO_2$ to epoxides without α-hydroxyl moieties in the absence of a nucleophilic halide, indicating that, for the case of glycidol, the reaction would no proceed *via* the "classical" cycloaddition mechanism but through the proton-shuttling manifold of Scheme 8. Kinetic investigation showed that the reaction catalyzed by $Na_3$-citrate was first order in glycidol concentration and zeroth order in $CO_2$ pressure, indicating that the rate-determining step was the initial epoxide activation (Scheme 9). The reaction order in $Na_3$-citrate concentration was fractional (likely because of its only partial solubility), indicating the involvement of the catalyst in the rate-determining step. Additional information was provided by the catalytic performance of strong organic bases such as DMAP and DBU that led exclusively to the polyether byproduct. The same observation applied to organic salts devoid of an H−bonding moiety, such as sodium benzoate and propionate. Overall, the moderate basicity of the citrate anion ($pK_b$=7.6) and the presence of a hydroxyl group as HBD were found to be crucial features of $Na_3$-citrate for the coordination and activation of glycidol and to prevent the undesired attack of the coordinated alkoxide to another glycidol molecule leading to the polyether by-product. The role of the metal cations ($Na^+$, $Ca^{2+}$, and $K^+$) was investigated. $Ca_3$-(citrate)$_2$ had a low solubility in the substrate, leading to poor catalytic performance. $K_3$-citrate was fully soluble in the reaction medium but lacked selectivity towards the desired GC, leading nearly exclusively to the formation of polyether. It was proposed that the larger potassium ion radius led to a weaker interaction between the activated alkoxide and the carboxylate, leading to an improved selectivity for the polyether.

Sodium citrate was further investigated in the cycloaddition of $CO_2$ to other epoxy alcohols (Scheme 10). Two distinct carbonate products were formed, whether it be internal or secondary, and tertiary epoxy alcohols employed as the epoxide substrate. These products consist of a mixture of carbonates obtained *via* the proton-shuttling mechanism (*i.e.* containing a secondary alcohol group) and the products that would be obtained *via* a "classical" cycloaddition mechanism (*i.e.* containing a primary alcohol group). Because the "classical" cycloaddition mechanism is not viable in the absence of halide nucleophiles, the latter carbonates were clearly generated *via* the "Payne rearrangement"[195] (Scheme 8) of the carbonates obtained *via* the proton-shuttling pathway.



**Scheme 9.** Proposed mechanism for the conversion of epoxy alcohol into cyclic carbonate over $Na_3$-citrate.

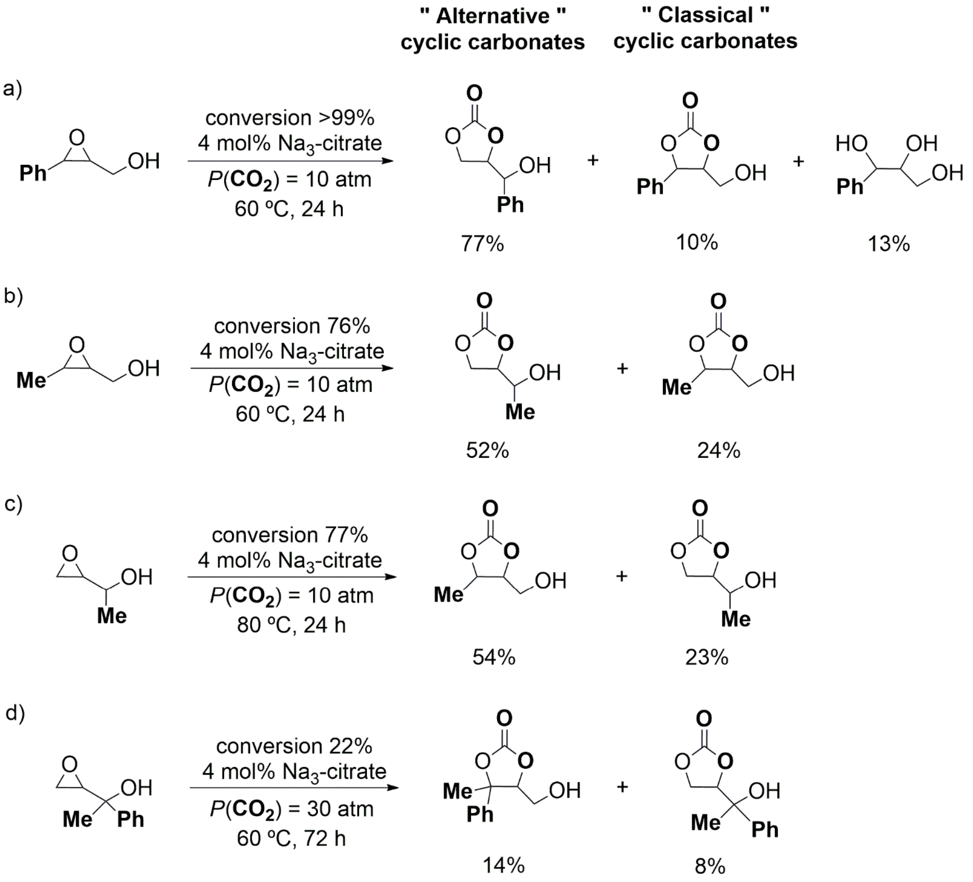
### 3.1 Recyclable biobased hydrogen−bond donors

Although biobased HBDs such as ascorbic acid serve as easily accessible green catalytic components for the cycloaddition of $CO_2$ to epoxides, their homogeneous nature prevents their recycling and requires purification of the carbonate product *via* chromatographic methods that are not convenient in the large scale. It is therefore convenient to look into recyclable and/or heterogeneous biobased HBDs. In this context, several studies in recent years have focused on the upcycling of hydroxyl-rich bioderived waste materials as heterogeneous, recyclable components for the synthesis of cyclic carbonates.[44]

Various studies have focused on using cellulose, lignin, and lignin-containing wastes such as sugar cane bagasse as heterogeneous HBDs.[197-199] Nevertheless, these catalytic systems required relatively harsh reaction conditions ($T$=80-120 °C, $P$=10-20 atm). More recently, phenolated lignin nanoparticles were found to promote the cycloaddition of $CO_2$ to epoxides at mild temperatures (60-80 °C) and atmospheric pressure.[200] Nevertheless, in all cases, the catalytic systems comprised a heterogeneous HBD material and soluble halide additives, which still commanded the purification of the carbonate after the removal of the HBD. Overall, traditional biobased HBD materials that are reviewed in detail in previously published works,[44, 97] are yet to provide efficient, homogeneous-additive free HBDs for the cycloaddition of $CO_2$ to epoxides under ambient or very mild conditions and are, therefore, not discussed further in this work.

Therefore, motivated by the enhanced activity observed for ascorbic acid **AsA-1**, our groups devised a method to create single-component ascorbic acid-based molecular catalysts (**AsA-2** and **AsA-3**, as shown in Figure 10) to serve as recyclable catalysts for the cycloaddition of $CO_2$ to epoxides in biphasic systems comprising an aqueous phase.[201] Structurally, **AsA-2** and **AsA-3** bear both hydrogen−bonding moieties and a halide nucleophile, enabling their use as single-component catalysts.

Despite their molecular nature, due to their high solubility in water compared to the carbonate product phase, **AsA-2** and **AsA-3** could be recovered just by phase separation and recycled as aqueous solutions for the next biphasic reaction. This biphasic approach simplified the retrieval of the catalyst and allowed to receive the cyclic carbonates under mild conditions without the need for additional purification steps. Interestingly, the developed catalytic approach belongs to the wider family of biphasic catalysis, where the catalyst operates at the interface between two different layers.[202,203] However, differently from the typical “on water”[204,205] processes where water is used in large excess to constrain the substrate into small droplets and the catalyst is soluble in the hydrophobic layer, **AsA-2** and **AsA-3** are water soluble and operate as quasi heterogeneous catalysts at the interface between water droplets and the epoxide phase.



**Scheme 10.** Overview of cyclic carbonate products formed by using sodium citrate as the catalysts in the cycloaddition of $CO_2$ to epoxy alcohols. The carbonates on the left are produced *via* proton-shuttling mechanism while the carbonate on the right (corresponding to the isomers that would form by the "classical" cycloaddition mechanism) are obtained *via* a Payne-like rearrangement of the products of proton-shuttling.

In particular, in the preliminary catalytic screening of the AsA-based catalysts in the cycloaddition of $CO_2$ to styrene oxide under atmospheric pressure without the addition of water (single organic phase), it was observed that **AsA-3** exhibited a higher SO conversion than **AsA-2**, primarily due to the catalyst solubility within the reaction mixture (Table 3, entries 8, 9). Indeed, **AsA-3** was fully soluble from the start, whereas **AsA-2** started as an insoluble compound but eventually dissolved before the end of the reaction. This difference in solubility stems from the varying lengths of the alkyl groups within the quaternary ammonium iodide moiety of the catalysts. Under mild conditions (80 °C, 10 atm $CO_2$), a small amount of water (0.5 mL) was added to the reaction mixture to create a biphasic medium. This addition enhanced the solubility of **AsA-2**, leading to an almost complete transformation of 1,2-epoxyhexane into the targeted carbonate product in a significant contrast to when no water was introduced (Table 3, entry 10). The addition of salts further enhanced the catalytic performance of the catalyst, as observed when the same amount of seawater was added instead of DI water to the reaction mixture. In the presence of salt in the aqueous layer, **AsA-2** showed the ability to convert 1,2-epoxyhexane into its carbonate even under atmospheric pressure, although the conversion was moderate (Table 3, entry 11). This salt-related effect was attributed to the formation of smaller water droplets in the substrate medium, increasing the surface of contact of the catalyst with the epoxide. The duration to achieve nearly complete conversion was twice reduced over the **AsA-2**/seawater catalytic system under identical reaction conditions (Table 3, entries 10, 12). The **AsA-2** (24 h) and **AsA-2**/seawater (12 h) systems under the same conditions (80 °C, 10 atm $CO_2$) demonstrated recyclability for up to 5 cycles, yielding notable quantitative conversions and selectivities. No significant decline in catalytic activity was observed for both systems following five consecutive cycles. **AsA-2** could catalyze the conversion of various terminal epoxides at 60 °C under mild pressure (10 atm), while glycidyl ethers and epoxides bearing long-chain substituents (*i.e.* butyl and decyl) necessitated higher reaction temperatures ranging from 80 to 100 °C for effective conversion. Moreover, highly challenging internal epoxides[51, 206] such as *cis*-epoxidized methyl oleate were successfully converted into the desired carbonate products under harsher settings (100-120 °C, 30 atm $CO_2$) with **AsA-2**/seawater serving as a recyclable system.

## 4. Conclusions and outlook

Cyclic organic carbonates play a crucial role in modern chemistry and industry because they are versatile functional compounds that can be obtained from readily available epoxides and $CO_2$ as a green feedstock. The main challenge for these compounds to become widely accessible commodity chemicals is represented by a general lack of inexpensive and ubiquitously available catalytic systems active under very mild conditions. For this reason, in this work we have reviewed the state-of-the-art of two classes of compounds that serve as convenient catalytic components for the cycloaddition of $CO_2$ to epoxides, *i.e.* coordination compound and biobased hydrogen−bond donors. The first, serves as inexpensive Lewis acids devoid of sophisticated organic frameworks for the activation of the epoxide substrate. They are active under ambient conditions in the homogeneous form and can be heterogenized *via* surface chemistry approaches such as SOMC leading to systems that are active under atmospheric pressure and even under ambient conditions. Hydrogen−bond donors activate the epoxide group *via* establishing (a network of) H−bonds and serve as green organocatalytic components for the cycloaddition of $CO_2$ to epoxides. This is especially the case of biobased HBDs such as ascorbic acid and sodium citrate, the latter, being active in the case of the cycloaddition of $CO_2$ to glycidol *via* proton-shuttling mechanism.

Further research will surely see further developments for both classes of compounds. For the case of grafted coordination compounds, the main challenge is to reduce leaching and deactivation of the metal complexes occurring *via* undesired processes such as dehalogenation. To reduce the impact of these undesired processes, grafting the complexes on mesoporous materials could contribute to avoid metal leaching by protecting the metal centers in the channels of the material. Additionally, using metal alkoxides ($MOR_n$) or metal amides in place of metal halides as grafting precursors may lead to more stable complexes towards deactivation by avoiding dehalogenation. In the case of biobased hydrogen−bond donors, it is desirable that further developments will focus on the heterogenization of the biobased compounds rather than on the further discovery of more homogeneous structures. Attempts to develop heterogeneous biobased hydrogen−bond donors have, thus far, not led to fully heterogeneous systems active under ambient conditions. Nevertheless, ascorbic acid-based single-component catalysts were designed that served as molecular recyclable systems for the target cycloaddition reaction under biphasic conditions. Therefore, it is expected that alternative catalytic methodologies such as biphasic catalysis may be further developed in the future to overcome the limitations of traditional heterogeneous systems.

Overall the cycloaddition of $CO_2$ to epoxides will continue to represent a vibrant field of investigation in year to come; it is desirable that the focus of further research will be on the preparation of realistic, durable, recyclable inexpensive catalysts to support the industrial synthesis of cyclic carbonates under sustainable conditions by using impure sources of $CO_2$.

## Acknowledgment

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