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Recent progress in the catalytic transformation of carbon dioxide into biosourced organic carbonates

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Cyclic organic carbonates are among the most widely studied targets in the nonreductive conversion of carbon dioxide using oxiranes as the common reaction partners. Apart from using fossil fuel based precursors, recent developments have shown that biomass related feedstock can also serve as coupling partner for CO_2 allowing the preparation of more functional and complex types of carbonate architectures. This tutorial review places this latter development in the current context of new and more sustainable material designs, and highlights the main types of biomass that have been examined using primarily homogeneous catalysis approaches.

1. Introduction

Cyclic organic carbonates, more typically denoted as cyclic carbonates (CCs), have become a major target in the area of catalytic valorization of (waste) carbon dioxide.[1–8] The most common way to prepare such carbonates is through the coupling of epoxides and CO_2,[9–11] a reaction that has reached a high level of sophistication thanks to the development of improved catalysts,[12–16] and new concepts.[17–19] A more recent trend shows a shift towards the use of biosourced feedstock in the synthesis of organic carbonates, *i.e.*, so-called bio-carbonates. These biosourced carbonates are believed to give new impetus for the development of a variety of new applications such as their use as drop-in monomers for sustainable polymers,[20,21] the creation of isocyanate-free polyurethanes (NIPUs),[22,23] new types of plasticizers,[24] green and biodegradable solvents and surfactants,[25] and functionalized building blocks for organic synthesis.[26,27]

With this context in mind, we decided to capture the most recent and important advances in this area in this review. The focal point will be on selected biosourced feedstock that has been utilized to prepare cyclic carbonate structures including glycerol, fatty acids, terpenes and carbohydrates (Fig. 1).

Here, biosourced feedstock is defined as those starting materials produced by the growth of microorganisms, plants or animals or derived thereof.[28,29] Each of these specific categories of biocarbonates is shortly introduced followed by a detailed description of the state-of-the-art. Mechanistic details on the formation of CCs from CO_2 and epoxides are provided where necessary, since this topic has been recently and extensively reviewed.[30] This article thus summarizes the most frequently used feedstock to build biobased organic carbonates serving as an inspiring stepping stone towards a greener development of CO_2-derived heterocyclic building blocks.

2. Glycerol carbonate

The utilization of glycerol to produce valuable chemicals is an inspiring goal for chemists. Glycerol is the main byproduct

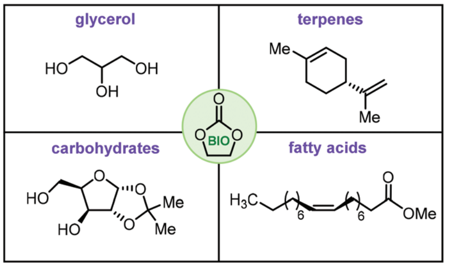

Fig. 1 Biobased feedstock used to prepare bio-carbonates. Apart from glycerol, exemplary cases of the other categories are shown.

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derived from the production of biodiesel (*i.e.*, through the transesterification of triglycerides, present in vegetable oils, with alcohols such as methanol), and is produced at a higher rate than it is consumed. Therefore, it is important to find ways that transform low-value glycerol into high-value products. Regarding the chemical transformations of glycerol, one of the most attractive conversion processes is its conversion into glycerol carbonate (**GC**).[31–39] This cyclic organic carbonate finds interesting use in cosmetics and lubricants, coating materials and as a polar solvent.[40] In addition, **GC** can also be used as building block in organic synthesis through ring-opening, decarboxylation, esterification or polymerization reactions.[41–43]

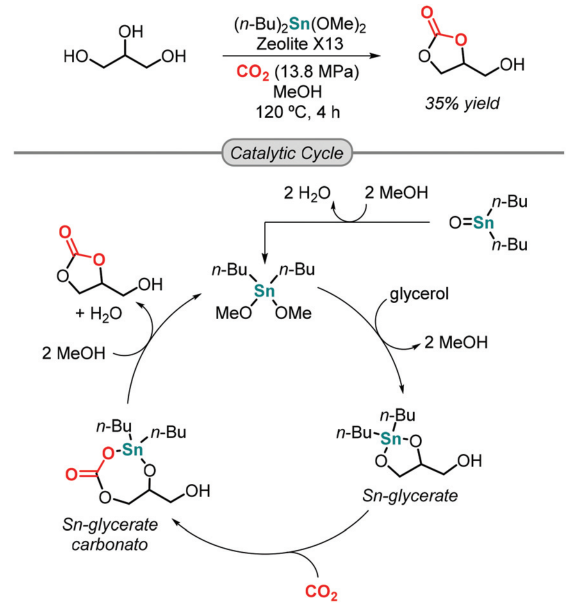
The most common way to produce **GC** is by transesterification of glycerol with dimethyl carbonate (DMC) or urea with the aid of a catalyst.[44–48] The most desirable sustainable and straightforward route to produce **GC** would be from glycerol and carbon dioxide combining two waste molecules. However, the direct coupling of CO_2 and glycerol is an equilibrium-limited reaction making it difficult to achieve high conversions and yields unless sacrificial dehydrating agent are used (*vide infra*). Despite significant advances that have been achieved in the direct glycerol-to-**GC** conversion, an alternative route towards **GC** utilizes glycidol and CO_2. Glycidol has much higher reactivity towards CO_2 and, moreover, it can also be produced from biomass. The subsequent sections discuss the pros and cons of both formation routes.

2.1. Glycerol carbonate from glycerol and CO_2

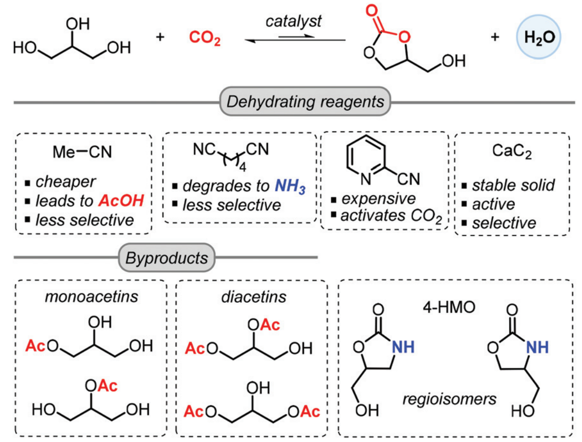
The first attempt towards the synthesis of **GC** from glycerol and CO_2 was reported by Mouloungui in 1998.[49] Unfortunately, under supercritical CO_2 conditions, the reaction did not occur. It was not until 2006 when Dibenedetto successfully reported that Sn-based catalysts of the formula $(n\text{-Bu})_2SnO$ or $(n\text{-Bu})_2Sn(OMe)_2$ were able to catalyze the formation of **GC** at 5 MPa of CO_2 pressure and 180 °C to obtain a maximum of 5.7% isolated yield of **GC** under solvent-free conditions using molecular sieves to remove water from the reaction mixture.[50] The Sn-based catalyst activates glycerol by forming an active Sn-glycerate intermediate that allows for CO_2 insertion. This process was greatly improved by Munshi in 2009 using MeOH as medium, which increased the yield of **GC** to 35% (Scheme 1).[51] The addition of MeOH is believed to help preventing catalyst deactivation by avoiding oligomerization of the mononuclear catalytic species.

Up to now, many catalytic systems have been reported that are based on metal oxides/complexes,[52–57] supported metal catalysts,[58,59] or modified zeolites or hydrotalcites,[60–62] in combination with a dehydrating reagent. Most of the reported heterogeneous catalysts typically require harsh reaction conditions for **GC** synthesis, *i.e.* a CO_2 pressure above 40 bar and temperatures above 150 °C.

Another notable feature of these processes is the introduction of a dehydrating reagent, which was found to be more effective than molecular sieves, but on the other hand lowered in some cases the chemoselectivity towards **GC** (Scheme 2).[57]



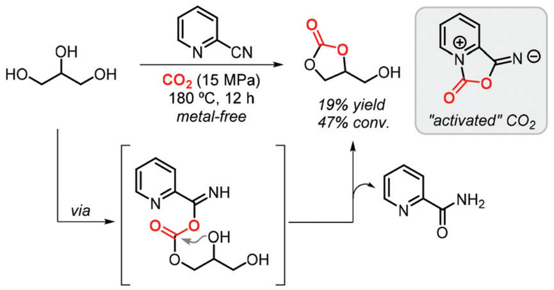
Scheme 1 Formation of **GC** from glycerol using $(n\text{-Bu})_2Sn(OMe)_2$ as catalyst.



Scheme 2 Comparison of different dehydrating agents in the formation of **GC** from glycerol and CO_2.

In most reported approaches, acetonitrile is selected as an inexpensive dehydrating agent, which upon reaction with the *in situ* generated water forms acetamide. This in turn may further react with a second molecule of water to generate acetic acid. The latter can lower the selectivity towards **GC** through mono- and di-acetylation of glycerol.

Adiponitrile has been used as a dehydrating agent by McGregor,[57] who found that under the applied reaction conditions, adiponitrile degraded to NH_3 that upon reaction with glycerol produces 4-(hydroxymethyl)oxazolidin-2-one (**4-HMO**) as a mixture of two regioisomers. Apart from acetonitrile and adiponitrile, He and co-workers reported in 2016 the use of 2-cyanopyridine as a superior dehydrating reagent. In the presence of a CeO_2 based catalyst, the yield of **GC** is boosted up to



Scheme 3 Metal-free formation of **GC** using 2-cyanopyridine.

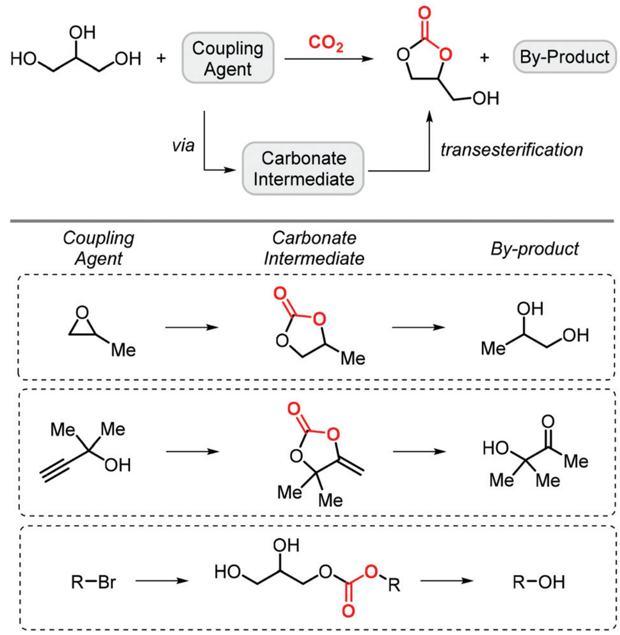
79% when using 3 equiv. of 2-cyanopyridine at 4 MPa of CO_2 and 150 °C in DMF.[63] Moreover, the CeO_2 catalyst could be recycled 5 times through a calcination process at 400 °C. Recently, Choi *et al.* demonstrated the advantage of using CaC_2 as a dehydrating agent for the synthesis of **GC**, which in combination of $Zn(OTf)_2$/phen (1,10-phenanthroline) in NMP (*N*-methyl-2-pyrrolidone) could achieve 88% isolated yield at 50 bar of CO_2 pressure at 180 °C for 24 h.[55]

One year later, Zhao *et al.* demonstrated that the formation of **GC** (*via* 2-cyanopyridine) also occurs in the absence of a metal catalyst achieving a 19% yield at 15 MPa of CO_2 and 180 °C (Scheme 3).[64] The authors confirmed by FTIR that 2-cyanopyridine activates CO_2 to form a five-membered ring which then reacts with glycerol to produce **GC**. Interestingly, switching to 3-cyanopyridine, 4-cyanopyridine or acetonitrile did not provide such potential. Theoretical calculations pointed indeed to the formation of a five-membered heterocycle as the "activated" form of CO_2, which is subsequently involved in a transesterification reaction of glycerol.

2.2. Glycerol carbonate using coupling agents

Glycerol carbonate can also be successfully prepared by reaction of glycerol and carbon dioxide in the presence of a coupling agent, which is used to produce a cyclic carbonate intermediate *in situ* allowing for transesterification of glycerol to form glycerol carbonate and a by-product (Scheme 4). The involvement of a third reactant allows to overcome the intrinsic thermodynamic limitation for the direct reaction between glycerol and CO_2, whereas it also produces a new byproduct derived from this additional component.

In this context, propylene oxide (**PO**) was the first additive to be reported by Han and co-workers in 2012 (entry 1, Table 1).[65] Although **PO** constitutes an inexpensive precursor, the process would not be entirely biobased since **PO** is primarily produced from fossil fuel feedstock. The reaction uses KI as a catalyst and is carried out at 2 MPa of CO_2 pressure and 115 °C affording **GC** in 75% yield. The catalyst promotes the formation of propylene carbonate (**PC**), which then engages in a transesterification of glycerol producing both **GC** and propylene glycol. In 2018, Xiao *et al.* improved the process by introducing a bromide-based heterogeneous catalyst obtained through the polymerization of divinyl benzene and 1-vinyl-3-butylimidazolium bromide (entry 2, Table 1).[66] Importantly,



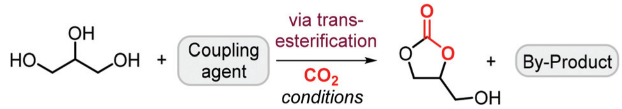
Scheme 4 General reaction of glycerol with CO_2 in the presence of a coupling agent.

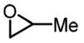
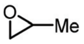
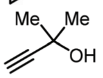
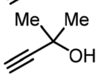
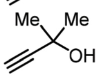
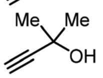
not only the yield of **GC** could be improved to 81%, but also the catalyst could be recycled up to 5 times while maintaining the same level of activity.

Apart from the use of **PO**, dimethylethynyl carbinol (*i.e.*, a propargylic alcohol) has also been applied as a reagent to generate **GC** in high yield, along with 3-hydroxy-3-methyl-2-butanone as the byproduct. The reaction proceeds through the intermediacy of a cyclic alkenyl carbonate, which allows for the transesterification of glycerol. Since 3-hydroxy-3-methyl-2-butanone contains a tertiary alcohol group, it is less nucleophilic than propylene glycol, and thus does not readily react with the formed **GC** to return the carbonate intermediate. Initially, the group of He reported in 2017 the use of a Ag_2CO_3/Xantphos as a catalyst promoting this transformation in MeCN at 80 °C under 1 MPa of CO_2 pressure to give **GC** in 82% yield (entry 3, Table 1).[67] A solvent-free version was later reported by Song and Zhang using a silver sulfadiazine/Et_4NBr catalytic system, although a lower yield for **GC** was obtained (entry 4, Table 1).[68]

On the other hand, the groups of Lu,[69] and Liu,[70] independently reported an organocatalytic approach to prepare **GC**. In the case of Lu, a one-pot approach was applied by formation of the intermediate carbonate using a catalytic amount of an amidine-CO_2 adduct, followed by the transesterification with glycerol catalyzed by MTBD (entry 5, Table 1; MTBD = methyl-1,5,7-triazabicyclo[4.4.0]dec-5-ene). In this way, 85% yield of **GC** was obtained under very mild reaction conditions. The system of Liu and co-workers was based on DBU (8-diazabicyclo[5.4.0]undec-7-ene) and was also found to promote both steps to deliver **GC** in 97% yield albeit under harsher reaction conditions (entry 6, Table 1).

Table 1 Results for the synthesis of **GC** using various coupling agents. NR = not reported



Entry[a]	Coupling agent	Conditions	Yield of **GC** (%)	Yield of byproduct (%)
1 [65]		CO_2 (2 MPa), KI 115 °C, 1.5 h	77	39[b]
2 [66]		CO_2 (2 MPa) *P*-DVB-(vIm-BuBr) 100 °C, 4 h	81	20[c]
3 [67]		CO_2 (1 MPa) Ag_2CO_3, XantPhos MeCN, 80 °C, 16 h	82	83
4 [68]		CO_2 (1 MPa) Ag sulfadiazene, Et_4NBr 80 °C, 24 h	56	69
5 [69]		**1.** CO_2 (0.1 MPa) Amidine-CO_2 25 °C, 24 h **2.** MTBD MeCN, 25 °C, 24 h	85	NR
6 [70]		CO_2 (3 MPa), DBU DMF, 120 °C, 10 h	97	63
7 [71]	CH_2Br_2	CO_2 (1 MPa) DBU, $BmimPF_6$ 70 °C, 18 h	86	NR
8 [72]	*n*-BuBr	CO_2 (0.1 MPa) Guanidine cat. NMP, 50 °C, 4 h	74	NR

[a] Corresponding reference in parentheses. [b] 59% yield of propylene carbonate. [c] 76% yield of propylene carbonate.

The last example of this strategy illustrates that alkyl halides are also effective reactants. Compared to the other methods, the use of halogenated reagents implies the generation of halogen-containing waste, which is not ideal from a sustainable point of view. Initially, Jang reported in 2014 one example using $BmimPF_6$ (an ionic liquid), DBU as a homogeneous base and CH_2Br_2 as both the reactant and solvent to afford **GC** in 86% isolated yield (entry 7, Table 1).[71] An intermediary linear carbonate salt attacks the CH_2Br_2 reagent following ring-closure leading to the CC. The authors propose that the ionic liquid helps to improve the solubility of CO_2 although under basic conditions, it is possible that an NHC-carbene forms able to capture/activate CO_2, which can then react with glycidol. In another approach, Mihara *et al.* used *n*-BuBr as the additional component, together with a guanidine-based catalyst (entry 8, Table 1).[72] By adjusting the reaction conditions, it was possible to selectively form **GC** in 74% yield at 50 °C under 0.1 MPa of CO_2 pressure and using NMP (*N*-methyl pyrrolidone) as solvent.

2.3. Glycerol carbonate from glycidol

Apart from the conversion of bio-glycerol into glycerol carbonate, an alternative and popular route starts from its epoxy alcohol derivative, *viz*. glycidol (**Gly**). This precursor can be derived from glycerol present in industrial waste produced in the synthesis of epichlorohydrin, thus providing an opportunity for recycling it into valuable glycerol carbonate in two steps.[73] This route based on **Gly** features excellent atom-economy and, additionally, since many highly efficient catalytic systems have been developed over the years for the coupling of oxiranes and CO_2, glycidol has often been included in the substrate scope.

Gly has distinct reactivity compared to other common epoxides such as **PO** or styrene oxide. The non-innocent hydroxyl group can actively participate in the reaction in two distinct ways. Capacchione and co-workers found that ring-opening of glycidol by an external nucleophile was faster than with other epoxides (Table 2).[74] By means of NMR and DFT studies, they concluded that glycidol dimers were present under the catalytic reaction conditions. Intermolecular hydrogen bonds between the **Gly** molecules are important to explain the activation the oxirane ring of **Gly** towards nucleophilic ring-opening by bromide (Fig. 3). Hence, using simple TBAB (tetrabutylammonium bromide, 5 mol%) at 60 °C and 1 MPa of CO_2 pressure it was possible to convert **Gly** in >99% conversion and selectivity producing **GC** (entry 1, Table 2). Lowering the temperature to 40 °C or reducing the loading of TBAB to 1 mol% while heating at 80 °C for 1 h reduced the conversion to 87% and 85%, respectively (entries 2 and 3, Table 2). Lowering the pressure to 0.1 MPa had a negative impact on the **Gly** conversion, which reached 52% after stirring for 24 h at 40 °C. The authors also examined the conversion of **PO** at the optimized reaction conditions but noted only 4% of conversion. This **Gly**/TBAB derived binary catalyst was then successfully applied to other epoxide/CO_2 combinations, and significantly better substrate conversion levels were achieved compared to the reactions performed without **Gly**.

The group of Kleij discovered that the hydroxyl group of **Gly** can be involved in the activation of CO_2 by forming a transient hemi-carbonate species (Scheme 5) that acts as an intramolecular nucleophile able to ring-open the oxirane ring under mild conditions: as such, no external nucleophilic additive is required facilitating thus a halide-free route.[17] The use of the aminotriphenolate aluminum catalyst $\mathbf{1}^{t\mathrm{Bu}}$ (1 mol%) at

Table 2 Upper part: effects on the conversion by changing the reaction parameters in the synthesis of **GC** using **Gly**

Entry	TBAB (mol%)	*T* (°C)	CO_2 (MPa)	Time (h)	Conversion (%)
1	5	60	1	3	>99%
2	5	40	1	3	87
3	1	80	1	1	85
4	5	40	0.1	24	52
5[a]	5	60	1	3	4

>99% selectivity towards GC in all the cases. [a] **PO** as substrate.

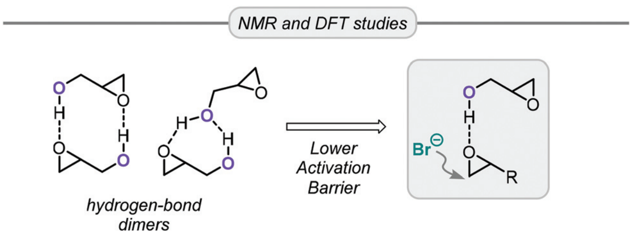
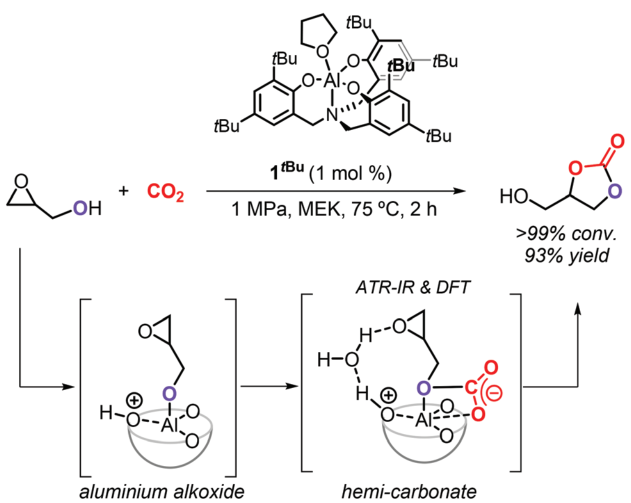
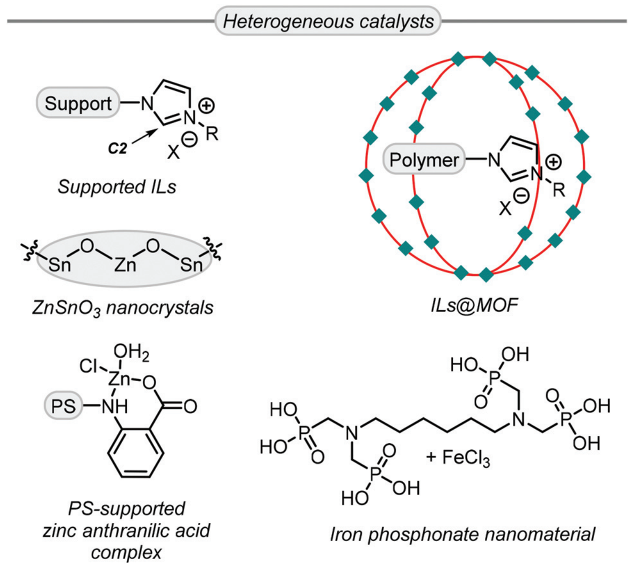


Fig. 3 Lower part: Hydrogen bonding in **Gly** and implications for the overall reaction.



Scheme 5 Halide-free carboxylation of glycerol using the aluminum aminotriphenolate catalyst **1**[tBu].

75 °C and 1 MPa of CO_2 pressure in methylethyl ketone (MEK) as solvent enabled to obtain >99% **Gly** conversion in 2 h and provided **GC** in 93% isolated yield. The mechanism of the reaction was studied in detail by ATR-IR, kinetic studies, DFT analysis and X-ray crystallography, which provided proof that a hemi-carbonate intermediate forms under the reaction conditions aiding the intramolecular ring-opening of the oxirane ring of **Gly** and being facilitated by a hydrogen bond network between the catalyst, **Gly** and co-catalytic H_2O.[75]



Scheme 6 Highly efficient heterogeneous catalysts for the synthesis of **GC** from **Gly**. ILs = ionic liquids, MOF = metal–organic framework, PS = polystyrene.

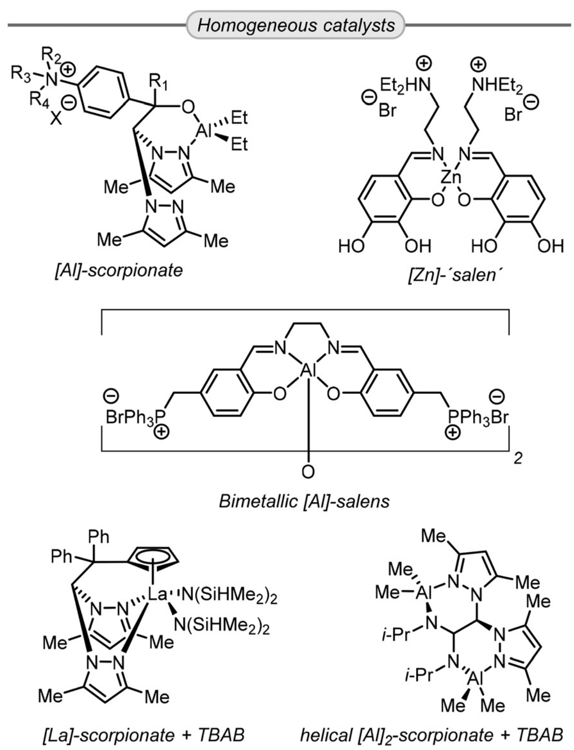
While more than 140 publications have been reported that discuss the conversion of **Gly** into **GC**, not all the catalyst systems proved to be superior to simple TBAB. However, some catalyst systems provide other advantages, such as recyclability, reduced catalyst loading and/or milder reaction conditions among others. For example, the use of heterogeneous catalysts (Scheme 6) allows for easy catalyst recovery after some postsynthetic treatment such as filtration or product extraction. Most of these heterogeneous systems for **GC** synthesis from **Gly** are derived from ionic liquids (ILs),[76–82] which accelerate the reaction in two ways.

First, a nucleophilic anion helps to ring-open the oxirane ring and, second, an appropriate IL can establish hydrogen bonds between the oxirane ring and the acidic C2 proton (Scheme 6) of the imidazolium ring. The group of Jiang reported an efficient supported ionic liquid catalyst which was confined inside a metal–organic framework (MOF), and this multi-component system displayed synergistic effects between the CO_2 capturing capability of the MOF, the Lewis acidic sites of the MOF and the basic sites of the poly-IL.[83] Islam *et al.* reported three examples of active heterogeneous catalysts that are not based on ILs. An iron-phosphonate nanomaterial,[84] and a polystyrene supported zinc catalyst,[85] showed good activity as Lewis acidic materials with TBAB used as a co-catalyst. Conversely, the catalyst based on $ZnSnO_3$,[86] did not require any additive.

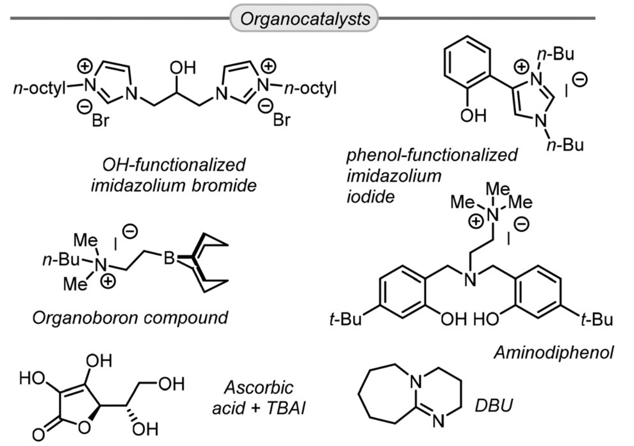
Compared to heterogeneous catalysts, homogeneous catalysts derived from earth-abundant metals show superior activity and, thus, reduced catalyst loadings are typically utilized. Moreover, bifunctional catalysts, which have the halide anion incorporated within the catalyst structure, have demonstrated good activity and selectivity towards the formation of **GC**. For instance, aluminum scorpionate complexes (Scheme 7) reported by Lara-Sánchez and co-workers can achieve an excellent **GC** yield using 0.25–0.5 mol% of catalyst loading at 70–85 °C.[87–89] Similar results were obtained by the group of He, who reported a bifunctional zinc salen-like complex that shows appreciable activity at 0.3 mol% catalyst loading and 0.1 MPa of CO_2 pressure, though heating to 100 °C was necessary.[90] Another type of bifunctional catalyst was reported by North *et al.* showing that a bimetallic aluminum salen complex displays high activity in the synthesis of **GC** from **Gly**, achieving full conversion in 3 h at only 27 °C and 0.1 MPa.[91]

Other homogeneous metal catalysts combined with a co-catalytic amount of halide also exhibit high activity such as the aluminum,[92] and lanthanum,[93] based scorpionate catalysts reported by Otero, Lara-Sánchez *et al.* In particular the La-based catalyst shows good activity at remarkably low catalyst loading (0.05 mol%) achieving 98% yield of **GC** at 70 °C and 1 MPa CO_2 pressure in 4 h.

Lastly, some organocatalysts have also been demonstrated as competitive systems for metal-based catalysts. Most of these organocatalysts effectively activate the oxirane ring by establishing hydrogen bonds that facilitate the ring-opening by a halide nucleophile. For instance, Cokoja,[94] and Lara-Sánchez,[95] reported recyclable organocatalysts that contain imidazolium rings featuring halide counter anions (Scheme 8). Similarly, the group of Kim published a scorpionate type organocatalyst comprising of an aminodiphenol scaffold which acts as a hydrogen-bond activator, and additionally contains a quaternary ammonium salt in its structure.[96]



Scheme 7 Highly efficient homogeneous catalysts for the synthesis of **GC** from **Gly**.



Scheme 8 Efficient reported organocatalysts for the conversion of **Gly** into **GC**.

D'Elia reported that ascorbic acid is an efficient hydrogen bond donor which, in combination with a co-catalytic amount of TBAI, could achieve high yield of **GC** at room temperature and 0.1 MPa of CO_2.[97] On the other hand, the group of Wu reported a bifunctional organoboron organocatalyst able to achieve full conversion and excellent yield of **GC** at remarkably low (0.02 mol%) catalyst loading though under somewhat harsher reaction conditions (120 °C, 20 MPa CO_2).[98] In the latter case, mechanistic studies indicated that the boron acts as a Lewis acid and activates the oxirane ring near a closely positioned ammonium iodide unit (Scheme 8). Lastly, Kleij *et al.* showed that DBU can promote the formation of **GC** from **Gly** and other epoxy alcohols through the formation of a hemi-carbonate intermediate under mild reaction conditions (45 °C, 1 MPa CO_2).[99]

3. Terpene based carbonates

As stated before, the synthesis of CCs from CO_2 has become a mature research field. In most contributions, there has been a primary focus on the preparation of relatively simple five- and six-membered CCs with a low degree of substitution/functionality. To explore new applications of CCs, the preparation of structurally more complex products is currently an emerging topic in the area of CO_2 utilization. In this regard, terpenes represent attracting starting materials for the preparation of new, more complex and partially biobased CCs.

The isolation of 4-muurolen-7,15-diol-7,15-carbonate in 1994 demonstrated that there are naturally occurring terpenoid carbonates (Fig. 2).[100] Since then, several other examples of terpene carbonates have been reported,[101,102] ranging from compounds having five- to eight-membered CC moieties

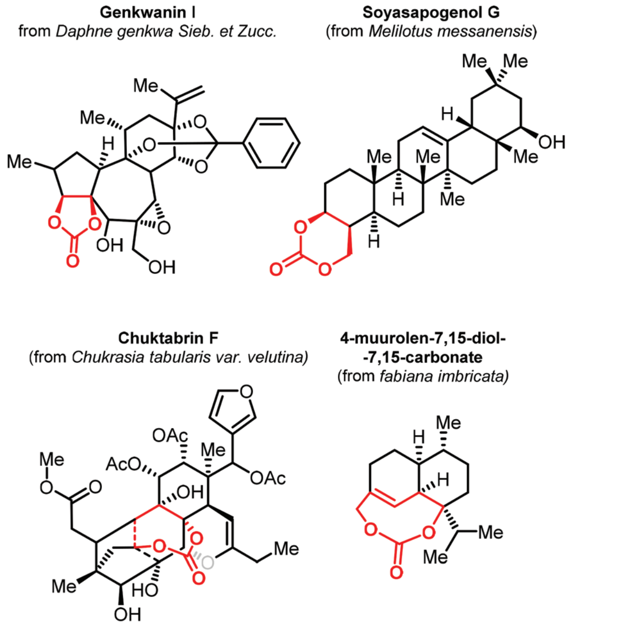
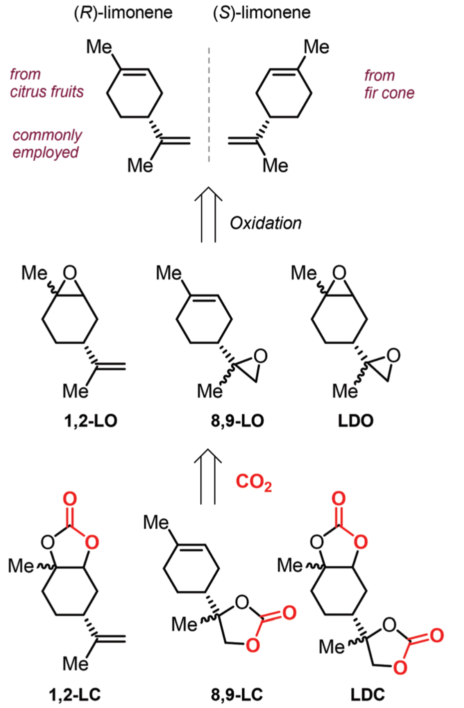


Fig. 2 Examples of naturally occurring terpenoid carbonates. The cyclic carbonate rings are highlighted in red.



Scheme 9 Structures of both limonene enantiomers, limonene-based oxides and limonene-based cyclic carbonates, and their abbreviations.

within their structure with some of them showing biological activity such as Genkwanin I,[103] Soyasapogenol G,[104] and Chuktabrin F (Fig. 2).[105] These findings triggered the effort of several research groups to use terpene scaffolds for the preparation of new types of CCs. The high-structural modularity of terpenes and the almost ubiquitous presence of double bonds that can be easily oxidized and further functionalized, offer an ideal starting point for the preparation of CCs using CO_2.[106,107]

In addition to these attractive structural features, it must be noted that terpenes can be isolated from natural sources, rendering these molecules an attracting alternative to fossil fuel-based raw materials. In particular, the cyclic terpene limonene (both enantiomers) can be conveniently isolated from natural sources such as citrus fruit and fir cone oil (Scheme 9).[108,109] It is likely for this reason that limonene has been the most studied terpene in the coupling reaction with CO_2, and especially in the synthesis of polycarbonates.[110–116]

The extraction of (*R*)-limonene from orange peel has resulted as economically feasible, and thus the use of this enantiomer is predominant in literature. The structure of limonene shows the presence of two different double bonds, that can be selectively epoxidized to afford either 1,2-limonene oxide (**1,2-LO**), 8,9-limonene oxide (**8,9-LO**) and limonene dioxide (**LDO**, being a mixtures of *cis*/*trans* isomers), and their coupling with CO_2 leads to the formation of the corresponding 1,2-limonene carbonate (**1,2-LC**), 8,9-limonene carbonate (**8,9-LC**) and limonene dicarbonate (**LDC**) (Scheme 9).

Due to the higher reactivity of the endocyclic double bond and hence the easier synthetic access to **1,2-LO**, this particular limonene oxide has been investigated preferentially. A summary of metal-based catalytic systems reported to promote the coupling of **1,2-LO** with CO_2 is given in Fig. 4.[92,93,117–121] With respect to other epoxides commonly used for the preparation of CCs, sterically demanding **1,2-LO** shows substantially lower reactivity during its coupling with CO_2. This results in the typical use of relatively high temperatures (75–100 °C) and pressures (10–30 bar) and relatively long reaction times (16–66 hours); therefore, achieving full substrate conversion remains a challenge.

Selective formation of *trans*-**1,2-LC** has been observed in several cases such as with catalysts based on $\mathbf{1}^{t\mathbf{Bu}}$, **2**, **6** and **8** (Fig. 4). This suggests that the *cis* and *trans* isomers of **1,2-LO** exhibit different reactivity as previously described in the preparation of poly(limonene carbonate).[114,115] Indeed, reactions conducted with the binary system $\mathbf{1}^{t\mathbf{Bu}}$/PPNCl [bis(triphenylphosphine)iminium chloride] using either the pure *trans*-**1,2-LO** or *cis*-**1,2-LO** resulted in higher conversion (73%) and stereoselectivity (*cis*/*trans* > 1 : 99), and only very low conversion (4%), respectively.[116] The formation of *trans*-**1,2-LC** was confirmed by X-ray analysis, and more recently the same reactivity difference was observed with the binary catalyst **8**/PPNCl.[93]

In 2016, Fiorani *et al.* extended the use of the binary systems $\mathbf{1}^{\mathbf{R}}$/PPNCl to the synthesis of other CCs from CO_2 and both bicyclic and acyclic terpene epoxides (Scheme 10).[116] Under the optimized conditions, the conversion of these bicyclic substrates typically proceeds with high chemoselectivity and moderate isolated yields between 45–52% providing thus access to carvone (**c1**), limonene dioxide (**c3**) and menthene (**c4**) based CCs. Attempts to produce limonene dicarbonate **c2**

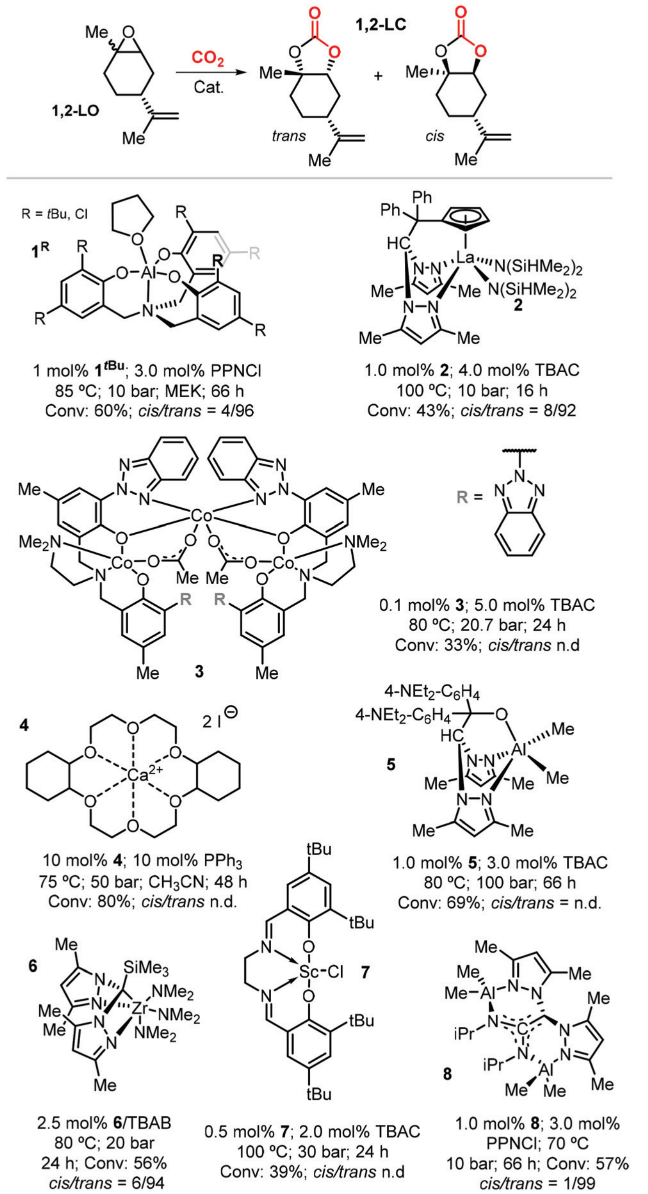
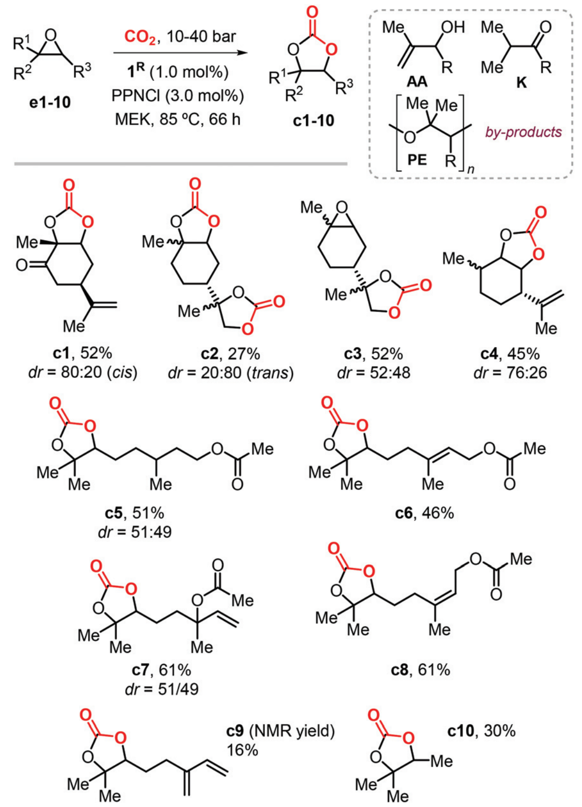


Fig. 4 Metal-based catalytic systems reported for the preparation of **1,2-LC**, comparative reaction conditions and product stereochemistry. N.d. stands for not determined.



Scheme 10 Terpene-based CCs obtained with binary catalysts $\mathbf{1^R}$/PPNCl.

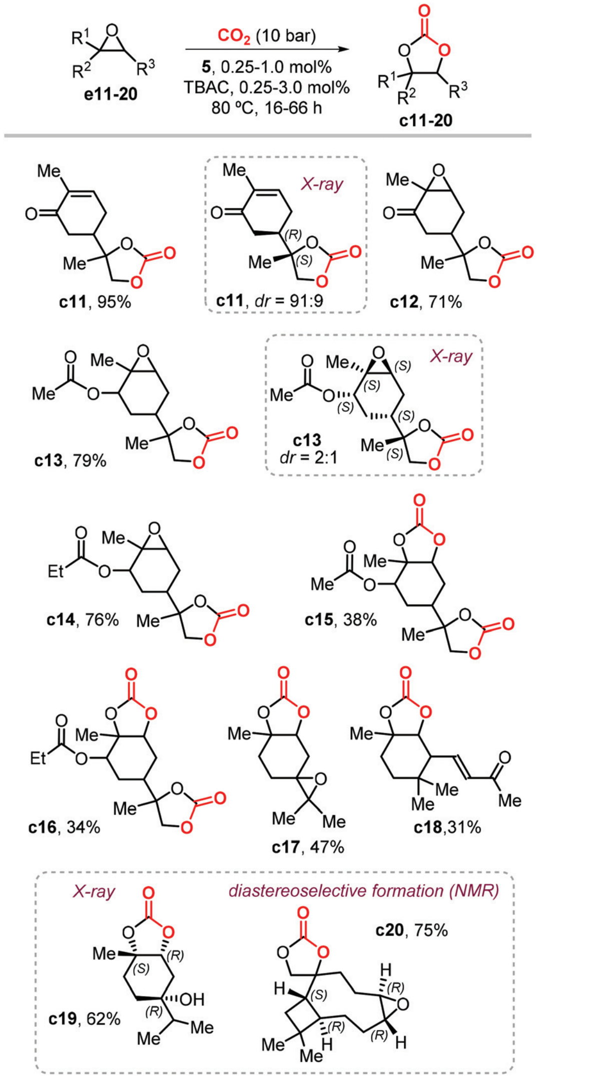
were less successful because of the competitive formation of a polyether (**PE**) product. The crystal structures of *cis*-**c1**, *trans*-**c2** and **c3** were elucidated by X-ray analysis for the first time, and confirmed the assigned stereochemistry on the basis of NMR spectroscopic studies.

The conversion of acyclic substrates proceeded with lower chemoselectivities, and generally higher pressure of CO_2 (4.0 MPa) was necessary to obtain appreciable yields. In the conversion of these acyclic terpene oxide substrates apart from the formation of a **PE**, the formation of allylic alcohol (**AA**) and ketone (**K**) side-products was also detected (Scheme 10). The formation of **AA** and **K** by-products was attributed to the phenolate-assisted,[122,123] and the Lewis-acid induced Meinwald-type rearrangements of the starting epoxide,[124,125] respectively.

The preparation of model compound **c10** resulted into a similar product distribution, thus ruling out that by-product formation depends on the nature of the substrate. Despite the issue with the overall chemoselectivity, the synthesis of terpene CCs derived from citronellyl acetate (**c5**), geranyl acetate (**c6**), linalyl acetate (**c7**) and neryl acetate (**c8**) was possible in moderately high yields. The conversion of myrcene gave a complex reaction mixture, resulting in low yield of CC **c9** due to additional side-reactions likely involving the conjugated double-bond.

Following this study, Werner *et al.* reported the preparation of carbonate **c2** (78%) and **c4** (81%) in high yields in the presence of 10 mol% of the catalyst **4**/PPh_3 (Fig. 4) and at 50 bar of CO_2 and 75 °C.[118] Under the same reaction conditions, the preparation of **c5** (19%) and **c6** (23%) was less efficient and provided only low yields. In 2019, Lara-Sánchez *et al.* reported the preparation and characterization of several new terpene-based CCs obtained through the use of binary catalyst **5**/TBAC (Fig. 4).[119] Carvone-based carbonates **c11–14** (Scheme 11) were obtained in good to high yields.

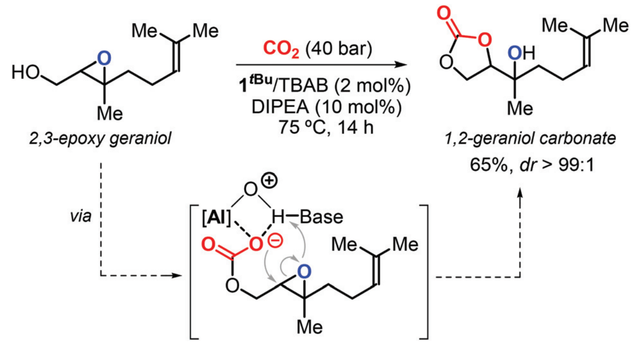
Diastereo-enriched samples of **c11** and **c13** were obtained after crystallization, and their atom connectivities were revealed by X-ray analysis. Carbonates **c15** and **c16** were only



Scheme 11 New terpene-based CCs obtained with the binary catalyst 5/TBAC.

isolated in low yield because of the low stability of the bicyclic carbonates derived from the *endo* epoxide. These latter products undergo a decarboxylative decomposition toward the formation of the corresponding *syn* diols. The challenging carbonates **c17** and **c18**, derived from terpinolene and ionone were obtained in moderate yields, whereas the preparation of terpinene-4-ol and caryophellene carbonates **c19** and **c20** were found to proceed in a diastereo-selective fashion as presented in the bottom part of Scheme 11.

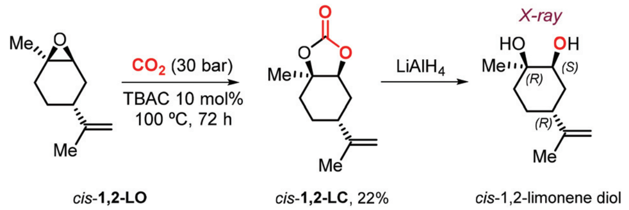
In 2016, Kleij *et al.* described a new protocol for the synthesis of highly substituted CCs using epoxy alcohols as substrates *via* a "substrate-directed" mechanism promoted by complex $\mathbf{1^R}$ (Fig. 4).[17,126] In this context, the authors reported the diastereoselective synthesis of 1,2-geraniol carbonate from 2,3-epoxy geraniol and CO_2 (Scheme 12). Notably, this regio-divergent method achieved the conversion of a sterically demanding terpene-based substrate under mild conditions.



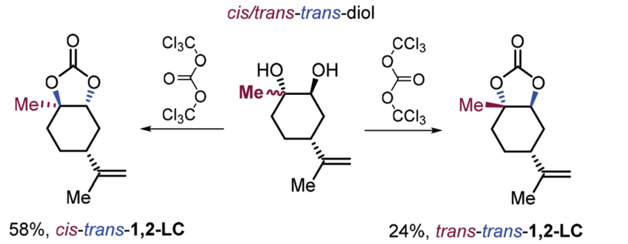
Scheme 12 Diastereoselective synthesis of 1,2-geraniol carbonate *via* a substrate-directed CO_2 activation in the presence of $\mathbf{1^{tBu}}$ as catalyst.

Metal-based catalysts may offer several advantages such as the use of milder reaction conditions, shorter reaction times and higher stereocontrol. At the same time, drawbacks such as high(er) cost, multistep synthesis and air/moisture sensitivity create incentives to select more simple catalysts of commercial interest and a practical point of view. In 2018, Morikawa *et al.* described the reaction of **1,2-LO** with CO_2 in the presence of TBAC, TBAB or TBAI as catalyst.[127] In the presence of 10 mol% of halide salt, the reaction at 100 °C and 30 bar proceeds more efficiently with TBAC. Due to the steric impediment of **LO**, the smaller radius chloride anion gives the best trade-off in terms of nucleophilicity, leaving group ability and size features. Under these conditions, the reactions using pure *trans*-**1,2-LO** and *cis*-**1,2-LO** provided higher (76%) and lower (19%) conversions, respectively, compared with the commercial *cis*/*trans* mixture (51%). This finding is in line with the different reactivity reported for both **LO** stereoisomers in the case of metal-based catalysts.[93,116] Interestingly, pure *cis*-**1,2-LC** was isolated for the first time and characterized by NMR spectroscopy. In addition, the relative configuration of the chiral centers in *cis*-**1,2-LC** was confirmed by X-ray analysis of the corresponding diol obtained by reduction with $LiAlH_4$ (Scheme 13).

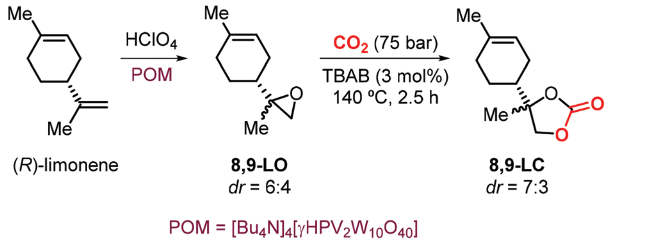
For comparative reasons only, the same research group reported, for the first time the synthesis of two **1,2-LC** diastereoisomers in which the oxygen atoms of the carbonate ring are in a *trans* configuration by treatment of 1,2-diols stereoisomers with triphosgene rather than using a more preferred CO_2/epoxide coupling strategy (Scheme 14).[128]



Scheme 13 Synthesis of *cis*-**1,2-LO** and reduction towards the corresponding *syn* diol.



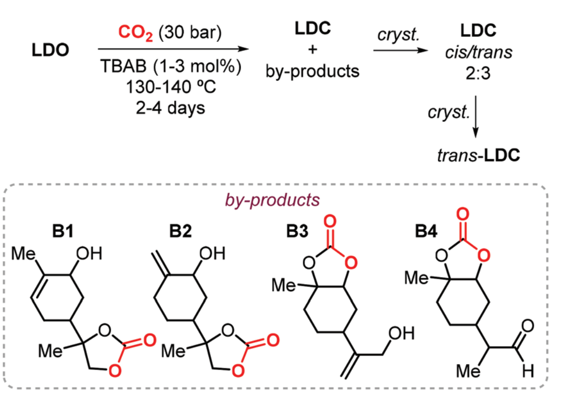
Scheme 14 Synthesis of **1,2-LC** diastereoisomers having a *trans* configured carbonate ring.



Scheme 16 Selective epoxidation of (*R*)-limonene and synthesis of **8,9-LC**.

Recently, Rehman *et al.* reported a detailed kinetic study of the **1,2-LO**/CO_2 coupling reaction in the presence of TBAC.[129] This investigation confirmed the higher reactivity of the *trans* isomer in the formation of **1,2-LC**. It was found that the reaction kinetics show a first-order dependence with respect to all the reaction components (**1,2-LO**, CO_2 and TBAC). In addition, the thermodynamic parameters of this conversion were determined using the Eyring equation, providing activation enthalpy and entropy values of 60.6 kJ mol^{-1} and −103.6 J $(mol\ K)^{-1}$, respectively.

In the last decade, the use of CCs have emerged as an attracting, more sustainable alternative for the production of the so-called non-isocyanate based polyurethanes (NIPUs), and the preparation of CCs from renewable feedstock is of importance to develop more sustainable materials.[22,130,131] In this respect, the research group of Mülhaupt investigated the use of limonene dicarbonate (**LDC**) for the synthesis of new types of NIPUs.[132,133] They investigated the synthesis of **LDC** from **LDO** and CO_2 catalyzed by TBAB on a kilogram scale. First, the reaction parameters (CO_2 pressure, temperature and catalyst loading) where optimized, after which full **LDO** conversion could be achieved using 3 mol% of TBAB in less than 50 h at 140 °C and 30 bar of CO_2. A brownish oil was is obtained this way, and it was initially directly used (without purification) for the preparation of NIPUs preparation.[132] Afterwards, a more detailed analysis of the reaction products based on NMR and mass spectrometry was carried out revealing the formation of several by-products (**B1–4**, Scheme 15).[133] The authors proposed that the formation of these products occurs by bromide elimination after initial bromide-assisted epoxide ring-opening being essentially the first step of the catalytic cycle leading to **LDC**. Therefore, in order to obtain a pure compound, **LDC** was crystallized obtaining a mixture of *cis* and *trans* isomers in a 2 : 3 ratio. Further crystallization led to the isolation of pure *trans*-**LDC** as confirmed by X-ray analysis.



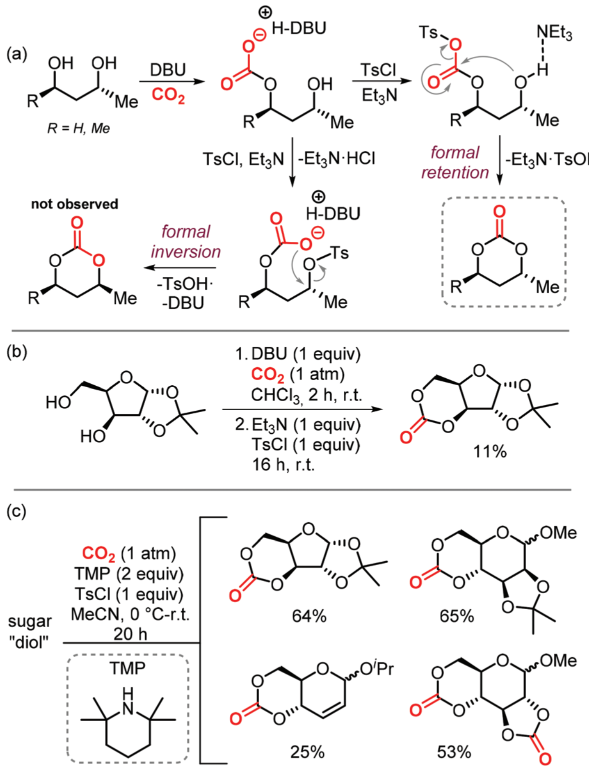
Scheme 15 Synthesis of **LDC** catalyzed by TBAB followed by crystallization of *trans*-**LDC**, and structures of reaction by-products **B1–B4**.

The use of limonene-based CCs in the preparations of NIPUs was also investigated by Hintermair *et al.*[134] The authors reported the preparation of **8,9-LC** by reaction of **8,9-LO** and CO_2 mediated by TBAB. The key step for the synthesis of the desired carbonate was the selective epoxidation of (*R*)-limonene at the less hindered terminal alkene. This reaction was performed using perchloric acid as the oxidant in the presence of a bulky polyoxometalate (POM) catalyst previously reported by Mizuno and coworkers (Scheme 16).[135] Because of a lower degree of steric hindrance, the formation of **8,9-LC** occurs comparatively much faster than the formation of **1,2-LC** under the same reaction conditions reaching 80% conversion in 2.5 hours. Remarkably, the two different **8,9-LO** diastereoisomers generated during the epoxidation reaction show similar reactivity in their coupling reaction with CO_2, which is in contrast to the behaviour typically observed for *cis* and *trans* **1,2-LO**.

4. Carbohydrate derived carbonates

Sugars are another interesting and ubiquitous source for CCs. Different from terpenes or fatty acids, these compounds bear multiple alcoholic functionalities, and therefore the preparation of cyclic carbonates on sugars is generally performed using phosgene-derived reagents.[136–139] Well-defined, non-toxic and biodegradable poly-glycocarbonates with a narrow distribution of molecular weights can be prepared from sugar-based monomers bearing a six-membered carbonate,[136,137,140–142] or a *trans*-positioned five-membered carbonate,[138,143] showing the huge potential of functional polymers from such substrates. In addition, the sugar molecules can first be converted into simpler compounds, which can then be converted into polymerizable monomers.[144–147]

Recently, a protocol to replace phosgene-derivatives was developed (Scheme 17).[148] In this process, CO_2 and an organic base (DBU) form an ionic hemi-carbonate intermediate, after which tosyl-chloride is added to yield a cyclic carbonate.



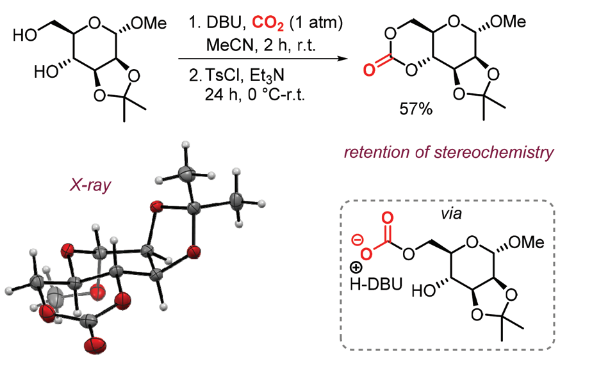
Scheme 17 (a) and (b): Conversion of 1,3-diols to 6-membered cyclic carbonates by a stepwise, 1-pot procedure. (c) 1-step procedure to form cyclic carbonates from sugars.

^{1}H NMR spectroscopy was used to monitor the formation of the ionic intermediate of 1,3-butanediol, showing that under optimized conditions, 49% of the *in situ* product is carbonated on the primary alcohol, 24% on the secondary alcohol, and 5% is bis-carbonated. Subsequent tosylation rapidly led to cyclic carbonate formation, without the observation of any intermediates. To discriminate between two mechanistic possibilities where either the hemi-carbonate or the remaining free alcohol is tosylated, enantiopure (*R*)-1,3-butanediol or (*R,R*)-2,4-pentanediol were employed. Interestingly, the stereochemistry was preserved during the reaction, indicating that the hemi-carbonate group is likely tosylated instead of the remaining free alcohol (Scheme 17a, top pathway).[148] The proposed mechanism was further supported by DFT calculations. The reaction proved to be capable of providing the 6-membered cyclic carbonate derivative of D-xylose (Scheme 17b), albeit in low yield, showing the potential of the overall transformation.

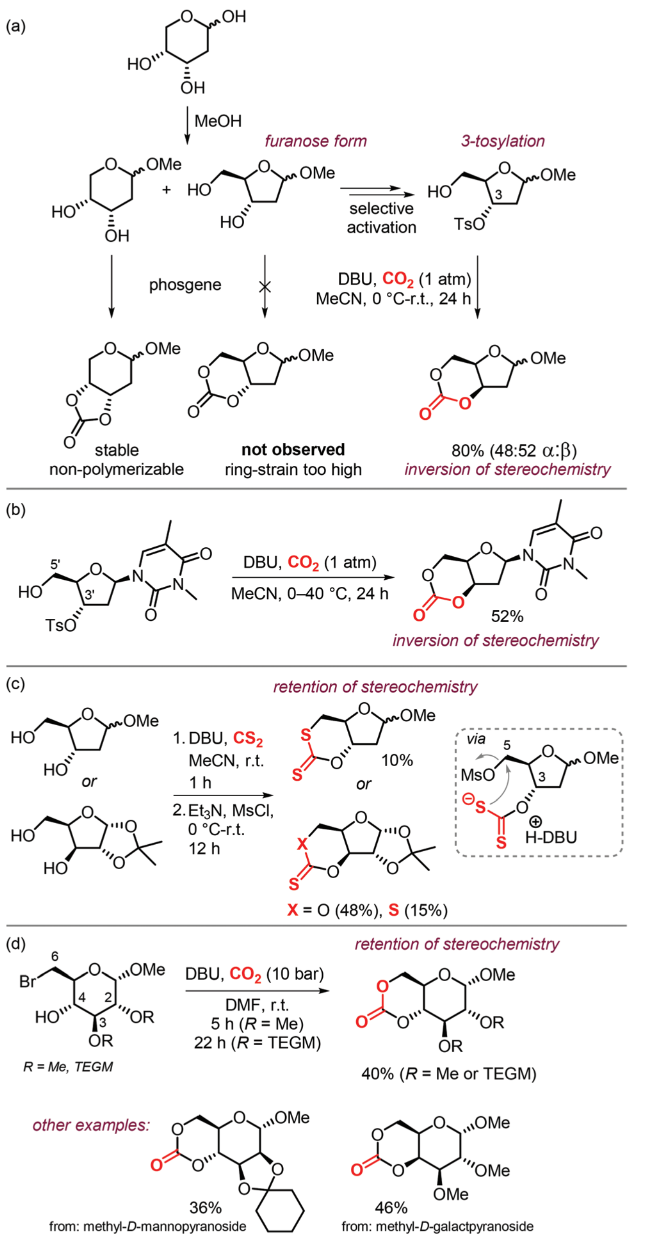
Later on, the process was improved significantly as to allow the carbonation to occur in one step, and higher yields of the cyclic carbonate *versus* byproducts such as oligomeric species or tosylation of the alcohols were reported.[149] The use of a weaker base such as Et_3N or 2,2,6,6-tetramethylpiperidine (TMP) proved to be essential for the overall chemoselectivity. Even though the initial formation of the hemi-carbonate is strongly disfavored in the presence of weaker bases (2% or 4% for TMP or Et_3N, respectively *vs.* 85% for DBU), the selective tosylation of the hemi-carbonate over the alcohol and the ring-closure step are strongly favored energetically as calculated by DFT. A comparison between the mechanism using Et_3N,[149] *vs.* DBU,[148] shows that the barriers for formation of the tosylated carbonate are 18.4 and 23.8 kcal mol^{-1}, and the ring-closure step is subject to a barrier of 15.4 and 18.9 kcal mol^{-1}, respectively. Using this new strategy, the authors synthesized a series of 5- to 8-membered cyclic carbonates, amongst which four sugar-based CCs (Scheme 17c) in good yields comparable to or exceeding the yields obtained using phosgene-reagent based syntheses.

The possibility to convert diols to carbonates by this method rapidly led to further development of CO_2- and sugar-based CCs. A first report describes the synthesis and ring-opening polymerization (ROP) of a cyclic carbonate-functionalized mannose derivative.[150] 1-*O*-Methyl-α-D-mannose was protected at position 2 and 3 by an isopropylidene acetal. Subsequently, a six-membered cyclic carbonate was formed by subjecting the compound to DBU and CO_2 followed by tosylation with TsCl and Et_3N (Scheme 18). The stereochemistry was retained, which suggests that the mechanism discussed above is operative. The yield of the product (57%) was higher than in similar syntheses for D-glucose (36%) and D-xylose (41%) derived CCs mediated by phosgene-reagents. An X-ray molecular structure was obtained, confirming the *trans*-positioning of the carbonate on the mannose ring. These types of bicyclic carbonates are easily polymerized through ROP. Indeed, the authors showed that a controlled polymerization of the obtained cyclic carbonate is feasible under organocatalytic conditions using TBD (1,5,7-triazabicyclo[4.4.0]dec-5-ene) and 4-methylbenzyl alcohol as initiator.

In addition to pyranose-sugars, there has been interest in the use of furanoses due to their stiffness in the backbone for potential polymers based on it. An interesting candidate is 2-deoxy-D-ribose. Naturally, this sugar exists in its pyranose form, which exposes a *cis*-diol, which can be converted into a CC through phosgene-based pathways. *cis*-5-Membered CCs, however, do not readily undergo ROP.[151] Therefore, this sugar was treated with MeOH in acidic conditions to transform it to its furanose-form (Scheme 19a). The furanose-form has a *trans* 1,3-diol that cannot be carbonated using phosgene-derived methods,[152] likely due to



Scheme 18 Synthesis of a 6-membered carbonate based on D-mannose. X-ray ellipsoids at 50% probability.



Scheme 19 (a) Synthesis of sugar-derived CCs through a DBU mediated insertion of CO_2 through S_N2 displacement of pre-activated alcohols or halides. (b) synthesis of a thymidine-based cyclic carbonate. (c) preparation of thiobased CCs. (d) synthesis of a D-glucose-based cyclic carbonate (TEGM = $-(CH_2CH_2O)_3CH_3$, a D-mannose-based cyclic carbonate and a D-galactose-based cyclic carbonate.

the high ring strain. Therefore, an alternative route was envisioned, based on selective preactivation of the secondary alcohol at the 3-position using tosyl chloride.[153]

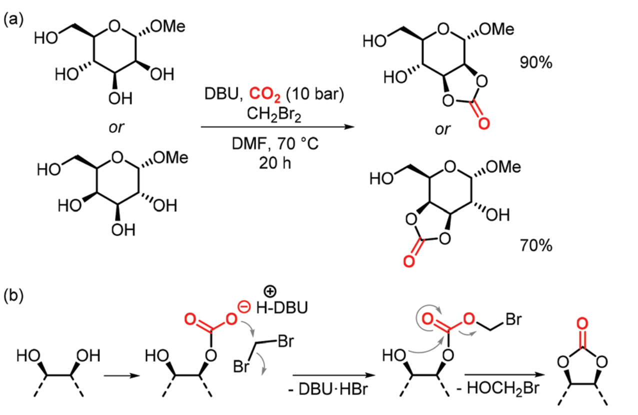
Using the activated sugar, the protocol based on DBU and CO_2 led to a 6-membered CC in one step as a mixture of anomers that could be separated by column chromatography. By reversing the order of tosylation and hemi-carbonate formation, the stereochemistry of the reaction can therefore be controlled. However, it is necessary to first isolate the tosylate, and the regioselectivity had to be forced by protection of the 5-alcohol. The reason for the successful synthesis lies in the fact that the stereochemistry is formally inverted in this process leading to a *cis*-configured carbonate of 2-deoxy-D-xylose that is less strained than its *trans*-analogue. ROP was attempted for both anomers, and it was shown that the β-anomer could not be polymerized. In contrast, the α-anomer was converted into a high-molecular weight polymer using trimethylene carbonate (TMC) as a comonomer in the presence of TBD as catalyst and benzyl alcohol as initiator.[153]

The same research group set out to investigate the possibility of generating CCs of thymidine, one of the bases of DNA containing the same 2-deoxy-D-ribose sugar backbone.[154] Both phosgene-reagent and DBU-CO_2 mediated syntheses were unsuccessful likely due to high ring strain of *trans*-fused CC units in furanose-sugars. In order to relieve the ring-strain but retain polymerization potential, the secondary alcohol at position 3′ of the thymidine was tosylated. Subsequent hemi-carbonate formation at alcohol 5′ and ring-closure led to a 6-membered CC with the stereochemistry at the 3′-position inverted (Scheme 19b). In addition, the free NH-group of thymidine required methylation as not to inhibit carbonate formation. As in other comparable cases, the cyclic carbonate monomer could be polymerized with a high control over the molecular weight of the resultant polycarbonate.

Later on, the ribose substrate was investigated for the formation of thiocarbonates or xanthates using CS_2 as a replacement for CO_2 (Scheme 19c).[155] The authors hypothesized that the larger C–S bond distance could better accommodate a *trans*-fused ring on the sugar. Reacting 1-*O*-methyl-2-deoxy-D-ribose with CS_2 and DBU, followed by MsCl (mesyl chloride) and Et_3N led to a single product in low yield (10%). The product was proven to contain a xanthate ring fused *trans* to the ribofuranose ring. When using a substrate where the diol is positioned *cis* (such as in 1,2-protected xylose) the xanthate product was obtained in similar yield (15%) but in addition the expected thiocarbonate product was formed in moderate yield (48%). The authors explain these results by proposing that the alcohol at the 5-position is mesylated, and the hemi-xanthate intermediate is formed at position 3, formed by ring-closure. Indeed, when the mesylated compound is prepared prior to reacting with DBU and CS_2, the same product is formed in higher yield.

The group of Gnanou published a similar strategy to obtaining carbonates of glucose by inclusion of CO_2.[156] By a protection-group strategy, they produced a fully protected glucopyranose with a benzylidene-acetal on alcohols 4 and 6, methylated anomeric alcohol and either a methyl or a methyl triethyleneglycol group on alcohols 2 and 3. Bromination of the acetal-group and hydrolysis of the resulting benzoyl-group on position 4 led to a halo-alcohol derivative. Under slightly elevated pressure of CO_2 (10 bar) and in the presence of DBU, this compound was carbonated to give the glucose-based cyclic carbonate with retention of stereochemistry (Scheme 19d). Although inversion of stereochemistry would be expected on position 6, this carbon center is achiral. The authors were able to generate hydrophilic or hydrophobic polymers by ROP of the cyclic-carbonate monomers, with R = Me, or TEGM, respectively or amphiphilic polymers by using both monomers. The new synthetic method proves a greener alternative to the method described by Wooley *et al.*, using phosgene derivatives to generate the carbonate.[136–138] Two more derivatives were later synthesized through the same method, *i.e.*, selective protection and bromination of the 6-position followed by reaction with DBU and CO_2 in DMF.[157] By this method, the authors could synthesize cyclic carbonates from a D-mannose and a D-galactose, and polymerize them through ROP.

In the same article, the authors report a procedure to generate 5-membered cyclic carbonates regioselectively from galactose and mannose that were only methylated at the anomeric position (Scheme 20a).[157] The simple one-step reaction involves CH_2Br_2 to generate a productive leaving group in the hemi-carbonate fragment that allows for subsequent ring-closure to yield the cyclic carbonate (Scheme 20b).[158] The procedure is selective for the formation of *cis*-5-membered carbonates, no *trans*-cyclic carbonates or 6-membered (even if they are *cis* in the case of galactose) were observed. Although not polymerizable, the authors show that the carbonates can react with amines to afford linear carbamates, which holds promise for their use in the production of isocyanate-free hydroxypolyurethanes.[157]



Scheme 20 (a) one-step synthesis to form *cis*-5-membered CCs from a D-mannose and a D-galactose.(b) Proposed mechanism of the reaction.

5. Fatty acid based carbonates

As can be judged from the preceding sections, the partial replacement of fossil fuels-based chemicals with compounds sourced from bio-based, renewable sources is an attractive and rewarding target in chemical research in the pursuit of increased sustainability.[159–162] It is clear that the realization of such a target requires the use of feedstock that are available in large volumes such as biogenic and food waste materials,[163–165] or those derivable from mass production crops.[166,167]

In this context, vegetable oils (**VOs**, Fig. 5), with a global production of over 200 Mt per year,[168,169] represent a valuable feedstock for the production of several chemicals.[170] The transesterification of **VOs** leads to fatty acid methyl esters (**FAMEs**, Fig. 5) that find wide application as commodity chemicals,[171] biodiesel fuel,[172] and as intermediates for further chemical diversification.[173–177] In particular, epoxidized fatty acid esters (**EFAs**, Fig. 5) can be easily obtained and display potential for applications such as lubricants, additives and plasticizers.[178] Similarly, triglycerides in vegetables oils can be epoxidized to afford epoxidized vegetable oils (**EVOs**, Fig. 5), that find application as green materials for the preparation of PVC [poly(vinyl chloride)], plasticizers,[179] elastomers,[180] coatings,[181] epoxy

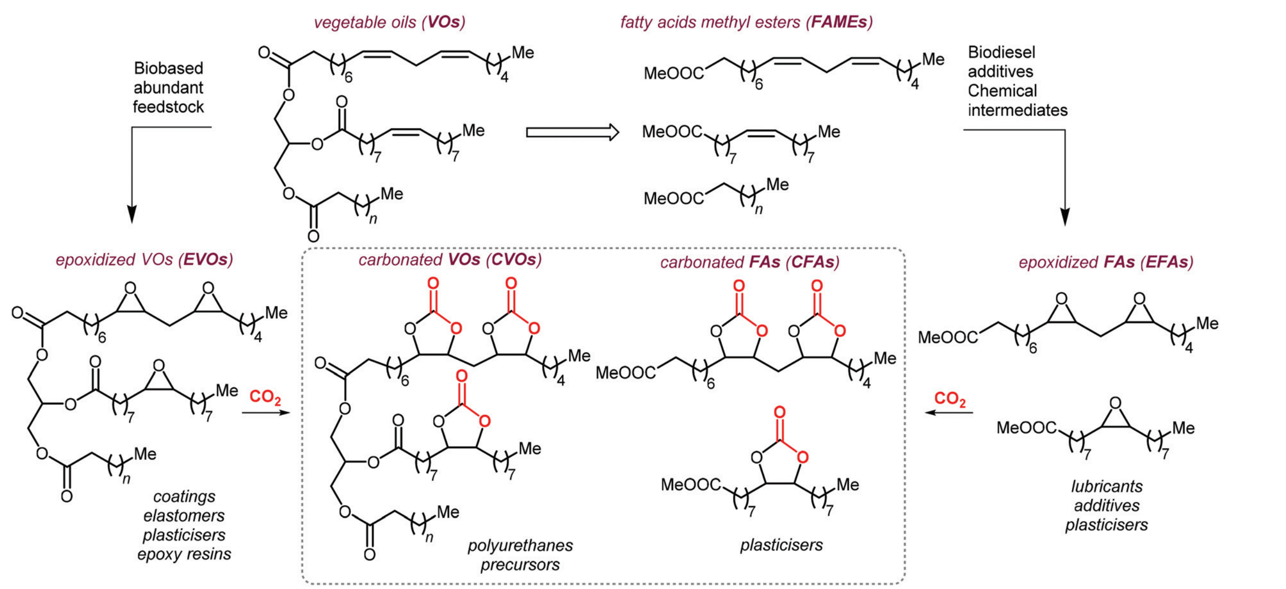


Fig. 5 Products from transesterification and functionalization of vegetables oils depicted as triglycerides of saturated, mono- and poly-unsaturated fatty acids.

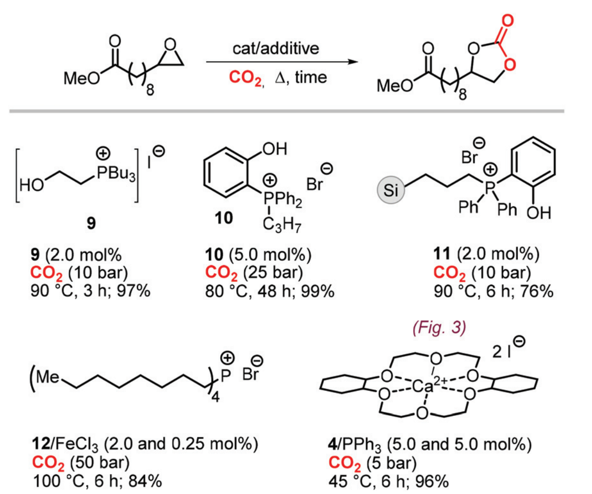
resins and blends.[182] Finally, both **EFAs** and **EVOs** can be carbonated *via* catalytic cycloaddition chemistry using CO_2,[1,2,4,181,183] leading to carbonated fatty acids and carbonated vegetable oils (**CFAs** and **CVOs**, Fig. 5). These latter compounds can serve as plasticizers for PVC,[24] and as building blocks for the synthesis of NIPUs, respectively.[185,186] Importantly, the latter processes have received increasing attention in recent years,[118,187,188] as they enable the integration between highly sought-after recycling of CO_2 into chemicals,[189–191] and the use of renewable substrates as building blocks for commodity chemicals with a low(er) carbon footprint.[24,192,193]

In this section, we review the catalytic processes that have been developed (mostly in the last decade) for the cycloaddition of CO_2 to **EFAs** and **EVOs** providing oleochemical carbonates. For the sake of clarity, terminal cyclic carbonates prepared from epoxidized fatty acid derivatives are initially discussed whereas the carbonation of internal epoxides present in fatty acids and vegetable oils is discussed separately.

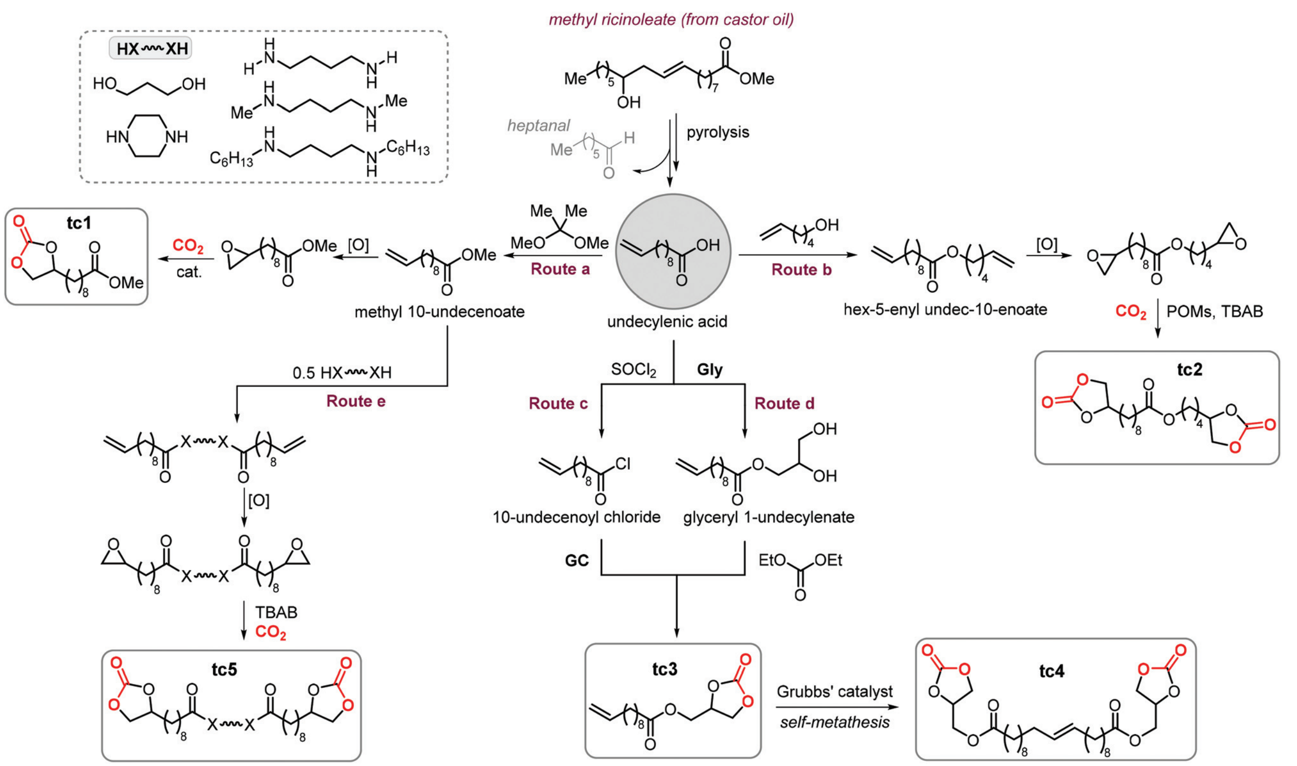
5.1 Terminal carbonates from EFA derivatives

A variety of terminal carbonates can be generated from methyl 10-undecenoate, a terminal fatty acid (**tEFA**) that in turn can be obtained from the pyrolysis of methyl ricinoleate, which is a main fatty acid component of renewable castor oil.[194] In Scheme 21, several possible synthetic routes are illustrated leading to (terminal) mono- and bis-carbonates. Terminal carbonate **tc1** can be obtained from the carbonation of epoxidized methyl 10-undecenoate (route a, Scheme 21). In recent years, the synthesis of **tc1** was studied by Werner *et al.* by employing various organocatalysts derived from phosphonium salts, or calcium-based catalysts (**9**, Scheme 22).[118,195–197]

The first attempt to prepare **tc1** was carried out by using bifunctional single-component organocatalysts based on tetraalkylphosphonium salts bearing an alcoholic moiety acting as hydrogen bond donor (HBD) for the activation of the epoxide (**9**, Scheme 22).[195] The latter class of organocatalysts is structurally tunable and accessible through the simple reaction



Scheme 22 Catalysts for the formation of fatty acid based CC **tc1**.



Scheme 21 Five-membered CC diversity derived from castor oil.

between trialkylphosphines and halogenated alcohols under ambient conditions. Using catalyst **9**, the coupling of the epoxy precursor and CO_2 was carried out in the temperature range 45–90 °C and at 10 bar of CO_2 pressure. A different single-component organocatalyst for the carbonation of this epoxidized fatty acid is the triphenylphosphine derivative **10** bearing an *ortho*-hydroxy functionality (Scheme 22).[198] Importantly, due to an optimal pK_a, phenolic hydroxyl groups have been found among the best H-bonding activating moieties in the conversion of epoxides into CCs.[199] The presence and the position of the hydroxy substituent in **10** was found to be crucial for its catalytic performance likely because it allows activation of the epoxide in the proximity of the bromide anion associated to the phosphonium group, with the halide acting as nucleophile for the ring-opening of the epoxide. The latter aspect allowed the use of **10** also as organocatalyst for the carbonation of more challenging internal bio-based epoxides (*vide infra*). However, in comparison to the previously discussed single-component organocatalyst **9**, the carbonation of epoxidized methyl 10-undecenoate using **10** required higher pressure (25 bar) and longer reaction times.

In order to avoid the limitations related to the use of homogeneous catalysts in terms of cost and product purification, immobilization of **10** onto polystyrene and a silica based support was carried out to ease separation from the reaction products and to allow for its recycling (**11**, Scheme 22) with the silica-supported catalyst **11** found to perform better than the polystyrene-supported one.[197] Catalyst **11** proved to be even more active than its homogeneous counterpart achieving a satisfactory yield in the carbonation of the same epoxide in 6 h at 10 bar of CO_2 pressure. The increased activity of the supported catalyst was attributed to the presence of abundant Si–OH moieties on thermally untreated silica likely acting as additional hydrogen-bonding moieties.[200,201] Catalyst **11** could be recovered and reused for over ten catalytic cycles, albeit some leaching and deactivation was noted.

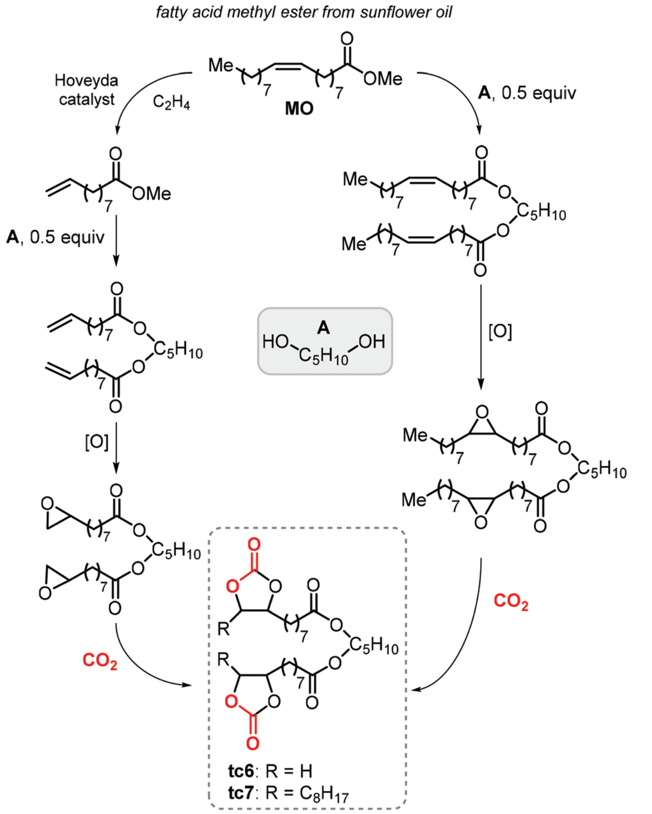
As an alternative to the application of organocatalysts, inexpensive and readily available coordination compounds in combination with ammonium and phosphonium salts have frequently found to act as highly active catalysts for the cycloaddition of CO_2 to epoxides.[202–204] Additionally, Lewis acids based on earth-abundant iron-derived complexes are particularly attractive.[2,7,205,206] On the other hand, catalysts based on metal halides are potentially corrosive and unlikely to find application in industrial reactors.[207,208] In this context, within a study on the application of iron-based coordination compounds as Lewis acids for the carbonation of several bio-based epoxides, Werner *et al.* investigated the catalytic performance of the binary catalyst tetra-*n*-octylphosphonium bromide **12**/$FeCl_3$ (Scheme 22) for the carbonation of epoxidized methyl 10-undecenoate.[196] The complete carbonation of this substrate was achieved in 6 h albeit under harsh reaction conditions (100 °C, 50 bar of CO_2).

More recently, the *in situ* complexation of calcium halides by crown ethers allows to prepare soluble calcium-based catalysts (**4**, Scheme 22 and Fig. 4).[209] This system was able to convert several internal and terminal epoxides to their corresponding CCs under ambient or very mild conditions without the need for additional quaternary salts. Later on, **4**/PPh_3 was applied for the conversion of several bio-based epoxides including epoxidized methyl 10-undecenoate (Scheme 22).[118] Whereas the calcium based complex **4**, formed by the reaction of CaI_2 with dicyclohexyl-functionalized 18-crown-6 ether (DCFCE), performed well in the carbonation of a benchmark substrate (*i.e.*, methyl oleate), the addition of triphenylphosphine (PPh_3, 5 mol%) allowed for reducing the CO_2 pressure from 20 to 5 bar and the reaction temperature from 60 to 45 °C. Under such conditions, epoxidized methyl 10-undecenoate was efficiently converted into **tc1** in 6 h.

Bis-carbonates containing two terminal cyclic carbonate moieties are useful synthons for the preparation of non-isocyanate based polyurethanes (NIPUs) by step-growth polymerization using diamine reagents.[185,186,210,211] Leitner *et al.* studied the carbonation of bis-epoxidized hex-5-enyl undec-10-enoate (route b, Scheme 21) to afford **tc2**, and this process was carried out under relatively harsh conditions using supercritical CO_2 ($scCO_2$) at 100 °C.[212] In this case, the authors chose tetraheptylammonium silicotungstate containing chromium (a polyoxometalate, POM, abbreviated as THA-Cr-Si-POM) in combination with TBAB as the catalyst. The authors proposed that the POM is capable of activating CO_2 by binding it to the catalyst surface. However, this aspect was not experimentally proven and it should be considered that the metal atoms (W, Cr) on the surface of the POM could, alternatively, accelerate the cycloaddition reaction by acting as Lewis acids. This could facilitate the ring-opening of the epoxide in a similar way as observed in MOFs,[213,214] and metalated porous polymers.[215,216] Despite the harsh reaction conditions, the advantage of the binary, heterogeneous system THA-Cr-Si-POM/TBAB was its simple separation from the products and the potential implementation of a flow process.

Cramail *et al.* carried out the coupling between **GC**, a versatile biobased building block,[217,218] with 10-undecenoyl chloride leading to the preparation of CC **tc3** (route c, Scheme 21) bearing both terminal carbonate and alkene moieties.[219] The same CC (**tc3**) was also prepared by Plasseraud *et al.* using a different strategy that involves the ring opening of glycidol (**Gly**) by undecylenic acid followed by carbonation of the obtained diol with diethyl carbonate (route d, Scheme 21).[220] Dimerization of **tc3** *via* self-metathesis using Grubbs catalyst gave access to bis-carbonate **tc4** that could be used to produce NIPUs by treatment with diamines. Cramail *et al.* also utilized 6-membered bis CCs derived from undecylenic acid using a procedure similar to route d giving other types of NIPUs precursors.[221]

A different strategy to advance the synthesis of cyclic bis-carbonates for NIPUs using undecylenic acid derivatives was followed by Cramail and coworkers (route e, Scheme 21). This strategy consists of bridging two undecylenic acid units by flexible "diamino or diol" linkers *via* transamidation or transesterification reactions.[222] Following epoxidation of the terminal alkenes to afford a bis-epoxide precursor, the bis-carbonate product (**tc5**) was produced quantitatively under harsh reaction conditions (80–140 °C, 50–60 bar of CO_2) using TBAB as the catalyst.



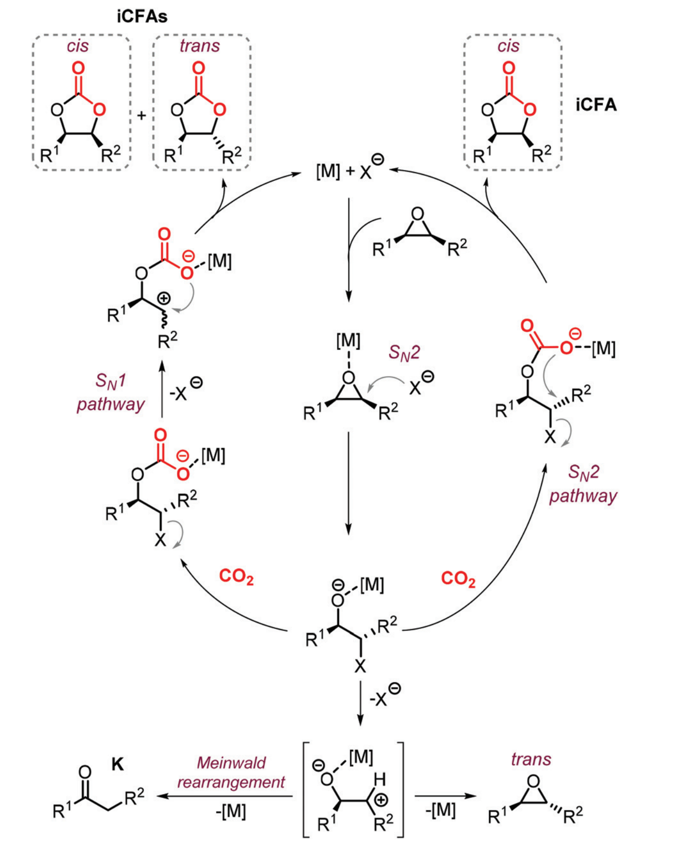
Scheme 23 Synthesis of terminal carbonated fatty acid diester (**tc6**) and internal carbonated fatty acid diester (**tc7**).

Finally, terminal cyclic bis-carbonates were prepared also from the methyl ester of oleic acid (**MO**, Scheme 23). The ethenolysis of the latter is known to produce useful synthons such as 9-decanoic acid methyl ester (9-DAME) and 1-decene.[173] Cramail *et al.* coupled two molecules of 9-DAME by transesterification with pentanediol catalyzed by $Zn(OAc)_2$ at 140 °C. Alternatively, parent **MO** was directly transesterified with pentanediol to afford an intermediate with internal double bonds.[223] Epoxidation of both compounds led to bis-epoxides serving as precursors for their respective CCs, which was carried out under close-to-supercritical or supercritical conditions using TBAB as a catalyst. Terminal bis-carbonate **tc6** was found to be more reactive than the bis-internal one **tc7** despite the latter being more soluble in the liquid CO_2 phase.

5.2 Internal carbonates from EFA derivatives

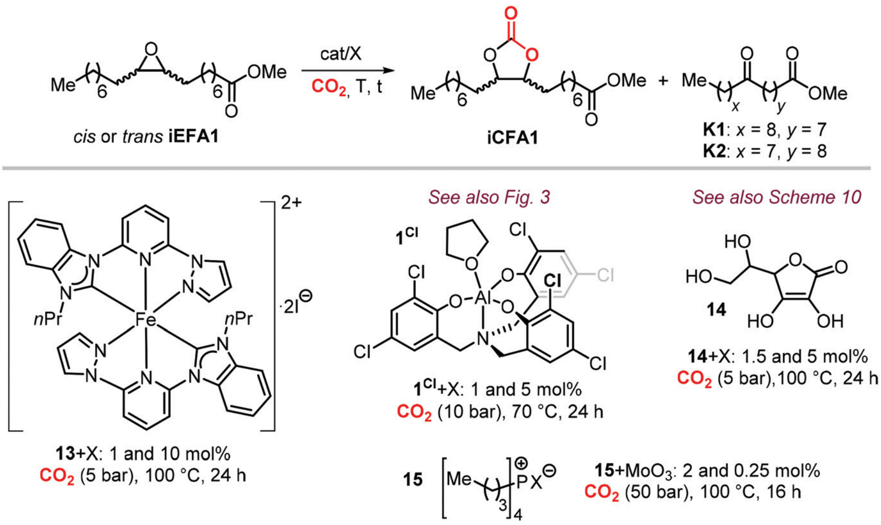
The synthesis of cyclic carbonates from epoxidized fatty acids with internal epoxy groups (**iEFAs**) is more complex than from terminal ones (**tEFAs**) because of the increased steric hindrance around the epoxy groups and the occurrence of rearrangement and/or isomerization processes compromising the selectivity and thus the yield of the targeted product. In the case of **iEFAs**, the internal epoxides are generally available in the stereochemically pure *cis*-configuration, and an attractive challenge is to perform the carbonation reaction with control over the stereoselectivity to obtain the fatty acid based cyclic carbonates as pure *cis*- or *trans*-isomers.

A general mechanism along with competitive side-reactions is shown in Scheme 24 for a reaction catalyzed by a binary catalyst comprising of a Lewis acid [M] and a nucleophilic halide(x).[224] Starting from a pure *cis*-epoxide, both *cis* and *trans* configured CCs can be formed after an initial S_N2-type epoxide ring-opening step mediated by the halide that affords a metal alkoxide.[225,226] In the subsequent step, a hemicarbonate intermediate is formed after CO_2 insertion into the metal–alkoxide bond. This linear carbonate species undergoes a second, intramolecular nucleophilic substitution having either S_N1 or S_N2 character that strongly depends on the choice of the halide nucleophiles.[227–229] Halides possessing excellent leaving group ability (*i.e.*, Br and I) may provide under suitable reaction conditions S_N1 type chemistry with the intermediacy of a carbocation. In this case, ring-closure of the carbocation affords either the *cis*- or *trans*-carbonates with the latter being typically the thermodynamically favored product. Conversely, an anion with reduced leaving group ability (*i.e.*, Cl) is less likely to provide an *in situ* generated carbocation. In this case, a second S_N2 at the same carbon atom of the



Scheme 24 General mechanism of the coupling reaction between a fatty acid containing internal epoxide units and CO_2 catalyzed by a binary system [M]/X. X is a halide source such as an ammonium or phosphonium salt. **iCFA** stands for internal carbonated fatty acid, **K** for a ketone byproduct.

Table 3 The catalytic comparison of the cycloaddition of CO_2 to **iEFA1** producing **iCFA1** depending on the metal complex/halide combinations



			I			Br			Cl			
							Selectivity					
Entry	iEFA1	Cat.	Conv.	Selectivity iCFA1[a]	*cis* : *trans*[b]	Conv.	iCFA1[a]	*cis* : *trans*[b]	Conv.	Selectivity iCFA1[a]	*cis* : *trans*[b]	Ref.
1	*cis*	**13**	91[c]	[d]	<1 : 99	85[c]	[d]	15 : 85	72[c]	[d]	76 : 24	230
2	*cis*	$\mathbf{1^{Cl}}$	[d]	[d]	[d]	94	>99	76 : 24	>99	>99	95 : 5	187
3	*cis*	**14**	>99	19	17 : 83	98	74	24 : 76	69	>99	85 : 15	231
4	*cis*	**15**	89	79	39 : 61	95	91	64 : 36	64	92	94 : 6	224
5	*trans*	$\mathbf{1^{Cl}}$	[d]	[d]	[d]	[d]	[d]	[d]	65	99	<1 : 99	187
6	*trans*	**13**	78[c]	[d]	17 : 83	81[c]	[d]	11 : 89	79[c]	[d]	7 : 93	230

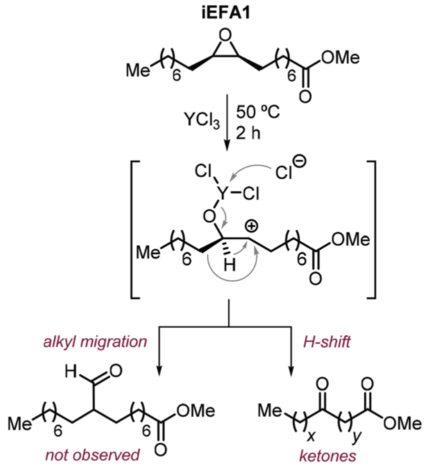
[a] Determined by ^1H NMR from the integration of the peaks corresponding to the carbonates (*cis* **iCFA1** + *trans* **iCFA1**) and ketone (**K**) by-product. [b] *Cis* : *trans* ratio determined by ^1H NMR by integration of the corresponding signals of *cis* and *trans* carbonate products. [c] Isolated yield. [d] Not reported.

metallo-hemicarbonate will undergo ring-closure while restoring the initial configuration leading thus to a *cis* CC product.

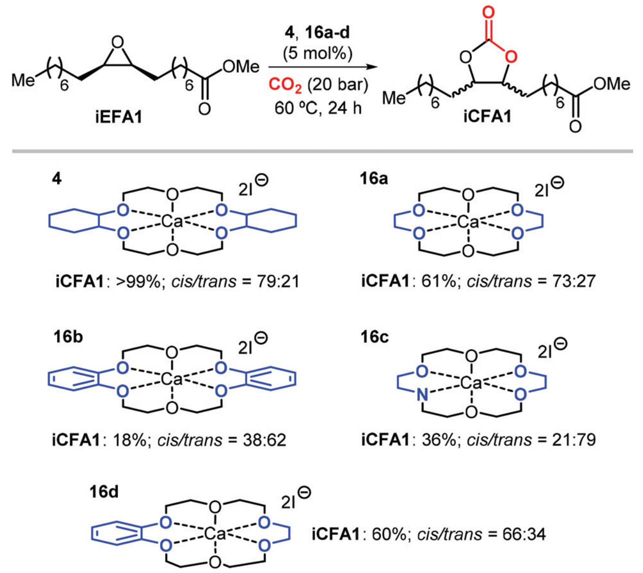
To further substantiate these concepts, the catalytic performance of several binary/bifunctional catalysts ($\mathbf{1^{Cl}}$ and **13–15**) incorporating different nucleophilic halides(x) is compared in Table 3. For all catalysts featuring chloride nucleophiles, the *cis*-**iCFA1** was observed as the main product (entries 1–4). Furthermore, the use of **13**/TBAI allowed the formation of *trans*-**iCFA1** with nearly complete diastereoselectivity.[230] In agreement with the mechanistic picture of Scheme 24, the use of bromide or iodide as the nucleophilic anion should lead to a decreased selectivity for the *cis*-isomer and thus increased selectivity for the *trans* isomer by partially favoring the S_N1 pathway (entries 1–4), and this appears to be generally the case.

Among the catalysts, simple and readily available L-ascorbic acid **14**/TBAC allowed the synthesis of the *cis*-**iCFA1** from *cis*-**iEFA1** with high diastereoselectivity (*cis* : *trans* = 85 : 15).[231] The system **14**/TBAC showed (expectedly) lower substrate conversion than **14**/TBAB and **14**/TBAI but higher chemoselectivity towards *cis*-**iCFA1** (>99%), whereas in the other two cases a significant amount of the side products were formed (entry 3). When **13**/TBAI or **14**/TBAI were selected as catalysts, *trans*-**iCFA1** was observed as the main carbonate product (entries 1 and 3), whereas **iCFA1** was preferentially formed when utilizing bifunctional catalyst **15** regardless of the nature of the halide (entry 4) though with the lowest stereocontrol towards *cis*-**iCFA1** in the presence of iodide. These results suggest that the use of iodide based catalysts have higher preference for the *trans*-carbonate product by favoring an S_N1 pathway.[229,230]

The nature of the halide has thus a clear impact on the overall selectivity of the process, and ketones **K** are typical by-products in the formation of **iCFAs.**[24,116,118,196,212,224,231,232] Ketone formation is attributed to Meinwald rearrangement *via* a 1,2-hydride shift in the presence of Lewis- or Brønsted acids (Scheme 24, below).[124,233] For example, the formation mechanism of **K** proposed for YCl_3 is shown in Scheme 25.[234–236] In the case of CO_2 cycloaddition to internal epoxides catalyzed by Lewis acids in the presence of halides as nucleophiles, the carbocation species (precursor of the ketone *via* hydride shift) may be formed by dissociation of the halide from the alkoxide intermediate similar to what discussed for the S_N1 mechanism. Therefore, catalysts with halides that can serve as good leaving groups (Br and I) are expected to favor the formation of a ketone by-product (**K**), whereas catalysts delivering a chloride nucleophile should suppress this side-product formation.



Scheme 25 Plausible formation of ketone side-products *via* Meinwald rearrangement in the presence of YCl_3.[234]



Scheme 26 Dependency of catalytic activity and stereocontrol on the macrocyclic ligand structure in calcium-based crown ether complexes in the cycloaddition of CO_2 to **iEFA1** to afford **iCFA1**.[118]

This is in agreement with the observations when using catalysts **14**,[231] and **15**,[224] with the selectivity for the carbonate product *cis*-**iCFA1** progressively decreasing in the series Cl > Br > I (entries 3 and 4) in line with the ability of Cl-derived catalysts to suppress the occurrence of undesired Meinwald rearrangement.

Interestingly, the use of Lewis acid complex $\mathbf{1}^{\mathbf{Cl}}$ led preferentially to carbonate *cis*-**iCFA1** as the major product independent of the use of chloride or bromide anions as nucleophiles (entry 2). Finally, the formation of a carbocation from the crucial alkoxide intermediate can also lead to *cis*-to-*trans* isomerization of the epoxide (Scheme 24, below). Indeed, *trans*-**iEFA1** is often observed as minor by-product along with the formation of *trans*-**iCFA1** and ketones **K**.[224]

Apart from the nature of the nucleophilic halide anion, modifications of the (Lewis acid) structure can also play a role in controlling the stereoselectivity and kinetics of the carbonation reaction. In the case of calcium-based crown ether complexes, the use of complexes **4** and **16a** (Scheme 26) containing fully aliphatic crown ether ligands and iodide as co-catalyst principally led to carbonate product **iCFA1** with high *cis*-selectivity, which is somehow different from the results obtained using catalysts **13** and **14** in the presence of TBAI where the principal product was the *trans* isomer of **iCFA1**.[118] When part of the bridging groups were aromatic (**16b**), the selectivity switched from mostly *cis* to *trans* product though the overall yield (18%) of **iCFA1** was low, likely due to the low solubility of **16c** in the reaction mixture. Similarly, by replacing one oxygen for a nitrogen atom (**16c**) largely the formation of *trans*-**iCFA1** was noted. Finally, compound **16d** with a single aromatic bridging unit displayed a catalytic performance similar to that observed for **16a**. All these results combined indicate that, beside the choice of the nucleophilic halide anion, other structural factors can contribute to the overall efficacy and stereo-outcome of the process.

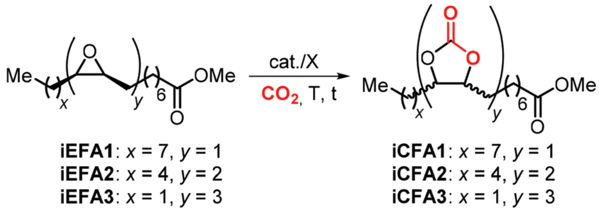
Some authors examined the cycloaddition of CO_2 to *trans*-**iEFA1** (Table 3) as a way to confirm the occurrence of a double inversion (or: double S_N2) pathway in the formation of **iCFAs**. The binary catalytic system $\mathbf{1}^{\mathbf{Cl}}$/PPNCl, that converts *cis*-**iEFA1** mostly to its corresponding carbonate *cis*-**iCFA1** (entry 2, Table 3), led to almost total diastereoselective formation of *trans*-**iCFA1** from *trans*-**iEFA1** (entry 5, Table 3) in agreement with a double inversion pathway. Interestingly, the application of complex **13** for the carbonation of *trans*-**iEFA1** led principally to *trans*-**iCFA1** as the thermodynamically most stable isomer regardless of the type of halide employed (entry 6). This observation is somewhat in contrast with that observed for the carbonation of *cis*-**iEFA1** where the use of iodide and bromide as nucleophiles led to substantial degrees of inversion of configuration *via* a *pseudo*-S_N1 mechanism (entry 1). These results suggest that the outcome of the cycloaddition process may be subject to a more complex set of interactions between the catalyst components and the substrate.

5.3 Catalytic performances in the cycloaddition of CO_2 to various iEFAs and EVOs: the role of quaternary salts

Initial attempts to carry out the carbonation of **EFAs** where carried out using quaternary ammonium, phosphonium or other salts in the absence of Lewis acidic catalysts or HBDs. An overview of quaternary salts applied under various reaction conditions for the carbonation of **iEFAs1–3** derived from mono-unsaturated **MO** (**iEFA1**), bis-unsaturated methyl linoleate (**iEFA2**) and, more rarely, tris-unsaturated methyl linolenate (**iEFA3**) is given in Table 4.[223]

The obvious advantage of using quaternary salts as catalysts is that they are metal-free, generally inexpensive, and commercially available. In addition, Doll and Erhan found that TBAB can be conveniently removed from the product mixture by thermal breakdown into volatile compounds at 190 °C by

Table 4 The catalytic performance of quaternary salts in the cycloaddition of CO_2 to **iEFA1–3**



Entry	iEFA	cat. (mol%)	Reaction conditions T (°C), CO_2 (bar), time (h)	Conversion[a] (%)	Selectivity for iCFA	Selectivity (*cis* : *trans*)[b]	Ref.
1	**1**	TBAB (5)	100, 103, 15	93[c]	[d]	[d]	238
2	**1**	TBAF (5)	100, 117, 24	62	0	[d]	212
3	**1**	TBAC (5)	100, 117, 24	21	95	77 : 23	212
4	**1**	TBAB (5)	100, 117, 24	97	≥99	72 : 28	212
5	**1**	TBAI (5)	100, 117, 17	80	92	20 : 80	212
6	**1**	NH_4Br	100, 117, 24	4	75	[d]	212
7	**1**	$((n\text{-}C_7H_{15})_4N)Br$	100, 117, 24	99	≥99	70 : 30	212
8	**1**	$(C^{14}mim)Br$[e]	100, 117, 24	97	96	74 : 26	212
9	**1**	$((n\text{-}C_{14}H_{29})(n\text{-}C_6H_{13})_3P)Br$	100, 117, 24	97	97	69 : 31	212
10	**2**	TBAB (5)	100, 117, 24	71	95	[d]	212
11	**3**	TBAB (5)	100, 117, 24	68	89	[d]	212
12	**1**	TBAB (2)	100, 50, 16	39	82	46 : 56	224
13	**1**	**15**-Br (2)	100, 50, 16	49	94	71 : 29	224
14	**1**	**15**-Cl (2)	100, 50, 16	39	99	90 : 10	224
15	**1**	**15**-I (2)	100, 50, 16	35	71	57 : 43	224
16	**1**	TBAB (7)	130, 30, 8	99	[d]	[d]	239
17	**1**	TBAB (5)	70, 10, 24	>99	>99	51 : 49	187
18	**1**	TBAC (5)	70, 10, 24	6	>99	>99 : 1	187
19	**1**	PPNCl (5)	70, 10, 24	53	>99	96 : 4	187
20	**2**	PPNCl (5)	85, 10, 24	95	>99	95 : 5	187
21	**3**	PPNCl (5)	70, 10, 24	75	>99	90 : 10	187
22	**1**	TBAI (5)	100, 5, 24	70	59	22 : 78	231
23	**1**	TBAB (5)	100, 5, 24	83	87	36 : 64	231
24	**1**	TBAC (5)	100, 5, 24	44	>99	90 : 10	231

[a] Conversion determined by titration and/or ^1H NMR. [b] *Cis* : *trans* ratio determined by ^1H NMR by integration of the corresponding signals of *cis* and *trans* carbonate products. [c] Isolated yield. [d] Not reported. [e] $(C^{14}mim)Br$ = 1-*n*-tetradecyl-3-methylimidazolium bromide.

Hofmann elimination.[237] In different studies, the use of halide salts often required harsh reaction conditions such as the use of $scCO_2$ (entries 1–11, Table 4) or temperatures above 100 °C (entry 16) to convert **iEFA1–3** to their corresponding carbonates **iCFA1–3** in reasonable to high yields.

Based on the earlier report by Doll and Erhan highlighting the catalytic competence of TBAB in the carbonation of **iEFA1** under supercritical conditions (entry 1),[238] Leitner *et al.* showed that the employment of several quaternary ammonium halides for the cycloaddition of CO_2 to **iEFA1** under $scCO_2$ conditions generally provided the target carbonate with good conversion rates and selectivities (entries 2–9). Exceptions in this series were NH_4Br and tetra-*n*-butylammonium fluoride (TBAF) because of the poor leaving group character of the fluoride anion (see entries 2 and 6) and the tighter ion pair when using ammonium cations.[212] In line with earlier results discussed in section 5, all salts employed provided *cis*-**iEFA1** as the main stereoisomer with the exception of TBAI for which the *trans*-isomer was found to be the main product (entry 5). The use of ammonium or phosphonium salts bearing longer alkyl chains compared to TBAB did not lead to any significant improvement of the catalytic activity (entries 7–9). Therefore, TBAB was selected as catalyst for the conversion of other substrates such as *cis*-**iEFA2** and *cis*-**iEFA3**, obtaining satisfactory performances despite a slight drop in conversion and carbonate selectivity (entries 10 and 11).

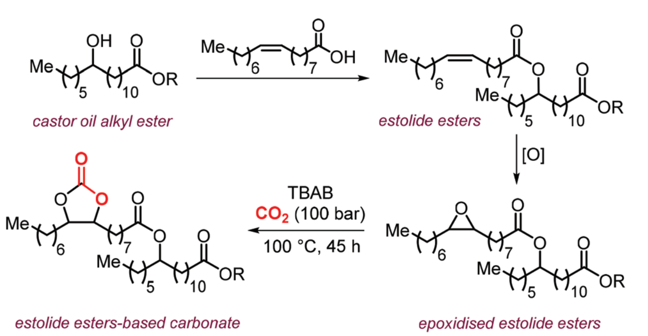
Similar results under comparable reaction conditions were found for substrate *cis*-**iEFA2** in a later study by Buchholz *et al.*[24] However, Werner and coworkers demonstrated that the catalytic performance is strongly reduced together with some loss of selectivity for **iCFA1** when using TBAB for the carbonation of *cis*-**iEFA1** at 100 °C but lower CO_2 pressure (50 bar) and lower catalyst loading (2 mol%; *cf.*, entries 4 and 12).[224] In the same study it was observed that the use of tetrabutylphosphonium halides, in particular **15**-Br and **15**-Cl, leads to slight improvement in terms of epoxide conversion and **iCFA** selectivity compared to TBAB under identical conditions (*cf.*, entry 12 and 13–15). In addition, Leveneur *et al.* showed that the use of a slightly higher TBAB loading (7 mol%) at 130 °C allowed complete conversion of *cis*-**iEFA1** under 30 bar CO_2 pressure as an alternative for supercritical conditions, though the selectivity towards **iCFA1** was not reported (entry 16).[239]

Recently, the group of Kleij studied the performance of various halide salts in an attempt to develop catalysts able to operate under milder conditions.[187] They found that TBAB converts *cis*-**iEFA1** quantitatively into **iCFA1** at 70 °C and 10 bar of CO_2, although without any observable stereocontrol (entry 17). The use of TBAC, however, provided *cis*-**iCFA1** selectively but only at very low epoxide conversion, while the use of PPNCl as chloride source led to higher conversion of *cis*-**iEFA1** maintaining very high selectivity for *cis*-**iCFA1** (*cf.*, entries 18 and 19). PPNCl served also as an efficient and stereoselective catalyst for carbonation of *cis*-**iEFA2** and *cis*-**iEFA3** at 70–85 °C and 10 bar of CO_2 (entries 20 and 21).

Recently, it was shown that quaternary ammonium salts give appreciable conversion levels of *cis*-**iEFA1** at 5 bar of CO_2 and 100 °C. Under these conditions, the stereocontrol exerted by TBAI in the preparation of *cis*-**iCFA1** is moderately high, and similar results are obtained switching to TBAB though with significantly higher chemoselectivity for **iCFA1**. The use of TBAC led to moderate epoxide conversion but with very high overall selectivity for *cis*-**iCFA1** (*cf.*, entries 22–24).

A further expansion of the portfolio of fatty acid-derived CCs can be realized by using epoxidized estolides as starting point. This class of compounds is generated by the reaction between a carboxylic acid of a fatty acid with a double bond or hydroxyl moiety of another one.[232,240] The estolide compounds are attractive functional fluids when compared to standard vegetable oils because of a higher stability towards oxidation and lower pour points.[241] The epoxidation and carbonation of estolides can be used to further tune crucial properties of these compounds such as viscosity.[242]

In an initial study, Isbell *et al.* used 2-ethylhexyl estolide esters of oleic acids constituted by a complex mixture of oligomers generated by the addition of the carboxylic acid of oleic acid to the double bond of other oleate chains.[242] Following epoxidation using *in situ* generated performic acid, the epoxidized estolide was successfully carbonated using TBAB as the catalyst under $scCO_2$ conditions at ∼100 bar of CO_2 and 100 °C. The viscosity of the carbonated estolide was substantially higher than that of the parent epoxidized estolide. The same group developed the synthesis of estolide esters obtained through the reaction between oleic acid and the hydroxyl group of saturated and unsaturated alkyl esters of castor oil (Scheme 27).[232] The resulting compounds were epoxidized and carbonated using TBAB as catalyst under supercritical conditions as described in the previous example. The resulting carbonated estolides displayed increased viscosity and higher oxidation stability (oxidation onset around 200 °C) compared to the non-functionalized estolides and its epoxy derivatives, thus offering good candidates for application as industrial fluids.



Scheme 27 The synthesis of estolides from oleic acid and castor oil alkyl esters.

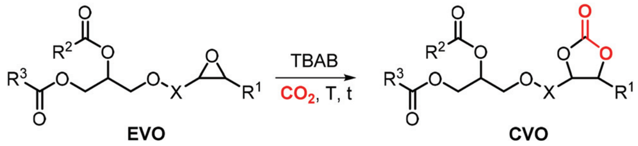
Beside the case of **EFAs**, the carbonation of **EVOs** (Table 5) such as epoxidized vernonia, castor, soybean, linseed, sunflower, cottonseed and olive oils has been extensively studied.[243] The resulting **CVOs** (Table 5) are attractive synthons for the synthesis of NIPUs by reaction with diamines,[23,185,211,244–251] and find applications in paints, coatings, and bio-based materials.[252,253] Remarkably, some properties such as the thermal stability and oxidative stability of polyurethanes (PUs) derived from soybean oil were found to rival those of PUs derived from poly(propylene oxide).[254]

The synthesis of **CVOs** has been principally carried out on epoxidized linseed, sunflower and soybean oils due to the relatively high epoxy content that can be introduced in the fatty acid alkyl chains. The cycloaddition reaction of CO_2 to such **EVOs** has often been carried out using TBAB as the catalyst (Table 5). As in the case of **EFAs** (see entries Table 4), these reactions are conveniently performed at high pressure ($CO_2 \geq$ 50 bar) or under sc-CO_2 conditions (entries 1–10, Table 5) often in combination with high reaction temperatures (120–140 °C). However, the CO_2 pressure can be reduced to 4 bar when the carbonation reaction is carried out at ≥110 °C (entries 11–15). Under these conditions, high to nearly quantitative conversion of the epoxide groups was generally observed, however the selectivities for the carbonate products have seldom been reported. Leitner *et al.* observed a relatively low selectivity (73%) for carbonate formation in the cycloaddition of CO_2 to epoxidized soybean oil (**ESBO**) under supercritical conditions (entry 5).[212] Further attempts were carried out for the carbonation of **EVOs** under atmospheric pressure at $T \geq$ 110 °C using TBAB or TBAI as catalyst by extending the reaction time to 40–70 h (entries 16–19). In some of these cases, despite the disappearance of epoxide and the appearance of IR-bands for the carbonate C═O stretching were observed, the actual chemoselectivity for the CC was not reported.[255,256]

Mazo and Rios observed that the addition of water (about 33 mol%) significantly accelerates the carbonation of **ESBO** thus obtaining the corresponding **CVO** under atmospheric pressure with good conversion and selectivity in 70 h (entry 18).[257] This result is in line with the known ability of water to serve as a HBD in the cycloaddition of CO_2 to epoxides.[258] Additionally, the same authors have shown that a further acceleration of the reaction rate can be achieved by combining the addition of water to the use of a microwave reactor resulting in a reduction of the reaction time to 40 h without affecting the selectivity for the carbonated product (entry 19).[259]

Finally, several examples of comprehensive physicochemical studies on the carbonation of **EVOs** in the presence of TBAB have been carried out. These studies concern reaction kinetics modelling, the role of mass transfer, CO_2 solubility,

Table 5 Catalytic comparison of cycloaddition of CO_2 to **EVOs** catalyzed by TBAB



Entry	EVO	TBAB (mol%)	Reaction conditions T (°C), CO_2 (bar), time (h)	Conversion[a] (%)	Selectivity[a] for CVOs	Ref.
1	Soybean	5[b]	140, 152, 18	96[c]	[d]	263
2	Sucrose soyate	5[b]	140, 131, 20	70[c]	[d]	263
3	Soybean	16.6	100, 138, 46	96	[d]	264
4	Soybean	4.5	140, 124, 54	99	[d]	265
5	Soybean	5	100, 117, 24	47	73	212
6	Soybean	2.7[i]	120, 100, 9	100	[d]	266
7	Soybean	5	100, 100, 20	94	[d]	237
8	Soybean	0.18	140, 56.5, 22	98	[d]	267
9	Cottonseed	3.5	130, 50, 7	94	[d]	268
10	Sunflower	3.5	120, 50, 12	86	[d]	269
11	Cottonseed	5	140, 30, 24	99.9	[d]	270
12	Linseed	3	140, 30, 20	100	[d]	271
13	Soybean	3.4[i]	140, 10, 23	97	[d]	272
14	Castor	5	130, 5, 8	93	[d]	273
15	Soybean	5	110, 4, 12	100[e]	[d]	274
16	Soybean	5[f]	110, 1, 70	100	[d]	255
17	Linseed	5	100, 1, 72	100[g]	[d]	256
18	Soybean[h]	5	120, 1, 70	77	89	257
19	Soybean[h]	5	120, 1, 40	80	92	259

[a] Conversion/selectivity determined by titration and/or ^{1}H NMR. [b] Weight percent (wt%) loading. [c] Weight percent (wt%), epoxide conversion determined by epoxy titration according to ASTM D 1652. [d] Not Reported. [e] Conversion determined by FTIR. [f] TBAI loading in mol%. [g] Conversion determined by FTIR analysis of the reaction mixture at intervals of 24 h until completion. [h] Addition of water, with a molar ratio H_2O : **EVO** of 1 : 3. [i] Weight percent.

substrate viscosity, the differences between **EFAs** and **EVOs** and the effect of microwave irradiation on the process kinetics, and were carried out by Leveneur *et al.*[260–262] These important, but rather technical studies are not described in detail in this section.

5.4 Catalytic performance of binary catalytic systems in the cycloaddition of CO_2 to iEFA1: metal salts and coordination compounds

The vast majority of catalytic systems for the cycloaddition of CO_2 to epoxides are binary systems. These systems typically involve one component (Lewis acid or HBD) coordinating or better activating the epoxide substrate, and a nucleophilic component that serves to ring-open the activated epoxide.[30,183,184] These bicomponent catalysts often allow for the cycloaddition reactions to take place under relatively mild or even ambient conditions when compared to the exclusive use of (quaternary) halide salts.[1]

In recent years, several examples of binary catalytic systems suitable for the mild and stereoselective carbonation of **EFAs** and **EVOs** have been developed and are discussed in this and following sections, by taking **iEFA1** as a model substrate, according to the kind of epoxide-activator including metal coordination compounds, metal–organic catalysts and organocatalysts.

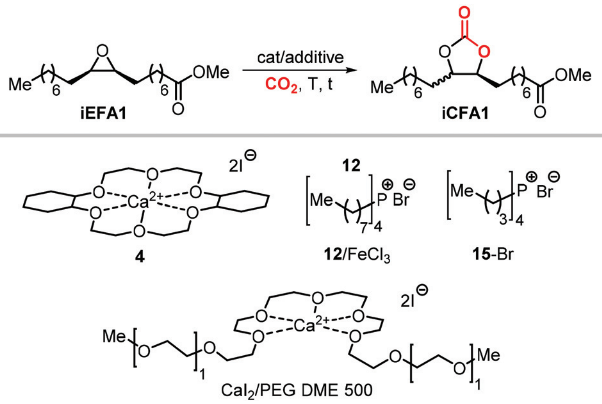
Coordination compounds and metal salts represent readily available and inexpensive compounds for the cycloaddition of CO_2 to epoxides.[202,203,229] They are usually commercially available and can be easily immobilized onto silica supports.[225,275,276] However, in the case of metal halide salts, their large-scale application could be limited by their relatively low moisture stability and by the risk of reactor corrosion.[207]

Polyoxometalates (POMs) are clusters of metal atoms connected by oxo-bridges and terminated by anionic MO moieties. Such compounds are able to activate CO_2/epoxides *via* interaction with the basic oxygen atoms and Lewis acidic metal centers of the POM.[277] Based on this dual activation ability, the halogen-free cycloaddition of CO_2 to epoxides catalyzed by transition-metal-substituted silicotungstates ($[(n\text{-}C_7H_{15})_4N]_6[\alpha\text{-}SiW_{11}O_{39}M(\textsc{ii})]$, with M = Mn, Co) was demonstrated by Sakakura *et al.* already in 2005.[278] The sustainable character of this approach was limited by the harsh reaction conditions (150 °C, 35 bar of CO_2) and the need for a reaction solvent.

Later in 2013, Leitner *et al.* employed $[(n\text{-}C_7H_{15})_4N]_5[\alpha\text{-}SiW_{11}O_{39}Cr(\textsc{iii})]$ (THA-Cr-Si-POM) for the carbonation of **iEFAs** in $scCO_2$.[212] As expected, under harsh conditions (100 °C, ~130 bar of CO_2), THA-Cr-Si-POM (2 mol%) was able to catalyze the quantitative conversion of **iEFA1** to *cis*-**iCFA1** in 20 h. However, the authors also observed that the addition of equimolar, catalytic amounts of TBAB could accelerate the reaction that was complete in 6 h (entry 1, Table 6).

More recent, the use of coordination compounds and metal salts for the carbonation of fatty acids has led to the discovery

Table 6 The comparison of the cycloaddition of CO_2 to epoxidized **MO** (**iEFA1**) catalyzed by coordination compounds and metal salts



Entry	Cat/add. (mol%)	T, p, t (°C, bar, h)	Yield **iCFA1** (%)	Sel.[a] **iCFA1** (%)	Sel.[a] *cis* vs *trans*	Ref.
1	THA-Cr-Si-POM (2.0) TBAB (2.0)	100, 130, 6	95	98	96 : 4	212
2	**15**-Br (2.0) MoO_3 (0.25)	100, 50 20	98	98	77 : 23	224
3	**12** (2.0) $FeCl_3$ (0.25)	100, 50 24	96	96	68 : 32	196
4	CaI_2 PEG-DME 500 (5.0)[b]	90, 50 48	91	[c]	53 : 47	280
5	**4** (5.0) Ph_3P (5.0)	45, 5 24	86	[c]	84 : 16	118
6	KI (2.0) TEA (2/2)	100, 50 16	8[d]	[c]	[c]	281

[a] *Cis* : *trans* ratios and selectivity towards **iCFA1** determined by ^{1}H NMR from the integration of the corresponding signals of *cis* and *trans* carbonate products. [b] PEG DME 500: oligo(ethyleneglycol) dimethyl ether with $M_n \sim 400$ g mol^{-1}. [c] Not reported. [d] Conversion determined by GC analysis. THA = tetra-*n*-heptyl ammonium, p is the partial pressure of CO_2 and TEA is triethanolamine.

of binary systems operating under milder conditions than the THA-Cr-Si-POM reported by Leitner. Werner *et al.* extensively studied the application of coordination compounds as additives for the cycloaddition of CO_2 to **iEFA1**. Initial studies involved the application of phosphonium salts **12** and **15** in combination with commercially available coordination metal compounds of transition metals such as MoO_3 and $FeCl_3$ under relatively harsh conditions (100 °C, 50 bar of CO_2; entries 2 and 3 in Table 6).[196,224] The presence of MoO_3 appeared as a more convenient choice for **iEFA1** conversion and carbonate selectivity in a wider screening of metal salts (mostly Al- and Mo-based) in the presence of **15**-Br (see also Table 3) as the nucleophile.

Interestingly, compared to the exclusive use of phosphonium salts as catalysts, the addition of coordination compounds accelerate **iEFA1** conversion at the cost of a slight drop in carbonate selectivity.[224] Under the same reaction conditions, the use of $FeCl_3$ in the presence of phosphonium salts (**12** or **15**-Br) led to a similar result as MoO_3.[196] The use of iron-based catalysts is considered advantageous, since Fe is an earth-abundant, non-toxic and non-endangered metal.[2,7,205,279]

Similarly, the application of calcium may be seen as more sustainable compared to the use of transition metals in catalyst systems. Whereas most coordination compounds of calcium are generally insoluble in most reaction media, Werner *et al.* showed that the use of chelating ligands (crown ethers) in combination with calcium halides leads to soluble and highly active Lewis acids for CO_2/epoxide cycloaddition.[118,209,280–282] The *in situ* complexation of CaI_2 by poly(ethylene glycol)dimethyl ether (PEG-DME-500) further promotes the nucleophilicity of the iodide anion leading to a system able to mediate the cycloaddition of CO_2 to terminal and internal epoxides including **iEFA1** (entry 4, Table 6).[280] Alternatively, crown ethers are effective complexing agents for CaI_2 leading to highly active calcium catalysts such as **4** for the cycloaddition of CO_2 to terminal epoxides under ambient conditions.[209] Catalyst **4** can be successfully applied for the carbonation of **iEFA1** under relatively mild conditions (60 °C, 20 bar of CO_2). In addition, it was found to work under even milder conditions (45 °C, 5 bar of CO_2, entry 5) when used in the presence of a relatively high loading (5 mol%) of PPh_3 obtaining **iCFA1** mostly as the *cis*-isomer.[118] In a previous study, the same group showed that KI, a frequently used source of nucleophilic iodide,[283] forms an efficient catalyst for the carbonation of terminal epoxides when combined with triethanolamine as HBD, although this catalyst was virtually inactive for the conversion of **iEFA1** (entry 6),[281] justifying the design of more sophisticated binary catalyst architectures.

5.5 Catalytic performance of binary catalytic systems in the CO_2 cycloaddition to iEFA1: metal complexes

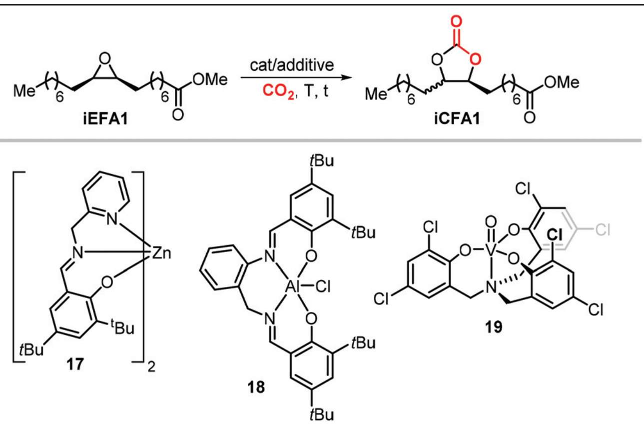
Metal complexes based on Schiff-base ligands are among the most studied metal–organic compounds often displaying remarkable catalytic activity for the cycloaddition of CO_2 to terminal epoxides.[121,284,285] Thus, it is not surprising that these complexes have also been studied for the carbonation of **EFAs**.

Masdeu-Bultó *et al.* prepared NN′O- and N_2O_2-type Schiff-base ligands that were used for the complexation of earth-abundant metals such as zinc,[286] and aluminum, respectively (complexes **17** and **18**, Table 7).[287] These complexes were found to be active Lewis acidic catalysts for the cycloaddition of CO_2 to terminal epoxides, but their application for the carbonation of **iEFA1** required harsh reaction conditions (100 °C, 100 bar of CO_2) to afford only moderate yields of **iCFA1** (entries 1 and 2). Under these conditions, catalyst **18**/TBAB proved to be much faster with reaction times as short as 30 min.[287]

Aminotriphenolates (TPA) complexes, extensively studied by the group of Kleij,[206,288–291] are a different class of highly efficient and strongly Lewis acidic metal complexes for the cycloaddition of CO_2 to internal epoxides. In particular, TPA complexes derived from aluminum (1^R, Table 3) and vanadium (**19**, Table 7) are highly chemo- and stereoselective Lewis acids for the carbonation of **iEFA1** under comparatively mild conditions (75–80 °C, 10 bar of CO_2) in the presence of TBAB, obtaining *cis*-**iCFA1** (entries 3 and 4), with the V-based binary catalyst **19**/TBAB only providing moderate conversion.

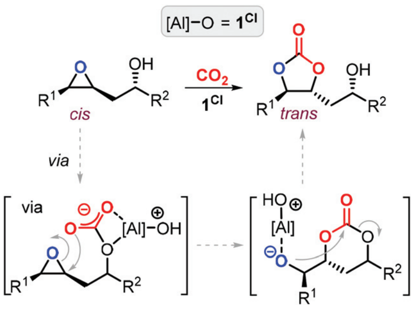
One peculiar feature of Al-aminotriphenolate complexes is their capability to catalyze the conversion of CO_2 and epoxy alcohols such as glycidol and its derivative, to cyclic carbonates in the absence of nucleophilic additives. The conversion of epoxy alcohols has been proposed to take place by formation of a carbonic acid hemi-ester stabilized by the metal–organic Lewis acid.[17,18,75] A similar mechanism was proposed when epoxidized methyl ricinoleate was combined with CO_2 in the presence of 1^{Cl}.[187] Despite the initial *cis*-configuration of the epoxide precursor, in the absence of halide nucleophiles the *trans*-isomer of carbonate product was obtained in high yield and selectivity indicating effective inversion of configuration (entry 5, Table 7). To explain this observation and in line with their previous findings,[17,75] the authors postulated a mechanism in which an Al-stabilized carbonic acid-like intermediate, formed by reaction of the substrate with CO_2, first evolves into a six-membered carbonate intermediate by nucleophilic attack on the nearest epoxide carbon (Scheme 28). A

Table 7 Comparison of the catalytic cycloaddition of CO_2 to epoxidized **MO** (**iEFA1**) in the presence of various Schiff base and aminotriphenolate metal complexes



Entry	Cat/add. (mol%)	T, p, t (°C, bar, h)	Yield/sel.[a] for **iCFA1** (%)	Sel.[a] *cis* : *trans*	Ref.
1	**17** (2.0) TBAB (2.0)	100, 100, 24	53, [b]	95 : 5	286
2	**18** (2.0) TBAB (2.0)	100, 100, 0.5	63, [b]	52 : 48	287
3	**19** (0.5) TBAB (5.0)	85, 10, 18	46, >99	>99 : 1	291
4	1^{Cl} (0.5) PPNCl (3.0)	70, 10, 24	99[d], >99	97 : 3	187
5[c]	1^{Cl} (1.0)	70, 10, 24	99 [d], 99	< 1 : 99	187
6	**13** (1.0) TBAI (10)	100, 5, 24	91, [b]	< 1 : 99	230

[a] *Cis* : *trans* ratio and selectivity for **iCFA1** determined by ^1H NMR from the integration of the corresponding signals of *cis* and *trans* carbonate products, and substrate/side-products. [b] Not reported. [c] Using epoxidized methyl ricinoleate (*cis*) as the substrate. Note that p is the partial pressure of CO_2. [d] Conversion, determined by ^1H NMR.



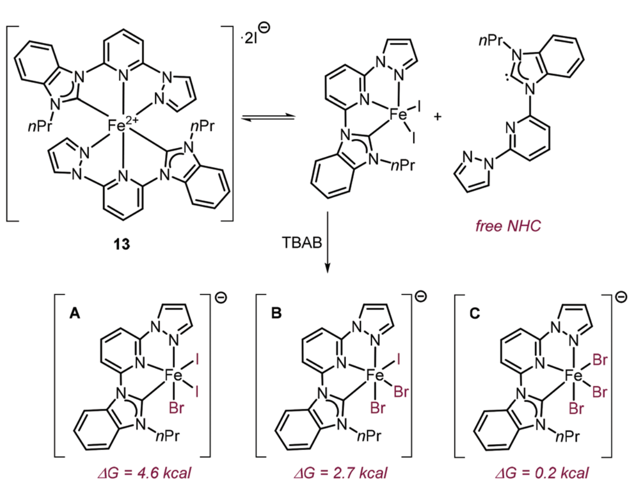
Scheme 28 Proposed mechanism for the conversion of CO_2 to epoxidized methyl ricinoleate catalyzed by Al-complex 1^{Cl}.

subsequent nucleophilic attack of the produced oxyanion on the electrophilic carbon center of the latter carbonate would then lead to formation of the final *trans*-carbonate with stereo-inversion.

Recently, Liu and coworkers reported the cycloaddition of CO_2 to **iEFAs** catalyzed by the iron bis-pincer complex **13** (Table 3).[230] By using a large amount of TBAI (10 mol%, entry 6, Table 7) at 100 °C and low CO_2 pressure (5 bar), **iEFA1** was fully converted to *trans*-**iCFA1** (entry 6, Table 7) according to an S_N1 pathway described in Scheme 24. Independent from the substrate, the authors managed to control the stereochemistry of the final carbonate **iCFA1** by proper selection of a suitable nucleophilic halide as described in section 5.2.

Based on previous investigations, the authors proposed that **13** acts as a precatalyst in this cycloaddition process by generating an iron-based Lewis acid (LA) and a (free) N-heterocyclic carbene (NHC), see Scheme 29.[292]

In the presence of TBAB, the Lewis acid is supposed to evolve into hexa-coordinated tri-halide –ate complexes of type $[Fe(CNN)X_3]$ (structures **A**–**C** in Scheme 29). According to DFT calculations, compound **C** is the most stable one. After dissociation of one of the halide anions, a coordination site on the Fe-center becomes available for the coordination (activation) of the epoxide prior to nucleophilic attack by the liberated halide. In principle, the free NHC fragment stemming from **13** can also play a role in the reaction by capturing and activating CO_2,[293] but in this specific case this was not discussed or proven.



Scheme 29 Proposed catalytically competent species generated from **13** under the applied reaction conditions. Tetra-*n*-butylammonium cations (TBA) are omitted for clarity.

5.6 Catalytic performance of organocatalysts in the cycloaddition of CO_2 to iEFA1

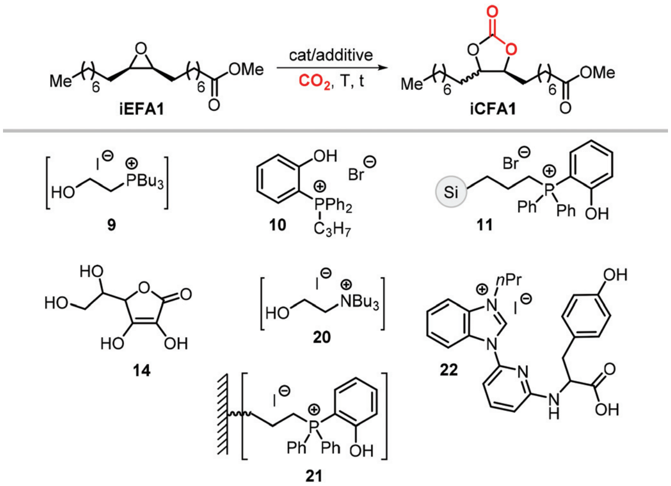
Organocatalysts have received considerable attention as relatively nontoxic, readily available, and in most cases moisture-insensitive compounds.[294–297] In the cycloaddition of CO_2 to epoxides, organocatalysts are often applied as single-component nucleophilic species, such as DBU, TBD and 4-dimethylamino-pyridine (DMAP), or as HBDs in the presence of nucleophilic halide sources.[1,5,31,298] Thus far, the organocatalyzed carbonation of fatty acids has been generally carried out using both binary and bifunctional catalytic systems, with the second category embedding halide nucleophiles and HBD moieties within the same molecule.

The Werner group developed two families of bifunctional phosphonium halides (such as **9**, Scheme 22),[195] and ammonium halides (such as **20**, Table 8),[299] bearing hydroxyl groups for the activation of epoxides. Such catalysts performed efficiently in the carbonation of terminal epoxides under mild conditions (45–90 °C, 5–10 bar of CO_2).

When using **iEFA1** as the substrate, **9** promotes its chemoselective carbonation in good yields under demanding reaction conditions (100 °C, 50 bar of CO_2), whereas **20** was less efficient under similar conditions providing only low yields of **iCFA1** (*cf.*, entries 1 and 2, Table 8). In both cases, the carbonate product was obtained as a mixture of *cis* and *trans* stereoisomers. Due to their higher acidity, phenolic hydroxyls are more active HBDs in the cycloaddition of CO_2 to epoxides than aliphatic hydroxyls.[199] Werner prepared bifunctional phenolic phosphonium salts (such as **10**; see also Scheme 22) and applied them for the cycloaddition of CO_2 to fatty acids. The carbonation of **iEFA1** proceed quantitatively under significantly milder conditions than for aliphatic HBDs (entry 3) though without any stereocontrol.[198] The same group reported the immobilization of **10** either on a traditional support such as silica (*i.e.*, catalyst structure **11**; see also Scheme 22),[197] or on amorphous hydrogenated carbon coating through a plasma-assisted method leading to recyclable catalysts **21**.[300] The application of these heterogeneous compounds for the carbonation of **iEFA1** at lower CO_2 pressure compared to the homogeneous catalyst **10** led to low yields of **iCFA1** (entries 4 and 5).

Dai *et al.* reported a multifunctional pincer-type organocatalyst (**22**) for the cycloaddition of CO_2 to **iEFA1**. This catalyst bears several active functionalities such as a nucleophilic imidazolium iodide, a pyridine moiety, –NH and –OH (carboxylic and phenolic) HBDs groups.[301] Higher loadings of **22** and TBAI were required to produce moderate yields of **iCFA1** mostly as the *trans*-isomer.

Table 8 The comparison of cycloaddition of CO_2 to epoxidized **MO** (**iEFA1**) catalyzed by various organocatalytic binary/bifunctional systems



Entry	Cat/add. (mol%)	*T*, *p*, t (°C, bar, h)	Yield/sel. of **iCFA1**[a] (%)	Sel.[a] *cis* : *trans*	Ref.
1	**9** (5.0)	100, 50, 24	65, >99	40 : 60	195
2	**20** (2.0)	100, 50, 16	20[b], >99	48 : 52	299
3	**10** (5.0)	80, 25, 24	98, [c]	54 : 46	198
4	**21** (1.0)	90, 10, 24	30, [c]	28 : 72	300
5	**11** (2.0)	90, 10, 24	26[d,c]	43 : 57	197
6	**22** (4.0) TBAI (12)	100, 5, 24	51, [c]	19 : 81	301
7	**14** (1.5) TBAC (5.0)	100, 5, 48	90, >99	77 : 23	231

[a] *Cis* : *trans* ratio determined by ^{1}H NMR by integration of the corresponding signals of *cis* and *trans* carbonate products, isolated yields of **iCFA1** are given. [b] GC yield. [c] Not reported. [d] Yield determined by ^{1}H NMR using mesitylene as the internal standard. Note that *p* is the partial pressure of CO_2.

Despite its excellent catalytic activity, compound **10** was prepared from the reaction between expensive and toxic (2-hydroxyphenyl)-diphenylphosphine (hazard: GSH07) and carcinogenic 1-bromopropane (hazard: GSH08). Similarly, the synthesis of **22** required 2,6-dibromopyridine as the starting material and a two-step CuI-mediated coupling process.[301] In order to better exploit the generally assumed benefits of organocatalysis (lower catalyst cost and toxicity), the application of ubiquitous biobased compounds such as amino acids,[302,303] peptides,[304–306] sugars,[307] and vitamins,[308] would be highly attractive.[309]

In this context, L-ascorbic acid (**14**), a well-established biobased HBD for the cycloaddition of heterocumulenes to epoxides under ambient or mild conditions,[310,311] was applied in combination with TBAC for the cycloaddition of CO_2 to **iEFAs**.[231] Ascorbic acid was found to accelerate the quaternary ammonium salt-catalyzed cycloaddition of CO_2 to **iEFA1**, with the binary combination **14**/TBAC showing the best performance in terms of **iCFA1** selectivity (see also Table 3). Under similar reaction conditions as reported for **22**/TBAI apart from the longer reaction time (48 h), the use of a lower loading of both catalyst components of **14**/TBAC led to quantitative **iEFA1** conversion at 5 bar CO_2 pressure at 100 °C (entry 7).

5.7 Catalytic performance of binary catalysts in the cycloaddition of CO_2 to polyunsaturated EFAs

Several of the catalytic systems discussed before were also applied for the carbonation of bis-unsaturated epoxidized linoleic acid methyl ester **iEFA2** (entries 1–10, Table 9). Generally, the reaction conditions optimized for the carbonation of **iEFA1** highlighted in the previous sections could be successfully applied to the conversion of **iEFA2**, therefore there will not be any detailed discussion of each example. For systems operating under supercritical conditions (entries 1 and 2), good epoxide conversion rates and **iCFA2** selectivities were obtained using alkali metals halides in combination with crown ethers.[24] The best results were obtained using KI/[18]crown-6 (entry 2). Whereas other catalytic systems could afford the carbonation of **iEFA2** under subcritical conditions (entries 3 and 4) or even at moderate CO_2 pressures (entries 5–10), the mildest conditions were reported for the *in situ* generated complex between CaI_2 and [18]crown-6 (**4**) combined with PPh_3 (entry 9).[118] It is worth noting that the combination of complex $\mathbf{1^{Cl}}$ and PPNCl performed also well in the carbonation of **iEFA2** at slightly higher temperature providing a shorter reaction time and with high (chemo)selectivity for *cis*-**10b** (entry 7).[187]

Finally, organocatalysts **10** (entry 5),[198] and **14**/TBAC (entry 6),[231] also performed well under different reaction conditions, with **14** achieving a selectivity for *cis*-**iCFA2** close to that observed with Al-based $\mathbf{1^{Cl}}$.

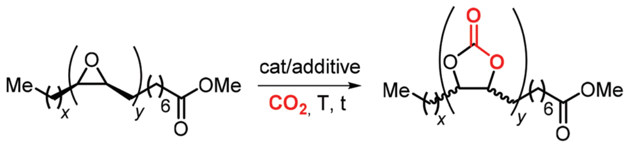
Few catalytic systems have been reported to date that are able to mediate the cycloaddition of CO_2 to tris-epoxide **iEFA3** derived from triply unsaturated linolenic acid (entries 11–14). To note, under $scCO_2$ conditions, the binary system THA-Cr-Si-POM/TBAB afforded only poor yields of **iCFA3** because of a low chemoselectivity for the tris-carbonate product (entry 11).[212] Under considerably milder conditions, the use of $\mathbf{1^{Cl}}$/PPNCl provided **iCFA3** with excellent conversion and carbonate selectivity with an approximate and overall 2 : 1 *cis*/*trans* isomer ratio (entry 12).[187] However, excellent selectivity for all-*cis* **iCFA3** in appreciable yield was achieved by replacing the chlorine for *tert*-butyl substituents in complex **1** (entry 13). The organocatalytic pair **14**/TBAC achieved comparable results by applying similar reaction conditions but using a longer reaction time (48 h *versus* 24 h, entry 14).[231]

5.8 Catalytic performance of binary catalytic systems in the cycloaddition of CO_2 to EVOs

Whereas the cycloaddition of CO_2 to **EVOs** produced from several vegetable oils (soybean, linseed, olive, sunflower *etc.*) has been reported, here we mostly focus on the carbonation of **ESBO** as a benchmark substrate. The catalytic performance of various catalyst systems for the carbonation of **EVOs** is summarized and discussed in Table 10.

Several catalytic systems already highlighted in Tables 7–9 could be successfully applied, under optimized conditions, for the conversion of **EVOs** into **CVOs** (entries 1, 4–6, 9–11),

Table 9 Comparison of the catalytic cycloaddition of CO_2 to epoxidized methyl linoleate (**iEFA2**) and epoxidized methyl linolenate (**iEFA3**)



iEFA2: *x* = 4, *y* = 2
iEFA3:, *x* = 1, *y* = 3

iCFA2: *x* = 4, *y* = 2
iCFA3:, *x* = 1, *y* = 3

Entry	iEFA	Cat/additive[a] (mol%)	*T*, *p*, t (°C, bar, h)	Conv.[b] (%)	Sel. For **iCFA**[b]	Yield (%)	Sel. (*cis* : *trans*)[c]	Ref.
1	**iEFA2**	THA-Cr-Si-POM (2.0)[d] TBAB (2.0)	100, 130, 6	85	50	[e]	[e]	212
2	**iEFA2**	KI (5.0 wt%) 18-C-6 (3.5 wt%)	100, 100, 17	90[f]	97	[e]	[e]	24
3	**iEFA2**	**12** (1.0) $FeCl_3$ (0.13)	100, 50, 48	99	[e]	85	[e]	196
4	**iEFA2**	**15**-Br (1.0) MoO_3 (0.13)	100, 50, 40	88	93	82	70 : 30	224
5	**iEFA2**	**10** (2.5)	80, 25, 48	>99	>99	99	[e]	198
6	**iEFA2**	**14** (0.75) TBAC (1.5)	100, 10, 48	>99	94	85	91 : 9	231
7	**iEFA2**	$\mathbf{1}^{\mathbf{Cl}}$ (0.30) PPNCl (5.0)	70, 10, 24	>99	>99	[e]	97 : 3	187
8	**iEFA2**	**22** (4.0) TBAI (12)	100, 5, 48	[e]	[e]	43	[e]	301
9	**iEFA2**	**4** (10) PPh_3 (10)	45, 5, 48	[e]	[e]	90	[e]	118
10	**iEFA2**	**13** (1.0) TBAI (10)	100, 5, 24	[e]	[e]	84	16 : 84	230
11	**iEFA3**	THA-Cr-Si-POM (2.0)[d] TBAB (2.0)	100, 130, 6	71	12	[e]	[e]	212
12	**iEFA3**	$\mathbf{1}^{\mathbf{Cl}}$ (0.20) PPNCl (5.0)	70, 10, 24	>99	>99	[e]	68 : 32	187
13	**iEFA3**	$\mathbf{1}^{t\mathbf{Bu}}$ (1.0) PPNCl (5.0)	70, 10, 24	92	>99	[e]	96 : 4	187
14	**iEFA3**	**14** (1.5) TBAC (5.0)	80, 10, 48	94	93	75	93 : 7	231

[a] The loading value in brackets is relative to the total amount of epoxides unit. [b] Conversion and selectivity determined by ^1H NMR. [c] Overall *cis* : *trans* ratio determined by ^1H NMR from the integration of the corresponding signals of *cis* and *trans* carbonate units. [d] THA = tetra-*n*-heptylammonium. [e] Not reported. [f] Conversion determined by ^1H NMR and GC. Note that *p* is the partial pressure of CO_2, 18-C-6 is short for 18-crown-6.

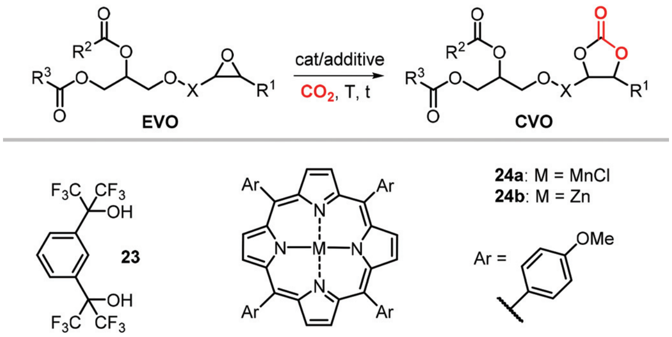
although in the case of THA-Cr-Si-POM/TBAB only a relatively modest yield of carbonated product was observed (entry 1).[212] Therefore, these examples will not be discussed in detail to avoid overlap with previous sections. A different system able to efficiently carbonate **ESBO** under supercritical conditions was developed by Jerome, Detrembleur *et al.* in a study targeting the preparation of NIPU foams from CVOs.[312] The authors used TBAB in the presence of fluorinated HBD [1,3-bis(2-hydroxyhexafluoroisopropyl)benzene, **23**],[313] providing quantitative carbonation of **ESBO** in 10 h (entry 2).

Rokicki *et al.* reported the carbonation of **ESBO** at lower CO_2 pressure than the previous example but a higher reaction temperature and longer reaction time (5 d) were needed employing KI/18-crown-6 as a catalyst. In this case, the CVO was obtained in high yield in the form of *cis*- and *trans* mixture (entry 3).[314]

Previously discussed coordination compounds (see also Table 6) displayed good performance in the carbonation of **EVOs** under relatively high pressure (entries 4–6, Table 10). A simple alkali salt ($CaCl_2$) displayed a catalytic activity comparable to these aforementioned Lewis acid based systems for the carbonation of **ESBO** in the presence of TBAB albeit at a significantly higher reaction temperature (entry 7).[315] In a related contribution, the same authors showed that $CaCl_2$/TBAB can be used for the synthesis of carbonated soybean oil (**CSBO**) under a flow of atmospheric CO_2 at 110 °C, although at the expense of the reaction time.[254]

A different, readily available and highly Lewis acidic compound, $SnCl_4 \cdot 5H_2O$, used in combination with TBAB allowed for quantitative conversion of **ESBO** into **CSBO** under moderate CO_2 pressure but at a high temperature (entry 8).[316] Previously discussed organocatalytic systems **10** and **14**/TBAC (entries 9 and 10) and coordination complex **4** combined with PPh_3 (entry 11) had attractive catalytic activity for the synthesis of **CSBO** under milder temperatures and/or CO_2 pressures with performances comparable to those observed for fatty acids (see Tables 6 and 8). Thus, it appears that the type of ester and the presence of saturated fatty acid chains in the starting material has a negligible impact on the reactivity of the epoxide moieties. As a testament for this hypothesis, **14**/TBAC proved to be

Table 10 Comparison of the cycloaddition of CO_2 to **EVOs** catalyzed by various binary catalysts



Entry	EVO	Cat/additive (mol%)	T, p, t (°C, bar, h)	Yield (%)	Sel.[a] for **CVO**	Ref.
1	Soybean	THA-Cr-Si-POM (2.0)[b] TBAB (2.0)	100, 130, 24	41[c]	60	212
2	Soybean	**23** (1.0) TBAB (1.0)	100, 100, 10	100	[d]	312
3	Soybean	KI (2.0) [18]crown-6 (1.0)	130, 60, 120	98[e]	[d]	314
4	Soybean	**12** (2.0) $FeCl_3$ (0.25)	100, 50, 24	94	>99	196
5	Soybean	**15**-Br (2.0) MoO_3 (0.25)	100, 50, 20	89	90	224
6	Sunflower	CaI_2 (5.0) PEG-DME-500 (5.0)[f]	90, 50, 120	83	[d]	282
7	Soybean	$CaCl_2$ (5.0) TBAB (2.5)	140, 40, 40	98	[d]	315
8	Soybean	$SnCl_4{\cdot}5H_2O$ (1.0) TBAB (3.0)	140, 15, 30	99[e]	[b]	316
9	Soybean	**10** (5.0)	80, 25, 24	77	[b]	198
10	Soybean	**14** (1.5) TBAC (5.0)	100, 5, 48	81	89	231
11	Soybean	**4** (5.0) PPh_3 (5.0)	45, 5, 24	81	>99	118
12	Sunflower	**24a** (4.0) TBAB (4.0)	100, 1, 30	99[g]	[d]	320
13	Sunflower	**24b** (4.0) TBAB (4.0)	100, 1, 30	8[g]	[d]	320

[a] Selectivity determined by ^1H NMR. [b] THA: tetra-*n*-heptylammonium. [c] Conversion determined by ^1H NMR. [d] Not reported. [e] Conversion determined by standard titration. [f] PEG DME 500: poly(ethyleneglycol) dimethyl ether with $M_n \sim 400$ g mol^{-1}. [g] Yield determined by ^1H NMR.

an efficient catalyst for the carbonation of epoxidized **FAME**.[231]

Finally, Lewis acidic metal complexes were tested for the carbonation of epoxidized sunflower oil (**ESFO**) under atmospheric pressure in the presence of TBAB. Metalloporphyrins are known as efficient catalysts for the cycloaddition of CO_2 to epoxides under ambient pressure.[1,317–319] Safari *et al.* showed that the Mn(II) metalloporphyrin complex **24a** in the presence of TBAB permits full carbonation of **ESFO** under atmospheric pressure at 100 °C in 30 h, whereas the analogous Zn(II) complex **24b** is inactive under identical conditions (entries 12 and 13).[320]

5.9 Recyclable catalytic systems for the carbonation of EFAs and EVOs

Whereas most of the highlighted catalytic systems are homogeneous, the development of recoverable and recyclable heterogeneous catalysts is crucial for easier purification of the products and for the sake of cost and sustainability, especially in the context of large-scale application. The development and communication of recyclable catalysts for the carbonation of fatty acids is rare.

In the case of TBAB as homogeneous catalyst for the carbonation of **ESBO**, Doll and Erhan were able to recover TBAB from the products mixture by liquid–liquid extraction using water followed by freeze-drying (96% recovery rate). However, they did not report the catalyst reuse for the same reaction.[237] Similarly, D'Elia *et al.* attempted to recover **14**/TBAC from the crude reaction mixture containing **iCFA1** by extraction with water.[231] In this case, the recovered catalyst showed poor reusability as it converted only 38% of **iEFA1** into **iCFA1** without altering the chemoselectivity for the carbonate product.

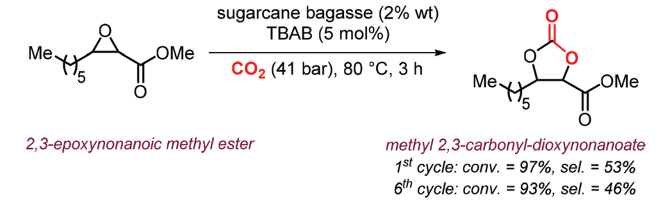
Some homogeneous catalysts highlighted in the previous sections such as **20**,[299] **24a**,[320] CaI_2/PEG-DME-500,[282] and KI/hydroxyl-functionalized imidazoles,[281] can be recovered after the synthesis of the respective CCs by methods such as column chromatography, product distillation and liquid–liquid extraction, and reused for the same cycloaddition reaction. However, their recyclability for the synthesis of **CFAs** and **CVOs** has not been specifically addressed. Catalyst separation protocols that require evaporation of large volumes of water or distillation of high-boiling carbonates are likely not convenient or sustainable for commercial exploitation. Along similar lines, Werner *et al.* prepared some heterogeneous, reusable catalysts such as **11**,[197] and **21**,[300] but their recyclability was not demonstrated for processes that focus on carbonated oleochemicals.

Bähr and Mülhaupt reported the application of silica-supported 4-pyrrolidinopyridinium iodide (previously developed by Motokura)[321] as a heterogeneous catalyst for the carbonation of **ESBO** and epoxidized linseed oils (**ELSO**) with full conversion of the respective **EVO** realized at high temperature and moderate pressure (140 °C, 30 bar of CO_2, 45 h).[271] Whereas the catalyst could be easily recovered by simple filtration after the reaction and thus avoid product purification by liquid–liquid extraction, the performance of the recycled catalyst for a new run of carbonation was not reported.

As a rare example of a recyclable catalyst for the coupling of CO_2 and epoxidized oleochemicals, Wang *et al.* reported a ZrO_2-supported heteropolyacid ($H_3PW_{12}O_{40}/ZrO_2$) that was successfully applied for the carbonation of **ESBO** at high temperature (150 °C) and moderate CO_2 pressure (10 bar) in the presence of DMF.[322] Its catalytic performance was attributed to the synergy between the strong acidic metal centers of the heteropolyacid and the basic zirconia surface providing sites for CO_2 adsorption and activation. Nonetheless, $H_3PW_{12}O_{40}/ZrO_2$ showed poor reuse features due to the strong adsorption of bulky reaction by-products at the active sites of the catalyst surface that could not be efficiently regenerated even after calcination.

To improve the regeneration of an active catalyst, the catalyst was modified by doping it with platinum (5%) *via* a co-impregnation approach. As expected, the addition of platinum increased the ability of the material to oxidize hydrocarbons, and the undesired adsorbed organic molecules could be removed below 300 °C.[323] At the same time, the presence of platinum did not affect the efficiency of the carbonation reaction. The Pt-doped $H_3PW_{12}O_{40}/ZrO_2$ displayed significantly better recyclability despite the gradual decrease in catalytic activity upon reuse with the **ESBO** conversion dropping from 93 to 78% after four catalytic cycles. An obvious drawback of this catalytic system is the need for expensive noble metal dopant to achieve reusability.

A different way to generate internal carbonates from fatty acids was reported by Cádiz *et al.* by using heptanal, a product of the thermal cracking of castor oil, as a novel precursor for NIPU synthesis.[324] The Horner–Wadsworth–Emmons reaction between heptanal and trimethyl phosphonoacetate yielded methyl 2-nonenoate that was further oxidized to achieve the corresponding 2,3-epoxynonanoic methyl ester (see Scheme 30) as a short-chain epoxidized fatty acid derivative.



Scheme 30 The coupling of 2,3-epoxynonanoic methyl ester with CO_2 catalyzed by a recyclable sugarcane bagasse/TBAB binary catalyst.

Interestingly, the carbonation of the latter compound can be performed by employing sugarcane bagasse as a heterogeneous HBD in combination with TBAB at 80 °C and about 41 bar of CO_2 pressure (Scheme 30). The insolubility of sugarcane bagasse allows for easy separation from the crude reaction mixture by simple filtration. This catalyst component can be reused for at least six runs with only slight loss of activity. However, the chemoselectivity toward carbonate for this system was only moderate due to secondary reactions (such as hydrolysis) taking place involving the epoxy groups. Additionally, fresh TBAB, likely the most expensive catalyst component, had to be added in each consecutive cycle.

6. Conclusions and perspectives

This tutorial review demonstrates that the area of biobased carbonate synthesis has tremendously advanced over the last decade. Key to the success has been and will continue to be the development of suitable catalysts that, according to the principles of green chemistry and commercial applications, should preferentially be low-cost, readily available, scalable and sustainable in terms of their components. The incorporation of carbon dioxide in biobased feedstock such as terpenes, sugar-derived architectures, glycerol and fatty acids (including vegetable oils) offers a way to increase the application potential of low-value materials into high-value functional additives, solvents and polymer precursors for, *inter alia*, NIPUs.

There are several aspects that still deserve attention. Most of the catalytic processes developed to date are operated with purified and single-component substrates, whereas larger scale commercially available feedstock are often mixtures containing impurities that may affect the stability, activity and reuse of the involved catalyst system. Therefore, it is important to further develop catalysts that are not only able to combine high (chemo)selectivity and sufficient activity, but are also compatible with less defined mixtures of waste streams such as the case for fatty acids that are available from the biodiesel industry. As catalyst cost is paramount for scale up, cheap(er) catalyst design is a crucial aspect and particularly when bulk chemical applications are foreseen for biocarbonates attained by integration of CO_2 into biomolecules.

In the following sections we present a summary of key advances and future perspectives for each class of compounds.

6.1 Glycerol carbonate

Glycerol carbonate is a promising outlet for the valorization of waste glycerol from saponification reactions, and it is expected to represent a valuable bio-refinery product.[325] The ideal route to prepare **GC**, *i.e.* the combination of two renewable substrates such as glycerol and CO_2, is affected by thermodynamic limitations that lead to low **GC** yields under typically harsh reaction conditions. Such limitations can be partially eased by the use of dehydrating agents or by the presence of additional reaction components that, however, unavoidably negatively affect the overall sustainability, cost, and purification requirements of the product. In this context, the atom-economic cycloaddition of CO_2 to glycidol appears as a convenient approach as it can be carried out under relatively mild conditions using molecular catalysts based on readily available organic compounds such as ascorbic acid. Moreover, recent advances in the synthesis of **GC** from glycidol and CO_2 *via* Payne rearrangement chemistry rather than the traditional cycloaddition mechanism,[99] demonstrate that this reaction can be carried out using single-component and halogen-free systems. Therefore, the development of bio-based homogeneous and heterogeneous catalysts exploiting such a reaction manifold for the synthesis of **GC** is highly promising. To note, the sustainability of the glycidol-based approach can be increased by the implementation of green routes to produce the latter compound; for instance using 2-chloro-1,3-propanediol, a waste product of the Epicerol process, as the substrate,[326] or from glycerol deoxydehydration affording allyl alcohol.[327]

6.2 Terpene-derived carbonates

Terpene compounds have been used for a long time for the preparation of fragrances, flavors and pharmaceuticals. Some terpenes, such as pinene, carvone, myrcene and limonene are currently obtained from turpentine oil, paper pulping process and extraction from citrus fruits.[328] Such terpenes are produced on million tons per year, and have been also proposed for the production of biofuels.[329] Interesting, terpene-based cyclic carbonates have been isolated from natural sources with some of them showing biological activity. In comparison with other biobased feedstock, terpenes present an impressive structural diversity, which offers the possibility to produce complex cyclic carbonate structures by relatively easy transformations (*i.e.*, oxidation followed by coupling with CO_2). Consequently, the synthesis of terpene-based CCs has gained momentum, and future investigations could lead to the discovery of compounds with promising pharmaceutical activity. However, most of the current reports focus on limonene- and pinene-derived carbonates. Thus, future investigations are required to expand the portfolio of terpene-based carbonates. To date, different catalytic methodologies for the coupling of CO_2 with terpene oxides have been reported, with in several cases significant byproduct formation when more complex substrates were employed. This clearly calls for further development of more efficient and selective catalytic systems.

In recent years, the use of terpene oxides in the field of sustainable polymer chemistry has also emerged.[110] In particular, polycarbonates such as poly(limonene carbonate) and poly (menth-2-ene carbonate) have been obtained by direct coupling with CO_2.[111,330] Unfortunately, up to now these reactions can only be promoted by two types of catalytic systems. Alternatively, polycarbonates can be obtained *via* ROP of reactive cyclic carbonates in the presence of simple catalytic systems.[331,332] We believe that further investigations should focus on the discovery of terpene-based cyclic carbonates that will serve as monomers for the production of polycarbonates by easy-to-tune ROP protocols. This will offer an alternative strategy for the production of polymeric materials with attractive properties.

6.3 Sugar-derived carbonates

Thanks to the ubiquity of sugars in nature, this class of compounds has been recognized as an attractive sustainable feedstock. However, in order to avoid competition with the food processing industry, a lot of research is still needed that should focus on sugar-based biofuels, chemicals and polymers obtained from widely-available cellulose and lignocellulose.[333–335] Sugar structures are characterized by the presence of hydroxyl groups and, consequently, their transformation into cyclic carbonates has been mainly conducted by well-known stoichiometric procedures in the presence of non-ideal reactants such as phosgene. During the last few years, alternative methodologies have been reported for the carbonation of sugars under milder conditions. In general, these procedures are based on the reaction of low pressure carbon dioxide (1–10 bar) with an *in situ* formed activated alcohol species, followed by cyclization promoted by elimination of a suitable leaving group (*e.g.*, OTs and OMs). These reactions do avoid the use of phosgene-related compounds, though they still require the presence of stoichiometric amounts of base (*e.g.*, DBU and Et_3N) and halogenated reactants (*e.g.*, TsCl and CH_2Br_2). Future development of catalytic methodologies are likely needed to improve the potential application and scale up of this synthetic process. Interestingly, the possibility to control the stereochemistry during the synthesis of sugar-based CCs has also been demonstrated. This aspect is highly relevant, especially with respect to the use of such carbonates as monomers in polycarbonate synthesis. Indeed, the stereochemistry of bicyclic carbonates strongly influences their reactivity during the polymerization process, and the possibility to compare compounds with different stereochemistry will offer the possibility to further investigate structure–reactivity relationships. In addition, phosgene-free routes for sugar-based carbonates render these molecules as an attracting platform for the synthesis of bio-based NIPUs.

6.4 Fatty acid and vegetable oil-based carbonates

The attractive aspects of these feedstock is that they are available in large volumes either as-produced or from the recovery of spent cooking oils. Carbonated vegetable oils are versatile substrates for the preparation of NIPUs *via* aminolysis reactions (*i.e.,* amine-promoted ring-opening of the cyclic carbonate). With NIPUs being regarded as ideal green polymers for the replacement of phosgene-based PUs, it is expected that the demand for these types of biocarbonates will considerably increase in the near future when current process issues such as low molecular weights, low aminolysis rates and side reactions can be adequately solved.[336] Additionally we foresee that carbonated fatty acids could be suitable substrates for the preparation of additives to improve the anti-wear properties of group II base oils.[337]

In the last decade, the synthesis of fatty acid/vegetable oil based CCs has been characterized by a remarkable development of several binary homogeneous systems able to catalyze the carbonation reactions of oils under practical reaction conditions (45–100 °C, 5–10 bar). This is especially relevant when comparing to the exclusive use of quaternary ammonium or phosphonium salts and, often, binary systems provide better/improved control of the stereochemistry of the final products. As a drawback, and due to the low reactivity of the substrates, long reaction times (24–48 h) are generally required to reach high degrees of conversion (>80%). Therefore, substantial improvement of the performance of homogeneous (binary) catalysts for the carbonation of vegetable oil-derived epoxides is a future requisite. It can be anticipated that a substantial increase in the demand for carbonated vegetable oils should be met by the development of heterogeneous, or at least, recyclable catalysts with powerful reactivity profiles. As discussed in section 5.8, there is limited knowledge on the development of heterogeneous catalysts for the carbonation of epoxidized fatty acids, and up to now no viable catalyst has been developed for application in large-scale production. This may be related to the more challenging nature of internal epoxide conversion in the presence of CO_2 mediated by heterogeneous catalysts, making the latter much less efficient than their homogeneous counterparts.[338] A different and promising approach to the development of recoverable and reusable catalysts for the carbonation of epoxidized fatty acids was recently proposed by Duguet *et al.* by using a thermomorphic polyethylene-supported catalyst.[339] In this latter example, the polymeric catalyst is soluble in the reaction mixture (T = 100 °C) but insoluble in the product at room temperature. Therefore, it can essentially be recovered by filtration and its recyclability for the carbonation of epoxidized methyl oleate was indeed demonstrated. Whereas such polymeric catalysts are still limited by relatively modest molecular weights (~1000 g mol^{-1}) and low product stereoselectivity, the concept of using a catalyst that can be separated from the carbonated fatty acid after reaction is a promising molecular approach and could be further developed in the future.

An interesting direction for all the categories of biobased substrates presented in this account could be to merge flow catalysis approaches with biocarbonate synthesis, with catalyst recycling and a continuous operation mode helping to increase the overall sustainability. Parallel flow catalysis may help to scale up the preparation of any desired target, but market demands will likely determine which type of process will be preferred to create critical amounts of the biocarbonate for eventual (commercial) use.

From the diversity and functionality of biobased structures that can be accessed *via* catalytic process, and the prospect of biocarbonates in various academic and commercial applications, a bright future is ahead of these CO_2 based cyclic carbonates.

Conflicts of interest

There are no conflicts to declare by the authors.

Acknowledgements

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