Published in : Angew. Chem. Int. Ed. 2022 61 e202116066
DOI: 10.1002/anie.202116066
Status : Postprint (Author's version)

EXOVINYLENE CYCLIC CARBONATES: MULTIFACETED CO2-BASED BUILDING BLOCKS FOR MODERN CHEMISTRY AND POLYMER SCIENCE

Charlène Ngassam Tounzoua, Bruno Grignard and Christophe Detrembleur

Center for Education and Research on Macromolecules (CERM) CESAM Research Unit, Department of Chemistry University of Liege, 13 allée du 6 août, buiding B6a, 4000 Liège (Belgium)

Abstract: Carbon dioxide is a renewable, inexhaustible, and cheap alternative to fossil resources for the production of fine chemicals and plastics. It can notably be converted into exovinylene cyclic carbonates, unique synthons gaining momentum for the preparation of an impressive range of important organic molecules and functional polymers, in reactions proceeding with 100 % atom economy under mild operating conditions in most cases. This Review summarizes the recent advances in their synthesis with particular attention on describing the catalysts needed for their preparation and discussing the unique reactivity of these CO_2-based heterocycles for the construction of diverse organic building blocks and (functional) polymers. We also discuss the challenges and the future perspectives in the field.

Keywords: CO2 Conversion · Exovinylene Carbonates · Organic Transformations · Polycarbonates · Polyurethanes

1. Introduction

On the path to sustainability and circularity, the upgrading of CO_2 into value-added organic scaffolds and polymers has become a vibrant field of research. The development of new catalytic systems and efficient CO_2 activation modes has made it possible to overcome the kinetic and thermodynamic stability of this highest oxidized state of carbon. A variety of products are now accessible, ranging from commodities (methanol, formic acid, urea)[1–3] to more sophisticated products (organic carbonates, polyurethanes, polycarbonates).[4–10] Amongst the multitude of CO_2-sourced molecules, cyclic carbonates have emerged as important building blocks for fine chemistry (e.g. to construct carbamates, key intermediates for the pharmaceutical and agro-industries)[11] and polymer design (e.g. polyols used to formulate polyurethane foams),[12–14] as solvents and electrolytes for batteries.[11] Three main routes are implemented to prepare cyclic carbonates by the direct reaction of CO_2 with a substrate (Scheme 1).

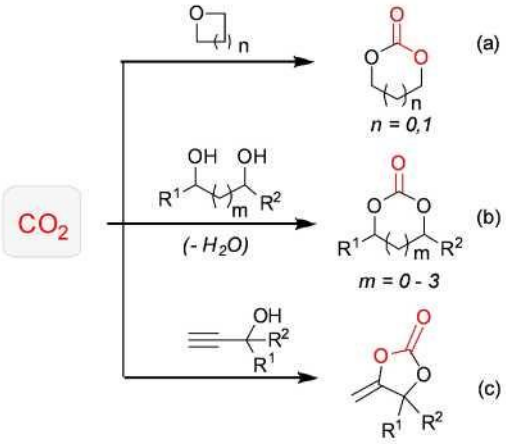
The predominant method consists in coupling CO_2 to oxiranes in the presence of metal or organocatalysts.[4, 6, 9] The 100 % atom economy [3+2] fixation of CO_2 onto epoxides affords selectively and quantitatively five-membered cyclic carbonates even under mild and solvent-free conditions (Scheme 1a). Six-membered cyclic carbonates are also obtained from oxetanes.[15,16] The great availability of oxiranes of petro- or bio-based origin gives access to a large library of cyclic carbonates with diverse structures and functionalities. The second approach involves the challenging condensation of CO_2 with polyols into five- to eightmembered cyclic carbonates (Scheme 1b).[17–20] Although potentially the most interesting in terms of the valorization of natural polyols (e.g. glycerol, sorbitol), this second approach remains less explored. Indeed, this reaction is thermodynamically limited by the release of water, whose removal is mandatory to prepare the cyclic carbonates in quantitative yields. Some strategies have been developed to partly overcome this problem, notably by activating the alcohol using metal-based catalysts in combination with dehydrating agents,[20] or by using bases (tertiary amine or superbases) in combination with alkylating agents (e.g. alkyl halides, sulfonyl halides).[18,19] Nonetheless, these processes require harsh conditions and release considerable amounts of waste, rendering them not sustainable. The third route provides α-exovinylene cyclic carbonates (αCCs) by the carboxylative coupling of CO_2 to propargylic alcohols (Scheme 1c). These synthons are promising and appealing, even from an industrial perspective, as they offer multiple opportunities in organic and polymer chemistry for the design of advanced CO_2-derived products. The presence of an exocyclic olefin renders these heterocycles highly reactive towards S-, N-, and O-nucleophiles via the ring-opening of the cyclic carbonate, as well as towards radicals or aryl halides via additions onto the olefin. This makes them central building blocks for the design of linear and cyclic carbamates and carbonates, and important polymer families (e.g. polyurethanes, polycarbonates, polyvinyls, and sulfurcontaining polymers). This Review discusses the general concepts for the synthesis of this emerging class of cyclic carbonates and their exploitation in organic synthesis and polymer sciences.

2. Synthesis of Exovinylene Cyclic Carbonates

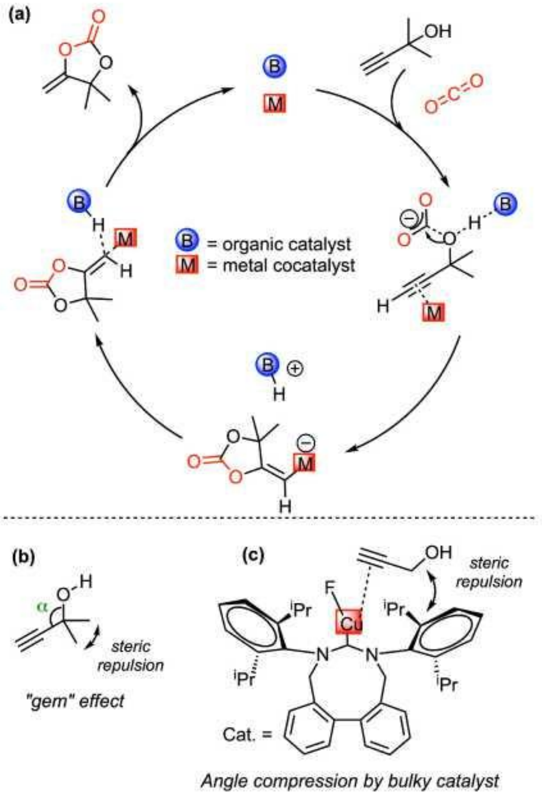
The mechanism of αCC formation from CO_2 and a propargylic alcohol is illustrated in Scheme 2. It involves first the formation of a carbonate salt intermediate via the reaction between a propargylic alcohol, CO_2, and a base, which activates the alcohol for the carbonation. Then, the carbonate ion undergoes a conformational rotation, followed by a ring-closure step via an intramolecular nucleophilic addition onto the triple bond. The resulting exocyclic alkenyl anion generates the cyclic carbonate upon protonation and completes the catalytic cycle.[21, 22] Alternatively, a dual activation mechanism makes use of a metal-based cocatalyst that coordinates to the triple bond and facilitates the cyclization of the carbonate ion, yielding an alkenyl metal intermediate, which gives the αCC upon proto- demetalation.[23] The carboxylative coupling was long restricted to tertiary propargylic alcohols, the driving force of the carboxylation being the presence of the two *gem* substituents on the substrate that create a compression angle via the Thorpe–Ingold effect, hence facilitating the carbonate ring closure (Scheme 2b).[24] With secondary and primary propargylic alcohols, this effect is absent, rendering their cyclization more challenging. To overcome these hurdles, recent findings by Schaub et al. utilize dual catalysts made of a metal salt and a sterically congested ligand which causes an angle torsion of the substrate similar to the "*gem*" effect and allows for the efficient carboxylative cyclization of secondary and primary propargylic alcohols (Scheme 2c).[25,26] The choice of the catalyst and the reaction conditions is crucial to prevent side reactions, i.e. the hydrolysis of αCC by residual water to give the hydroxy ketone **1**, the alcoholysis of αCC either by the in situ formed hydroxyketone **1** to furnish the symmetrical acyclic carbonate **2** or by the unreacted propargylic alcohol yielding the acyclic carbonate **3** (Scheme 3).

In the next section, we first benchmark the performances of a selection of relevant homogeneous catalysts, using customized spider charts to highlight their strengths and weaknesses, without extensive discussions. While these illustrations give an "instant" comparison of the activities of state-of-the-art catalysts, we underline that most of the reactions are realized under different operating conditions which complicates this benchmarking task. Furthermore, parameters that can be highlighted as weaknesses (long reaction time, high temperature, low yields…) might result from non-optimized conditions. Therefore, we believe that these charts will provide guidelines for the readers to identify the most relevant parameters to turn the less efficient catalysts into more competitive systems. These data are also summarized in traditional form as tables in the Supporting Information. Next, heterogeneous catalysts are briefly considered and their performance and recycling are correlated to the type of support and the nature of the immobilized catalyst. For ease of comparison and to identify the main trends, we have selected works dealing with the formation of a model αCC that is frequently reported in the literature, 4,4-dimethyl-5-methylene-1,3-dioxolan-2-one (DMACC) prepared by coupling CO_2 to 2-methyl-3-butyn- 2-ol.

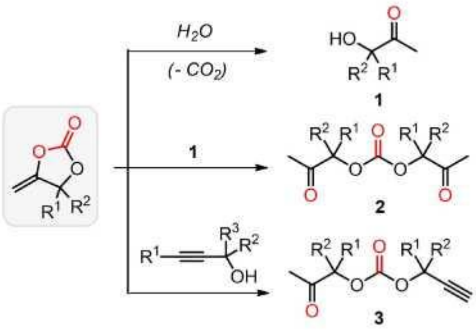
Scheme 1. *Synthesis of cyclic organic carbonates a) from oxiranes, b) diols, and c) propargylic alcohols.*



Scheme 2. a) General mechanism for the formation of αCC (shown for a dual activation mechanism), b) steric repulsions induced by the "*gem*" or c) catalyst-driven "angle compression" effects.



Scheme 3. Side reactions that may occur during the carboxylation of propargylic alcohols by CO_2.



3. Catalysts for αCC synthesis

3.1. *Homogenous Single Activation Catalysts*

3.1.1. *Organic Bases*

Phosphines (**4 a**–**c**) and nitrogen bases such as amines (**5**), guanidine (**6**), and amidines (**7** and **8**) are evaluated for the transformation of CO_2 into αCCs (Scheme 4). Phosphines provide DMACC with yields of 8–99 % within 8–15 h using 50-100 bar of CO_2 at 100-140 °C and a catalyst loading of 5 to 9 mol%.[27–29] In his seminal work, Dixneuf highlighted the significantly higher activity of $P(C_4H_9)_3$ compared that of triphenyl- or tricyclohexylphosphine.[28] The weak base NEt_3 is inefficient in catalyzing the formation of DMACC in organic medium or under neat conditions (T = 30-80 °C, p_{CO2} = 5–10 bar, catalyst loading = 0.25–1 eq., t = 5–10 h).[30] Superbases such as TBD and MTBD promote the total conversion of the propargylic alcohol at 10 mol%, 100 °C for 24 h with 50 bar of CO_2; however, the reaction was non- selective, with a DMACC yield of only 21 to 25 %.[31] Both bases favor the side alcoholysis of DMACC by the propargylic alcohol or the hydroxyketone. The selectivity of MTBD for DMACC is significantly improved by reducing the catalyst loading to 1 mol% and the temperature to 60 °C at a p_{CO2} = 30 bar or by working under dilute conditions in acetonitrile for a shorter time at 80 °C, 30 bar, and a catalyst loading of 5 mol%.[32]

The performances of selected organobases are benchmarked in Figure 1 (Table S1). On the basis of the data reported under conditions specific to each catalyst, tributylphosphine emerges as one of the most efficient bases, affording DMACC selectively with a yield close to 100 % in a reasonable time frame; nevertheless, moderate to high pressure and temperature are required. With nitrogen bases, the basicity of the catalyst is a crucial factor. Low pK_a amines exhibit no catalytic activity, while stronger (super)- bases (TBD and MTBD) catalyze the reaction, however, with moderate selectivity. Therefore, the ideal organic base should display sufficient basicity to activate the OH moiety of the propargylic alcohol and facilitate the fixation of CO_2. However, the basicity should remain low enough to avoid competitive side alcoholysis of the DMACC with the unreacted precursors or hydroxylated side products **1**.

Scheme 4. Selected organic bases used as catalysts for the carboxylative coupling of CO_2 with propargylic alcohols.

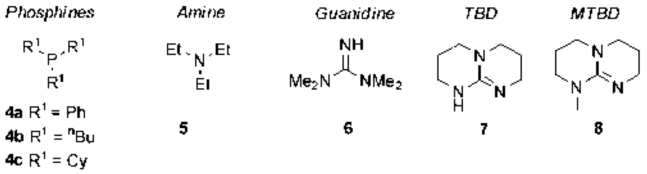
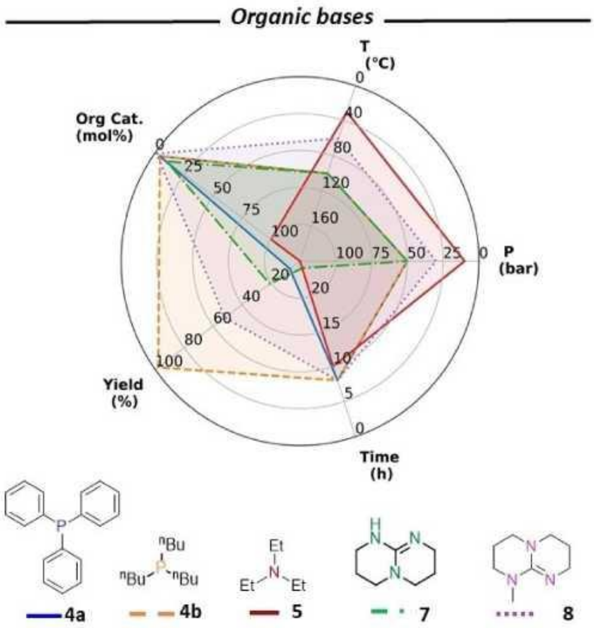


Figure 1. Comparison of the activity of some selected bases for the solvent-free synthesis of DMACC.



3.1.2. Lewis Base–CO_2 adducts

Owing to the high electrophilicity of the carbon atom in CO_2, Lewis bases (LB) of nitrogen-containing heterocycles react with CO_2 to form zwitterionic adducts. The diversity of the LB-CO_2 adducts and the facile structural modulation of their flanking groups make them efficient catalysts in organic synthesis, including for CO_2 conversion. The most common LB-CO_2 adducts are based on the (unsaturated) *N*- heterocyclic carbene templates (NHC-CO_2, **9 a**–**d**) (Scheme 5). NHC-CO_2 adducts catalyze the fixation of CO_2 onto propargylic alcohols at 60-80 °C and 45-60 bar. DMACC is obtained with an excellent yield of 99 % in 15 h, especially with catalyst **9c** at a loading of 5 mol%.[33] Other Lewis base–CO_2 adducts have also been designed. The carbodicarbene–CO_2 adducts (CDC-CO_2, **10 a**–**d**) appear less efficient than NHC-CO_2 adducts and afford DMACC in 94% yield within 12 h at a loading of 5 mol% and 20 bar of CO_2 at 80 °C.[34] The most efficient catalytic systems are *N*- heterocyclic olefin–CO_2 adducts (NHO-CO_2, **11 a**–**f**),[35] alk-oxide-functionalized imidazolium betaine–CO_2 adducts (AFIB-CO_2, **12 a**–**d**)[36] and tetrahydropyrimidin-2-ylidene– CO_2 adducts derived from 5-diazabicyclo[4.3.0]non-5-ene (DBN-CO2, **13 a**–**d**).[37] All the Lewis base–CO2 adducts especially **11d**, **12d**, and **13a** operate under smoother conditions compared to NHC-CO_2 (20 bar of CO_2, *T* = 60 °C, catalyst loading of 5 mol% except AFIB-CO_2 (2 mol%)) and provide DMACC with excellent yields of 91–96 % in 1 to 5 h. Figure 2 (Table S2) benchmarks the activity of the various LB-CO_2 adducts, which follows in the order CDC- CO_2 < NHC-CO_2 < NHO-CO_2 ≈ AFIB-CO_2 ≈ DBN-CO_2.

Some authors attributed the higher activity observed for NHOs in comparison to NHCs to the increased nucleophilicity of the α-carbon in NHOs arising from the aromatization of the *N*-heterocyclic ring in *N*,*N*-disubstituted 2-methylene imidazolines.[38] In addition, they proposed that the longer Ccarboxylate–CNHO bond in comparison to Ccarboxylate– C_{NHC}, as well as the presence of electron-donating (bulky) substituents on their *α* carbon, rendered NHO-CO_2 adducts less stable and hence more prone to liberate free carbene. Ikariya et al. also demonstrated the existence of a cut-off temperature for NHC-CO_2 adducts at 60 °C and 45 bar, above and beyond which the yield of the αCC decreased.[33] This observation is further confirmed by Tommassi, who obtained lower αCC yields when working at a higher temperature of 100 °C and 60 bar.[39] Reducing the catalyst loading influences the selectivity of the reaction, with the side formation of acyclic carbonates. The high activity of DBN-CO_2 adducts is probably due to the high basicity of free DBN.[37] It has to be noted that phosphorus ylide–CO_2 adducts (P-Ylide–CO_2) have been also evaluated; however, they are not included in this benchmarking because they have not been tested for the preparation of DMACC.[40] However, their catalytic activities do not differ from those of NHC-CO_2 adducts that are tested under identical conditions using a similar substrate.

Scheme 5. Non-exhaustive LB–CO_2 adducts used for the carboxylative coupling of CO_2 to propargylic alcohols.

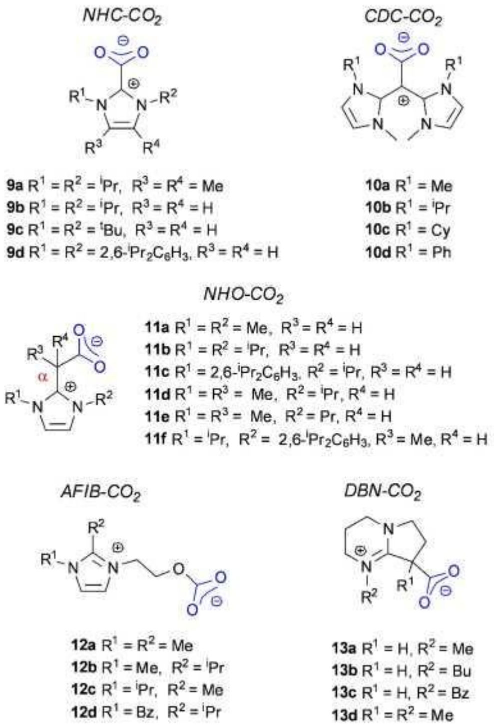
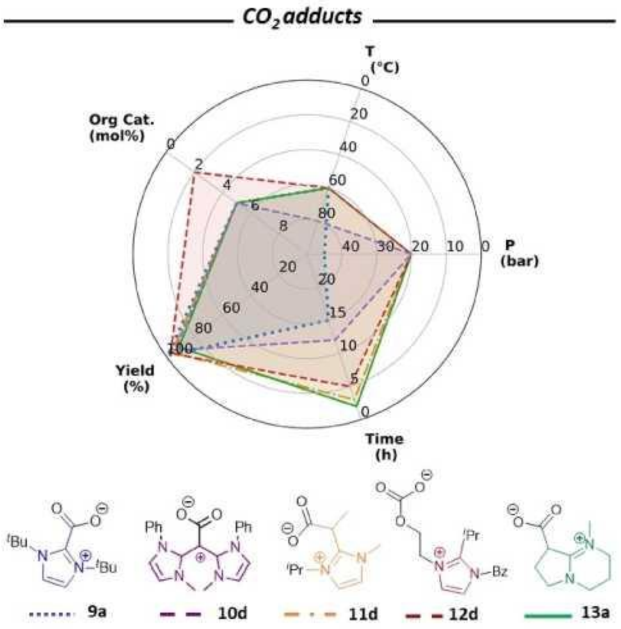
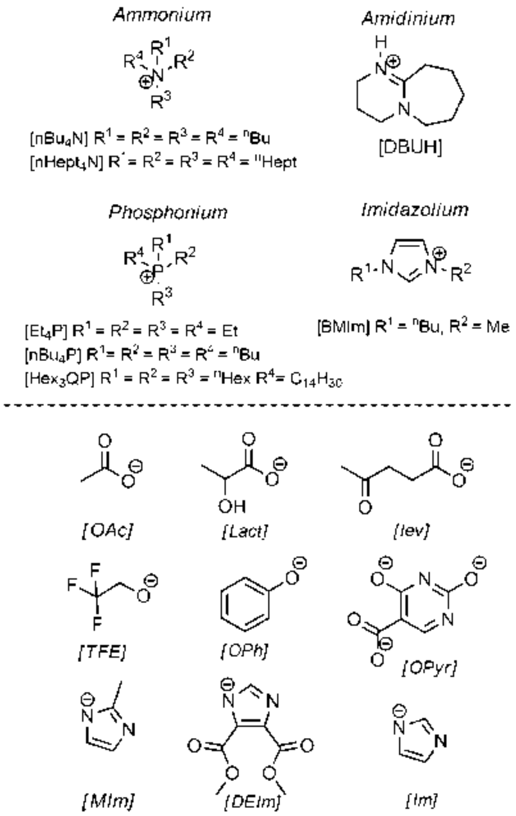


Figure 2. Comparison of the activity of selected Lewis base–CO_2 adducts for the solvent-free synthesis of DMACC.



Scheme 6. Selected cations and anions for the design of ionic liquid catalysts.

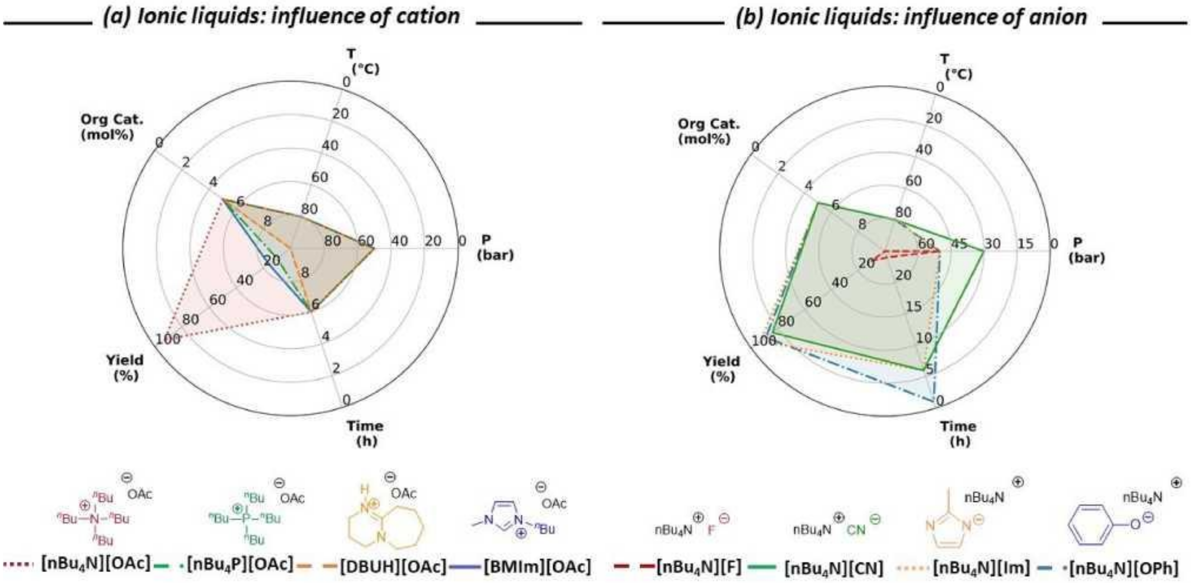


3.1.3. Ionic Liquids

Due to their intrinsic properties such as non-volatility, recyclability, tunability, and thermal stability, ionic liquids (IL) have gained in popularity for CO_2 transformation. Their catalytic activity is easily modulated by the nature of the cation/anion pair, which influences the salt dissociation and hence the basicity of the anion. Moreover, ILs show a propensity to solubilize significant amounts of CO_2. Various ILs made of phosphonium,[41] imidazolium,[23] ammonium,[42] or amidinium[43] cations, and carboxylate, alcoholate/pheno- late, halide, azide, thio-/isocyanate, cyanide, azole, imidazo- lide, or other anions featuring multiple active sites[44] catalyze the coupling of CO_2 with propargylic alcohols (Scheme 6). To benchmark the activity of ILs, we have selected those that are used in low amounts (i.e. 5 mol%) only. Indeed, at high loading, the IL may influence the reactions by acting as a solvent, potentially influencing the overall reaction mechanism, e.g. by (de)stabilizing some transition states/reactive intermediates. Acetate-type ILs are chosen as representative organocatalysts to evaluate the influence of the cation on their performance. This is justified by the rather large scope of acetate/cation pairs that have been tested under strictly identical experimental conditions (T = 80 °C, ***pCO2*** = 50 bar, t = 6 h), which facilitates the benchmarking of the IL activity.

As illustrated in Figure 3a (Table S3), the DMACC yield increases with the cation structure in the order [*N*-butylimidazolium] < [$DBUH^+$] < [nBu_4P^+] < [nBu_4N^+]. [nBu_4N][OAc] is identified as the only IL that afforded DMACC quantitatively and selectively, while the other systems are poorly active (DMACC yield < 20%) or even inactive.[42] The influence of the alkyl substituent of the quaternary ammonium also reveals an optimum chain length at C_4, above and beyond which the conversion of propargylic alcohol declines. Note that this trend is only valid for acetate-type ILs with ammonium cations, as comparable studies for other types of ILs differing in the structure of both the cation and the anion have not been reported. Therefore, any generalization of this trend to other IL families might give inadequate guidelines for tailoring more active organocatalysts. The basicity of the anion is a key parameter in determining the reaction rate. Generally, the higher the basicity, the faster the reaction rate. This is reflected in Figure 3b (Table S4), wherein the very low basicity of fluoride led to the lowest DMACC yield (≈ 10%). Switching to anions with stronger basicity such as cyanide (pK_a = 7), phenolate (pK_a = 9.95), or imidazolide (pK_a = 9.2), significantly accelerates the reaction and enables quantitative conversion, however, with detrimental selectivity in DMACC which decreased to 87–93 %. Anions of intermediate basicity such as azide (pK_a=4.6) or carboxylates (pK_a = 4.6-4.9) provided ILs of moderate activity; nonetheless, they are highly selective for DMACC. The above observations are in line with Chen's postulate, which proposed an optimum pK_a value of the anion of ≈ 7.6, above which the selectivity in the αCC significantly declines, and beyond which the reaction rate slows down.[45] The pK_a value of the anions thus provides a guide to design ILs for the selective conversion of CO_2 into αCCs. The catalytic activity also depends on the catalyst dissociation in the reaction medium. Determining relationships between the catalyst performance and its dissociation requires the ion pair dissociation constants and/or the ion partial charges of the ILs which are not available in the literature. One can only refer to more general considerations to guide the reader in designing more competitive IL catalysts. According to Watanabe, the "ionicity" of ILs reflects the strength of coulombic interactions in ion pairing.[46] This is correlated to the Lewis acidity and basicity of the cation and anion which greatly depends on their ionic structure. The ionicity and consequently the dissociation ability of ILs is favored by selecting weak basic anions and acid organic cations. Beside the steric hindrance, longer alkyl chain lengths usually found in the organic cations impact van der Waals interactions. These may create segregation of the ILs into polar and nonpolar domains, affecting not only the partial charges of the ions but also their solvation.[47] Importantly, the reactant, i.e. the propargylic alcohol, may also act as a polar solvent for the catalyst. Its OH moiety creates a solvation shell surrounding the anion via H-bonding interactions, furnishing solvent-separated ion pairs.[47]

Figure 3. Comparison of the activity of selected ionic liquid catalysts for the solvent-free synthesis of DMACC: influence of the nature of the cation and the anion.



3.2. Dual Activation by Ag- and Cu-Based Catalysts

A large variety of transition metal salts derived from ruthenium,[48] cobalt,[49] palladium,[50] and zinc[30] have been tested for the envisioned reaction; however, silver and copper salts are the most preferred cocatalysts, justifying the focus for further reviewing. Nonetheless, one can refer to Vessaly's review for details on the other metal-based dual systems.[51]

CuX, AgX, and Ag_2Y (with X = I^-, Br^-, Cl^-, SO_4^-, NO_3^-, OAc^- etc. and Y = CO_3^{2-}, WO_4^{2-}, O^{2-}) are typical salts used in combination with basic additives (ILs, PPh_3, nitrogen bases) to drive the formation of DMACC. Three main catalytic scenarios have been identified:

- Low-activity dual catalysts relying on a low content of Ag or Cu salts (2 mol%) with a (large) excess of IL (50 to

200 mol%) that simultaneously acts as a base, a solvent, and CO_2 absorbent. This type of catalyst provides DMACC with yields > 91-97% in 2.5-8 h at 25-120 °C and 1–10 bar of CO2;[23,52,53]

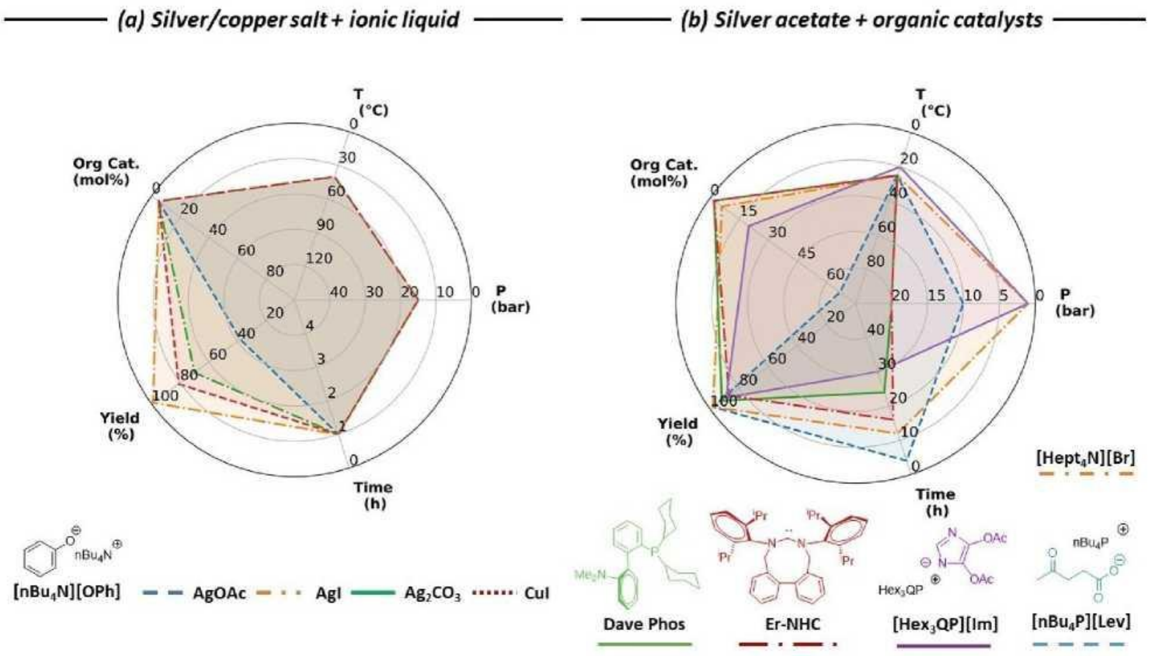
- Moderate-activity catalysts based on a high loading of metal salt (10 mol%) and basic ILs (20 mol%) that deliver DMACC with 91-93 % yield in 5-24 h at 30 °C and 1 bar CO2;[45]
- Highly active catalysts consisting of a (very) low loading of Cu or Ag salts (1–5 mol%) and some base additives (1– 5 mol%) that produce DMACC with 89–100 % yield in 1– 12 h at 25-60 °C and 1-15 bar of CO_2;[54-56]

The literature survey highlights some key features and trends to guide the design of more active systems. Regardless of the organobase, the activity of dual systems made of Cu^I or Ag^I halide salts is influenced by the counter anion and follows in the order I > Br > Cl in line with the easier dissociation ability of iodide versus bromide or chloride salts.[23, 53, 54, 57] In addition, Han et al. illustrated that introducing an oxo moiety within the microstructure of carboxylatetype ILs or using acetone as solvent further improves the dissociation of CuI, due to the coordination ability of the carbonyl group with Cu^+.[53]

One also notes the crucial role of the WO_4^{2} anion, which provides a unique interaction with CO_2 that is beneficial for CO_2 insertion and carbonate formation.[56]

Figure 4a (Table S5) benchmarks the efficiency of some relevant Cu^I and Ag^I dual systems (5 mol%) using $[nBu_4N]$-[PhO] as basic IL (5 mol%) for the synthesis of DMACC at 40 °C and 15 bar of CO_2 for 1 h. The co-catalytic activity of the metal salts follows in the order AgI > CuI > Ag2CO3 > AgOAc. Despite being limited to Ag salts, this trend is also (partly) supported by Verpoort[23] and He,[58] who utilized acetate-type and PPh_3 organic cocatalysts, respectively. Finally, Figure 4b (Table S6) underlines the role of the base cocatalyst on the formation of DMACC using AgOAc, which is one of the most frequently used Ag salts. ILs of weak basicity $[hex_3QP]$[Im] are required in large amounts to drive the reaction slowly to completion under ambient conditions (rt and 1 bar CO_2). The ammonium salt $[nHept_4N]$[Br] appears to be a good compromise in terms of activity under mild conditions. However, as this salt displays no basicity, we believe that an exchange between the acetate and bromine anions occurs in the reaction medium yielding AgBr and $[nHept_4N]$[OAc], which were the catalytic species.[55] In our opinion, the systems based on phosphine (Dave Phos)[25] or expanded-ring NHC (Er-NHC),[26] although not the best performing and used in combination with a solvent, are remarkable catalytic options as they are active for the transformation of the challenging primary, secondary, and internal propargylic alcohols and they present a high tolerance towards various functional groups (e.g. acetate, acrylate, carbonates). Their sensitivity to moisture is pointed out as a weakness, and does not facilitate their recyclability (50 % loss of activity after the first reuse). In a recent study, Schaub et al. proposed a recyclable catalytic system based on the use of lipophilic Ag- based catalysts and a biphasic organic reactive medium (acetonitrile/cyclohexane). The catalyst is recovered by liquid–liquid extraction in the cyclohexane phase, while the cyclic carbonates remain in the acetonitrile phase (average yields of 86–90 %).[59]

Figure 4. Comparison of the activity of selected dual catalysts for the synthesis of DMACC. Dave Phos and Er-NHC catalysts used in combination with ACN.



3.3. *Mixed Heterogeneous/Homogeneous Dual Activation Catalysts*

As a result of the limited recyclability of homogeneous catalysts, most of the systems are costly, limiting their industrial interest. This limitation is overcome by using heterogeneous catalysts wherein a base or an active metal is anchored onto an inert support or mixed heterogeneous/ homogeneous systems combining an immobilized metal (salt) and a free base additive. These catalysts have the advantage of being easily separated and recovered from products, in most cases by simple filtration. The preparation of heterogeneous catalysts relies on the development of efficient inert supports. A variety of supports exist, which includes polymers, carbon materials, and metal/covalent organic frameworks (MOFs/COFs). The supports can either be nonporous, in which case the catalytic reaction takes place at the surface, or porous, wherein the reaction takes place at the inner surface of the pores and at the outer surface of the support. The porous supports have the advantage of a larger surface area available for catalysis. Furthermore, they can either be directly grafted with an organic base or a ligand that coordinates to the metal center or decorated with metallic nanoparticles or simply with a precipitated metal salt and used in combination with a free base.

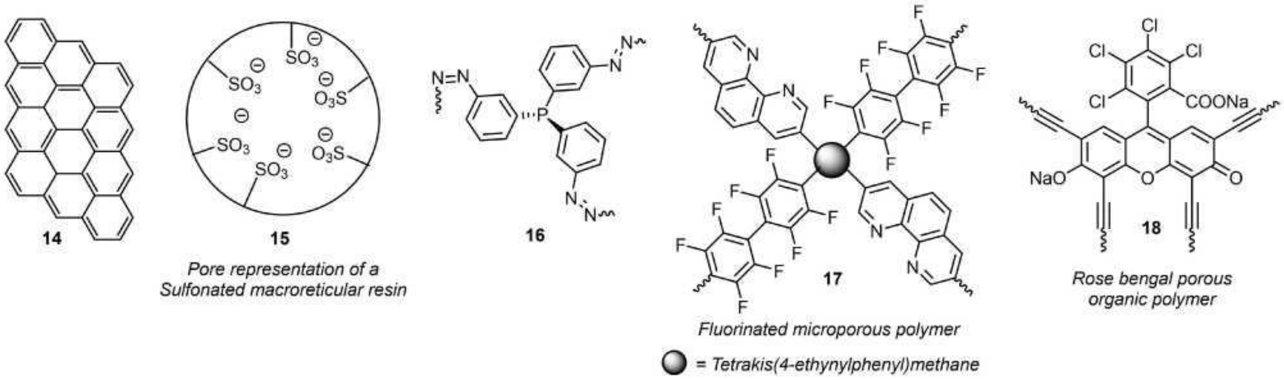
3.3.1. Ag^0-Decorated (Porous) Supports

In 2016, Wang et al. underlined the ability of Ag^0 nanoparticles to activate the propargylic alcohol triple bond and act as a cocatalyst in its transformation with CO$_2$.[60] This discovery opened a new avenue in the development of heterogeneous catalysts via the deposition of Ag^0 nanoparticles on various supports including (porous) activated carbon,[60] reduced graphene nanosheets (**14**),[61] ion-exchange resin,[62] (meso)porous polymers,[63–66] and covalent organic frameworks (COFs)[67,68] (Scheme 7). The textural properties of the supports (meso-, micro-, or macroporosity, absence of porosity, support size, and shape) as well as the particle size (from 1 to 50 nm) are the key features determining the distribution of Ag^0 either at the inner surface of the pores (internal surface) and/or the outer surface of the support (external surface) and hence the efficiency of the catalyst. Nanoparticles with small diameters (1–3 nm) are generally embedded within the meso- to macropores (pore size in the range of 10 to 90 nm, with a pore size distribution centered at 26 nm) or macropores ($d > 50$ nm) of the substrate (such as sulfonated resins **15**), and at the outer surface of the support. Exclusive outer surface decoration of the support is observed with Ag^0 particles of diameter > 20-50 nm or when carbon, COFs, or porous polymers with micro- and mesoporosity (pore diameter < 9 nm) are used. The catalytic activity also benefits from the presence of additional surface functional groups such as azo, phosphine, (**16**), and carboxylate.[64] These moieties favor the nanoparticle–support interactions, further enhancing the metal dispersion, minimizing the metal leaching, and adjusting the catalyst activity/selectivity by the metal– support charge transfer.[69–71]

The presence of heteroatoms such as nitrogen or fluorine (**17**) lining the pores of the substrates favors synergistic host (support)–guest (CO_2) interactions and consequently CO_2 adsorption.[65] Indeed, the electron lone pair on the N atom is an attractive site for the electron-deficient carbon atom of CO_2.[72] Fluorine interacts with CO_2 through the interplay of 1) halogen bonding (O···F) between electron-deficient σ- holes on fluorine and CO_2 and 2) electrostatic C···F interactions between the electrophilic carbons of CO_2 and the electron-rich fluorine atoms.[73]

Similar to the metal salt/base dual systems, two catalytic scenarios can be distinguished: heterogeneous supports with low Ag^0 content (0.01–0.14 mol%) in combination with a large amount of DBU (100 mol%) or supports decorated with a high metal loading (3–10 mol% of Ag^0) and 10– 30 mol% of DBU. All catalytic systems operated at low CO_2 pressure (1-10 bar) and temperature (25 °C), affording DMACC in moderate to excellent yields (78–100 %) in 3 to 18 h. A general classification of their performances is rather difficult as the catalytic activity results from a complex interplay between the Ag° particle size and the properties of the support. In addition, the CO_2 adsorption capacity and turnover number (TON) are not reported for all systems.

Scheme 7. Types of supports used in the design of Ag^0-decorated (porous) supports.



Nonetheless, the Ag^0-decorated (micro)porous organic polymer derived from Rose Bengal[63] (**18**) and also Ag^0 COF catalysts used in combination with DBU seem promising.[67,68] Remarkably, these catalysts were reused up to 5–10 times without any significant loss in activity. This suggested the absence of leaching or aggregation of the Ag^0 particles. As illustrated by Wang, the next generation of this family of catalysts might rely on the physisorption of AgX nanoparticles (X = Cl, Br, or I) onto supports; these catalysts were more efficient than analogous mixed heterogeneous/ homogeneous catalysts made of Ag^0 nanoparticles.[60]

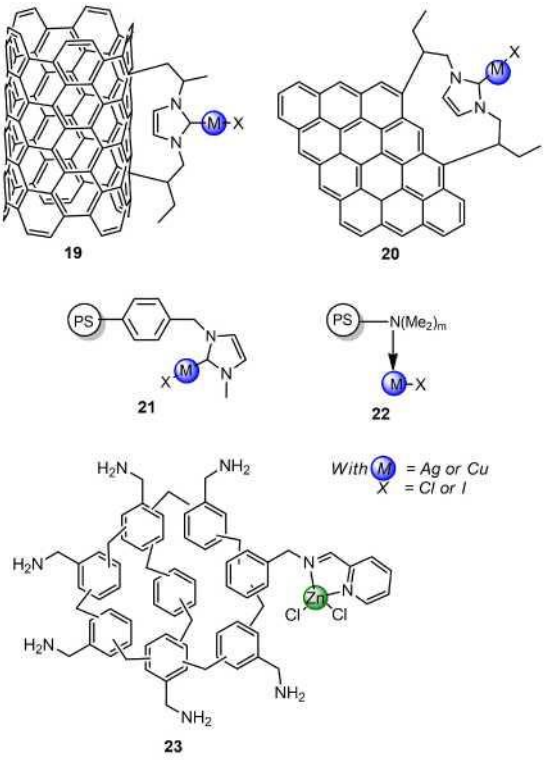
3.3.2. Heterogeneous Catalysts Containing Metal–N Chelates

N-heterocyclic carbene–Ag^I or Cu^I complexes have been immobilized onto multiwall carbon nanotubes (CNTs, **19**), graphene nanosheets (GNs, **20**),[74] and polystyrene beads (PSs, **21**)[75] (Scheme 8). These systems perform remarkably for the carboxylation of propargylic alcohols without an added base. The CO_2 transformation is realized at 30– 50 bar, 40-80 °C for 24 h. CNT-NHC- and GN-NHC-AgCl catalysts (Ag loading ≈ 1.5 mol%) and PS-NHC-AgCl (Ag loading 2 mol%) deliver DMACC with a yield of 96–99 %. With analogous heterogeneous systems made of immobilized NHC-CuI complexes (Cu loading ≈ 3 mol%) on the carbon-type supports, the conversion of the propargylic alcohol decreased to 88–91 % under identical conditions and the reaction is slightly less selective. Surprisingly, no reaction is observed with PS-NHC-CuI. All these catalysts can be reused for ten cycles without any significant decline in activity.

Other Cu^I or Zn^{II} metal-anchored polymer catalysts, such as (dimethylamino)methyl-polystyrene-supported copper(I) iodide (DMAM-PS-CuI, **22**)[76] and ZnI_2-grafted benzene-benzylamine porous organic polymers

(Zn@BBA-PA, **23**),[77] have been also employed as heterogeneous catalysts. **22** afforded DMACC with a 97 % yield under supercritical conditions (T=40 °C, p_{CO2} = 100 bar) within 24 h at 8 mol% loading of CuI. Unfortunately, its reusability is affected by Cu leaching and destruction of the PS beads caused by the stirring. Catalyst **23** was only effective in the presence of DBU (100 mol%) and delivered quantitatively DMACC in 6 h at 30 °C and 10 bar of CO_2. This heterogeneous catalyst can be reused up to five cycles with only marginal loss of activity. However, none of these catalysts competes with the Ag^I complexes of NHC immobilized onto CNT or GN or PS.

Scheme 8. Structure of selected heterogeneous carbon- and polymerbased catalysts reported for the synthesis of αCCs.

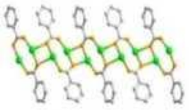


3.3.3. MOFs and COFs

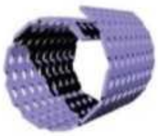
In 2017, Duan et al. pioneered the utilization of MOF catalysts to synthesize αCCs (Figure 5). Ag^I chains are embedded in a tubular 3D framework with large quadrilateral channels.[78] The proximity of the Ag nodes facilitated long-range charge and electron transfer endowing the support with strong activating capacity. The specific MOF topology which embeds unsaturated metal sites and some defects, increased the CO_2 uptake and is beneficial for the activation of the propargylic alcohol via π-activation of the triple bond. The silver-metalated MOF (**24**) (0.5 mol% loading of Ag) used in combination with PPh_3 (2.5 mol%) delivers quantitatively DMACC at 50 °C and 5 bar of CO_2 in 20 h.[78, 79] More recent reports describe the design of Ag- metalated tubular porous MOF distinguished by a curved 2D π-conjugated honeycombed metal framework with a dense distribution of Ag cations at the tube surface (**25**)[80] and organosulfonated 3D frameworks with cubic topology for dual CO_2 capture/activation and Ag metalation (**26**).[81, 82]

Figure 5. Selected MOF- and COF-based catalysts reported for the synthesis of αCCs. Acronyms of catalysts reproduced from the original publications. **24** is reproduced from ref. [79]; **25** is adapted from ref. [80] with permission from the Royal Society of Chemistry, Copyright 2020; **26** is reproduced from ref. [82] with permission from the American Chemical Society, Copyright 2020; **27** is reproduced from ref. [85] with permission from the Royal Society of Chemistry, Copyright 2020; **28** is reproduced from ref. [83] with permission from Wiley-VCH, Copyright 2019; **29** is reproduced from ref. [84] with permission from the Royal Society of Chemistry, Copyright

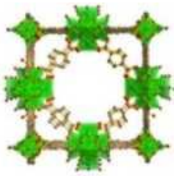
2019.



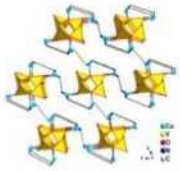
24
Ag-H$_4$TCPE



25
Ag-TPPB

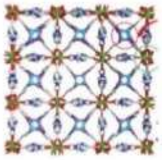


26
Ag-Zr-MOF-SO$_3$



27
V-Cu-MOF

28
In-Cu$_4$I$_4$-MOF

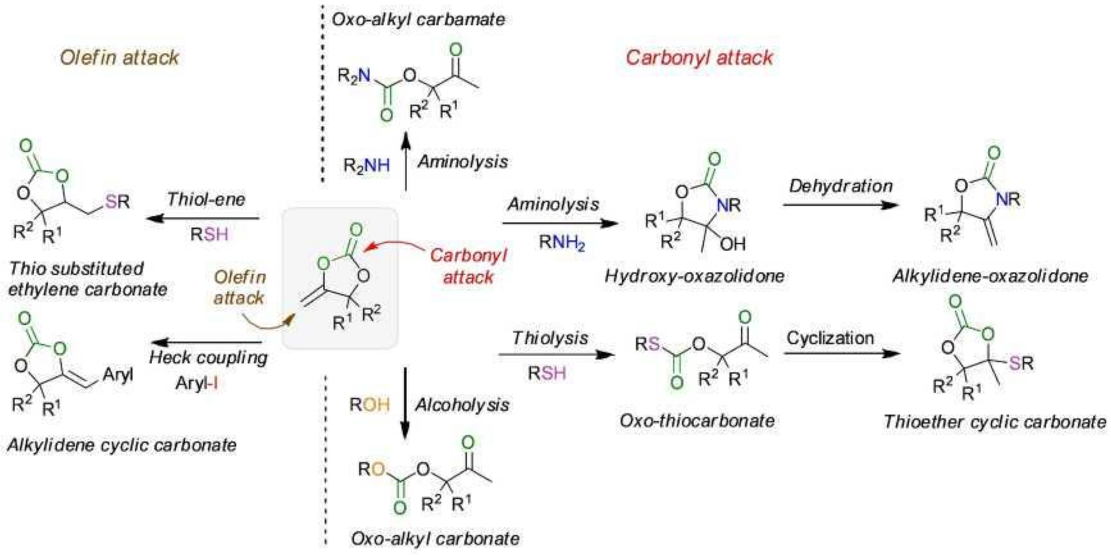


29
Dy-Cu$_4$I$_4$-MOF

All MOF catalysts (0.1 to 10 mol% Ag loading) are mixed systems using 10 to 20 mol% of DBU to provide DMACC in excellent yields (90–99 %) within 1 to 24 h at 1 bar CO$_2$ pressure and 25-40 °C.

Although unlikely to be used for the large-scale production of αCCs, systems embedding Cu$_n$I$_n$ (with n=2 or 4) clusters,[83,84] Cu^{I} chains,[85] or Cu^{I}X moieties[86] (with X = CN, Cl, I) into various polyoxovanadate- (**27**), lanthanide- (Dy^{III} (**28**) or Gd^{III}), and In-based MOFs (**29**) are also employed in combination with a base (DBU or TEA) for the fixation of CO$_2$ onto propargylic alcohols. All these catalysts operate under similar conditions as the Ag-type MOF/DBU dual catalysts (low CO$_2$ pressure < 10 bar, temperature = 25-50 °C) and deliver DMACC with comparable yields. Although research on MOF catalysts for the synthesis of αCCs is very recent, some trends are observed. Firstly, the presence of sulfonated or cyanide groups displaying electron-rich sites that interact with the electrophilic carbon of CO$_2$ favors the adsorption of CO$_2$ within the MOF channels.[72] Secondly, the embedding of tetrahedral Cu$_4$I$_4$ clusters within the 3D framework seems preferable for the design of high-performance catalysts. Lastly, the construction of heterometallic MOFs displaying additional Lewis acid sites (Dy^{III}, Zn^{II}, or In^{III}) provides undeniable synergistic catalytic effects, thereby boosting the reaction.

Scheme 9. Transformations of αCCs.



4. Chemical Transformation of Exovinylene Cyclic Carbonates in Organic Synthesis

αCCs present two distinct reactive sites, i.e. the carbonate and the olefin group, which can undergo selective reactions. Scheme 9 summarizes the main transformations of αCCs and the families of products that have been obtained. The presence of the exovinylene moiety associated with the strain release enables the facile and regioselective ringopening of the cyclic carbonate by nucleophiles (amines, alcohols, thiols). The driving force lies in the spontaneous tautomerization of an enol into the corresponding ketone upon ring opening. The olefin group can also be involved in other transformations, such as thiol–ene and Heck coupling reactions, although only few of them have been explored.

4.1. Aminolysis

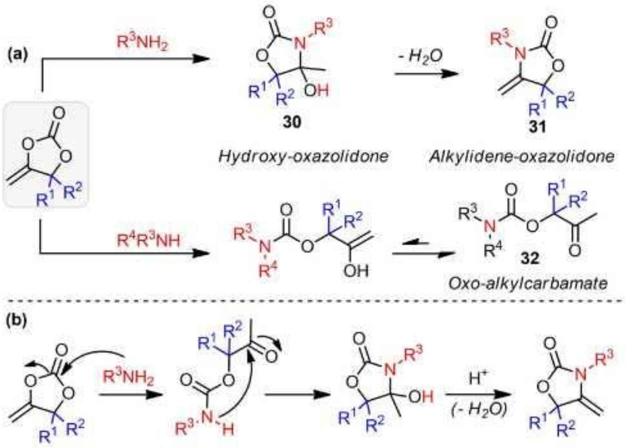
αCCs offer a new attractive alternative to toxic phosgene,[87] carbamoyl chlorides, and isocyanates[88, 89] for the construction of (cyclic) carbamates, which are important scaffolds in the agrochemical and pharmaceutical industries.[90] Their transformation with primary amines delivers hydroxy-oxazo- lidones (Scheme 10a). The heterocycle formation proceeds through a formal domino process involving ring-opening of the αCC to create an oxo-alkyl carbamate intermediate. Then, the latest undergoes a spontaneous cyclization by reaction between the secondary NH of the carbamate group and the adjacent ketone (Scheme 10b). With heptyl-, benzyl, or cyclohexylamine, the whole transformation is complete within few hours at room temperature (r.T.) without any catalyst (Scheme 11, **30 a**–**c**).[91, 92] When heated at reflux in glacial acetic acid, the hydroxy-oxazolidone undergoes quantitative dehydration into the corresponding α-alkyli- dene oxazolidone (**31 a**–**c**).[91] With secondary amines, the catalyst-free aminolysis of αCCs at r.T. furnishes exclusively oxo-carbamates. This is exemplified by the conversion of 4,4-dimethyl-5-methylene-1,3-dioxolan-2-one with *N*-methyl- butylamine[92] or secondary diamines such as piperazine and *N,N*-dimethyl-1,6-hexanediamine (cf. Section 5.3).[93] Optionally, with less reactive primary or secondary amines, both transformations can be accelerated by addition of a superbase (DBU).[91]

Examples addressing the direct aminolysis of preformed αCCs are rare. To date, few multicomponent reactions involving the in situ formation of αCCs from propargylic alcohols and CO_2 followed in cascade by their aminolysis are privileged. These made it possible to access a portfolio of organic carbamates and oxazolidones with ample structural diversity. To be successful, this concept necessitates the selection of an efficient catalyst to drive the CO_2 fixation onto the propargylic substrate that does not impede the αCC's ring-opening by the *N*-nucleophile, as well as optimized conditions (high T, p_{CO2}, t) to drive both steps of the process to completion with a high degree of selectivity.

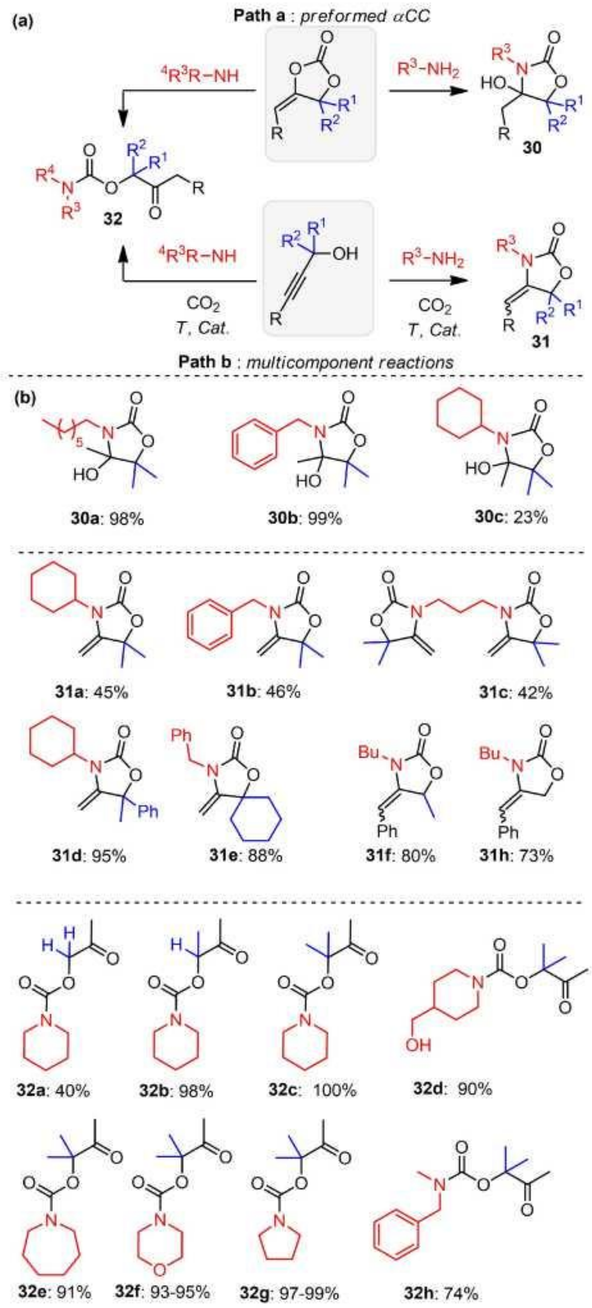
Metal complexes (Ru, Ag, Cu etc.), organic bases, or cooperatives systems (as reported in Section 3.2) represent valuable catalytic options for the preparation of the envisioned scaffolds. In this section, we will illustrate the concept with selected examples, and we invite the reader to refer to Arshadi's review for a more exhaustive picture of the existing works.[94] As a main trend, the propargylic alcohol/CO_2/primary amine three-component reaction delivers alkylidene oxazolidones (**31d** and **e**) in moderate to good yields (42–95 %) using bases (phosphines,[95] pyridines,[96] [DMIm]- [BF4],[97] etc.) or a cooperative system ($CuCl_2$/ [BMIm][BF4])[98] at 110-140 °C and p_{co2} of 25-50 bar. Jiang et al. utilized CuI[99] and AgOAc salts[100] to convert internal propargylic alcohols into the corresponding alkylidene oxazolidones (products **31f** and **g**) in moderate to high yields (70-96 %) at 80 bar of CO_2 and 60-120 °C. In these catalytic systems, the primary amine was used in excess and served both as the reagent and the basic additive required to drive the carboxylative cyclization. As a variant, Xu et al. have synthesized alkylidene oxazolidones with yields of up to 88 % in 48 h under metal-free conditions, by the use of supercritical conditions (140 bar, 120 °C) with an excess of amine.[101]

When secondary amines replace primary ones in multicomponent reactions, oxo-carbamates with structural analogy to those obtained by direct aminolysis of preformed αCCs are synthesized. Various metal complexes ([$RuCl_2$ (norbornadiene)]$_n$,[102] ([$Cu(MeCN)_4$]PF_6)),[103] cooperative systems (Ag2CO3/PPh3[58] or (*p*-MeOC6H4)3P,[104] AgCl/ Et_4NCl[105]), heterogeneous silver/copper-based catalysts (CNT-NHC-Ag/Cu),[74] and even immobilized metallo-en- zyme (laccase) used in synergy with TEMPO[106] illustrate the large diversity of catalytic options that have been engineered to fabricate the carbamate scaffolds. As a trend, Ru and Cu catalysts require demanding operative conditions (40-50 bar, 70-100 °C) to deliver the envisioned products with high yields. Ag-based catalysts appear more efficient under mild conditions (1 bar, 30-60 °C). Yields in carbamates up to 98 % are generally achieved with tertiary propargylic alcohols are lower with secondary and primary propargylic alcohols (40–57 %) under identical conditions (**32 a**–**c**). With CNT-NHC-Ag/Cu, Zhang et al. highlighted an influence of the R substituent of the secondary amines on the yields, with a slight decrease in the order pyrrolidine (99 %) > diethylamine > di-n-propylamine (96 %) > di-n- butylamine (92 %).[74] Remarkably, the immobilized biocatalyst is active at low CO_2 pressure of 15 bar for 30 days and affords a large scope of carbamates (**32 d**–**h**) with yields up to 99 %. This system can be reused 10 times without a significant loss of activity.[106]

Scheme 10. a) Reactions of primary and secondary amines with αCCs and b) mechanistic aspects.



Scheme 11. a) Synthetis of oxo-alkylcarbamates and oxazolidones from exovinylene cyclic carbonates or via multicomponent reactions. b) Product scope (non-exhaustive list from refs. [91, 92, 98, 100, 103– 106]).



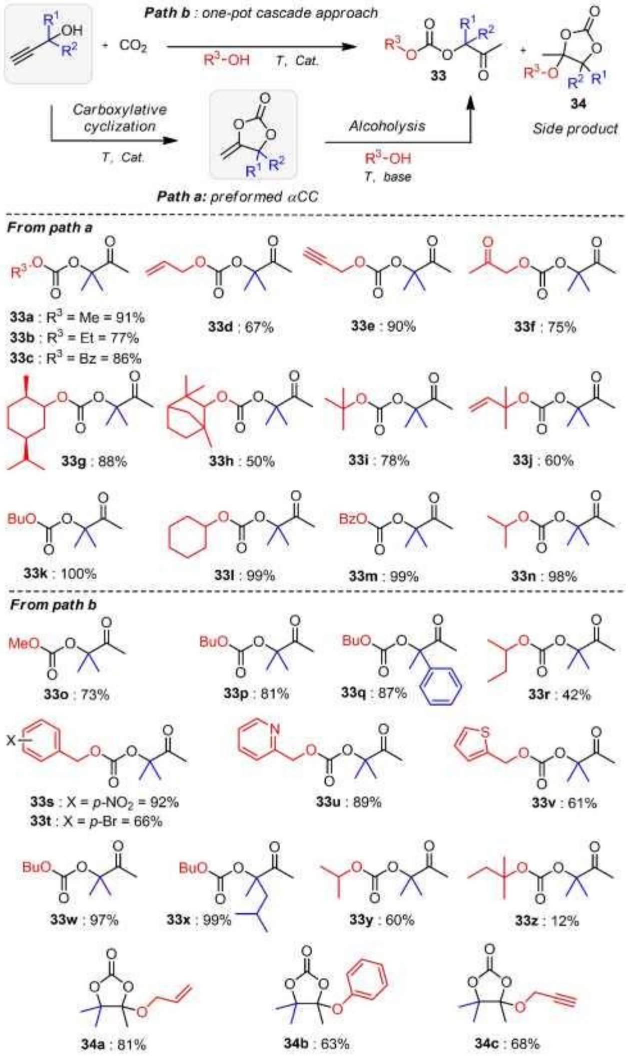
4.2. Alcoholysis

Acyclic carbonates are useful synthons in fine chemistry and deserve interest as solvents for organic synthesis and in Li- ion batteries. These scaffolds are now accessible by the transformation of αCCs either from the preformed substrate, or via the multicomponent cascade approach (Scheme 12). Unlike aminolysis, the alcoholysis of αCCs is not spontaneous and requires a base to activate the weak *O-* nucleophile and promote the ring-opening of the cyclic carbonate.

Dixneuf et al. pioneered the synthesis of oxo-alkyl carbonates from αCCs and primary or secondary alcohols.[107] By using triethylamine (70 mol% vs αCC), the

Scheme 12. Synthesis of oxo-alkylcarbonates and tetrasubstituted ethylene carbonates from αCCs and alcohols.

Selected examples from refs. [31, 54, 107–109, 111].



authors delivered the corresponding acyclic carbonates under relatively mild conditions (0-40 °C, 4-20 h) in moderate to high yields (67–90 %, **33 a**–**f**). The synthetic approach is also found to be tolerant to functional groups, allowing the introduction of an olefin, alkyne, or ketone to the product skeleton (**33 d**–**f**). The same research group further synthesized oxo-alkyl carbonates in good yields (60–70 %) from challenging bulky tertiary and/or sterically congested alcohols, respectively, by switching from NEt_3 to KCN, 2- hydroxypyridine (10 mol%) or DBN (40 mol%) catalyst at 20-60 °C (products **33g**-**j**).[10 8] Recently, the alcoholysis of αCC was revisited by Detrembleur who utilized an organic (super)base (DBU)[109] or nBu_4NOPh[54] (5 mol% vs αCC). Various oxo-alkyl carbonates were easily fabricated from αCCs and 1-butanol at 25 °C (within hours) or with less reactive benzyl alcohol or cyclohexanol at 80 °C (within 15 min) (**33 k**–**n**).

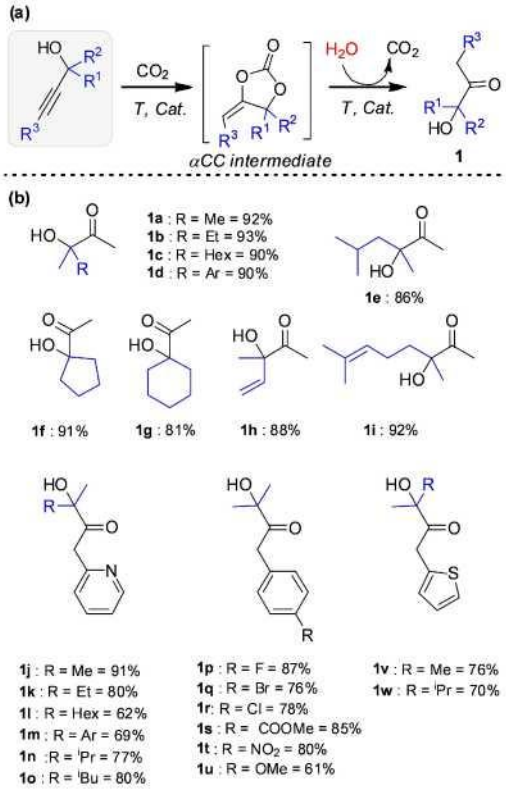
In the multicomponent approach, the oxo-alkyl carbonates selectivity and yield are strongly dependent on the catalyst. With DBU, TBD, and MTBD superbases, oxo-alkyl carbonates are exclusively formed at 100 °C under supercritical CO_2 conditions with yields of 42–81 % in 24 h from mixtures of propargylic alcohol, CO_2, and primary (MeOH or 1-butanol) or secondary (butan-2-ol) alcohols (**33 o**–**r**).[31]

With allylic alcohols, phenol or excess propargylic alcohol, the product selectivity switches to the exclusive formation of the tetrasubstituted ethylene carbonate (63– 81 %) when MTBD is employed (**34 a**–**c**).[31] Cooperative catalysts made of zinc[110] or silver[54,111–113] salts and basic additives are by far more selective and promote the formation of a large portfolio of asymmetric oxo-alkyl carbonates even with high yields (up to 98 %) (**33 s**–**z**). AgCl with 1-butyl-3-methylimidazolium acetate (acting both as a catalyst and solvent) promotes the tandem reaction with a large scope of aliphatic alcohols at rt and 1 bar of CO_2, delivering organic carbonates with yields approaching 100 %.[112] The Ag_2CO_3/PPh_3 catalyst is found effective (80 °C, 10 bar) in the formation of oxo-alkyl carbonates (6197 % yields) from (hetero)aromatic alcohols, such as (substituted) benzyl alcohols, pyridin-2-ylmethanol, and thio- phen-2-ylmethanol (**33 s**–**v**).[113] More recently, catalytic amount of AgI with nBu_4NOPh promoted the in situ formation of (sterically congested) αCCs and their cascade transformation into the acyclic carbonates at 1 bar of CO_2 and 60°C in 10 h.[54] High yields (> 97%) were obtained for primary alcohols but decreased to 60 % and 12 %, respectively, for less reactive secondary and tertiary alcohols (products **33 w**–**z**).

4.3. Acetylenic Hydration

α-Hydroxy ketones are a class of biologically active fragments in natural or pharmaceutical products and are important building blocks in fine organic chemistry.[114] Usually delivered by the nasty Hg-catalyzed hydration of propargylic alcohols,[115,116] these synthons are now accessible in a more sustainable way directly from CO_2, water, and propargylic alcohols through in situ hydrolysable αCC intermediates (Scheme 13a). Recent task-specific ionic liquids ([Bu_4P][Im]),[117] silver salt/base dual systems (AgOAc/DBU[118] and AgOAc/1-ethyl-3-methylimidazolium acetate[119]), ZnCl2/DBU,[110] and a Cu2O/phosphine/DBU[120] ternary catalyst were used to transform a series of diverse propargylic alcohols into the corresponding α-hydroxy ketones with moderate to excellent yields under mild conditions (1-20 bar, 60-90 °C). However, all systems display sufficient activity at high base loading (from 0.5 to 3 equivalent-fold excess) and/or with less hindered substrates. Scheme 13b illustrates the scope of ketones derived from terminal (bulky) propargylic alcohols with different (cyclo-)alkyl, vinyl, and aryl substituents (**1 a**–**i**) and from internal propargylic alcohols substituted at the acetylenic terminus by an aromatic moiety (**1 j**–**w**).

Scheme 13. a) Formation of α-hydroxy ketones by hydrolysis of in situ generated αCCs and b) product scope (non-exhaustive list from refs. [117–120]).



4.4. Carbonylation

αCCs serve as carbonylation agents in the construction of multifaceted heterocyclic compounds from secondary ethanolamines or vicinal diols. Conceptually, the *N*- or *O*- nucleophile of the ethanolamine or diol substrate is intercepted by the reactive αCC. This creates an oxo-alkyl carbamate or carbonate intermediate with an additional hydroxyl functionality that undergoes a cascade domino cyclization to deliver an oxazolidone or cyclic carbonate, respectively (Scheme 14).

To date, the carbonylation of aminoalcohols was only achieved via the multicomponent approach; αCCs were obtained in situ from propargylic alcohols and CO_2 prior to reaction with 2-aminoethanol and further cyclization. Taskspecific basic ILs,[121] Ag^I salts with xantphos,[122]

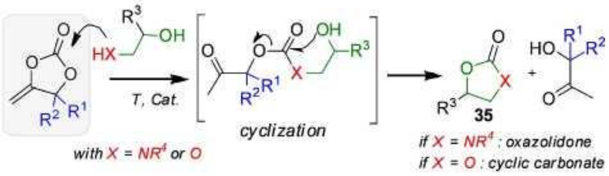
guanidines,[123] or acetate-type IL additives,[124] as well as Cu^I salt/1,10-phenanthroline/base[125] and Cu^I/IL[126] systems were used to form oxazolidone scaffolds (Scheme 15, **35 a**–**g**) with moderate to high yields (>97 %) even at atmospheric CO_2 pressure, low metal salt loading, and mild temperatures of 60-80 °C in less than 24 h. As illustrated by Verpoort, the overall reaction is influenced by the steric congestion of the αCC or propargylic alcohol and slows down with bulky R^1 and R^2 substituents (Et, Ph, ^{i}Bu, cyclohexyl).

Vicinal diols react in a cascade fashion with propargylic alcohols and CO_2 to deliver mono- or disubstituted ethylene carbonates with high yields (63–98 %) (Scheme 16, **36 a**–**m**). This carbonylation utilizes similar operative conditions and task-specific basic ILs, cooperative Ag^I[127, 128] or Cu^I salt/ basic additive/ligand[125] systems as those reported for ethanolamines, and Zn^{II}/superbase dual systems[110] that were shown efficient in the formation of oxo-alkyl carbonates and in acetylenic hydration. Recently, Lu et al. reported an elegant LB-CO_2/MTBD tandem catalyst for the CO_2/propargylic alcohol/vicinal diol three-component reaction, which opened a route to structurally diverse polycyclic carbonates with high chemo- and stereoselectivity from natural sugar polyols (e.g. glycerol, erythritol, xylitol) (**36 j**– **m**).[129] The carbonylation of 1,3-diols is also proven in concept by the synthesis of two six-membered cyclic carbonates either by using presynthesized αCCs (**37 a**)[108] or via the multicomponent cascade scenario (**37 b**).[110, 127]

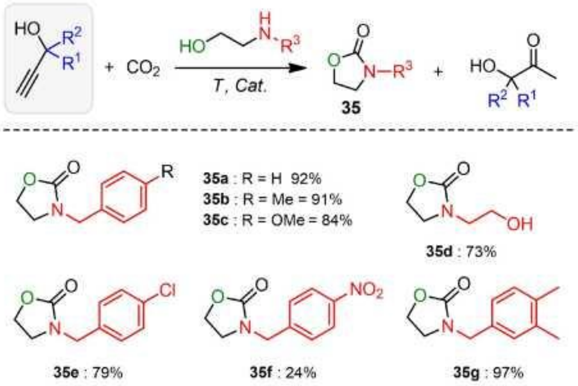
4.5. Addition of S-Nucleophiles

Organosulfur compounds play a key role in the biochemistry of most living organisms and are widely present in synthetic drugs and bioactive natural products.[130–132] The construction of carbon–sulfur bonds from thiols and αCCs was recently introduced. The presence of the carbonyl and olefinic site in αCCs, both of which react with R-SH reagents, makes it possible to form structurally divergent products using appropriate catalysts and/or operative conditions (Scheme 17). DBU promotes the fast thiolysis of αCCs, delivering oxo-thiocarbonates (kinetic product) with high yields (89–99 %, **38 a**–**g**) in less than 1 min at rt.[133] The reversibility of the reaction is proven in concept by the dynamic exchange of the thiol fragments of two structurally different oxo-thiocarbonates, producing four new scaffolds. After an extended reaction time, oxo-thiocarbonates are almost quantitatively transformed into elusive sulfur-containing tetrasubstituted ethylene carbonates (thermodynamic product) with a medium to high selectivity (43–100 %; **39 a**–**g**). When DBU is replaced with 2,2-dimethoxy-2-phenylacetophenone (DMPA) photocatalyst, i.e. a radical generator, the thiol addition onto the αCC occurs exclusively via the thiol–ene reaction, furnishing a trisubstituted ethylene carbonate with a thioether moiety (**40 a**) at r.T. with high yield (95 %).[133]

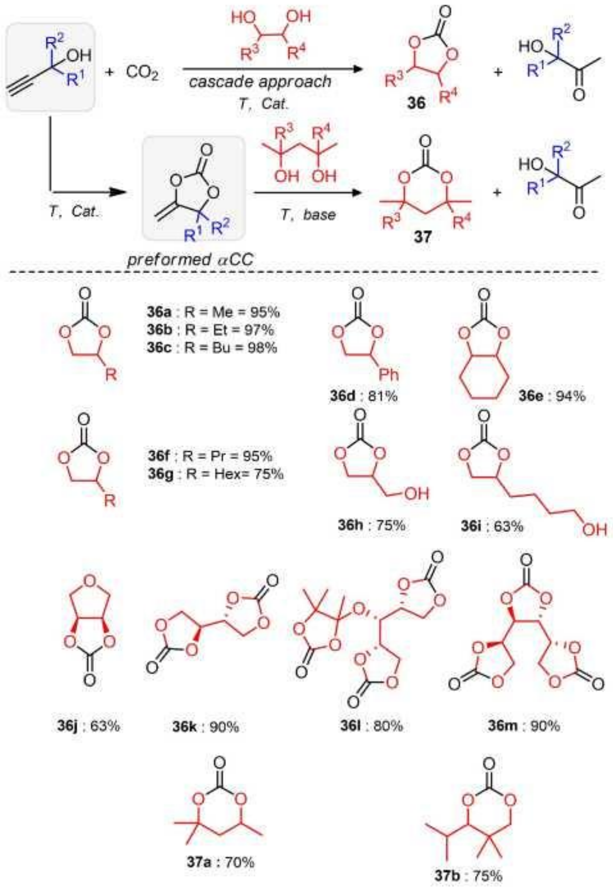
Scheme 14. Oxazolidones and cyclic carbonates synthesized by carbonylation of diols and ethanolamines with αCCs.



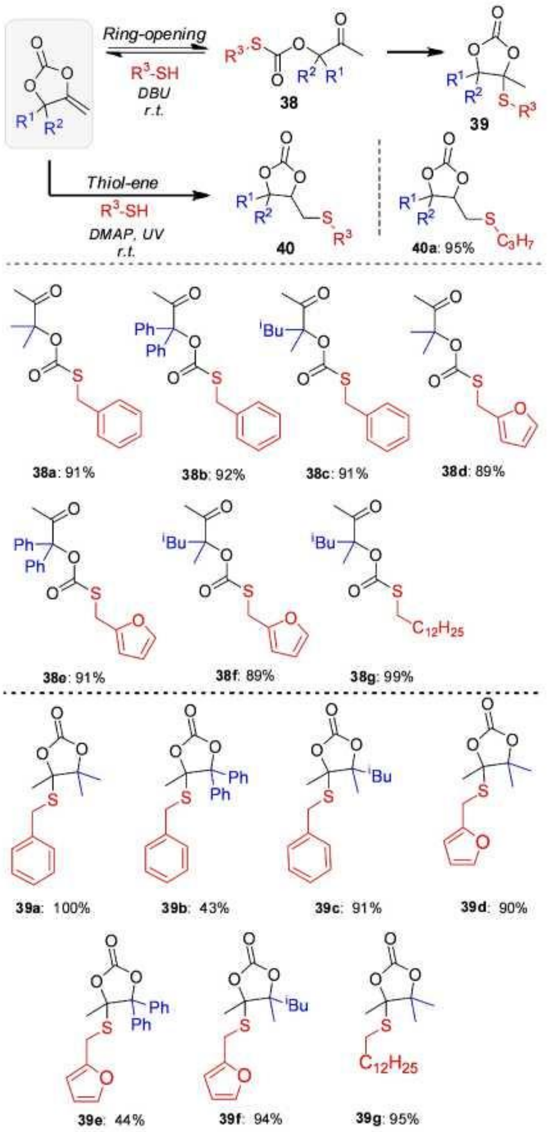
Scheme 15. Scope of oxazolidones synthesized by carbonylation of ethanolamines (selected from refs. [121–126]).



Scheme 16. Scope of cyclic carbonates synthesized by carbonylation of diols (selected examples from refs. [108, 110, 125–129]).



Scheme 17. Reaction of αCCs with thiols: general scheme and product scope.

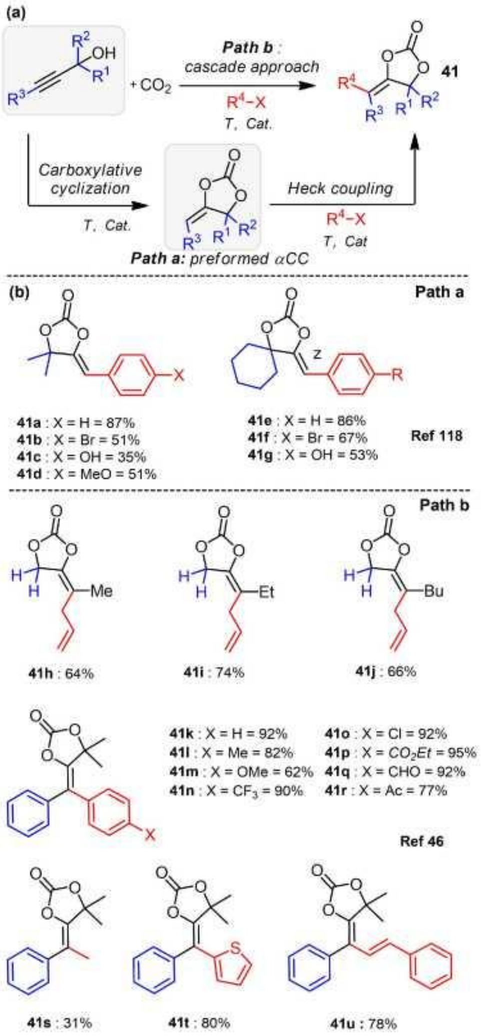


4.6. Heck Coupling

The palladium-catalyzed Heck reaction, which couples organohalides to vinylic compounds, has been exploited to fabricate functional αCCs with stereo-defined alkylidene substituents (Scheme 18). Dixneuf has synthesized trisubstituted alkylidene (bis)cyclic carbonates with stereoselective *Z* configuration in moderate to good yields (40–87 %, **41a**– **g**) by treating preformed αCCs with various aryl iodides

using PdOAc, PPh$_3$, and CF$_3$COOAg as the catalytic system at 100 °C.[134] However, with classical aryl bromide Heck substrates, no reaction was observed. In one-pot approaches, a single Pd catalyst combined with a base promotes both the carboxylation of propargylic alcohols and the Heck coupling. For example, the Pd(PPh$_3$)$_4$/NaH system allows the stereoselective formation of *E*-trisubstituted alkylidene carbonates with moderate yields (9–68 %) from bromo- or iodoaryl reagents, terminal tertiary propargylic alcohols, and 10 bar of CO$_2$ at 100 °C in 8 h (**41h**-**j**). Switching to a strong base (BuLi, LiO^{t}Bu) and a Pd^{II} complex (PdCl$_2$(MeCN)$_2$, Pd$_2$(dba)$_3$) permits the formation of *E*-tetrasubstituted alkylidene carbonates (50–92 % yield) from internal propargylic alcohols and aryl or alkyl halides under atmospheric pressure of CO$_2$ (**41 k–u**).[135, 136]

Scheme 18. Synthesis of tri- or tetrasubstituted alkylidene cyclic carbonates by Heck-type reaction: a) general strategy and b) product scope.



5. Exovinylene Cyclic Carbonates in Macromolecular Engineering

The multiple transformation options of αCCs with carboncentered radicals, nucleophiles, and aryl halides are extended to the construction of a multitude of polymers with diverse functionalities. Remarkably, from a limited set of monomers, a library of polycarbonates of different microstructures, polyurethanes, elusive sulfur-containing polymers, functional poly(vinyl alcohol)s, and even polar poly-

ethylene analogues is now accessible, most often under mild operating conditions.

5.1. Chain-Growth Polymerizations

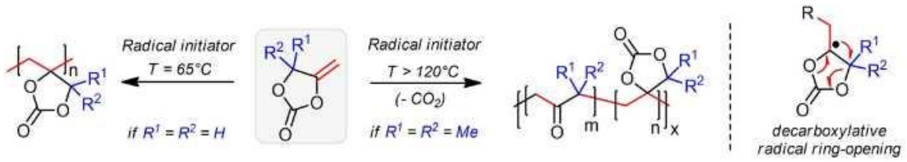
The olefinic moiety of αCCs offers a site for radical attack. This feature is exploited to polymerize 4-methylene-1,3- dioxolan-2-one, i.e. the simplest αCC structure (R^1=R^2=H) via a free-radical pathway using conventional azo or peroxide initiators at 65 °C and fabricate polyvinylic chains with pending cyclic carbonates (Scheme 19).[137] Further extension of the radical process to sterically congested αCCs is challenging. The presence of bulky substituents (methyl or phenyl) creates a sterically congested environment and a highly stabilized propagating radical is formed upon decarboxylation (with R = aryl group) which prevents the polymerization of the monomer units at low temperature. Only 4,4-dimethyl-5-methylene-1,3-dioxolan-2-one (R^1=R^2=Me, DMACC) homopolymerizes when the temperature is increased to 120 °C, affording oligomers (M_n = 11002100 gmol ^{1}) with microstructures of alternating cyclic carbonates and ketones repeating units, the latest being formed upon decarboxylative radical ring-opening of αCC.[137,138]

Decarboxylations can be suppressed by driving the controlled cobalt-mediated radical copolymerization (CMRP)[139] of DMACC with vinyl acetate (VAc)[140] or ethylene (E)[141] as co-monomers (Scheme 20). With the Co complex, it is possible to lower the operative temperature to 40 °C and design various random copolymers of precise composition (≈ 6 to 62% of DMACC insertion) and controlled molar masses (2000 gmol ^{1} <M_n<20000 gmol ^{1}). The selective hydrolysis of VAc units of P(VAc-*co*- DMACC) furnished a poly(vinyl alcohol) (PVOH) bearing cyclic carbonate pendants that are further post-functionalized into hydroxyurethanes by aminolysis.[140] Under basic methanolysis, both VAc and DMACC units are hydrolyzed, leading to PVOH bearing vicinal diols. Similar procedures applied to P(E-*co*-DMACC) yielded polar polyethylene with vicinal diols.[141]

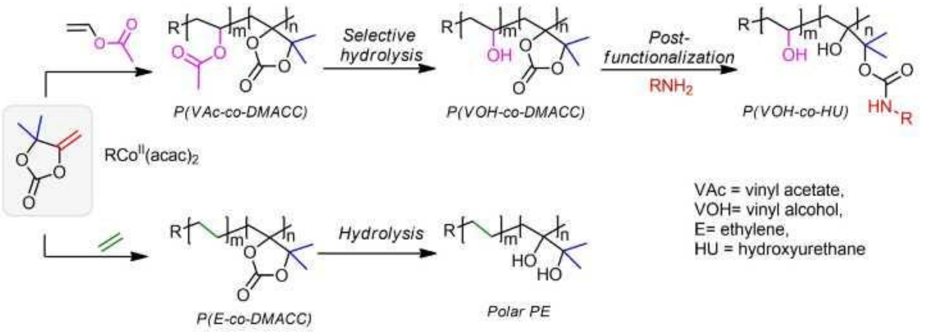
5.2. Polyadditions

5.2.1. Synthesis of BisαCCs

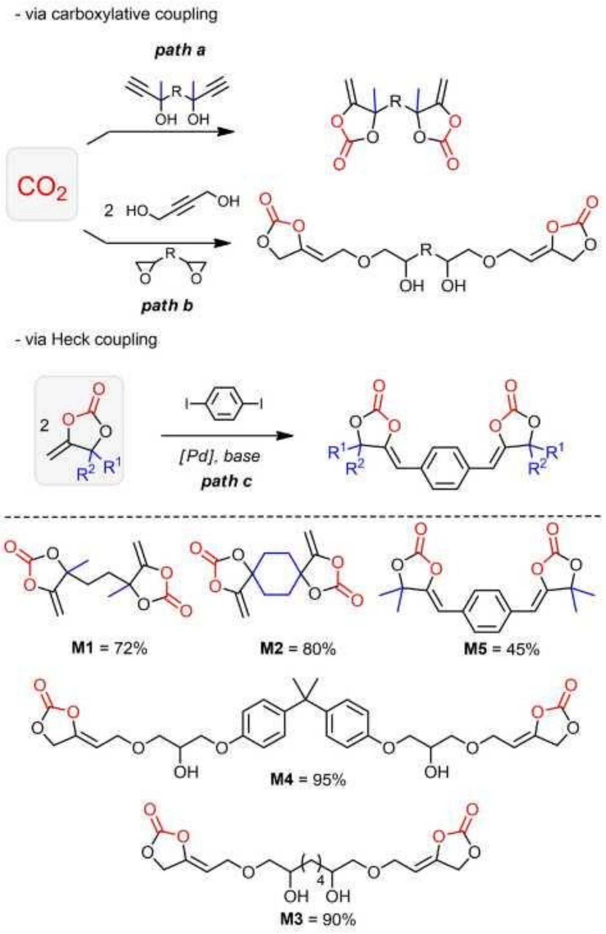
Scheme 19. Free-radical polymerization of αCCs.



Scheme 20. Cobalt-mediated radical polymerization of DMACC with VAc or E, and further copolymer derivatizations.



Scheme 21. Synthetic pathways to bisαCCs and product scope.



Capitalizing on the catalyst findings for the CO$_2$ transformation (Section 3) and the transformation of αCCs (Section 4), bis-α-alkylidene cyclic carbonates (bisαCCs) have been synthesized either by carboxylative cyclization of CO$_2$ with bispropargylic alcohols or via Heck reaction of αCCs with 1,4-diiodobenzene (Scheme 21). For the first methodology, bispropargylic alcohols with terminal or internal alkyne functionality have been synthesized by the Grignard reaction of diketones with ethynylmagnesium bromide (path a)[91, 92, 109] or via the ring-opening of bisepoxides by butynediol (an industrial waste) (path b).[142] These templates have been further transformed into the corresponding bisαCCs **M1–M4** with yields of 72–95 % by catalytic CO$_2$ fixation *(p***CO2** = 20-100 bar, *T*=25-40 °C) using binary catalysts (CuI/nBu$_4$NPhO or AgOAc/Dave Phos). The Heck approach exploits Dixneuf's catalysts and provides the aromatic bisαCCs **M5** with 45 % yield (path c).[92,134]

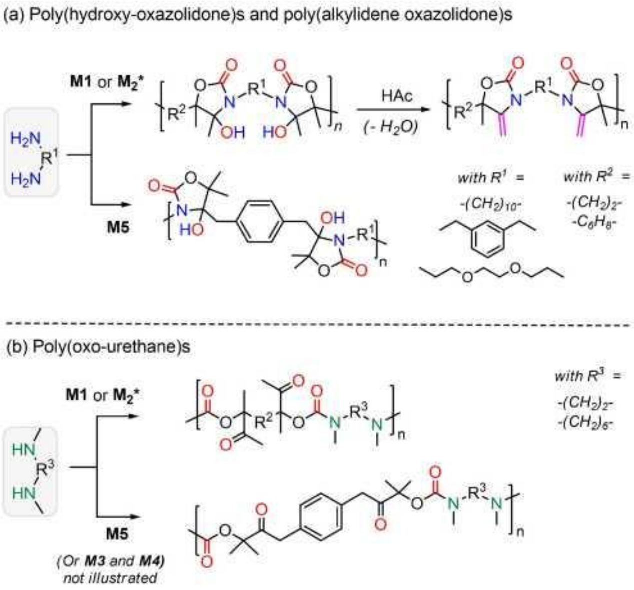
5.2.2. Polyurethanes

Polyurethanes (PU) are key constituents of paints, adhesives, and foams.[143–146] They are industrially produced by the polyaddition of diols to diisocyanates.[147] However, isocyanates are nasty toxic compounds facing restrictive changes in REACH regulations. This urges researchers to develop alternative isocyanate-free routes for their production, for example the transurethanization of dialkylcarbamates, the ring-opening polymerization of cyclic carbamates, and the polyaddition of bicyclic carbonates with diamines.[148] In this context, the reactivity of bisαCCs towards amines provides new opportunities for the design of non-isocyanate polyurethanes under mild conditions.

5.2.2.1. Poly(hydroxy-oxazolidone)s and Poly(oxo-urethane)s

Poly(oxazolidone)s, i.e. polymers characterized by cyclic carbamate repeating linkages, display unique thermal and chemical features making them valuable options for the design of new high-performances materials.[149, 150] Commonly prepared through the thermal copolymerization of epoxides with isocyanates,[151,152] they are now accessible by the r.T. polyaddition of bisαCCs (**M1**, **M2, M5**) to primary diamines under catalyst-free conditions (Scheme 22a).[91, 92] The resulting polymers, showing M_n up to 79 000 gmol ^{1}, differ slightly from conventional polyoxazolidones owing to the presence of additional hydroxyl moieties and undergo facile post dehydration in acetic acid at reflux.[91] This results in poly(α- alkylidene oxazolidone)s with remarkable thermal stability up to 400 °C. By analogy to the transformation of αCCs with primary amines, the polymerization follows the same mechanistic pathways and is accelerated by addition of DBU (5 mol%). However, less reactive or sterically congested diamines, e.g. 1,4- or 1,2-cyclohexanediamine, induce only partial intramolecular cyclization, furnishing chains with randomly distributed hydroxy-oxazolidone and oxourethane linkages. Secondary diamines are also exploited to construct regioregular poly(oxo-urethane)s by r.T. polyaddition with the bisαCCs **M1**–**M5** (Scheme 22b).[92, 142] Structurally, the location of the ketone within or along the polymer backbone is guided by the bisαCC monomer. **M1** and **M2** with terminal exovinylene groups provide the corresponding PUs with pending ketone moieties, while **M3**–**M5** with internal exocyclic olefins promote the ketone insertion within the main skeleton. Linear poly(oxo-urethane)s with M_n from 4000 to 25 000 gmol ^{1} and no noticeable defects were reported.

Scheme 22. Synthesis of poly(hydroxy-oxazolidone)s, poly(alkylidene oxazolidone)s and poly(oxo-urethane)s. * Polymer structure with **M2** not represented.



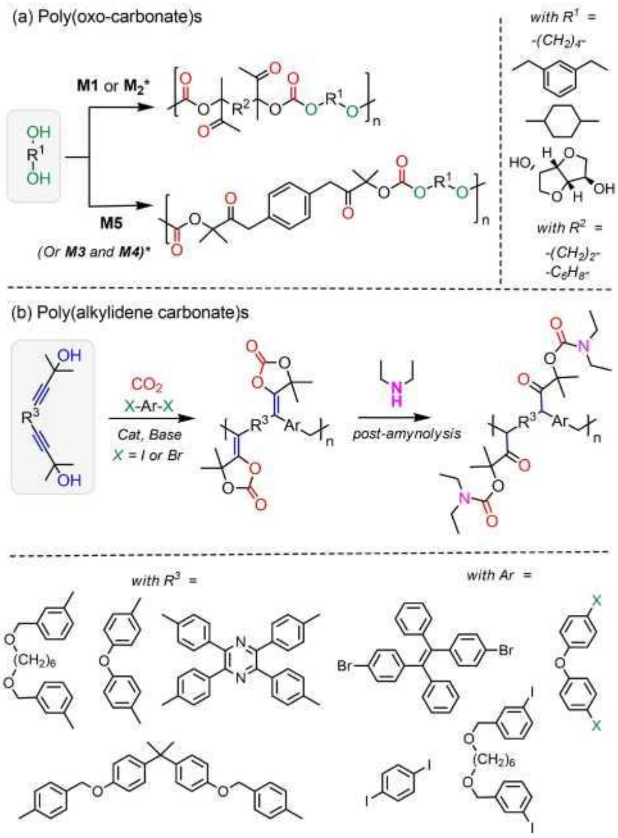
5.2.3. Polycarbonates

Aromatic polycarbonates (PCs) are commodity polymers used mainly in electronics, construction, and the automotive industry. Traditionally they are fabricated by polycondensation of the controversial bisphenol A or other aromatic diols with phosgene or dimethyl (or diphenyl) carbonate. Aliphatic polycarbonates are finding applications in the biomedical sector,[153] as building block (e.g. Cardyon®) for the construction of polyurethane foams,[12, 154] and as solid electrolytes for batteries.[155] They are produced by the ringopening polymerization (ROP) of cyclic carbonates,[155–157] the polycondensation of dialkyl/arylcarbonates with aliphatic diols,[158] and the ring-opening copolymerization (ROCOP) of epoxides with CO_2.[7, 8] Complementary to these approaches, the remarkable reactivity of bisαCCs gives momentum to the facile production of functional PCs.

5.2.3.1. Poly(oxo-carbonate)s and Poly(alkylidene cyclic carbonate)s

Similarly to poly(oxo-urethane)s, bisαCCs **M1–M5** copolymerize with diols via polyaddition to form linear regioregular poly(*oxo*-carbonate)s.[92, 109, 142] This polymerization necessitates a base catalyst (DBU) to activate the alcohols and promote the ring-opening of the cyclic carbonate. Introduced with 1,4-butanediol and **M1** or **M5** monomers, the concept was extended to bio-renewable diols derived from sugar (e.g. isosorbide) and lignin (e.g. 1,4-benzenedimetha- nol, 1,4-cyclohexanediol)[109] and to the utilization of **M3** or **M4** monomers (Scheme 23a).[142] A library of structurally diverse PCs with pending or in-chain ketones, with M_n of 2000 to 27 600 gmol ^{1}, have been fabricated, some of them are semicrystalline with a T_m ranging from 60 to 343 °C. Extension to α,ω-hydroxyl telechelic poly(ethylene glycol) with **M1** has enabled the design of low T_g flexible polymers serving as solid electrolytes for Li-ion batteries.[159] Recent works have also demonstrated that cascade polymerization was possible starting from a bis(propargylic alcohol), CO_2, and a diol at 60 °C and 15 bar using a nBu_4NPhO/AgI binary catalyst.[54] In this case, the bisαCC intermediate was formed in situ and subsequently ring-opened by alcoholysis, furnishing poly(oxo-carbonate) oligomers with M_n < 3000 gmol ^{1} in a one-pot process.

Scheme 23. a) Synthesis of poly(oxo-carbonate)s and b) poly(alkylidene cyclic carbonate)s. * Polymer structure with **M2** not represented.



Inspired by the Heck transformation of αCCs that couples aryl halides with the exocyclic olefin without damaging the structure of the five-membered carbonate ring, Tang has engineered a r.T. three-component cascade process utilizing di- or polyfunctional precursors and atmospheric CO_2 for the synthesis of linear and hyperbranched poly(alkylidene cyclic carbonate)s, i.e. PCs with intact inchain αCCs linkages (Scheme 23b).[160] To do this, various bis(propargylic alcohol), CO_2, and aryl dihalide formulations have been investigated using a PdOAc/LiO^{t}Bu catalyst and delivered chains displaying M_n of ≈ 6000 to 15000 gmol^{-1}. Through the suitable choice of the (poly)aromatic dihalide (binaphthyl halide or tetrakis(4-bromophenyl)methane)), it is possible to introduce chirality within the polymer microstructure as well as aggregation-induced emission properties making the PCs luminescent. Complementarily, the quantitative and regioselective post-polymerization aminolysis by secondary amines can be used to turn these poly(alkylidene cyclic carbonate)s into new poly(oxo-urethane)s.

5.2.4. Sulfur-Containing Polymers

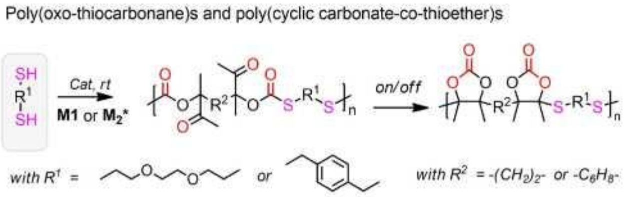
Sulfur is a key element in macromolecular engineering with the possibility to create a vast array of polymers such as poly(thioester)s, poly(thioether)s, poly(thiocarbonate)s, poly(thiourethane)s, and poly(sulfone)s/poly(sulfoxide)s for multiple purposes (biomaterials, vitrimers, self-healing, etc.).[161] Among them, poly(thiocarbonate)s, accessible from the ROCOP of COS or CS_2 with epoxides, are attractive for optics applications due to their high refractive index,[162, 163] and for water purification due to strong metal–sulfur binding.[164,165]

The polyaddition of bisαCC with thiols represents an alternative pathway for the fabrication of these sulfur polymers.[133] Using DBU catalyst (5 mol%) at r.T., novel poly(cyclic carbonate-*co*-thioether)s, with M_n of 16 000 to 75 000 g mol^{-1}, were obtained. By analogy to the thiolysis of αCCs (cf. Section 4.5), it is hypothesized that thiocarbonate linkages are initially formed, but progressively rearrange into the cyclic carbonate linkages during the polymerization. When a fluorinated alcohol (1,3-bis(2-hydroxyhexa- fluoroisopropyl)benzene; 3 mol%) is combined with a reduced amount of DBU (1 mol%), the linkage transformation is slowed down and sulfur polymers enriched in thiocarbonate entities (up to 82 mol%) are prepared (Scheme 24). The modulation of the thiocarbonate/cyclic carbonate linkages strongly influences the thermal properties of the materials. For example, the poly(cyclic carbonate- *co*-thioether) made from **M1** and 1,4-phenylenedimethane- thiol presents a T_g of 126 °C compared to 61 °C for the complementary poly(monothiocarbonate) of similar M_n (≈ 20000 gmol^{-1}) and contains 19 mol% of cyclic carbonate defects within its microstructure. The concept is extended to the DBU-catalyzed terpolymerization of bisαCCs (**M1**) with a mixture of a dithiol and PEGdiol to produce a hybrid polymer containing both oxo-carbonate and cyclic carbonate linkages which can serve as an electrolyte for Li-ion batteries.[166]

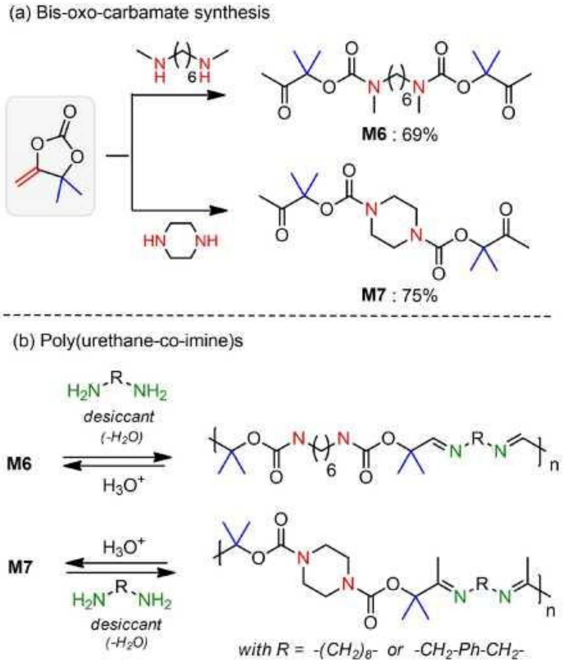
5.3. Polycondensations

Structurally, the carbamates synthesized by the regioselective addition of secondary amines with αCCs bear a ketone functionality (cf. Section 4.1), which like other ketones can be further transformed into imines by dehydrative condensation with primary amines. This feature is exploited by Detrembleur who has designed two novel polymerizable bis- oxo-carbamates by reacting *N,N*-dimethyl-1,6-hexanedi- amine or piperazine with 4-methylene-1,3-dioxolan-2-one at 25 °C (Scheme 25a).[93] Both monomers **M6** and **M7** were collected in 69–75 % yield and served to construct degradable PUs with in-chain pH-sensitive imine bonds by dehydrative polycondensation with a primary aliphatic or aromatic diamine, e.g. 1,8-octanediamine, *m*-xylylenedi- amine. When $Ti(OEt)_4$ was used as a desiccant, chains that are free of structural defects displaying M_n = 3400 to 8300gmol^{-1} were obtained at 60°C in 24 h (Scheme 25b). These materials completely degrade into the native bis(oxo- carbamate)s in 1 h when immersed in an acidic water solution (pH of 1) but the depolymerization rate decreased when the pH was adjusted to 4 and 7.[93]

Scheme 24. Synthesis of sulfur-containing polymers by polyaddition of bisαCCs with dithiols.



Scheme 25. a) Synthesis of new bis-oxo-carbamate monomers and b) access to degradable polyurethanes.



6. *Conclusion and Outlook*

Herein, we have reviewed the advances made in the synthesis of α-alkylidene cyclic carbonates (αCCs) from CO_2, their multiple options for transformation into structurally divergent organic scaffolds, and their brilliant potential for the construction of a broad diversity of novel polymers. The emerging success of αCCs in contemporary sciences highly depends on the catalytic breakthroughs needed to prepare them from CO_2 and propargylic alcohols. The state- of-the-art testifies that a large diversity of highly efficient and selective catalysts have been developed to promote this transformation. However, the lack of standardized protocols to access αCCs makes the benchmarking of the catalyst performance difficult. In this context, we have utilized customized spider charts to highlight the strengths and weaknesses of selected relevant homogeneous systems and propose further guidelines to improve their efficiency.

Single component catalysts including organic bases, taskspecific ionic liquids, and Lewis base–CO_2 adducts generally display moderate to good activity under demanding operative conditions. To overcome these hurdles, high loading or even excess of catalyst are proposed as a means to promote the transformation at milder temperature and/or under low CO_2 pressure. This feature is typically exemplified with ILs that are not only easy to recycle but also offer the benefit of solubilizing high contents of CO_2 which favors the overall CO_2 fixation. Binary catalysts using Ag^I or Cu^I salts in synergy with organic bases are by far more competitive, producing αCCs under milder conditions, even at room temperature and/or atmospheric CO_2. Ways to activate CO_2 (e.g. by using WO_4^{2} ions), and enhance salt dissociation (e.g. by utilizing ketone solvents) or the CO_2 solubility/ concentration within the reaction mixture (e.g. by using fluoro compounds) have been identified as some valuable options to further facilitate the reaction.

When the preparation of αCCs from tertiary propargylic alcohols is envisioned, one recommends the utilization of dual catalytic systems made of a Ag^IX or Cu^IX salt in combination with an organic base (superbase or basic ILs combining ammonium, phosphonium, or imidazolium cations, and carboxylate or phenolate anions). These catalysts are operative under mild conditions (p_{CO2} < 5–20 bar, T = 25-40 °C, t < 24 h) and generally provide the cyclic carbonates with high yields and excellent selectivity. For instance, AgI/[nBu_4N][PhO] is commonly used in our laboratory to produce mono-αCC (product c with R^1,R^2 = CH_3, Scheme 1)[42] or bis-αCCs (products **M1** and **M2**, Scheme 21) at the 10–100 g scale per batch.[109] The catalyst is facile to produce and to handle; however, its recovery and reuse has to be investigated.

Recent trends in catalyst developments rely on the development of heterogeneous systems embedding metal (Ag^0) nanoparticles within or onto porous polymeric or

silica supports. These are complemented by approaches focusing on the metalation of 3D frameworks (MOFs or COFs) with specific channels/cavities, shapes, and sizes or by surface immobilization of metal–nitrogen chelate complexes onto polymers or carbon-based materials. However, most of these systems requires the utilization of additional (large) amount of free bases to display sufficient activity under mild conditions. By now, classifying these catalysts according their performances and making any correlation to their textural properties and type of support is far from trivial. TON numbers, when mentioned, are not calculated under the same similar conditions, preventing us from drawing valuable guidelines to further develop more effective catalysts. Establishing a standardized methodology to calculate these TONs is now an absolute priority for further benchmarking the performances of future heterogeneous catalysts. One may suggest that the introduction of groups favoring host–guest interactions within the cavities or at the surface of the support may increase the catalyst efficiency by increasing locally the CO_2 or propargylic alcohol concentration close to the active sites. Although the fabrication of these MOF- or COF-based catalytic systems requires complex and multiple-step procedures and are far from being sustainable, there is room for improving the synthesis protocols. Moreover, the immobilization of the base additive is now needed to deliver fully heterogeneous systems. We believe that these fully heterogenized catalysts have the potential to be used for the continuous production of αCCs, for instance in flow devices. The purification of the final products (αCCs) will thus be facilitated and the production cost of the process will be minimized, provided that the catalyst does not deactivate significantly during multiple reuse. These fully heterogenized catalysts are thus particularly advantageous over homogeneous ones when large amounts of base are needed to catalyze the reactions.

Nonetheless, most of the homo- and heterogeneous catalysts are mainly efficient for the carboxylative coupling of CO_2 to tertiary propargylic alcohols. Recent findings utilize a smart catalyst made of a silver salt complexed by sterically congested phosphines or an expanded-ring NHC mimicking the "*gem*" effect encountered with tertiary alcohols to allow the transformation of challenging secondary and primary propargylic alcohols. When the large-scale carboxylation of secondary or primary acetylenic alcohols by CO_2 is considered, Ag(OAc)/Dave Phos systems[25] or Er- NHC complexes[26] of Cu^I used in synergy with CsF are currently the best options. They operate under mild conditions (r.T., $p_{CO2} < 15–20$ bar, $t < 24$ h) and provide the corresponding product in moderate to good yields with excellent selectivity. Moreover, when the Dave Phos ligand is modified with hydrophobic alkyl chains, the catalyst can be recycled by liquid–liquid extraction and reused a few times; this is a significant step towards the design of costeffective catalytic processes.[59]

Additional issues still remain unsolved, such as the evaluation of the catalyst toxicity and the sustainable supply of propargylic alcohols from bio-based or waste feedstocks. Currently, various propargylic alcohols are synthesized on the multi-thousand ton scale, for example by BASF, the

world's largest producer of propargylic alcohols, by alkyny- lation of ketones or aldehydes.[167] This company also produces 1,4-butynediol from CaC_2 and formaldehyde,[25] thus valorizing industrial wastes. The sourcing of these important products does not seem a limitation of the technology; however, further reducing their carbon footprint requires the utilization of renewable acetylene and ketones which currently necessitates further developments. Promising solutions are emerging to produce green acetylene, for example by electrochemical reduction of CO_2 and water.[168] It is attractive; however, the process must be optimized to increase yields and selectivity, and should use renewable electricity to decrease the carbon footprint. Ketones and aldehydes can be easily obtained by oxidation of alcohols,[169–172] ubiquitous scaffolds largely found in nature.

αCCs display two reactive sites that are easily discriminated to drive selective transformations, rendering them unique building blocks for organic synthesis and polymer design. The ring-strain release and the keto–enol equilibrium are the main driving forces that facilitate regioselective ring-opening, even at room temperature, by *N*-, *O*-, or *S*-nucleophiles. In reactions with amines, αCCs are converted into (a)cyclic carbamates (oxazolidones and *oxo*carbamates) under catalyst-free conditions or with an added organobase catalyst. With alcohols or thiols, the base is mandatory to produce acyclic (thio)carbonates or tetrasubstituted ethylene carbonates with a (thio)ether moiety. Importantly, these scaffolds are also accessible by the catalytic cascade in multicomponent reactions, in which αCCs are generated in situ prior to further transformation. The scope of ring-opening reactions is further complemented by the use of αCCs as carbonylation agents for vicinal or 1,3-diols and ethanolamines, furnishing five- or six-membered cyclic carbonates and oxazolidones, and as reactive intermediates in acetylenic hydrations to deliver α-hydroxyketones. In addition, the exovinylene moiety was also exploited for the thiol–ene "click" reaction and Heck coupling, further extending the product scope.

Most of these works concern the utility of αCCs for constructing important organic building blocks, not the applications of the resulting compounds. However, since these products are similar to conventional ones (carbamates, carbonates, hydro ketones, etc.), the applications are expected to be similar. This is exemplified by the easy access to oxazolidones, which are templates found in drugs, rendering αCCs attractive building blocks for designing therapeutics. Also, αCCs are efficient carbonylation agents, offering alternatives to toxic phosgene and derivatives, as well as to low-reactivity dialkyl- or diarylcarbonates.

The extension of this αCC chemistry to polymer synthesis is in its infancy; however, a diversity of functional polymers (polyurethanes, polycarbonates, polyvinyls and sulfur-containing polymers) are now easily accessible under mild operating conditions. First, the reactivity of the exovinylene moiety towards radicals is exploited for producing polymers bearing cyclic carbonates by (controlled) radical polymerization. Hydrolysis or aminolysis of the cyclic carbonate groups has given access to multiple modification possibilities, enlarging the scope of functional polymers. For instance, polyethylene bearing polar 1,2-diol groups are now accessible by copolymerizing αCCs with ethylene followed by hydrolysis of the cyclic carbonate hydrolysis, opening new perspectives in the preparation of polar polyolefins. Second, the facile regioselective ring-opening of αCCs by various nucleophiles has been utilized to furnish various regioregular polymers by step-growth copolymerization of bis(α-alkylidene cyclic carbonate)s (bisαCCs) with (biobased) nucleophilic co-monomers (i.e. diamines, diols, or dithiols). Remarkably, from a given bisαCC, five different polymer microstructures were prepared via the selection of the nucleophilic co-monomer, and from a given bisαCC/ nucleophile pair, the type of polymer linkages can be modulated on demand by the choice of the catalyst.

As most of the polymers accessible from (bis)- exovinylene cyclic carbonates are produced by conventional polymerization methods virtually compatible with existing industrial equipment, their cost will mainly depend on the production cost of the monomers and on the ability to easily and efficiently recycle the catalyst. Much effort must thus be devoted to utilizing cost-effective propargylic alcohols and to developing efficient routes to recycle the catalysts. We have to emphasize that most of the polymerizations involving (bis)exovinylene cyclic carbonates are performed under mild operating conditions (25 °C, ambient atmosphere), which is beneficial to decrease the carbon footprint of the process in comparison to the conventional procedures that involve high temperatures and vacuum, e.g. for the preparation of polycarbonates by polycondensation.

Currently, the sourcing of the bispropargylic alcohols remains the main bottleneck to accessing a wide range of bisαCCs monomers at reasonable cost and large volume in order to scale up the technology. Recent contributions by BASF have shown that the cheap bulk chemical 1,4- butynediol can be used to produce bisαCCs, which should contribute to accelerating the developments in the field.[25] Many questions still remain unanswered. For example, how can we design high-molar-mass polymers? What are the properties of these materials? How can we increase the range of bisαCCs from biosourced or waste chemical products? These answers are essential to define the scope of applications, e.g. for foams, adhesives, biomaterials, packaging, etc. Some poly(carbonate)s prepared by this αCC chemistry have already been evaluated as solid electrolytes for lithium-ion batteries working at room temperature with excellent cycling performance[159, 166] and for luminescent materials.[160] Isocyanate-free polyurethanes that are degradable on-demand by using pH as a trigger[93] and that present a high thermal stability[91] have also been developed.[173] It is important to note that not enough data are currently available to fairly compare the properties of the polymers prepared from αCCs to those obtained by the conventional techniques. They are also structurally different, e.g. αCC- based polycarbonates contain pendant or in-chain ketone groups, poly(oxazolidone)s contain hydroxyl moieties—functionalities that are difficult to obtain in a direct way by the conventional techniques. The properties of the new polymers are thus expected to be different; however, further investigation is needed here.

In conclusion, we have highlighted the extremely rich αCC chemistry that is expected to be impactful in the fields of organic and polymer chemistry as a multitude of important chemical groups can be easily installed mostly by 100 % atom economy reactions under mild operating conditions. This chemistry is no longer a curiosity and new products are expected in the next future in view of the recent patents of Henkel and BASF.[174–178]

Acknowledgements

The authors thank the "Fonds National pour la Recherche Scientifique" (F.R.S.-FNRS) and the Fonds Wetenschappe- lijk Onderzoek–Vlaanderen (FWO) for financial support in the frame of the Excellence of Science (EOS) project n° O019618F (ID EOS: 30902231) and for the support of the F.R.S-FRIA fellowship to C. Ngassam Tounzoua. C.D. thanks FNRS for financing the CO$_2$Switch project. The authors thank Robin Deprez and Arthur Detrembleur for coding the spider charts.

Conflict of Interest

The authors declare no conflict of interest.

References

[1] A. Dibenedetto, F. Nocito, *ChemSusChem* **2020**, *13*, 6219– 6228.
[2] E. C. Ra, K. Y. Kim, E. H. Kim, H. Lee, K. An, J. S. Lee, *ACS Catal.* **2020**, *10*, 11318–11345.
[3] X. Jiang, X. Nie, X. Guo, C. Song, J. G. Chen, *Chem. Rev.* **2020**, *120*, 7984–8034.
[4] M. Alves, B. Grignard, R. Méreau, C. Jérôme, T. Tassaing, C. Detrembleur, *Catal. Sci. Technol.* **2017**, *7*, 2651–2684.
[5] L. Guo, K. J. Lamb, M. North, *Green Chem.* **2021**, *23*, 77–118.
[6] V. Aomchad, À. Cristofol, F. Della Monica, B. Limburg, V. D'Elia, A. W. Kleij, *Green Chem.* **2021**, *23*, 1077–1113.
[7] A. J. Kamphuis, F. Picchioni, P. P. Pescarmona, *Green Chem.* **2019**, *21*, 406–448.
[8] B. Grignard, S. Gennen, C. Jerome, A. W. Kleij, C. Detrem- bleur, *Chem. Soc. Rev.* **2019**, *48*, 4466–4514.
[9] R. R. Shaikh, S. Pornpraprom, V. D'Elia, *ACS Catal.* **2018**, *8*, 419–450.
[10] F. D. Bobbink, A. P. van Muyden, P. J. Dyson, *Chem. Com- mun.* **2019**, *55*, 1360–1373.
[11] P. Rollin, L. K. Soares, A. M. Barcellos, D. R. Araujo, E. J. Lenardao, R. G. Jacob, G. Perin, *Appl. Sci.* **2021**, *11*, 5024.
[12] J. H. Jang, J. H. Ha, I. Kim, J. H. Baik, S. C. Hong, *ACS Omega* **2019**, *4*, 7944–7952.
[13] M. DeBolt, A. Kiziltas, D. Mielewski, S. Waddington, M. J. Nagridge, *J. Appl. Polym. Sci.* **2016**, *133*, 44086.
[14] D. H. Lee, J. H. Ha, I. Kim, J. H. Baik, S. C. Hong, *J. Polym. Environ.* **2020**, *28*, 1160–1168.
[15] C. J. Whiteoak, N. Kielland, V. Laserna, E. C. Escudero- Adan, E. Martin, A. W. Kleij, *J. Am. Chem. Soc.* **2013**, *135*, 1228–1231.
[16] J. Huang, C. Jehanno, J. C. Worch, F. Ruipérez, H. Sardon, A. P. Dove, O. Coulembier, *ACS Catal.* **2020**, *10*, 5399–5404.
[17] N. Kindermann, T. Jose, A. W. Kleij, *Top. Curr. Chem.* **2017**, *375*, 1–28.
[18] A. Brege, R. Méreau, K. McGehee, B. Grignard, C. Detrem- bleur, C. Jerome, T. Tassaing, *J. CO2 Util.* **2020**, *38*, 88–98.
[19] T. M. McGuire, E. M. Lopez-Vidal, G. L. Gregory, A. Buchard, *J. CO2 Util.* **2018**, *27*, 283–288.
[20] M. Honda, M. Tamura, K. Nakao, K. Suzuki, Y. Nakagawa, K. Tomishige, *ACS Catal.* **2014**, *4*, 1893–1896.
[21] W. Li, D. Huang, Y. Lyu, *Org. Biomol. Chem.* **2016**, *14*, 10875–10885.
[22] R. Méreau, B. Grignard, A. Boyaval, C. Detrembleur, C. Jerome, T. Tassaing, *ChemCatChem* **2018**, *10*, 956–960.
[23] Y. Yuan, Y. Xie, C. Zeng, D. Song, S. Chaemchuen, C. Chen, F. Verpoort, *Green Chem.* **2017**, *19*, 2936–2940.
[24] M. E. Jung, G. Piizzi, *Chem. Rev.* **2005**, *105*, 1735–1766.
[25] S. Dabral, B. Bayarmagnai, M. Hermsen, J. Schießl, V. Mormul, A. S. K. Hashmi, T. Schaub, *Org. Lett.* **2019**, *21*, 1422–1425.
[26] A. Cervantes-Reyes, K. Farshadfar, M. Rudolph, F. Ro- minger, T. Schaub, A. Ariafard, A. S. K. Hashmi, *Green Chem.* **2021**, *23*, 889–897.
[27] C. Bruneau, P. H. Dixneuf, *J. Mol. Catal.* **1992**, *74*, 97–107.
[28] J. Fournier, C. Bruneau, P. H. Dixneuf, *Tetrahedron Lett.* **1989**, *30*, 3981–3982.
[29] Y. Kayaki, M. Yamamoto, T. Ikariya, *J. Org. Chem.* **2007**, *72*, 647–649.
[30] J. Hu, J. Ma, Q. Zhu, Q. Qian, H. Han, Q. Mei, B. Han, *Green Chem.* **2016**, *18*, 382–385.
[31] N. Della Ca', B. Gabriele, G. Ruffolo, L. Veltri, T. Zanetta, M. Costa, *Adv. Synth. Catal.* **2011**, *353*, 133–146.
[32] A. Boyaval, R. Méreau, B. Grignard, C. Detrembleur, C. Jerome, T. Tassaing, *ChemSusChem* **2017**, *10*, 1241–1248.
[33] Y. Kayaki, M. Yamamoto, T. Ikariya, *Angew. Chem. Int. Ed.* **2009**, *48*, 4194–4197; *Angew. Chem.* **2009**, *121*, 4258–4261.
[34] A.-H. Liu, Y.-L. Dang, H. Zhou, J.-J. Zhang, X.-B. Lu, *ChemCatChem* **2018**, *10*, 2686–2692.
[35] H. Zhou, G.-X. Wang, X.-B. Lu, *Asian J. Org. Chem.* **2017**, *6*, 1264–1269.
[36] Y.-B. Wang, D.-S. Sun, H. Zhou, W.-Z. Zhang, X.-B. Lu, *Green Chem.* **2014**, *16*, 2266–2272.
[37] H. Zhou, R. Zhang, X.-B. Lu, *Adv. Synth. Catal.* **2019**, *361*, 326–334.

[38] Y.-B. Wang, Y.-M. Wang, W.-Z. Zhang, X.-B. Lu, *J. Am. Chem. Soc.* **2013**, *135*, 11996–12003.
[39] I. Tommasi, F. Sorrentino, *Tetrahedron Lett.* **2009**, *50*, 104– 107.
[40] H. Zhou, G.-X. Wang, W.-Z. Zhang, X.-B. Lu, *ACS Catal.* **2015**, *5*, 6773–6779.
[41] Y. Zhao, Y. Wu, G. Yuan, L. Hao, X. Gao, Z. Yang, B. Yu, H. Zhang, Z. Liu, *Chem. Asian J.* **2016**, *11*, 2735–2740.
[42] B. Grignard, C. Ngassam Tounzoua, S. Gennen, B. Gilbert, R. Mereau, C. Jerome, T. Tassaing, C. Detrembleur, *ChemCatChem* **2018**, *10*, 2584–2592.
[43] J. Qiu, Y. Zhao, Z. Li, H. Wang, M. Fan, J. Wang, *ChemSusChem* **2017**, *10*, 1120–1127.
[44] Y. Wu, Y. Zhao, R. Li, B. Yu, Y. Chen, X. Liu, C. Wu, X. Luo, Z. Liu, *ACS Catal.* **2017**, *7*, 6251–6255.
[45] K. Chen, G. Shi, R. Dao, K. Mei, X. Zhou, H. Li, C. Wang, *Chem. Commun.* **2016**, *52*, 7830–7833.
[46] K. Ueno, H. Tokuda, M. Watanabe, *Phys. Chem. Chem. Phys.* **2010**, *12*, 1649–1658.
[47] O. Nordness, J. F. Brennecke, *Chem. Rev.* **2020**, *120*, 12873– 12902.
[48] Y. Sasaki, *Tetrahedron Lett.* **1986**, *27*, 1573–1574.
[49] Y. Inoue, J. Ishikawa, M. Taniguchi, H. Hashimoto, *Bull. Chem. Soc. Jpn.* **1987**, *60*, 1204–1206.
[50] S. Sun, B. Wang, N. Gu, J.-T. Yu, J. Cheng, *Org. Lett.* **2017**, *19*, 1088–1091.
[51] M. Li, S. Abdolmohammadi, M. S. Hoseininezhad-Namin, F. Behmagham, E. Vessally, *J. CO2 Util.* **2020**, *38*, 220–231.
[52] Y. Gu, F. Shi, Y. Deng, *J. Org. Chem.* **2004**, *69*, 391–394.
[53] Y. Hu, J. Song, C. Xie, H. Wu, T. Jiang, G. Yang, B. Han, *ACS Sustainable Chem. Eng.* **2019**, *7*, 5614–5619.
[54] C. Ngassam Tounzoua, B. Grignard, A. Brege, C. Jerome, T. Tassaing, R. Mereau, C. Detrembleur, *ACS Sustainable Chem. Eng.* **2020**, *8*, 9698–9710.
[55] Q.-W. Song, L.-N. He, *Adv. Synth. Catal.* **2016**, *358*, 1251– 1258.
[56] Q.-W. Song, B. Yu, X.-D. Li, R. Ma, Z.-F. Diao, R.-G. Li, W. Li, L.-N. He, *Green Chem.* **2014**, *16*, 1633–1638.
[57] Y. Yuan, Y. Xie, C. Zeng, D. Song, S. Chaemchuen, C. Chen, F. Verpoort, *Catal. Sci. Technol.* **2017**, *7*, 2935–2939.
[58] Q.-W. Song, W.-Q. Chen, R. Ma, A. Yu, Q.-Y. Li, Y. Chang, L.-N. He, *ChemSusChem* **2015**, *8*, 821–827.
[59] C. Johnson, S. Dabral, P. Rudolf, U. Licht, A. S. K. Hashmi, T. Schaub, *ChemCatChem* **2021**, *13*, 353–361.
[60] J. Qiu, Y. Zhao, H. Wang, G. Cui, J. Wang, *RSC Adv.* **2016**, *6*, 54020–54026.
[61] X. Zhang, K.-H. Chen, Z.-H. Zhou, L.-N. He, *ChemCatChem* **2020**, *12*, 4825–4830.
[62] M. Cui, Q. Qian, Z. He, J. Ma, X. Kang, J. Hu, Z. Liu, B. Han, *Chem. Eur. J.* **2015**, *21*, 15924–15928.
[63] X. Yu, Z. Yang, F. Zhang, Z. Liu, P. Yang, H. Zhang, B. Yu, Y. Zhao, Z. Liu, *Chem. Commun.* **2019**, *55*, 12475–12478.
[64] Z. Yang, B. Yu, H. Zhang, Y. Zhao, Y. Chen, Z. Ma, G. Ji, X. Gao, B. Han, Z. Liu, *ACS Catal.* **2016**, *6*, 1268–1273.
[65] Z.-Z. Yang, Y. Zhao, H. Zhang, B. Yu, Z. Ma, G. Ji, Z. Liu, *Chem. Commun.* **2014**, *50*, 13910–13913.
[66] C. Xie, J. Song, H. Wu, Y. Hu, H. Liu, Y. Yang, Z. Zhang, B. Chen, B. Han, *Green Chem.* **2018**, *20*, 4655–4661.
[67] D. Chakraborty, P. Shekhar, H. D. Singh, R. Kushwaha, C. P. Vinod, R. Vaidhyanathan, *Chem. Asian J.* **2019**, *14*, 4767–4773.
[68] S. S. Islam, S. Biswas, R. Ali Molla, N. Yasmin, S. M. Islam, *ChemNanoMat* **2020**, *6*, 1386–1397.
[69] S. Li, Y. Xu, Y. Chen, W. Li, L. Lin, M. Li, Y. Deng, X. Wang, B. Ge, C. Yang, S. Yao, J. Xie, Y. Li, X. Liu, D. Ma, *Angew. Chem. Int. Ed.* **2017**, *56*, 10761–10765; *Angew. Chem.* **2017**, *129*, 10901–10905.
[70] N. Zheng, G. D. Stucky, *J. Am. Chem. Soc.* **2006**, *128*, 14278– 14280.
[71] J. Zhang, H. Wang, L. Wang, S. Ali, C. Wang, L. Wang, X. Meng, B. Li, D. S. Su, F.-S. Xiao, *J. Am. Chem. Soc.* **2019**, *141*, 2975–2983.
[72] B. Petrovic, M. Gorbounov, S. Masoudi Soltani, *Microporous Mesoporous Mater.* **2021**, *312*, 110751.
[73] S. S. Rao, S. P. Gejji, *J. Phys. Chem. A* **2016**, *120*, 1243–1260.
[74] Z. Zhang, H. Gao, H. Wu, Y. Qian, L. Chen, J. Chen, *ACS Appl. Nano Mater.* **2018**, *1*, 6463–6476.
[75] X. Tang, C. Qi, H. He, H. Jiang, Y. Ren, G. Yuan, *Adv. Synth. Catal.* **2013**, *355*, 2019–2028.
[76] H. F. Jiang, A. Z. Wang, H. L. Liu, C. R. Qi, *Eur. J. Org. Chem.* **2008**, 2309–2312.
[77] S. S. Islam, N. Salam, R. A. Molla, S. Riyajuddin, N. Yasmin, D. Das, K. Ghosh, S. M. Islam, *J. Mol. Catal.* **2019**, *477*, 110541.
[78] Z. Zhou, C. He, L. Yang, Y. Wang, T. Liu, C. Duan, *ACS Catal.* **2017**, *7*, 2248–2256.
[79] L. Yang, Y. Dou, Z. Zhou, D. Zhang, S. Wang, *Nanomaterials* **2019**, *9*, 1566.
[80] J. Bao, S. Wu, X. Xu, L. Huang, L. Zhang, J. Kim, X. Zhou, Y. Chen, H. Ji, Z. Huang, *Dalton Trans.* **2020**, *49*, 2403–2406.
[81] G. Zhang, H. Yang, H. Fei, *ACS Catal.* **2018**, *8*, 2519–2525.
[82] R. Das, C. M. Nagaraja, *Inorg. Chem.* **2020**, *59*, 9765–9773.
[83] S.-L. Hou, J. Dong, X.-L. Jiang, Z.-H. Jiao, B. Zhao, *Angew. Chem. Int. Ed.* **2019**, *58*, 577–581; *Angew. Chem.* **2019**, *131*, 587–591.
[84] Z. Wu, X. Lan, Y. Zhang, M. Li, G. Bai, *Dalton Trans.* **2019**, *48*, 11063–11069.
[85] H.-R. Tian, Z. Zhang, S.-M. Liu, T.-Y. Dang, Z. Li, Y. Lu, S.- X. Liu, *Green Chem.* **2020**, *22*, 7513–7520.
[86] Z. Shi, J. Jiao, Q. Han, Y. Xiao, L. Huang, M. Li, *J. Mol. Catal.* **2020**, *496*, 111190.
[87] H. Babad, A. G. Zeiler, *Chem. Rev.* **1973**, *73*, 75–91.
[88] Y. Ren, S. A. L. Rousseaux, *J. Org. Chem.* **2018**, *83*, 913–920.
[89] S. Yoganathan, S. J. Miller, *Org. Lett.* **2013**, *15*, 602–605.
[90] A. K. Ghosh, M. Brindisi, *J. Med. Chem.* **2015**, *58*, 2895–2940.
[91] T. Habets, F. Siragusa, B. Grignard, C. Detrembleur, *Macromolecules* **2020**, *53*, 6396–6408.
[92] S. Gennen, B. Grignard, T. Tassaing, C. Jerome, C. Detrem- bleur, *Angew. Chem. Int. Ed.* **2017**, *56*, 10394–10398; *Angew.*

Chem. **2017**, *129*, 10530–10534.

[93] S. Gennen, B. Grignard, C. Jérôme, C. Detrembleur, *Adv. Synth. Catal.* **2019**, *361*, 355–365.

[94] S. Arshadi, E. Vessally, A. Hosseinian, S. Soleimani-amiri, L. Edjlali, *J. CO2 Util.* **2017**, *21*, 108–118.

[95] J. Fournier, C. Bruneau, P. H. Dixneuf, *Tetrahedron Lett.* **1990**, *31*, 1721–1722.

[96] H. Liu, R. Hua, *Tetrahedron* **2016**, *72*, 1200–1204.

[97] Q. Zhang, F. Shi, Y. Gu, J. Yang, Y. Deng, *Tetrahedron Lett.* **2005**, *46*, 5907–5911.

[98] Y. Gu, Q. Zhang, Z. Duan, J. Zhang, S. Zhang, Y. Deng, *J. Org. Chem.* **2005**, *70*, 7376–7380.

[99] H. Jiang, J. Zhao, A. Wang, *Synthesis* **2008**, 763–769.

[100] H.-F. Jiang, J.-W. Zhao, *Tetrahedron Lett.* **2009**, *50*, 60–62.

[101] J. X. Xu, J. W. Zhao, Z. Bin Jia, *Chin. Chem. Lett.* **2011**, *22*, 1063–1066.

[102] C. Bruneau, P. H. Dixneuf, *Tetrahedron Lett.* **1987**, *28*, 2005– 2008.

[103] H.-S. Kim, J.-W. Kim, S.-C. Kwon, S.-C. Shim, T.-J. Kim, *J. Organomet. Chem.* **1997**, *545–546*, 337–344.

[104] Q.-W. Song, P. Liu, L.-H. Han, K. Zhang, L.-N. He, *Chin. J. Chem.* **2018**, *36*, 147–152.

[105] Q.-N. Zhao, Q.-W. Song, P. Liu, K. Zhang, J. Hao, *ChemistrySelect* **2018**, *3*, 6897–6901.

[106] L. Fan, J. Wang, X. Zhang, S. M. Sadeghzadeh, R. Zhiani, M. Shahroudi, F. Amarloo, *Catal. Lett.* **2019**, *149*, 3465–3475.

[107] J. M. Joumier, J. Fournier, C. Bruneau, P. H. Dixneuf, *J. Chem. Soc. Perkin Trans. 1* **1991**, 3271–3274.

[108] J. M. Joumier, C. Bruneau, P. H. Dixneuf, *J. Chem. Soc. Perkin Trans. 1* **1993**, 1749–1751.

[109] F. Siragusa, E. Van Den Broeck, C. Ocando, A. J. Müller, G. De Smet, B. U. W. Maes, J. De Winter, V. Van Speybroeck, B. Grignard, C. Detrembleur, *ACS Sustainable Chem. Eng.* **2021**, *9*, 1714–1728.

[110] Q.-W. Song, Q.-N. Zhao, J.-Y. Li, K. Zhang, P. Liu, *Synthesis* **2019**, *51*, 739–746.

[111] J. Li, Q. Song, H. Zhang, P. Liu, K. Zhang, J. Wang, D. Zhang, *Tetrahedron* **2019**, *75*, 2343–2349.

[112] J. Hu, J. Ma, L. Lu, Q. Qian, Z. Zhang, C. Xie, B. Han, *ChemSusChem* **2017**, *10*, 1292–1297.

[113] Z.-H. Zhou, Q.-W. Song, J.-N. Xie, R. Ma, L.-N. He, *Chem. Asian J.* **2016**, *11*, 2065–2071.

[114] P. Hoyos, J.-V. Sinisterra, F. Molinari, A. R. Alcantara, P. Domínguez de María, *Acc. Chem. Res.* **2010**, *43*, 288–299.

[115] M. Kutscheroff, *Ber. Dtsch. Chem. Ges.* **1881**, *14*, 1540–1542.

[116] R. J. Thomas, K. N. Campbell, G. F. Hennion, *J. Am. Chem. Soc.* **1938**, *60*, 718–720.

[117] Y. Zhao, Z. Yang, B. Yu, H. Zhang, H. Xu, L. Hao, B. Han, Z. Liu, *Chem. Sci.* **2015**, *6*, 2297–2301.

[118] H. He, C. Qi, X. Hu, Y. Guan, H. Jiang, *Green Chem.* **2014**, *16*, 3729–3733.

[119] D. Li, Y. Gong, M. Du, C. Bu, C. Chen, S. Chaemcheun, J. Hu, Y. Zhang, Y. Yuan, F. Verpoort, *ACS Sustainable Chem. Eng.* **2020**, *8*, 8148–8155.

[120] Z. Zhou, X. Zhang, Y. Huang, K. Chen, L. He, *Chin. J. Catal.* **2019**, *40*, 1345–1351.

[121] S. Xia, Y. Song, X. Li, H. Li, L.-N. He, *Mol.* **2018**, *23*, 3033.

[122] Q.-W. Song, Z.-H. Zhou, M.-Y. Wang, K. Zhang, P. Liu, J.-Y. Xun, L.-N. He, *ChemSusChem* **2016**, *9*, 2054–2058.

[123] X.-D. Li, Q.-W. Song, X.-D. Lang, Y. Chang, L.-N. He, *ChemPhysChem* **2017**, *18*, 3182–3188.

[124] M. Du, Y. Gong, C. Bu, J. Hu, Y. Zhang, C. Chen, S. Chaemchuen, Y. Yuan, F. Verpoort, *J. Catal.* **2021**, *393*, 70– 82.

[125] X.-D. Li, Y. Cao, R. Ma, L.-N. He, *J. CO2 Util.* **2018**, *25*, 338– 345.

[126] C. Bu, Y. Gong, M. Du, C. Chen, S. Chaemchuen, J. Hu, Y. Zhang, H. Díaz Velázquez, Y. Yuan, F. Verpoort, *Catal.* **2021**, *11*, 233.

[127] Z. H. Zhou, Q. W. Song, L. N. He, *ACS Omega* **2017**, *2*, 337– 345.

[128] J.-Y. Li, L.-H. Han, Q.-C. Xu, Q.-W. Song, P. Liu, K. Zhang, *ACS Sustainable Chem. Eng.* **2019**, *7*, 3378–3388.

[129] H. Zhou, H. Zhang, S. Mu, W.-Z. Zhang, W.-M. Ren, X.-B. Lu, *Green Chem.* **2019**, *21*, 6335–6341.

[130] P. Chauhan, S. Mahajan, D. Enders, *Chem. Rev.* **2014**, *114*, 8807–8864.

[131] J. Clayden, P. MacLellan, *Beilstein J. Org. Chem.* **2011**, *7*, 582–595.

[132] L. A. Damani, *Sulphur-Containing Drugs and Related Organic Compounds: Chemistry, Biochemistry and Toxicology, Vol. 3, Pt.A, Metabolism and Pharmokinetics of Sulphur- Containing Drugs.*, Ellis Horwood, Chichester, **1989**.

[133] F. Ouhib, B. Grignard, E. Van Den Broeck, A. Luxen, K. Robeyns, V. Van Speybroeck, C. Jerome, C. Detrembleur, *Angew. Chem. Int. Ed.* **2019**, *58*, 11768–11773; *Angew. Chem.* **2019**, *131*, 11894–11899.

[134] P. Toullec, A. Carbayo Martin, M. Gio-Batta, C. Bruneau, P. H. Dixneuf, *Tetrahedron Lett.* **2000**, *41*, 5527–5531.

[135] T. K. Hayes, A. J. Freyer, M. Parvez, S. M. Weinreb, *J. Org. Chem.* **1986**, *51*, 5501–5503.

[136] Y. Inoue, Y. Itoh, I.-F. Yen, S. Imaizumi, *J. Mol. Catal.* **1990**, *60*, L1–L3.

[137] I. Cho, T.-W. Lee, *Die Makromol. Chem., Rapid Commun.* **1989**, *10*, 453–456.

[138] B. Ochiai, Y. Sano, T. Endo, *J. Netw. Polym. Jpn.* **2005**, *26*, 132–137.

[139] J. Demarteau, A. Debuigne, C. Detrembleur, *Chem. Rev.* **2019**, *119*, 6906–6955.

[140] P. B. V. Scholten, J. Demarteau, S. Gennen, J. De Winter, B. Grignard, A. Debuigne, M. A. R. Meier, C. Detrembleur, *Macromolecules* **2018**, *51*, 3379–3393.

[141] P. B. V. Scholten, G. Cartigny, B. Grignard, A. Debuigne, H. Cramail, M. A. R. Meier, C. Detrembleur, *ACS Macro Lett.* **2021**, *10*, 313–320.

[142] S. Dabral, U. Licht, P. Rudolf, G. Bollmann, A. S. K. Hashmi, T. Schaub, *Green Chem.* **2020**, *22*, 1553–1558.

[143] D. M. Segura, A. D. Nurse, A. McCourt, R. Phelps, A. Segura, in *Adhes. Sealants*, Elsevier, Amsterdam, **2005**, pp. 101–162.

[144] F. E. Golling, R. Pires, A. Hecking, J. Weikard, F. Richter, K. Danielmeier, D. Dijkstra, *Polym. Int.* **2019**, *68*, 848–855.

[145] F. Monie, T. Vidil, B. Grignard, H. Cramail, C. Detrembleur, *Mater. Sci. Eng. R* **2021**, *145*, 100628.
[146] J. Peyrton, L. Avérous, *Mater. Sci. Eng. R* **2021**, *145*, 100608.
[147] E. Delebecq, J.-P. Pascault, B. Boutevin, F. Ganachaud, *Chem. Rev.* **2013**, *113*, 80–118.
[148] L. Maisonneuve, O. Lamarzelle, E. Rix, E. Grau, H. Cramail, *Chem. Rev.* **2015**, *115*, 12407–12439.
[149] S. R. Sandler, *J. Appl. Polym. Sci.* **1969**, *13*, 2699–2703.
[150] V. Sendijarevic, A. Sendijarevic, K. C. Frisch, P. Reulen, *Polym. Compos.* **1996**, *17*, 180–186.
[151] T. Pelzer, B. Eling, H.-J. Thomas, G. A. Luinstra, *Eur. Polym. J.* **2018**, *107*, 1–8.
[152] M. Kitayama, Y. Isda, F. Odaka, S. Anzai, K. Irako, *Rubber Chem. Technol.* **1980**, *53*, 1–13.
[153] W. Yu, E. Maynard, V. Chiaradia, M. C. Arno, A. P. Dove, *Chem. Rev.* **2021**, *121*, 10865–10907.
[154] J. Langanke, A. Wolf, J. Hofmann, K. Böhm, M. A. Subhani, T. E. Müller, W. Leitner, C. Gürtler, *Green Chem.* **2014**, *16*, 1865–1870.
[155] J. Zhang, J. Yang, T. Dong, M. Zhang, J. Chai, S. Dong, T. Wu, X. Zhou, G. Cui, *Small* **2018**, *14*, 1800821.
[156] J. Xu, E. Feng, J. Song, *J. Appl. Polym. Sci.* **2014**, *131*, 39822.
[157] S. M. Guillaume, *Eur. Polym. J.* **2013**, *49*, 768–779.
[158] J. H. Park, J. Y. Jeon, J. J. Lee, Y. Jang, J. K. Varghese, B. Y. Lee, *Macromolecules* **2013**, *46*, 3301–3308.
[159] F. Ouhib, L. Meabe, A. Mahmoud, N. Eshraghi, B. Grignard, J.-M. Thomassin, A. Aqil, F. Boschini, C. Jerome, D. Mecerreyes, C. Detrembleur, *J. Mater. Chem. A* **2019**, *7*, 9844–9853.
[160] B. Song, T. Bai, X. Xu, X. Chen, D. Liu, J. Guo, A. Qin, J. Ling, B. Z. Tang, *Macromolecules* **2019**, *52*, 5546–5554.
[161] P. T. X. Zhang, *Sulfur-Containing Polymers: From Synthesis to Functional Materials*, Wiley-VCH, Weinheim, **2021**.
[162] M. Luo, X.-H. Zhang, B.-Y. Du, Q. Wang, Z.-Q. Fan, *Polym. Chem.* **2015**, *6*, 4978–4983.
[163] L.-F. Hu, Y. Li, B. Liu, Y.-Y. Zhang, X.-H. Zhang, *RSC Adv.* **2017**, *7*, 49490–49497.
[164] K. R. Henke, *Water Environ. Res.* **1998**, *70*, 1178–1185.
[165] M. M. Matlock, K. R. Henke, D. A. Atwood, *J. Hazard. Mater.* **2002**, *92*, 129–142.
[166] F. Ouhib, L. Meabe, A. Mahmoud, B. Grignard, J.-M. Thomassin, F. Boschini, H. Zhu, M. Forsyth, D. Mecerreyes, C. Detrembleur, *ACS Appl. Polym. Mater.* **2020**, *2*, 922–931.
[167] https://chemicals.basf.com/global/en/Intermediates/Product_ groups/acetylenic-alcohols.html.
[168] J. M. McEnaney, B. A. Rohr, A. C. Nielander, A. R. Singh, L. A. King, J. K. Nørskov, T. F. Jaramillo, *Sustainable Energy Fuels* **2020**, *4*, 2752–2759.
[169] M. N. Kopylovich, A. P. C. Ribeiro, E. C. B. A. Alegria, N. M. R. Martins, L. M. D. R. S. Martins, A. J. L. Pombeiro, *Adv. Organomet. Chem.* **2015**, *63*, 91-174.
[170] K. Rajabimoghadam, Y. Darwish, U. Bashir, D. Pitman, S. Eichelberger, M. A. Siegler, M. Swart, I. Garcia-Bosch, *J. Am. Chem. Soc.* **2018**, *140*, 16625–16634.
[171] C. Parmeggiani, C. Matassini, F. Cardona, *Green Chem.* **2017**, *19*, 2030–2050.
[172] Q. Mei, H. Liu, Y. Yang, H. Liu, S. Li, P. Zhang, B. Han, *ACS Sustainable Chem. Eng.* **2018**, *6*, 2362–2369.
[173] B. Song, A. Qin, B. Z. Tang, *Cell Rep. Phys. Sci.* **2022**, *3*, 100719.
[174] K.-H. ela, Roberto; Kinzelmann, Hans-Georg; Garcia-Mir- alles, Jose; Kamm, Thomas; Seggewiss, Patrick; Hartmann, Olaf; Licht, Ulrike; Leonhardt, Viktoria; Mormul, Verena; Schumacher, *One Component Moisture Curable Composition Containing Exo-Vinylene Cyclic Carbonate Compounds for Coatings, Sealants or Adhesives*, WO 2018162205 A1 20180913, **2018**.
[175] G. Hartmann, Olaf; Garcia-Miralles, Jose; Kinzelmann, Hans- Georg; Struempf, Svenja; Kutter, Juliane; Licht, Ulrike; Leonhardt, Viktoria; Mormul, Verena; Schumacher, KarlHeinz; Boerzsoenyi, *Two-Component Composition Based on Compounds with at Least Two Exo-Vinylene Cyclic Carbonate Units*, WO 2018054609 A1 20180329, **2018**.
[176] D. Licht, Ulrike; Schumacher, Karl-Heinz; Klopsch, Rainer; Ghislieri, *Copolymer Made from Cyclic Exo-Vinyl Carbonate Acrylates*, WO 2016202652 A1 20161222, **2016**.
[177] S. Schaub, Thomas; Rudolf, Peter; Licht, Ulrike; Mormul, Verena; Dabral, *Monomers Comprising at Least One 4-(2-Oxyethylidene)-1,3-Dioxolan-2-One Unit and Use Thereof*, WO 2019219469 A1 20191121, **2019**.
[178] C. Schaub, Thomas; Rudolf, Peter; Licht, Ulrike; Hashmi, A. Stephen K.; Dabral, Saumya; Johnson, *Process for Preparing Cyclic Carbonates with an Exocyclic Vinylidene Group*, WO 2021144162 A1 20210722, **2021**.