Sustainable Conversion of Carbon Dioxide: The Advent of Organocatalysis

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The conversion of carbon dioxide (CO_2), an abundant renewable carbon reagent, into chemicals of academic and industrial interest is of imminent importance to create a higher degree of sustainability in chemical processing and production. Recent progress in this field is characterised by a plethora of organic molecules able to mediate the conversion of suitable substrates in the presence of CO_2 into a variety of value-added commodities with advantageous features combining cost-effectiveness, metal-free transformations and general substrate activation profiles. In this review, the latest developments are discussed in the field of CO_2 catalysis with a focus on organo-mediated conversions and their increasing importance as to serve as practicable alternatives for metal-based processes. Also a critical assessment of the state-of-the-art is presented with attention on those features that need further attention to lift the usefulness of organocatalysis in the production of organic molecules of potential commercial interest.

1. Introduction

Our current chemical needs depend highly on the availability of fossil fuels as feed stock. Predictions have been made that somewhere in the near future we will be running out of these reserves and/or their immediate availability can no longer fulfil the increasing global demand for these raw materials. As such, contemporary chemists are facing a huge challenge to develop more sustainable alternatives for chemical production. Carbon dioxide is a waste product from all combustion processes and represents a potential and alternative carbon feed stock[1,2] for the preparation of a variety of useful chemicals including MeOH,[3,4] urea,[5] lactones,[6] various heterocycles,[7-11] biodegradable polymers,[12-16] and carboxylated structures[17-21] among others.[22-24] In particular, direct CO_2 utilisation for the preparation of polycarbonates, poly(ether)carbonates and polyurethanes is a viable technology to access novel tailor-made CO_2-based materials.[25] The development of cost- and energy-efficient synthetic methodologies to exploit CO_2 as a C_1 synthon could eventually loosen the grip on our fossil fuel dependence, contributing to a reduction of the overall CO_2 emissions and offering tangible alternatives to physical sequestration methods.[26,27]

In nature, CO_2 is captured, converted and/or reduced to carbohydrates by a series of cascade reactions carried out by specific metalloenzymes present in photosynthetic organisms.[28] Similarly, the field of CO_2 conversion catalysis is dominated by the use of transition *metal*-based catalysts being either heterogeneous or homogeneous in nature.[29-32] While the use of a catalytic system generally implies a sustainability improvement, some marked differences can be foreseen between choosing metal-based or organo-catalysts. It has been shown that activation and/or stabilization of substrates/intermediates through metal complexes or immobilized metal species *via* coordination motifs is far more efficient compared with organo-based catalytic mediators. Organocatalysts, on the other hand, are generally low cost, non-toxic molecules, characterized by a good stability and inertness towards moisture and air. As such, from a reaction design point of view, they can be regarded as safer reaction components. Moreover, in some cases, they can be readily derived from renewable feed stocks, devising technically and economically practicable *ad hoc* procedures starting from biomass and CO_2, thus eventually developing "carbon-neutral" processes to produce sustainable chemicals, fuels, and materials.[33]

It is known that organocatalysis can sometimes lead to additional energy expenditure during reaction and work-up time, requiring higher catalyst loadings, higher operating temperatures and prolonged reaction times. Nevertheless, in some cases, (*e.g.* when using ionic liquids as reaction solvents and/or catalysts) the reagents/products can be recovered by simple distillation

devising more safe and atom-economical processes while avoiding commonly employed waste generating work-up procedures. Catalyst heterogenation has been extensively exploited to increase the lifetime of organo-catalyst simplifying reaction monitoring and work-up procedures, while providing a possible route towards the development of continuous flow reactions. Organocatalysis is especially advantageous to develop metal-free products or processes, since the incorporation of chemicals into consumer products require that the amount of metal residues to be present as low as possible to avoid any toxicity issues. Since these requirements are becoming more stringent by the year, alternative processes that can circumvent the use of metal catalysts would provide a means to produce targeted chemicals in a safer and potentially greener way. In this respect, organo-based catalysts (*i.e.*, organocatalysts) are of growing interest and importance in the area of CO_2 catalysis and conversion. Recently, the pace with which organocatalytic procedures are being utilized in organic preparations that involve CO_2 as a key reagent is unquestionably increasing. There are a number of structurally different organocatalyst systems that are considered as catalytic mediator including those based on ionic liquids (ILs),[33-35] *N*-heterocyclic carbenes (NHCs),[36] phenolic compounds[37] and sophisticated azaphosphatranes.[38] This is a true testimony of the increasing prominence of organocatalysis in the area of CO_2 fixation to create value-added organic matter from a waste material.

This review intends to showcase the most recent developments in CO_2 catalysis where organocatalytic systems have helped to increase the overall sustainability of the process in terms of more efficient energy usage, raw material conversion, avoiding solvent and/or metals and improvement of selectivity/reactivity features. A complete overview of all the literature is not feasible and therefore avoided; instead, the key contributions in specific areas of CO_2 research are highlighted. Also, a critical evaluation of the reported organocatalytic methodologies is a requisite for comparison with metal-based systems. This may help to identify, where possible, improvements that lead to a more widespread use of organocatalysts in CO_2 conversion. Other excellent reviews focusing on the use of hetero- and/or homogenous catalyst systems have recently appeared,[4,7-10,18,19,39-42] and may serve as a reference point.

In the first section, attention is given to the various activation modes that are the basis for the organocatalytic transformations. Hereafter, the main types of organocatalysed CO_2 coupling reactions are discussed followed by a section on the latest developments concerning new types of reactivity.

2. Activation modes of organocatalysts

Organocatalysis has become an essential tool for synthetic organic chemists as testified by the variety of organocatalysed organic transformations that can be performed with high chemo-, regio- and enantio-selectivities.[43-45] Although the currently available CO_2 conversion reactions are relatively simple from a chemical reactivity point of view, the continuous development of new and more efficient metal- and/or organo-catalysis is essential due to the kinetic inertness of CO_2. Although the array of available organo-catalysed CO_2 valorisation reactions is expanding constantly, currently the field is dominated by reductive and non-reductive coupling processes (see Figure 1).
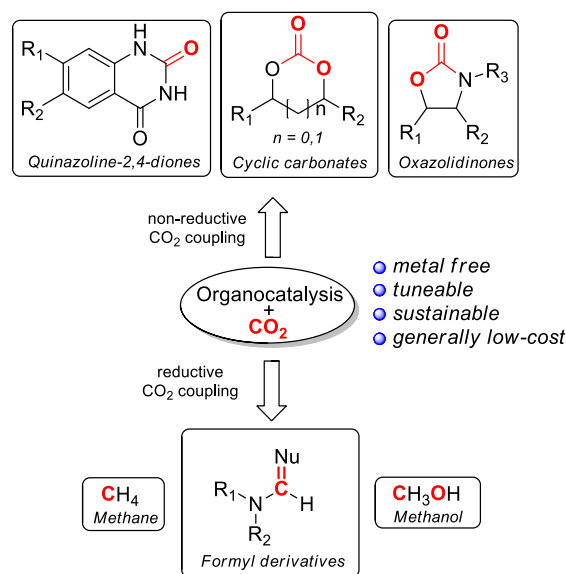

Fig. 1 CO_2 transformations mediated by organocatalysts.

Up to now, the reported organocatalysts active in CO_2 conversion catalysis can be roughly divided into three distinct categories: (1) nitrogen-based heterocycles (including organic bases and *N*-heterocyclic carbenes, NHCs); (2) organic salts, molten salts and ionic liquids (ILs); and (3) (poly)phenolic and poly-alcohol compounds. Most of these catalysts are active in a small series of CO_2 based synthetic processes which are illustrated in Figure 1. Beside the established heterocyclic synthesis based on CO_2 coupling to epoxides and aziridines (Figure 1, top), organocatalysis has also proved to be particularly attractive for CO_2 reduction (Figure 1, bottom). However, depending on the type of reaction (non-reductive *vs.* reductive coupling), the mechanistic hypothesis and the role of the catalyst can be quite different.

Similarly to what has been reported for metal-based catalysts, insights into the operative mechanism of organocatalysed CO_2/epoxide coupling reactions to afford cyclic carbonates have shown that the role of the catalytic species can be either (a) direct CO_2 activation; (b) activation of high energy co-reactants (*e.g.*, epoxides, aziridines, oxetanes and azetidines); or (c) dual activation of both CO_2 and the associated high-energy reactant as summarised in Scheme 1. Evidence of a dual activation mechanism has been seldom reported for CO_2 conversion catalysts; notable examples include polyoxometalate based systems developed by Mizuno[46] and Leitner,[47] respectively. While a general reactivity pattern may be readily derived for organocatalysed non-reductive CO_2 coupling reactions, a general mechanism for reductive CO_2 couplings has not yet been defined given the different reducing agents employed.
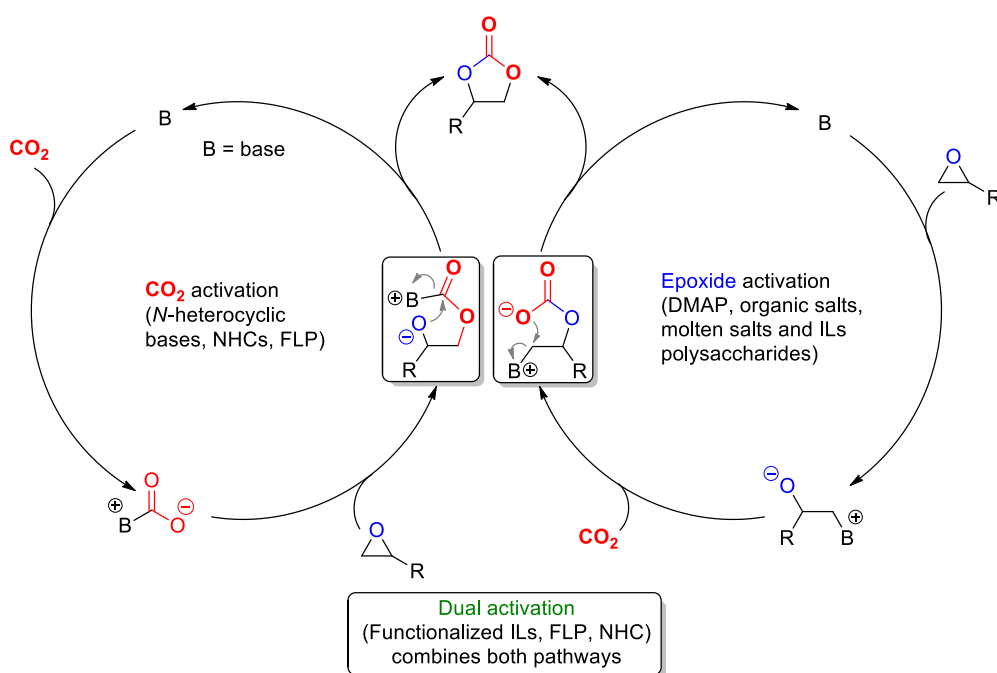
Scheme 1 General organocatalytic activation modes for the synthesis of cyclic carbonates from epoxides and CO_2.

2.1. Organic *N*-heterocyclic bases

Organic bases are probably the simplest organocatalysts studied in the context of CO_2 conversion as a result of their availability and structural diversity including alkyl/aryl mono- and polyamines, *N*-heterocyclic derivatives and amidine– and guanidine–like structures. So far, these compounds have proven to be useful in the epoxide/CO_2 couplings and reduction of CO_2 to methanol. Concerning the scope of this review, the most important class of organic bases reported to date are based on *N*-heterocyclic scaffolds, particularly the structures depicted in Figure 2.

The most commonly employed and effective organic catalysts for CO_2 valorisation are 4-dimethylamino-pyridine (DMAP) and amidine- and guanidine-derived superbases. Given the differences in Lewis basicity strength, the catalytic role of these two classes of compounds is quite different. DMAP has proven to be an efficient homogeneous[48] and heterogeneous[49] catalyst for the synthesis of cyclic carbonates from epoxides, even though high operating temperatures (120 ºC) and relatively high CO_2 pressures (17–40 bar) were required; however, in presence of Lewis acid co-catalysts such as phenols, this dual catalytic system showed a good catalytic activity for the preparation of cyclic carbonates from epoxides.[37,50] A definitive mechanism for the activation by DMAP has not been elucidated yet. One mechanistic hypothesis relies on the sole activation of the epoxide as depicted in Scheme 1. An

alternative mechanism based on a dual activation mode that involves both the epoxide and the CO_2 molecule has also been postulated.[50]
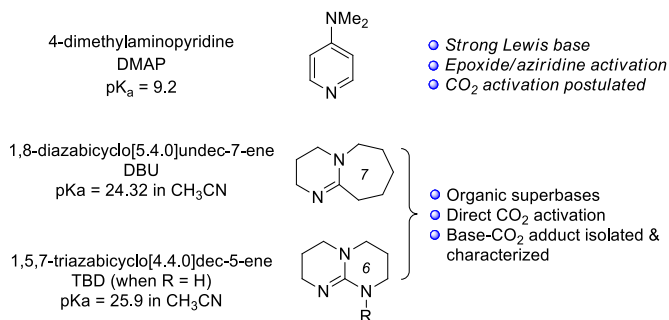

Fig. 2 *N*-heterocyclic bases commonly employed as organocatalysts. Note that the reactivity generally is higher when the pKa value is lower.

On the other hand, organic superbases such as DBU, TBD and *N*-methyl TBD (MTBD) (Figure 2) have been extensively employed as catalysts for CO_2 coupling reactions. As a typical example, Sartori *et al.* reported the use of MTBD as the sole catalyst for the synthesis of cyclic carbonates from CO_2 and epoxides.[51] When using both homogeneous and heterogeneous silica-supported MTBD catalysts, different terminal and internal epoxides were converted to the corresponding cyclic carbonate with good to excellent yield (60-98%) and high chemo-selectivities (90-98%) although the reaction conditions were quite harsh (T = 140 ºC, $p(CO_2)$ = 50 bar). Catalyst heterogenisation has been exploited as a straight-forward, feasible way to address recyclability issues and to work under milder conditions (T = 50 ºC),[52,53] while the addition of a co-catalyst has been generally shown to improve reaction rates, yields and selectivities. Recently, renewable based molecules such as cellulose, were successfully employed as co-catalytic mediators for the synthesis of cyclic carbonates.[54]

The catalytic role of guanidine-derived organic superbases is not limited to non-reductive CO_2 coupling reactions: these compounds are currently conquering a prominent role as CO_2 catalysts for the synthesis of methanol by reductive coupling of CO_2 with organosilanes[55] and organoboranes.[56] Regardless of the hydride donor employed, formation of a superbase-CO_2 salt is crucial to start the catalytic cycle forming a catalytically active CO_2 complex (Scheme 2).
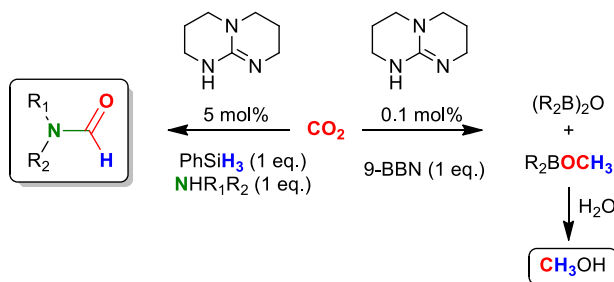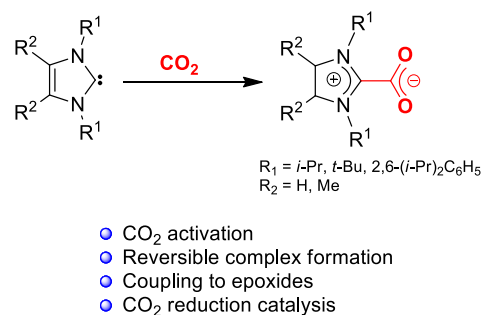

Scheme 2 CO_2 reduction catalysed by TBD.

Whether involved in catalytic CO_2 coupling or CO_2 reduction processes, the catalytic cycle involving superbases generally starts with an initial "coordination" of the CO_2 molecule. Stable organic superbase-CO_2 adducts have been isolated and fully characterized,[57,58] thus providing experimental proof that this class of compounds is capable of direct interaction with CO_2.

2.2. *N*-heterocyclic carbenes (NHCs)

Since their first isolation by Arduengo in 1991, NHCs have proved to be versatile ligands for homogeneous metal catalysis and organocatalysis.[59] Being highly nucleophilic in nature, NHCs need to bind suitable electrophiles to form air- and moisture-stable adducts: a classic example is the formation of a zwitterionic NHC–CO_2 adducts (Scheme 3).[60] These adducts are labile in solution, making them suitable for catalytic turnover.

R$_1$ = i-Pr, t-Bu, 2,6-(i-Pr)$_2$C$_6$H$_5$
R$_2$ = H, Me

○ CO_2 activation
○ Reversible complex formation
○ Coupling to epoxides
○ CO_2 reduction catalysis

Scheme 3 NHC-CO_2 adduct formation.

NHC-promoted CO_2 activation allows for CO_2 coupling reactions with high-energy reaction partners, including the preparation of cyclic carbonates and oxazolidinones from epoxides and aziridines,[61,62] respectively, and the synthesis of α-methylene-carbonates and α-methylene-oxazolidinones from propargylic alcohols.[62,63]

To further improve catalyst lifetime and recyclability, NHC-based catalysts have been heterogenised. When NHC scaffolds (Scheme 3; R[1] = i-Pr, R[2] = H) were grafted onto a silica MCM-41 support, the resultant catalyst was active towards cyclic carbonate formation at 0.5 mol % catalyst loading under relatively mild conditions (T = 120 ºC, $p(CO_2)$ = 20 bar, t = 24–48 h), whereas this supported catalyst was also used for the synthesis of oxazolidinones under even milder conditions (T = 80-100 ºC) affording N-substituted oxazolidinones in excellent yields.[64] A different NHC (R$_1$ = 2,6(i-Pr)$_2$C$_6$H$_5$; R$_2$ = H) was covalently embedded within a tubular, micro-porous organic network. When using this heterogeneous catalytic system, propylene oxide (PO) was quantitatively converted to propylene carbonate in 10 h with a catalyst load of only 0.065 mol % (Yield = 92%; TOF = 142 s$^-$^{1}, T = 160 ºC, $p(CO_2)$ = 30 bar).[65]

Since their catalytic activity is based on direct CO_2 activation, NHCs were also the first class of organocatalysts to show catalytic activity towards CO_2 reduction with different reduction partners, including mild reducing agents such as silanes. Cascade reactions have been reported in the presence of both a silane reductant (including polymethylhydrosiloxane (PHMS, an industrial by-product) and appropriate nucleophiles (amines, anilines, imines, hydrazines, hydrazones, N-heterocycles), thus employing CO_2 as a versatile C$_1$ synthon for the preparation of, *inter alia*, formamidine derivatives (Scheme 4).[23,66]
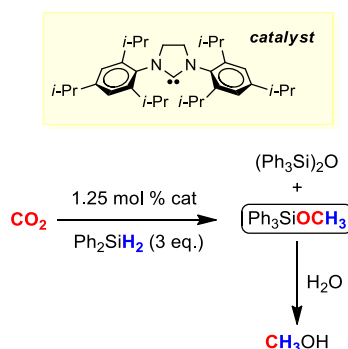
Scheme 4 CO_2 reduction catalysed by a NHC catalyst.

2.3. Catalysis by organic salts and ionic liquids

As highlighted in detail in a recent review by Kerton *et al.*,[32] the use of organic salts/ionic liquids as organocatalysts for CO_2 conversion has come a long way since the seminal work of Caló *et al.* published in 2002.[67] These catalysts have almost exclusively been employed for the coupling of CO_2 with strained heterocycles such as epoxides and aziridines. Their nucleophilic character mediates the ring-opening of the heterocycles while stabilizing the ring-opened alkoxide intermediate by ion-pairing interactions with the cationic part of the salt/IL.[68] Beside commercially available quaternary ammonium[68-70] and phosphonium halide salts,[69,71-73] a number of phosphonium,[74] imidazolium,[75-77] pyridinium,[76] pyrrolidinium[78] and superbases[10,79] derived ILs (including those based on DABCO, DBU and TBD; Figure 4) have also been prepared and employed as CO_2 coupling catalysts obtaining with, in some cases, excellent results in terms of conversion and selectivity. It is generally assumed that catalysis occurs through an

epoxide/aziridine activation pathway (Scheme 1, right), however, depending on the chosen anion/cation combination some peculiar behaviour has been observed.
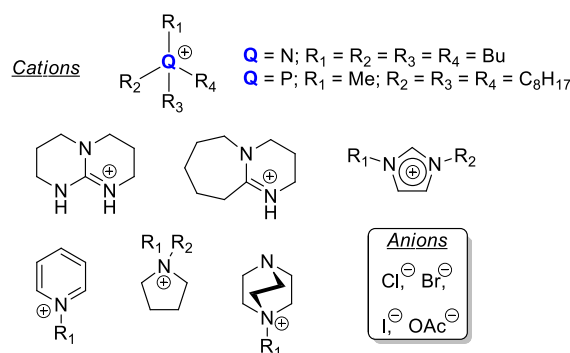

Fig. 4 Quaternary ammonium/iminium salts and ILs used as catalysts for CO_2 coupling reactions.

In most reported cases, the heterocycle/CO_2 coupling product can be recovered quantitatively from the reaction mixture by simple distillation. To address catalyst stability/recyclability issues, efforts have been made to develop heterogeneous IL-based catalysts including silica-supported,[72,80,81] co-polymerized,[73,82-84] PEG-ylated[85] and dendrimeric ILs.[86,87] Moreover, task-specific hydroxy-[88,89] and carboxy-functionalized ILs[90,91] have been designed, synthesized and tested as catalysts. These ILs have shown improved activity, mainly due to more efficient epoxide activation through H-bonding interactions (Scheme 5), and subsequently have been developed in their heterogeneous form.[81,92-94]
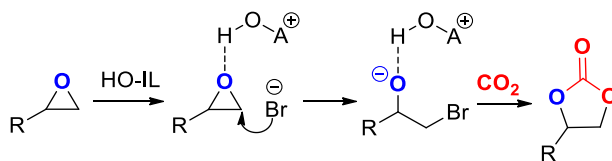
Scheme 5 Proposed mechanism for the activation of epoxides by hydroxy-functionalised ILs.

Direct CO_2 activation has also been achieved with Frustrated Lewis Pairs (FLPs), *i.e.* molecular systems incorporating Lewis acid and Lewis base functions which cannot interact directly due to steric constraints and/or backbone rigidity.[95] Their mechanism of action, as illustrated in Scheme 6 for aryl-bridged phosphine-borane FLPs, involves CO_2 binding and formation of a zwitterionic carboxylated FLP adduct.[96] Depending on the reaction partner, FLPs can be catalytically active towards CO_2 coupling to epoxides[97] or, in presence of an appropriate reducing agent, *i.e.* trialkylsilanes, towards its reduction.[98] Interestingly, up to date organo-catalysed reduction of CO_2 to methane has only been achieved in presence of an FLP catalyst[99] demonstrating their exceptional catalytic potential in CO_2 conversion catalysis.
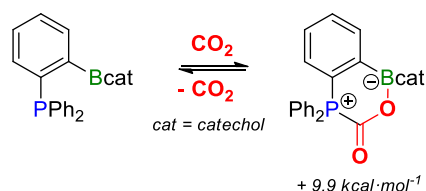
Scheme 6 CO_2 activation by FLPs: reversible activation of CO_2 by an aryl-bridged phosphine-borane ambiphilic molecule.

2.4. Phenolic and polyhydroxy compounds

This broad class of organocatalysts is quite attractive since most of them are naturally occurring or readily available from renewable resources. The term "polyhydroxy" compounds refers to several structurally different compounds (Figure 5) including pyrogallol,[100] linear non-conjugated polyols[101] and polysaccharides.[102-106] Due to their potential to form an (extended) hydrogen-bond network upon activation of the substrate, these catalysts have been employed almost exclusively for epoxide/CO_2 coupling reactions. This activation mechanism (*vide infra*) can be applied to all hydroxyl and polyhydroxy compounds, including the polysaccharide-based catalytic systems (cellulose, CMC and chitosan). In general, their catalytic behaviour is based on epoxide activation through the formation an H-bonding intermediate or network as for hydroxyl-functionalised ILs (Scheme 5).
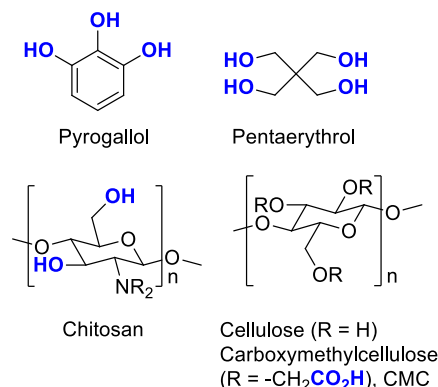

Fig. 5 Phenolic, polyhydroxy- and polysaccharide-based organocatalysts for CO_2 coupling reactions.

The extent of the H-bonding network depends on the type of polyhydroxy catalyst chosen. Generally, halide salts or organic bases are required as co-catalytic additives to ensure efficient catalysis. In the case of polysaccharides, however, the co-catalyst moiety can be embedded within the polysaccharide backbone by direct quaternization of the biopolymer, thus resulting in a bifunctional catalyst system. Polysaccharides (cellulose, carboxymethylcellulose (CMC) and chitosan) are particularly interesting for practical applications: they are easily obtained from renewable resources and they can be further functionalized by physical and chemical methods to improve the overall catalytic activity. These functionalization methods are based on the impregnation of ILs, electrostatic interactions with ILs,[102] organic superbases[54] or covalent incorporation of nucleophilic moieties within the macromolecular catalyst.[103,104,107] The possibility of multiple interactions between the catalyst and the substrates is exemplified in Scheme 7 for a heterogeneous chitosan catalyst functionalized with imidazolium moieties.[103]

3. Heterocyclic structures based on CO_2

Heterocyclic structures that incorporate a "carbonate" or "carbamate" fragment as highlighted in Scheme 8, can serve as valuable monomers of polyurethanes and polycarbonates, drugs, electrolytes or reagents in a wide range of chemical transformations,[108-112] and therefore have attracted a great deal of interest in industrial and academic research. The most elegant way of producing these heterocyclic scaffolds involves coupling reactions of CO_2 with readily available epoxides or aziridines in the presence of a suitable catalyst. One should keep in mind that non-exclusive selectivity in the ring-opening step of a mono-substituted aziridine may result in two regio-isomeric structures. However, virtually one isomeric form (generally the 5-substituted oxazolidinone) may be obtained when suitable reaction parameters and catalysts are used.
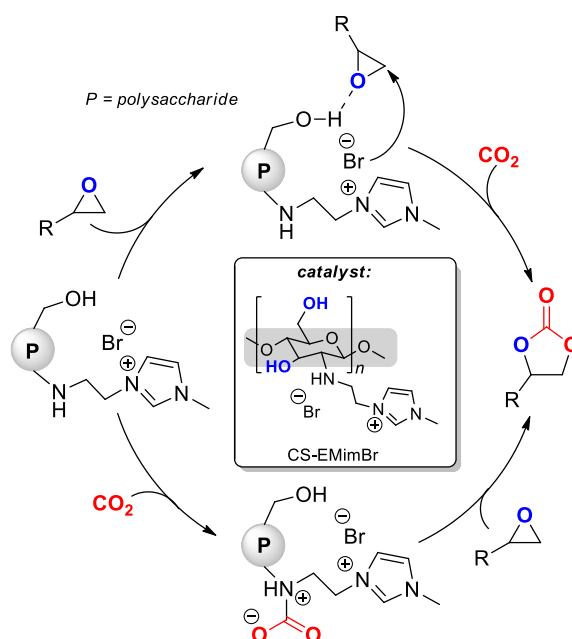
Scheme 7 Proposed mechanism for CS-EMIm-Br catalysed CO_2 coupling reactions. CS stands for cellulose and EMIm-Br for an imidazolium bromide unit.
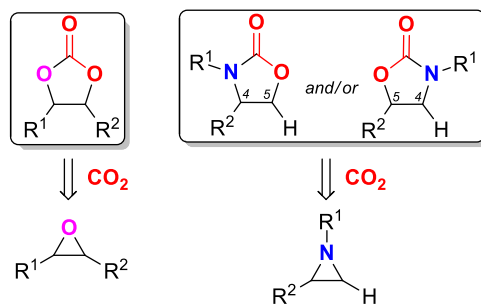
Scheme 8 Preparation of heterocyclic structures from the reactions of CO_2 and epoxides or aziridines.

Undoubtedly, ILs are the most widely studied organocatalysts for the formation of heterocyclic structures from CO_2 which has been reviewed in detail by Kerton and co-workers recently.[32] In this review, most of the ionic organocatalysts reported in the last eight years were listed and discussed, ranging from simple "onium" species to supported IL catalysts. In order to avoid unnecessary duplication, only some selected examples of IL catalysts are discussed here in the context of heterocyclic synthesis using CO_2.


activation of CO_2 and epoxide

○ 1 mol% cat, 120 °C, $p(CO_2)$ = 1-10 bar
○ complementary system
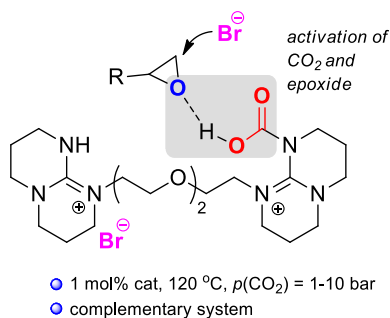
Scheme 9 PEG-bridged TBD as catalyst for CO_2-epoxides coupling reaction. PEG = polyethyleneglycol.

For instance, He's group reported[85] on the use of poly-ethylene-glycol (PEG) bridged basic ionic liquids: the most important structural feature is an ethylene glycol that ties two quaternary 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD) units (Figure 2, Scheme 9). These TBD units are known to interact with CO_2 to form an activated carbamate intermediate that may activate an epoxide substrate through H-bonding. Nucleophilic ring-opening of the activated epoxide may then easily occur using a bromide nucleophile providing a complementary activation pathway. The attack of the carbamate unit on the ring-opened epoxide (*i.e.*, an alkoxide) produces a hemi-carbonate that after ring-closure leads to a cyclic carbonate. This work is exemplary for the majority of the organocatalytic promoters reported to date: compared to metal based catalysts, the substrate activation potential is lower, generally requiring higher reaction temperatures for efficient catalytic turnover. However, despite this kinetic drawback, most organocatalysts are readily available and accessible from cheap and relatively non-toxic scaffolds.

A large improvement on the kinetic limitation in the organocatalyzed conversion of epoxides and CO_2 was provided by a pyrogallol (1,2,3-trihydroxybenzene) based binary catalyst comprising Bu_4NI.[100] Pyrogallol is a commercially available polyphenol and its excellent catalytic performance is a result of the adjacent nature of the phenolic groups. As with many other systems, the mode of activation of the epoxide substrate is through hydrogen-bonding. The three phenol units are all being involved in the stabilization of key intermediates (Scheme 10). Interestingly, the synthesis of the cyclic carbonate products could be done under highly mild conditions (T = 25–45 °C, $p(CO_2)$ = 10 bar), providing a low net CO_2 emission reaction setup. When compared to a previously reported metal based catalytic system, comprising of a Lewis acidic Zn(salphen) catalyst and using Bu_4NI as co-catalyst[113] employed under similar conditions (*i.e.*, MEK as solvent, T = 45 °C, $p(CO_2)$ = 10 bar, t = 18 h), both the metal based and organocatalytic systems showed similar activities: when using 2 mmol of 1,2-epoxyhexane as substrate in 5 mL of MEK, quantitative conversion to the corresponding cyclic carbonate (conversion > 99%) was observed with Zn(salphen)/Bu_4NI (both 2.5 mol%) as well as with pyrogallol/Bu_4NI (both 5.0 mol%). This simple comparison is further evidence of the exceptional potential of pyrogallol as a CO_2 coupling catalyst, exhibiting activities comparable to metal-based systems.

At a later stage,[114] a bifunctional, polystyrene-supported version of this pyrogallol catalyst was also successfully applied under comparable mild conditions with the advantage that the catalyst could be efficient recycled producing a more stable system and producing thus higher turnovers. Additionally, this organocatalysis protocol allowed for a multi-substrate campaign with minimal cross-contamination upon recycling the supported catalyst. These pyrogallol based catalysts are probably among the most active reported to date considering the low operating temperatures that are required. Other examples of phenol/catechol-mediated synthesis of cyclic carbonates have also appeared in recent literature,[37,115] though being generally less efficient compared to the aforementioned pyrogallol systems.
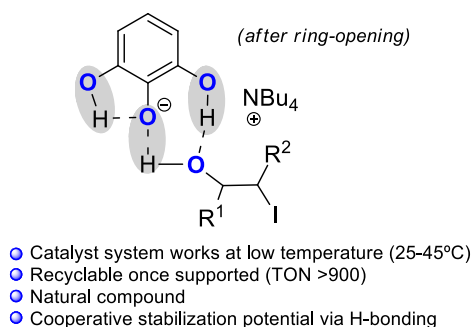

Scheme 10 Stabilization of a key intermediate through hydrogen-bonding involved in the synthesis of cyclic carbonates.

Dufaud *et al.*[116] recently developed a green method using azaphosphatranes as catalysts. This method allows for the efficient coupling of epoxides and CO_2 at 80 °C and atmospheric pressure of CO_2 using a 0.1 mol % of catalyst loading. Azaphosphatranes can be considered structurally tunable catalysts, and as such their catalytic activity can be optimised by changing the substituents attached to the peripheral *N*-atoms (R, Scheme 11). Whereas the presence of methyl substituents (R = Me) results in catalyst degradation during the reaction, bulkier R substituents such as *p*-methoxybenzyl and *neo*-pentyl result in azaphosphatranes with increased stability, thus developing longer-lived systems. Detailed optimization of the reaction conditions showed that the azaphosphatrane bearing *p*-methoxybenzyl groups exhibits the highest catalytic activity.

Insights into the reaction mechanism were provided on the basis of a series of detailed kinetic studies with the reaction between styrene oxide (SO) and CO_2 serving as a benchmark model. From the kinetic data it was deduced that SO first forms an adduct through a hydrogen-bond to the cationic P center. This first step is then followed by insertion of the CO_2 into the P–N bond, resulting in an unusual tricyclic phosphoryl- carbamate intermediate which is highly reactive and sensitive toward hydrolysis (Scheme 11). This intermediate can be stabilized more efficiently by bulkier R groups and the reaction then proceeds to the

product *via* a nucleophilic attack of the chloride anion, and subsequent attack of the resultant alkoxide species on the activated CO_2.

Given the low kinetic stability of the tricyclic phosphorylcarbamate intermediate in the absence of any steric protection, the same authors have come up with an alternative, successful strategy to stabilize this intermediate and to avoid degradation of the catalyst through encapsulation by means of self-assembly giving a nano-cage.[38] Thus, several hemicryptophane-caged azaphosphatranes were designed and tested in the coupling reaction of CO_2 and epoxide under reasonably mild conditions (T = 100 ^{o}C; $p(CO_2)$ = 1 bar; 0.1 mol % of catalyst loading) taking the corresponding non-caged catalysts as references. Indeed, the encapsulated azaphosphatrane systems showed much better catalytic activity and higher stability when compared to the corresponding non-caged catalysts. This study on supramolecular catalysis also provided new evidence concerning the previously proposed mechanism involving the simultaneous dual activation of the epoxide and CO_2.[116] The hemicryptophane was carefully chosen as a building block to construct the cages. This aspect deserves to be highlighted as it allowed the use of only 0.1 mol % of catalyst, although most of the known supramolecular catalysts suffer from product inhibition and have to be used in *stoichiometric* amounts. This strong structure-activity correlation sheds light on the design of new advanced, supramolecular catalysts for the synthesis of heterocyclic carbonates from CO_2.


R = bulky (p-methoxybenzyl)
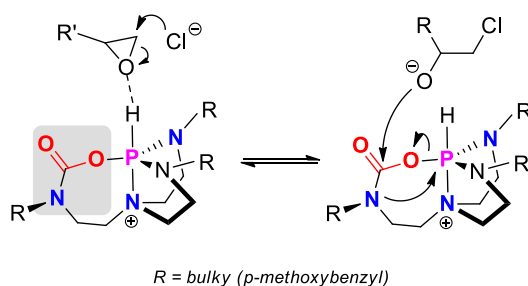
Scheme 11 Azaphosphatranes acting as catalysts in the coupling reaction between CO_2 and epoxides.

Alternative organocatalytic methodologies make use of NHCs and their derivatives as catalysts in the reaction of CO_2 and epoxides. Ikariya *et al.*[62] reported on imidazolium-2-carboxylates (NHC-CO_2 adducts) that can be employed as NHC surrogates to catalyze the cycloaddition of CO_2 and epoxides. The proposed mechanism involves the nucleophilic addition of the NHC–CO_2 adduct to the epoxide, followed by an intramolecular cyclization of the alkoxide intermediate (Scheme 12). The nucleophilic attack of the CO_2 moiety bound to the NHC on the substrates is thought to be the rate-limiting step: this hypothesis seems to be supported by a significant positive effect of electron-donating alkyl substituents on the NHC heteroatoms. Previously, Lu and coworkers[60] reported on the use of 1,3-diarylimidazolium-2-carboxylates as catalysts in similar transformations. At a later stage, the same group has shown that a NHC-CO_2 adduct could also be immobilized on a MCM-41 support and the catalytic activity of this hybrid material in the coupling between CO_2 and epoxides was investigated.[64] Although applicable, these protocols based on NHC catalysts and their corresponding derivatives require high CO_2 pressures (> 20 bar) and temperatures (> 100 ^{o}C). The hybrid silica material is indeed recyclable; however, its multi-step synthesis and isolation may result in extra energy and cost consumption, compromising to some extend the overall process sustainability.

○ 5 mol% catalyst, 100 ^{o}C, $p(CO_2)$ = 2.5-4.5 MPa
○ Yield of cyclic carbonate up to 89%
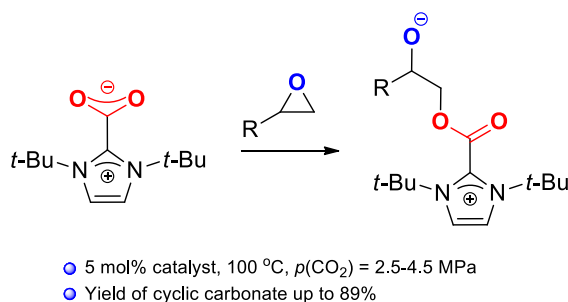
Scheme 12 Nucleophilic addition of NHC-CO_2 adducts to epoxides.

It is worth mentioning that cyclic α-alkylidene carbonates, can also be prepared from the reaction of propargylic alcohols with CO_2 ($p(CO_2)$ = 45 bar) under NHC or NHC–CO_2 catalysis at 60 °C.[56] Promisingly, Lu's group[117] found that _N-H_eterocyclic _O_lefin-CO_2 adducts (NHO–CO_2) work more efficiently as catalysts in this transformation (Scheme 13) under basically ambient reaction conditions. X-ray analysis of the NHO-CO_2 adduct revealed that the length of the C($_{carboxylate}$)-C($_{NHO}$) bond is significantly longer than that of the corresponding C($_{carboxylate}$)-C($_{NHC}$) bond. Therefore, the higher activity of the NHO–CO_2 adduct was tentatively ascribed to its lower stability compared to NHC-CO_2 adducts, thus facilitating the release of the CO_2 and/or the coupling product which may possible be rate-limiting in the catalytic cycle.
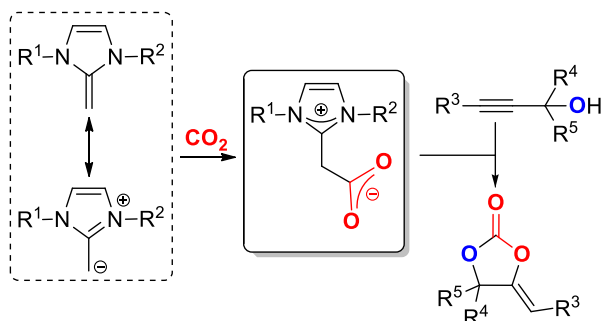

Scheme 13 Preparation of cyclic α-alkylidene carbonates from propargylic alcohols and CO_2 under NHO-CO_2 catalysis.

A creative approach towards cyclic carbonate synthesis using organic molecules as mediators was described by Jamison and his group.[118] Combination of _N_-bromosuccinimide (NBS) with a radical initiator (benzoyl peroxide, BPO) in the presence of dimethylformamide (DMF) as solvent in a continuous flow set up allows for the efficient coupling reaction between epoxides and CO_2. Under optimized conditions, high conversion levels and yields can be attained for various epoxide substrates. A series of (kinetic) experiments suggested epoxide activation by electrophilic attack from the bromine formed _in situ_. A slight drawback from this approach may be presented by the use of DMF as solvent/reactant requiring higher reaction temperatures (120 °C) as opposed to reactions carried out under milder, neat conditions. However, this method could pave the way towards continuous flow methodology for larger scale syntheses.

In contrast to epoxide/CO_2 couplings, aziridine/CO_2 couplings have been much less investigated, probably as a result of the easier access to epoxide reagents. As further detailed in the review by Kerton and coworkers,[32] a number of ILs and their polymer-supported derivatives has been used as catalysts in these aziridine/CO_2 coupling reactions. However, most of the reported catalytic systems either require high reaction temperatures (> 120 °C) and CO_2 pressures (> 50 bar) or deliver the heterocyclic products in low yields/conversions and with poor regio-selectivities.[10,119-121]

Gao's group recently reported[122,123] an alternative strategy for the selective preparation of 3-substituted cyclic carbamates from the reaction between a cyclic carbonate (made using CO_2) and aromatic amines using 1-butyl-3-methylimidazolium acetate (BmimOAc) as catalyst (Scheme 14). DFT calculations revealed that both the cationic and the anionic moieties of the catalyst activate in a cooperative fashion the substrates (_i.e._, cyclic carbonates and aromatic amines) by means of hydrogen-bonding. Despite the fact that this procedure is CO_2-free and requires relatively high reaction temperatures (140 °C), the use of metals and high-pressure reaction conditions can be avoided, thus developing a novel green method for the preparation of cyclic carbamates. Moreover, cyclic carbonates, which can be easily produced _via_ direct CO_2 coupling reactions with epoxides and/or oxetanes, are conveniently used as substrates for this type of reaction. Organocatalysts other than ILs including phenolic compounds[50] and NHCs[64] also have found applicability in this transformation but similar selectivity issues, as aforementioned, have been encountered.

The synthesis of five-membered cyclic carbonates and carbamates has been a highly active research area over the last five years. However, the formation of six-membered cyclic heterocycles based on direct coupling between suitable precursors (oxetanes or azetidines) and CO_2 is generally more difficult. It is further complicated by the lower accessibility and reactivity of oxetanes/azetidines compared with oxiranes/aziridines. Thus, this subfield of organic carbonate/carbamate formation is still in its infancy, though very recently several research teams have been able to design transition metal based catalytic protocols that allow for (substituted) oxetane-_into_-carbonate conversions.[29,124-125]
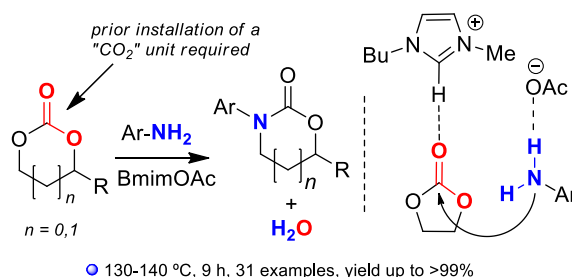
Scheme 14 Preparation of cyclic carbamates from the reaction of cyclic carbonates and aromatic amines with BmimOAc as catalyst.

4. Organocatalysed CO$_2$ reduction

Organocatalysis has also proven to be a powerful tool for CO$_2$ reduction. Various CO$_2$ reduction products have already been obtained including carbon monoxide (CO), formic acid, formamidine derivatives, methoxysilanes and methoxyboranes, of which the latter two can be easily converted to methanol and methane. Both MeOH and methane are energy vectors and the formation of these higher free energy molecules starting from CO$_2$ represents a possible alternative to fossil fuel based energy supply.

N-heterocyclic carbenes (NHCs) have been extensively applied as catalysts for the nucleophilic activation and subsequent reduction of CO$_2$. For example, NHC catalysts have been employed for the CO$_2$ reduction to CO in presence of inexpensive aldehyde reaction partners as (sacrificial) reductants. Although this reaction does not fall into the "reductive CO$_2$ coupling" category, it does show the potential of organocatalytic systems to access other type of transformations with formal reduction of the oxidation state of the CO$_2$ reactant. Initially, Zhang and Gu achieved the NHC-mediated catalytic reduction of CO$_2$ with aromatic aldehydes as oxygen acceptors.[126] The authors proposed that the NHC catalyst reacts with CO$_2$, resulting in an imidazolium carboxylate intermediate (Scheme 15, below left; cf. Scheme 12); this species attacks the 2-position of cinnamaldehyde realising through a [1,5] H−shift, the corresponding oxidation product as a potassium salt. The catalyst is regenerated by a quick decay of the NHC−CO adduct intermediate, with concomitant release of CO.
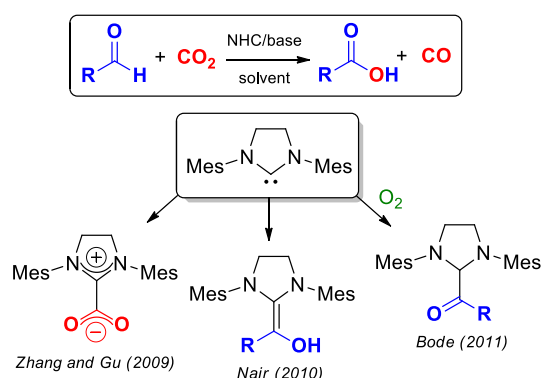
Scheme 15 Postulated intermediates for the oxidation of inactivated aldehydes in the presence of CO$_2$.

In 2010 Nair *et al.* reported a similar NHC−mediated oxidation of aromatic aldehydes with CO$_2$ leading to carboxylic acids.[127] The expected aryl glyoxylic acid product, resulting from trapping of the Breslow intermediate (Scheme 15, centre) with CO$_2$, was not observed. Different from what was previously reported, the postulated reaction mechanism relies on an initial addition of the catalyst to the aldehyde to form a nucleophilic Breslow intermediate which then reacts with CO$_2$. However, in 2011, both suggested mechanisms and experimental results were questioned by Bode and co-workers.[128] After detecting non-neglectable traces of air (and therefore oxygen) in both reported procedures, they suggested that exogenous molecular oxygen was likely the actual stoichiometric oxidant in the above-discussed reactions. In presence of oxygen, the NHC catalyst triggers the formation of NHC-acyl intermediates (Scheme 15, right), which are capable of transferring their acyl group to a nucleophile (traces of water) to produce the corresponding carboxylic acids.[129] In the mechanistic hypothesis of Bode *et al.* CO$_2$ only accounts for the reduction of aldehyde dimerization or oligomerisation side products. This particular chemistry therefore represents an interesting subject of debate likely to induce further detailed investigations into the role of the CO$_2$ reagent as oxidant.

Although organocatalyzed CO_2 reduction to MeOH is still not as powerful as transition metal based methodologies,[130-133] organocatalysis offers tangible and diverse approaches to reduced forms of carbon. For example, NHC catalysts have been employed for the reduction of CO_2 to methanol. Ying *et al.* reported on the reduction of imidazolium carboxylates by silanes yielding methanol.[36] The reaction is particularly interesting because the mesitylimidazolylidene carboxylate NHC catalyst (IMes–CO_2) employed is air stable, can be used in low concentration (0.05 mol %) while maintaining high TONs and TOFs (1840/25.5 h^{-1}, respectively). All these features help to overcome the typical drawbacks (catalyst deactivation, requirement of an air- and oxygen-free atmosphere) of metal-catalysed CO_2 reduction protocols. The proposed reaction mechanism, based on experimental and spectroscopic evidence, is based on the initial formation of a NHC-CO_2 adduct. Computational and experimental studies performed independently by different research groups led to distinct conclusions: Wang and co-workers postulated that the catalytic cycle starts with an initial attack of the NHC on the silane generating a pentavalent silicon species able to deliver a highly nucleophilic hydride to CO_2,[134] while a computational study by Zhang *et al.* supports an initial formation of an IMes–CO_2 adduct followed by a rate-determining [1,5] H-shift to give the corresponding formylsilane by hydrosilylation,[135] in agreement with the mechanism proposed initially.[40]
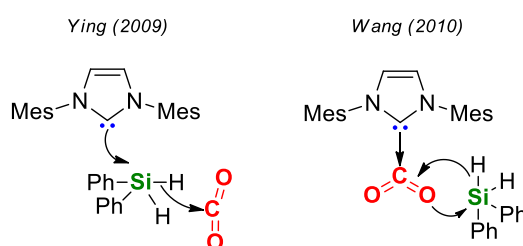
Scheme 16 Proposed NHC-catalysed CO_2 hydrosilylation intermediates.

Another class of organocatalysts active for the reduction of CO_2 to methoxysilanes and methoxyboranes (and thus, to methanol) are guanidine-based organic superbases (TBD and MTBD; see Figure 2). In an effort to broaden the range of compounds available from CO_2 reduction, Cantat *et al.* combined both reduction of CO_2 and formation of C−C, C−N, and C−O bonds reporting on the organocatalysed synthesis of formamidine derivatives starting from CO_2, trialkylsilane as reducing agents and *N*-based nucleophiles: with this approach they were able to synthesize different formamidine derivatives of amines, anilines, imines, hydrazines, hydrazones and *N*-heterocycles (Scheme 2 for an example).[55,66] This process is particularly appealing from a practical point of view because of its sustainable nature; in particular, it has been optimized to reuse two common industrial wastes: CO_2 being a by-product from all combustion processes involving organic matter and polymethylhydrosilane (PMHS).[23]

It has been recently demonstrated that rather mild (ambient) conditions can be used for organocatalytic CO_2 conversions. TBD or TMBD catalysts (0.025 mol%) have shown to be active towards CO_2 reduction using 9−BBN (9-borabicyclo[3.3.1]nonane) as reducing agent giving the corresponding dialkylmethoxyborane in >90% yield with TONs and TOFs up to 548 and 33 h^{-1}, respectively.[56] Although for both guanidine based catalysts the reduction of CO_2 with R_2BH and thus the first C−H bond formation is rate determining, with experimental and computational investigations revealing that TBD and MTBD follow different mechanisms. MTBD was proposed to promote the reduction of CO_2 through direct activation of the hydroborane reagent and formation of ion pairs, while TBD is converted into an FLP that first activates CO_2 and facilitates the hydride transfer from the boron to the carbon center (see Scheme 17).
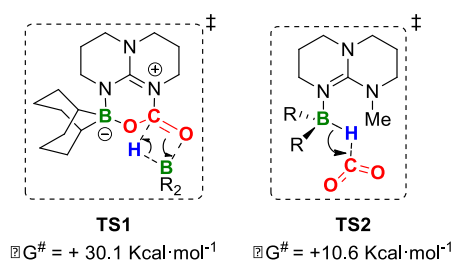
Scheme 17 Rate-determining step for the catalytic hydroboration of CO_2 with 9-BBN using (M)TBD as a catalyst precursor: CO_2 activation based mechanism (TBD, left) and hydroborane activation mechanism (MTBD, right).

In both cases formate type ($HCOOBR_2$) and acetal-like $H_2C(OBR_2)_2$ derivatives were identified as reaction intermediates.

In addition, stoichiometric and catalytic reductions of CO_2 have been reported which utilise frustrated Lewis pairs (FLPs) for CO_2 activation and dihydrogen, silanes, or boranes as the hydrogen source.[98] The first evidence of FLPs catalysing CO_2 reduction was reported by O'Hare et al. in 2009: when heated at 110 ºC at 1–2 bar of H_2 pressure, $B(C_6F_5)_3$ and TMP (TMP = 2,2,6,6-tetramethylpiperidine) were shown to bind CO_2 stoichiometrically and generate a formato-borate product. Extended heating at 160 ºC for several days yielded, after isolation by distillation, methanol as the sole C_1 product (Scheme 18, left).[61] Piers et al. reinvestigated the system using hydrosilanes as reductants in the presence of additional equivalents of the Lewis acid, and under those conditions the system effectively catalysed the reduction of CO_2 to methane (Scheme 18, right).[99] The reaction could be monitored spectroscopically (NMR), allowing the authors to propose a stepwise hydrosilylation process that was later supported computationally.[136] Unfortunately, the calculated turnover numbers are still far from those reached with transition metal-based systems based on, for instance, iridium.[132,137-139]
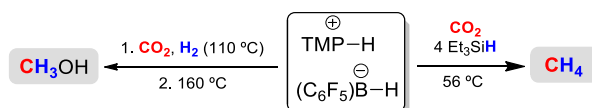
Scheme 18 FLP catalysed stoichiometric reduction of CO_2: to methanol with H_2 as a reductant (left), and to methane with triethylsilane as a reductant (right).

Milder Lewis acid/base FLP partners have also been proposed as catalyst systems. The preparation of 1-cathecolboryl-2-diphenylphosphinobenzene was reported and these kinds of FLP compounds catalyse the hydroboration of CO_2 in the presence of catecholborane to afford cat-BOB-cat and MeOB-cat (as depicted in Scheme 19), and the latter could be hydrolysed to methanol.[96] The reaction was performed under mild conditions ($p(CO_2)$ = 1 bar, T_{max} = 70 ºC) observing a maximum TOF of 973 h^{-1} (TONs up to 2950 using $BH_3 \cdot SMe_2$ as hydrogen source) reaching similar rates to the ones reported for transition-metal based catalysts.[140,141]
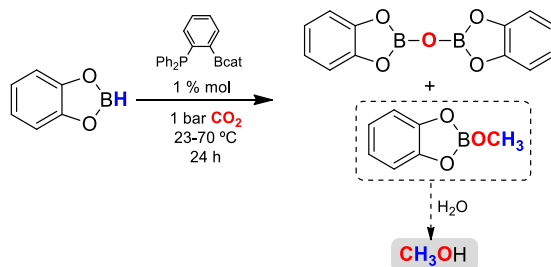
Scheme 19 CO_2 reduction with cathecolborane catalysed by an FLP organocatalyst.

This transformation was proposed to occur through simultaneous nucleophilic activation of the borane and electrophilic "fixation" of CO_2. It was postulated that the reduction process occurs through a stepwise process: initial CO_2 coordination forming a formatoborate intermediate which, upon rearrangement, loses the formaldehyde fragment necessary to generate the final methoxide derivative. More recently, the same authors reported a novel in situ generated FPL catalyst active towards reductive hydroboration of CO_2 based on a relatively non-nucleophilic proton sponge [= 1,8-bis(dimethylamino)naphthalene].[142] In the presence of stoichiometric quantities of a $BH_3 \cdot SMe_2$ reductant, at 80 ºC and 1 bar of CO_2 this system reached a TOF value of 64 h^{-1}. Here the postulated mechanism relies on the activation of $BH_3 \cdot SMe_2$ and converting it into a boronium–borohydride ion pair which, in the presence of CO_2, can evolve into a formate derivative. Final BH_2^+ abstraction from another FLP borane-proton sponge complex leads to elimination of the methoxyborane product.

The organocatalyzed N-methylation of amines using CO_2 and suitable reducing agents (hydroboranes) has recently emerged as another attractive catalysis route towards CO_2 valorisation. Contributions from Cantat et al.[143] and Dyson and co-workers[144] have set the stage for new conversions mediated by proazaphosphatrane superbases and NHC based organocatalysts. The results highlight the versatile catalytic use of NHCs towards the conversion of CO_2 into a variety of organic molecules such as alkylated amines, MeOH, formamidines and organic carbonates. As such they represent privileged catalyst systems with high potential in other types of CO_2 transformations.

5. Other reactions

The use of organocatalysis for other types of CO_2 conversion reactions is briefly discussed. Beside the formation of organic carbonates and products derived from reductive couplings, the formation of quinazoline–2,4(1H,3H)–diones (see Figure 1, Scheme 20) has also drawn considerable attention. Similar to organic carbonate formation, the formal oxidation state of the $C(CO_2)$ carbon centre does not change, however, mechanistic proposals[145] seem to indicate that water may play a role in the formation mechanism involving H_2CO_3 or bicarbonate. Though suggested by DFT analysis of the mechanism, it remains an open question whether the CO_2 is fully incorporated into the substrate.

Whereas metal based systems are known to catalyse the efficient formation of these heterocyclic structures from CO_2 generally using 2-amino-benzonitriles as reaction partners,[11,146] organocatalytic methods have been investigated successfully providing green alternatives. Quinazoline-2,4(1H,3H)-diones are considered as biologically and pharmacological relevant and thus represent interesting synthetic targets. To date various organocatalysts for the reaction between 2-amino-benzonitriles and CO_2 have been reported including IL based systems,[147-150] amine-based heterocycles[151,152] and carbonate bases/base impregnated clay minerals.[153,154] The use of water as a medium has been proposed for the non-catalytic formation of quinazoline–2,4(1H,3H)–diones.[155] In this latter case, the crucial role of the formation of H_2CO_3 acting as an intermediate was proposed, though higher reaction temperatures/pressures were required and relative longer reaction times were needed for high substrate conversion.
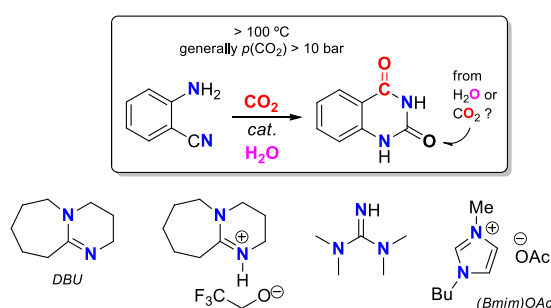
Scheme 20 Some of the reported organocatalysts used in the formation of quinazoline–2,4(1H,3H)–diones starting from 2-amino-benzonitriles and CO_2.

6. Summary and outlook

In the last five to ten years, the field of CO_2 chemistry and conversion catalysis has expanded enormously. Whereas homogeneous and heterogeneous metal catalysis still fulfil a prominent position within this vivid area of research, organocatalysis is emerging as a potential and useful alternative tool in specific CO_2 conversion reactions.

The current review shows that some organocatalyst structures such as NHCs and ILs can be regarded as "privileged" systems, as these are widely applicable systems for different organic transformations that are not limited to CO_2 couplings. However, the chemistry of other organocatalyst structures (including azaphosphatrane derivatives) seems highly promising, and the quest for a more diverse set of organocatalysts able to compete with metal catalysis is an ongoing challenge. In order to meet the challenges of sustainable though highly effective catalysis, new and conceptually different approaches may be warranted making clever use of cooperative, confinement and/or site–isolation effects. Without a doubt, there is a bright future for organocatalysis as a green alternative in CO_2 conversion catalysis, and this review will hopefully spur the catalysis community to develop new methodology of common interest to academic and industrial experts.

Acknowledgements

Giulia Fiorani studied chemistry at the Università degli Studi di Roma "Tor Vergata", where she obtained her MSc (Hons.) in 2006. In 2010 she completed her PhD in Chemical Sciences in the same University working on the synthesis and ap- plication of ionic liquids. Several different postdoctoral re- search assignments followed, working on nano-structured hydrid materials (Università degli Studi di Padova), functional hybrid membranes (ITM-CNR, Padova) and synthesis and synthetic applications of organic carbonates (Ca' Foscari University of Venice). Since March 2014, Giulia is working at ICIQ in the group of Prof. Arjan Kleij as a Marie Curie IEF Postdoctoral Fellow. Her research interests focus on the preparation of new molecules and materials based on CO_2 and renewable based feed stocks.
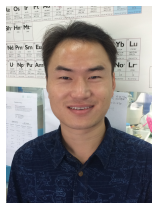
Wusheng Guo earned his MSc from South China University of Technology in 2010, and a PhD degree in organic chemistry in June 2014 from the Autonomous University of Barcelona under supervision of Prof. Roser Pleixats and Dr. Alexandr Shafir. His re- search focused on the use of hypervalent organoiodanes in oxidative processes and the use of metal nanoparticles based on Pd, Au and Rh in catalysis. Then, he joined the group of Prof. Arjan Kleij at the Institute of Chemical Research of Catalonia (ICIQ) in Tarragona as a CELLEX-supported postdoctoral associate working on the conversion of CO_2 for the formation of various value-added chemicals with carefully designed catalysts.

Arjan W. Kleij received his MSc (1996) and PhD degree (2000) in Chemistry from Utrecht University (The Netherlands) under the supervision of Prof. Gerard van Koten. Then he held several appointments as a postdoctoral fellow in Madrid (Prof. Javier de Mendoza) and Amsterdam (Prof. Joost Reek and Prof. Piet W.N.M. van Leeuwen), and as a scientist/project leader in industry at Avantium Technologies and Hexion Specialty Chemicals. In 2006 he was appointed Group Leader at ICIQ and ICREA fellow, and was promoted to ICREA professor in 2011. His main research interests are in the field of CO_2 conversion catalysis with a focus on heterocyclic synthesis, (bio)polymers and the development of new catalysts and new reactivity patterns.

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