

## REVIEW

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# Sustainable Conversion of Carbon Dioxide: The Advent of Organocatalysis

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The conversion of carbon dioxide (CO<sub>2</sub>), 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<sub>2</sub> 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<sub>2</sub> 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<sup>1,2</sup> for the preparation of a variety of useful chemicals including MeOH,<sup>3,4</sup> urea,<sup>5</sup> lactones,<sup>6</sup> various heterocycles,<sup>7-11</sup> biodegradable polymers,<sup>12-16</sup> and carboxylated structures<sup>17-21</sup> among others.<sup>22-24</sup> In particular, direct CO<sub>2</sub> utilisation for the preparation of polycarbonates, poly(ether)carbonates and polyurethanes is a viable technology to access novel tailor-made CO<sub>2</sub>-based materials.<sup>25</sup> The development of cost- and energy-efficient synthetic methodologies to exploit CO<sub>2</sub> as a C<sub>1</sub> synthon could eventually loosen the grip on our fossil fuel dependence, contributing to a reduction of the overall CO<sub>2</sub> emissions and offering tangible alternatives to physical sequestration methods.<sup>26,27</sup>

In nature, CO<sub>2</sub> is captured, converted and/or reduced to carbohydrates by a series of cascade reactions carried out by specific metalloenzymes present in photosynthetic organisms.<sup>28</sup> Similarly, the field of CO<sub>2</sub> conversion catalysis is dominated by the use of transition *metal*-based catalysts being either heterogeneous or homogeneous in nature.<sup>29-32</sup> 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<sub>2</sub>, thus eventually developing “carbon-neutral” processes to produce sustainable chemicals, fuels, and materials.<sup>33</sup>

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<sub>2</sub> catalysis and conversion. Recently, the pace with which organocatalytic procedures are being utilized in organic preparations that involve CO<sub>2</sub> 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),<sup>33-35</sup> *N*-heterocyclic carbenes (NHCs),<sup>36</sup> phenolic compounds<sup>37</sup> and sophisticated azaphosphatranes.<sup>38</sup> This is a true testimony of the increasing prominence of organocatalysis in the area of CO<sub>2</sub> fixation to create value-added organic matter from a waste material.

This review intends to showcase the most recent developments in CO<sub>2</sub> 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<sub>2</sub> 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<sub>2</sub> conversion. Other excellent reviews focusing on the use of hetero- and/or homogenous catalyst systems have recently appeared,<sup>4,7-10,18,19,39-42</sup> 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<sub>2</sub> 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.<sup>43-45</sup> Although the currently available CO<sub>2</sub> 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<sub>2</sub>. Although the array of available organo-catalysed CO<sub>2</sub> valorisation reactions is expanding constantly, currently the field is dominated by reductive and non-reductive coupling processes (see Figure 1).

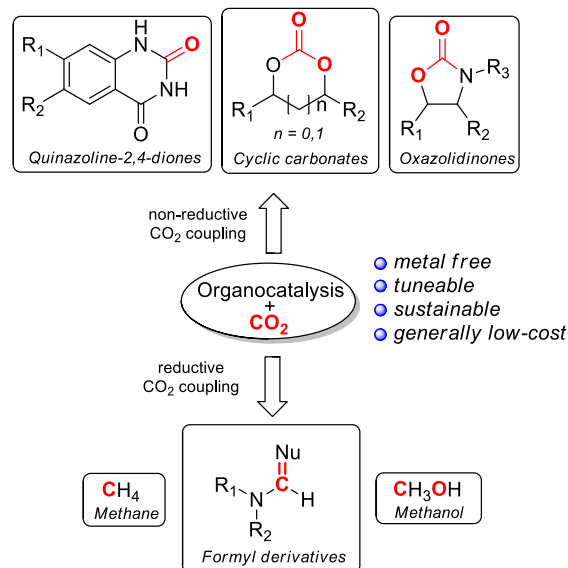
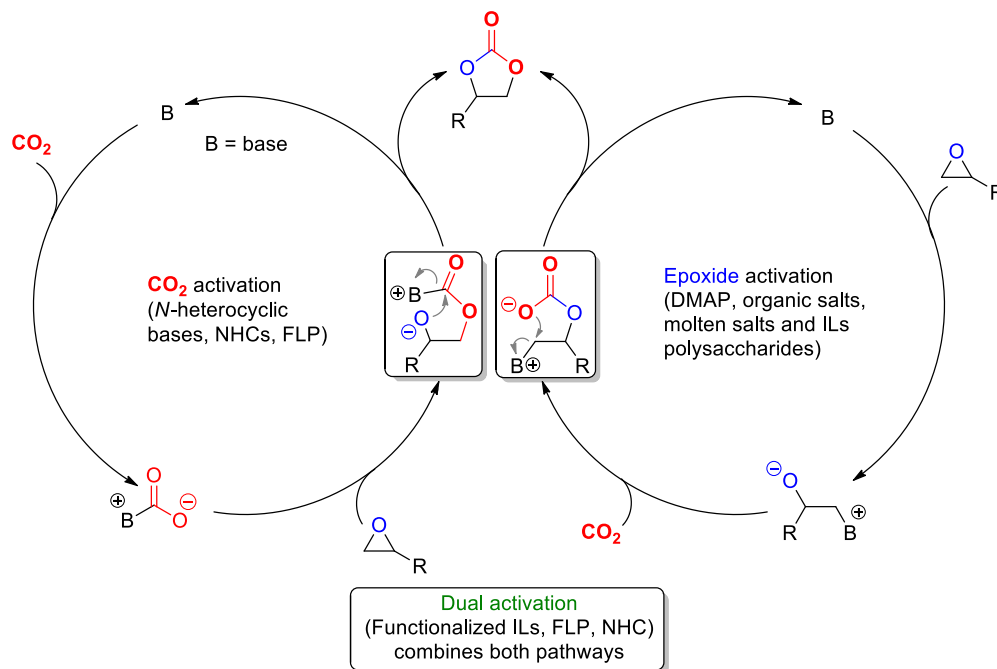


Fig. 1 CO<sub>2</sub> transformations mediated by organocatalysts.

Up to now, the reported organocatalysts active in CO<sub>2</sub> 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<sub>2</sub> based synthetic processes which are illustrated in Figure 1. Beside the established heterocyclic synthesis based on CO<sub>2</sub> coupling to epoxides and aziridines (Figure 1, top), organocatalysis has also proved to be particularly attractive for CO<sub>2</sub> 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<sub>2</sub>/epoxide coupling reactions to afford cyclic carbonates have shown that the role of the catalytic species can be either (a) direct CO<sub>2</sub> activation; (b) activation of high energy co-reactants (*e.g.*, epoxides, aziridines, oxetanes and azetidines); or (c) dual activation of both CO<sub>2</sub> and the associated high-energy reactant as summarised in Scheme 1. Evidence of a dual activation mechanism has been seldom reported for CO<sub>2</sub> conversion catalysts; notable examples include polyoxometalate based systems developed by Mizuno<sup>46</sup> and Leitner,<sup>47</sup> respectively. While a general reactivity pattern may be readily derived for organocatalysed non-reductive CO<sub>2</sub> coupling reactions, a general mechanism for reductive CO<sub>2</sub> couplings has not yet been defined given the different reducing agents employed.

## REVIEW



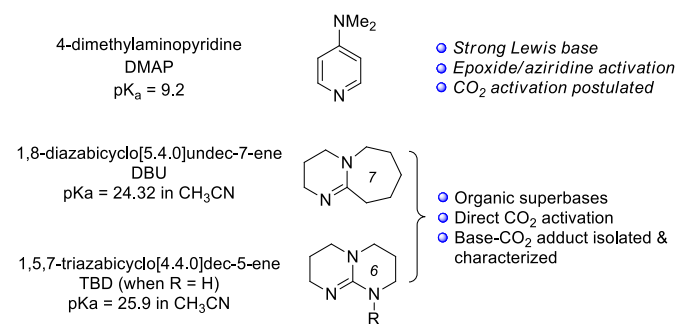
**Scheme 1** General organocatalytic activation modes for the synthesis of cyclic carbonates from epoxides and CO<sub>2</sub>.

## 2.1. Organic *N*-heterocyclic bases

Organic bases are probably the simplest organocatalysts studied in the context of CO<sub>2</sub> 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<sub>2</sub> couplings and reduction of CO<sub>2</sub> 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<sub>2</sub> 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<sup>48</sup> and heterogeneous<sup>49</sup> catalyst for the synthesis of cyclic carbonates from epoxides, even though high operating temperatures (120 °C) and relatively high CO<sub>2</sub> 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.<sup>37,50</sup> 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<sub>2</sub> molecule has also been postulated.<sup>50</sup>

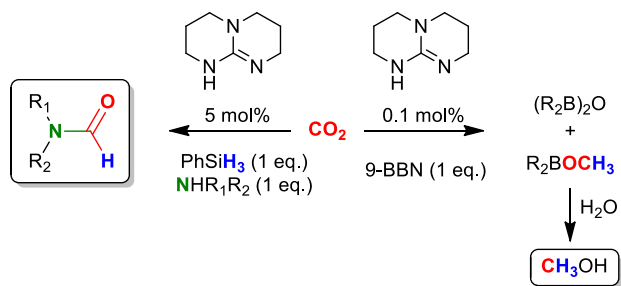


**Fig. 2** *N*-heterocyclic bases commonly employed as organocatalysts. Note that the reactivity generally is higher when the pK<sub>a</sub> value is lower.

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<sub>2</sub> 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<sub>2</sub> and epoxides.<sup>51</sup> 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 chemoselectivities (90–98%) although the reaction conditions were quite harsh ( $T = 140\text{ }^{\circ}\text{C}$ ,  $p(\text{CO}_2) = 50\text{ bar}$ ). Catalyst heterogenisation has been exploited as a straight-forward, feasible way to address recyclability issues and to work under milder conditions ( $T = 50\text{ }^{\circ}\text{C}$ ),<sup>52,53</sup> 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.<sup>54</sup>

The catalytic role of guanidine-derived organic superbases is not limited to non-reductive  $\text{CO}_2$  coupling reactions: these compounds are currently conquering a prominent role as  $\text{CO}_2$  catalysts for the synthesis of methanol by reductive coupling of  $\text{CO}_2$  with organosilanes<sup>55</sup> and organoboranes.<sup>56</sup> Regardless of the hydride donor employed, formation of a superbase- $\text{CO}_2$  salt is crucial to start the catalytic cycle forming a catalytically active  $\text{CO}_2$  complex (Scheme 2).

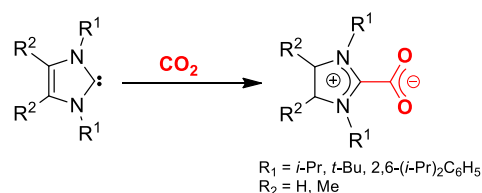


**Scheme 2**  $\text{CO}_2$  reduction catalysed by TBD.

Whether involved in catalytic  $\text{CO}_2$  coupling or  $\text{CO}_2$  reduction processes, the catalytic cycle involving superbases generally starts with an initial “coordination” of the  $\text{CO}_2$  molecule. Stable organic superbase- $\text{CO}_2$  adducts have been isolated and fully characterized,<sup>57,58</sup> thus providing experimental proof that this class of compounds is capable of direct interaction with  $\text{CO}_2$ .

## 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.<sup>59</sup> 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- $\text{CO}_2$  adducts (Scheme 3).<sup>60</sup> These adducts are labile in solution, making them suitable for catalytic turnover.



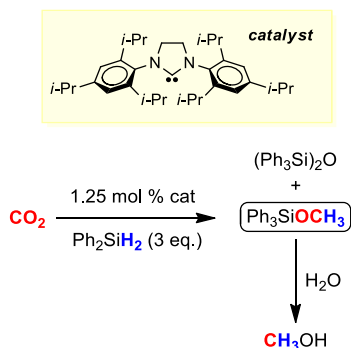
- $\text{CO}_2$  activation
- Reversible complex formation
- Coupling to epoxides
- $\text{CO}_2$  reduction catalysis

**Scheme 3** NHC- $\text{CO}_2$  adduct formation.

NHC-promoted  $\text{CO}_2$  activation allows for  $\text{CO}_2$  coupling reactions with high-energy reaction partners, including the preparation of cyclic carbonates and oxazolidinones from epoxides and aziridines,<sup>61,62</sup> respectively, and the synthesis of  $\alpha$ -methylene-carbonates and  $\alpha$ -methylene-oxazolidinones from propargylic alcohols.<sup>62,63</sup>

To further improve catalyst lifetime and recyclability, NHC-based catalysts have been heterogenised. When NHC scaffolds (Scheme 3;  $R^1 = i\text{-Pr}$ ,  $R^2 = \text{H}$ ) 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 ( $T = 120\text{ }^{\circ}\text{C}$ ,  $p(\text{CO}_2) = 20\text{ bar}$ ,  $t = 24\text{--}48\text{ h}$ ), whereas this supported catalyst was also used for the synthesis of oxazolidinones under even milder conditions ( $T = 80\text{--}100\text{ }^{\circ}\text{C}$ ) affording *N*-substituted oxazolidinones in excellent yields.<sup>64</sup> A different NHC ( $R_1 = 2,6\text{-}(i\text{-Pr})_2\text{C}_6\text{H}_5$ ;  $R_2 = \text{H}$ ) 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 =  $142\text{ s}^{-1}$ ,  $T = 160\text{ }^{\circ}\text{C}$ ,  $p(\text{CO}_2) = 30\text{ bar}$ ).<sup>65</sup>

Since their catalytic activity is based on direct  $\text{CO}_2$  activation, NHCs were also the first class of organocatalysts to show catalytic activity towards  $\text{CO}_2$  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  $\text{CO}_2$  as a versatile  $\text{C}_1$  synthon for the preparation of, *inter alia*, formamidine derivatives (Scheme 4).<sup>23,66</sup>



Scheme 4 CO<sub>2</sub> 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.*,<sup>32</sup> the use of organic salts/ionic liquids as organocatalysts for CO<sub>2</sub> conversion has come a long way since the seminal work of Caló *et al.* published in 2002.<sup>67</sup> These catalysts have almost exclusively been employed for the coupling of CO<sub>2</sub> 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.<sup>68</sup> Beside commercially available quaternary ammonium<sup>68-70</sup> and phosphonium halide salts,<sup>69,71-73</sup> a number of phosphonium,<sup>74</sup> imidazolium,<sup>75-77</sup> pyridinium,<sup>76</sup> pyrrolidinium<sup>78</sup> and superbases<sup>10,79</sup> derived ILs (including those based on DABCO, DBU and TBD; Figure 4) have also been prepared and employed as CO<sub>2</sub> 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.

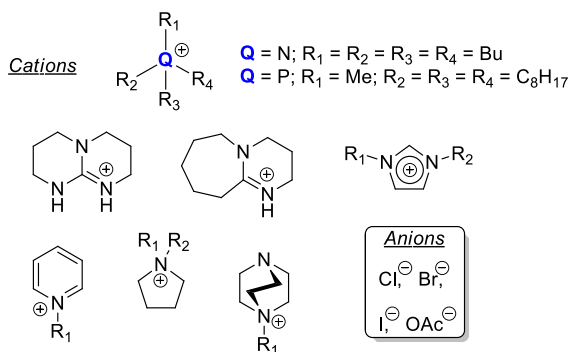
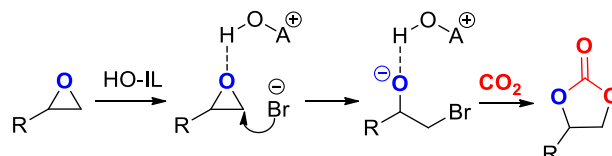


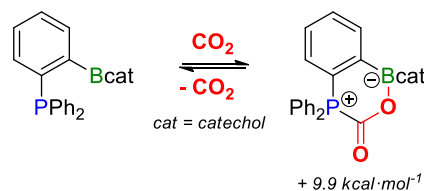
Fig. 4 Quaternary ammonium/iminium salts and ILs used as catalysts for CO<sub>2</sub> coupling reactions.

In most reported cases, the heterocycle/CO<sub>2</sub> 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,<sup>72,80,81</sup> copolymerized,<sup>73,82-84</sup> PEG-ylated<sup>85</sup> and dendrimeric ILs.<sup>86,87</sup> Moreover, task-specific hydroxy-<sup>88,89</sup> and carboxy-functionalized ILs<sup>90,91</sup> 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.<sup>81,92-94</sup>



Scheme 5 Proposed mechanism for the activation of epoxides by hydroxy-functionalised ILs.

Direct CO<sub>2</sub> 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.<sup>95</sup> Their mechanism of action, as illustrated in Scheme 6 for aryl-bridged phosphine-borane FLPs, involves CO<sub>2</sub> binding and formation of a zwitterionic carboxylated FLP adduct.<sup>96</sup> Depending on the reaction partner, FLPs can be catalytically active towards CO<sub>2</sub> coupling to epoxides<sup>97</sup> or, in presence of an appropriate reducing agent, *i.e.* trialkylsilanes, towards its reduction.<sup>98</sup> Interestingly, up to date organo-catalysed reduction of CO<sub>2</sub> to methane has only been achieved in presence of an FLP catalyst<sup>99</sup> demonstrating their exceptional catalytic potential in CO<sub>2</sub> conversion catalysis.



Scheme 6 CO<sub>2</sub> activation by FLPs: reversible activation of CO<sub>2</sub> 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,<sup>100</sup> linear non-conjugated polyols<sup>101</sup> and

polysaccharides.<sup>102-106</sup> 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<sub>2</sub> 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).

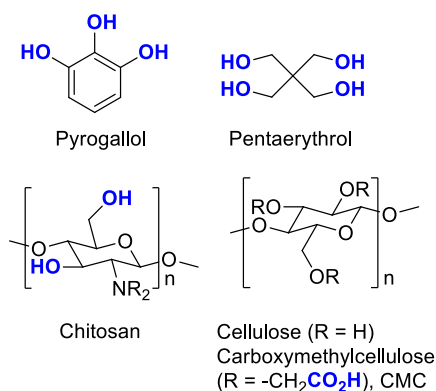


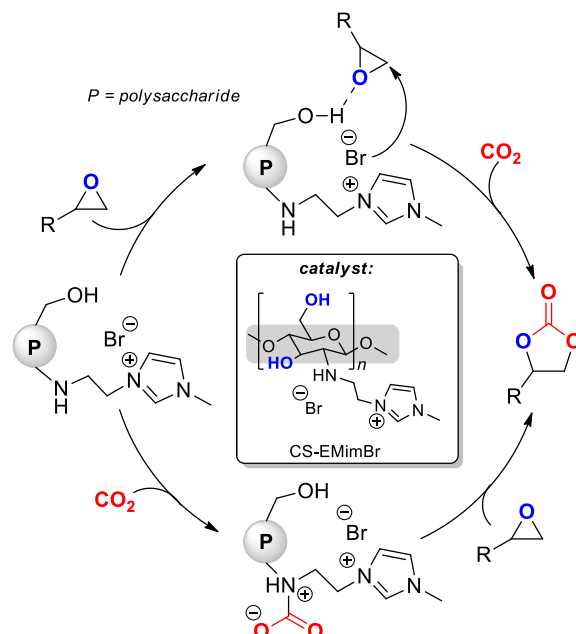
Fig. 5 Phenolic, polyhydroxy- and polysaccharide-based organocatalysts for CO<sub>2</sub> coupling reactions.

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,<sup>102</sup> organic superbases<sup>54</sup> or covalent incorporation of nucleophilic moieties within the macromolecular catalyst.<sup>103,104,107</sup> 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.<sup>103</sup>

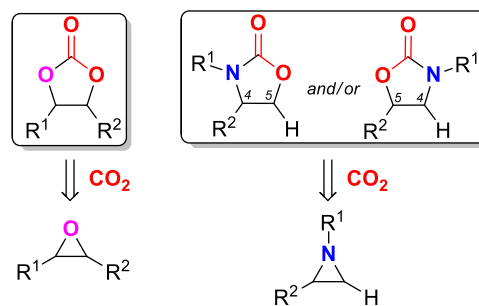
### 3. Heterocyclic structures based on CO<sub>2</sub>

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,<sup>108-112</sup> 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<sub>2</sub> 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.



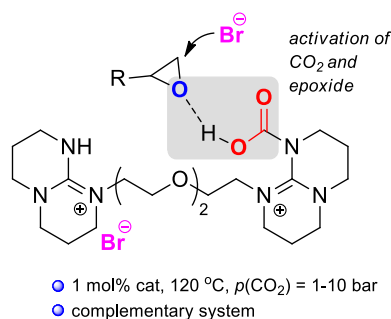
Scheme 7 Proposed mechanism for CS-EMIm-Br catalysed CO<sub>2</sub> coupling reactions. CS stands for cellulose and EMIm-Br for an imidazolium bromide unit.



Scheme 8 Preparation of heterocyclic structures from the reactions of CO<sub>2</sub> and epoxides or aziridines.

Undoubtedly, ILs are the most widely studied organocatalysts for the formation of heterocyclic structures from CO<sub>2</sub> which has been reviewed in detail by Kerton and co-workers recently.<sup>32</sup> 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<sub>2</sub>.





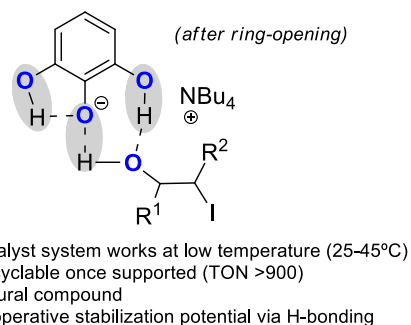
**Scheme 9** PEG-bridged TBD as catalyst for CO<sub>2</sub>-epoxides coupling reaction. PEG = polyethyleneglycol.

For instance, He's group reported<sup>85</sup> on the use of polyethylene-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<sub>2</sub> 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<sub>2</sub> was provided by a pyrogallol (1,2,3-trihydroxybenzene) based binary catalyst comprising Bu<sub>4</sub>NI.<sup>100</sup> 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 ( $T = 25\text{--}45\text{ }^{\circ}\text{C}$ ,  $p(\text{CO}_2) = 10\text{ bar}$ ), providing a low net CO<sub>2</sub> emission reaction setup. When compared to a previously reported metal based catalytic system, comprising of a Lewis acidic Zn(salphen) catalyst and using Bu<sub>4</sub>NI as co-catalyst<sup>113</sup> employed under similar conditions (*i.e.*, MEK as solvent,  $T = 45\text{ }^{\circ}\text{C}$ ,  $p(\text{CO}_2) = 10\text{ bar}$ ,  $t = 18\text{ h}$ ), 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<sub>4</sub>NI (both 2.5 mol%) as well as with pyrogallol/Bu<sub>4</sub>NI (both 5.0 mol%). This simple comparison is further evidence of the exceptional potential of

pyrogallol as a CO<sub>2</sub> coupling catalyst, exhibiting activities comparable to metal-based systems.

At a later stage,<sup>114</sup> 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 efficiently 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,<sup>37,115</sup> 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.

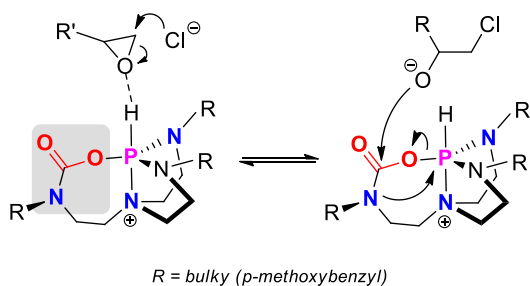
Dufaud *et al.*<sup>116</sup> recently developed a green method using azaphosphatranes as catalysts. This method allows for the efficient coupling of epoxides and CO<sub>2</sub> at 80°C and atmospheric pressure of CO<sub>2</sub> using a 0.1 mol % of catalyst loading. Azaphosphatranes can be considered structurally tunable catalysts, and as such their catalytic activity can be optimized by changing the substituents attached to the peripheral *N*-atoms (R, Scheme 11). Whereas the presence of methyl substituents ( $R = \text{Me}$ ) 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<sub>2</sub> 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<sub>2</sub> 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<sub>2</sub>.

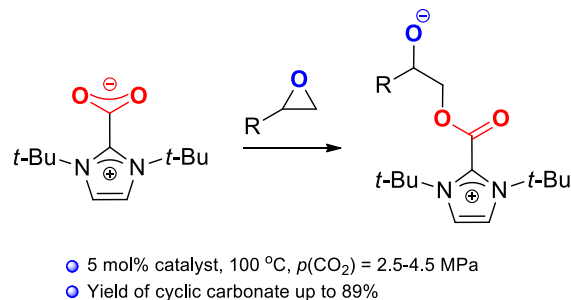
Given the low kinetic stability of the tricyclic phosphorylcarbamate intermediate in the absence of any steric protection, the same authors have come up with an alternative, successful strategy to stabilize this intermediate and to avoid degradation of the catalyst through encapsulation by means of self-assembly giving a nano-cage.<sup>38</sup> Thus, several hemicyptophane-caged azaphosphatranes were designed and tested in the coupling reaction of CO<sub>2</sub> and epoxide under reasonably mild conditions (T = 100 °C; p(CO<sub>2</sub>) = 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<sub>2</sub>.<sup>116</sup> The hemicyptophane 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<sub>2</sub>.



**Scheme 11** Azaphosphatranes acting as catalysts in the coupling reaction between CO<sub>2</sub> and epoxides.

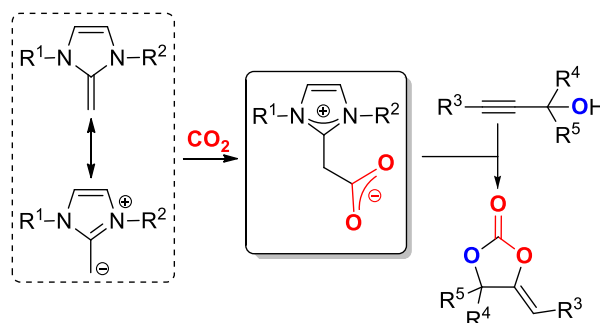
Alternative organocatalytic methodologies make use of NHCs and their derivatives as catalysts in the reaction of CO<sub>2</sub> and epoxides. Ikariya *et al.*<sup>62</sup> reported on imidazolium-2-carboxylates (NHC-CO<sub>2</sub> adducts) that can be employed as NHC surrogates to catalyze the cycloaddition of CO<sub>2</sub> and epoxides. The proposed mechanism involves the nucleophilic addition of the NHC-CO<sub>2</sub> adduct to the epoxide, followed by an intramolecular cyclization of the alkoxide intermediate (Scheme 12). The nucleophilic attack of the CO<sub>2</sub> 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<sup>60</sup> 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<sub>2</sub> adduct could also be immobilized on a MCM-41 support and the catalytic activity of this hybrid material in the coupling between CO<sub>2</sub> and epoxides was investigated.<sup>64</sup> Although applicable, these protocols based on NHC catalysts and their corresponding derivatives require high CO<sub>2</sub> pressures (> 20 bar) and temperatures (> 100 °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 extent the overall process sustainability.



**Scheme 12** Nucleophilic addition of NHC-CO<sub>2</sub> adducts to epoxides.

It is worth mentioning that cyclic  $\alpha$ -alkylidene carbonates, can also be prepared from the reaction of propargylic alcohols with CO<sub>2</sub> (p(CO<sub>2</sub>) = 45 bar) under NHC or NHC-CO<sub>2</sub> catalysis at 60 °C.<sup>56</sup> Promisingly, Lu's group<sup>117</sup> found that *N*-Heterocyclic *O*lefin-CO<sub>2</sub> adducts (NHO-CO<sub>2</sub>) work more efficiently as catalysts in this transformation (Scheme 13) under basically ambient reaction conditions. X-ray analysis of the NHO-CO<sub>2</sub> 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<sub>2</sub> adduct was tentatively ascribed to its lower stability compared to NHC-CO<sub>2</sub> adducts, thus facilitating the release of the CO<sub>2</sub> and/or the coupling product which may possible be rate-limiting in the catalytic cycle.



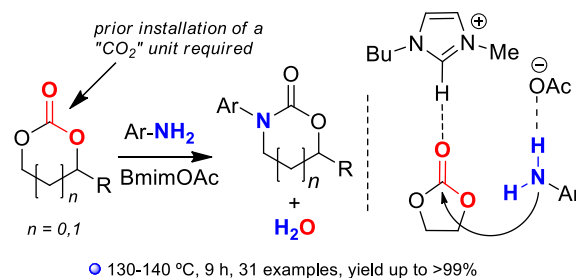
**Scheme 13** Preparation of cyclic  $\alpha$ -alkylidene carbonates from propargylic alcohols and CO<sub>2</sub> under NHO-CO<sub>2</sub> catalysis.

A creative approach towards cyclic carbonate synthesis using organic molecules as mediators was described by Jamison and his group.<sup>118</sup> 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<sub>2</sub>. 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<sub>2</sub> couplings, aziridine/CO<sub>2</sub> 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,<sup>32</sup> a number of ILs and their polymer-supported derivatives has been used as catalysts in these aziridine/CO<sub>2</sub> coupling reactions. However, most of the reported catalytic systems either require high reaction temperatures (> 120 °C) and CO<sub>2</sub> pressures (> 50 bar) or deliver the heterocyclic products in low yields/conversions and with poor regioselectivities.<sup>10,119-121</sup>

Gao's group recently reported<sup>122,123</sup> an alternative strategy for the selective preparation of 3-substituted cyclic carbamates from the reaction between a cyclic carbonate (made using CO<sub>2</sub>) 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<sub>2</sub>-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<sub>2</sub> coupling reactions with epoxides and/or oxetanes, are conveniently used as substrates for this type of reaction. Organocatalysts other than ILs including phenolic compounds<sup>50</sup> and NHCs<sup>64</sup> 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<sub>2</sub> 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.<sup>29,124-125</sup>

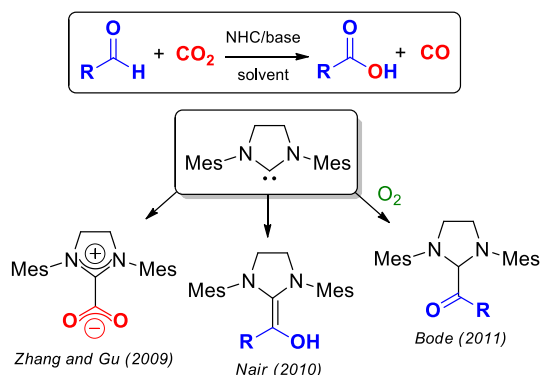


**Scheme 14** Preparation of cyclic carbamates from the reaction of cyclic carbonates and aromatic amines with BmimOAc as catalyst.

#### 4. Organocatalysed CO<sub>2</sub> reduction

Organocatalysis has also proven to be a powerful tool for CO<sub>2</sub> reduction. Various CO<sub>2</sub> 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<sub>2</sub> 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<sub>2</sub>. For example, NHC catalysts have been employed for the CO<sub>2</sub> reduction to CO in presence of inexpensive aldehyde reaction partners as (sacrificial) reductants. Although this reaction does not fall into the “reductive CO<sub>2</sub> 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<sub>2</sub> reactant. Initially, Zhang and Gu achieved the NHC-mediated catalytic reduction of CO<sub>2</sub> with aromatic aldehydes as oxygen acceptors.<sup>126</sup> The authors proposed that the NHC catalyst reacts with CO<sub>2</sub>, 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.

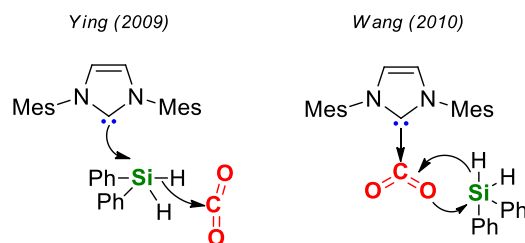


**Scheme 15** Postulated intermediates for the oxidation of inactivated aldehydes in the presence of CO<sub>2</sub>.

In 2010 Nair *et al.* reported a similar NHC-mediated oxidation of aromatic aldehydes with CO<sub>2</sub> leading to carboxylic acids.<sup>127</sup> The expected aryl glyoxylic acid product, resulting from trapping of the Breslow intermediate (Scheme 15, centre) with CO<sub>2</sub>, 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<sub>2</sub>. However, in 2011, both suggested mechanisms and experimental results were questioned by Bode and co-workers.<sup>128</sup> After detecting non-negligible 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.<sup>129</sup> In the mechanistic hypothesis of Bode *et al.* CO<sub>2</sub> 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<sub>2</sub> reagent as oxidant.

Although organocatalyzed CO<sub>2</sub> reduction to MeOH is still not as powerful as transition metal based methodologies,<sup>130-133</sup> organocatalysis offers tangible and diverse approaches to reduced forms of carbon. For example, NHC catalysts have been employed for the reduction of CO<sub>2</sub> to methanol. Ying *et al.* reported on the reduction of imidazolium carboxylates by silanes yielding methanol.<sup>36</sup> The reaction is particularly interesting because the mesitylimidazolylidene carboxylate NHC catalyst (IMes-CO<sub>2</sub>) employed is air stable, can be used in low concentration (0.05 mol %) while maintaining high TONs and TOFs (1840/25.5 h<sup>-1</sup>, respectively). All these features help to overcome the typical drawbacks (catalyst deactivation, requirement of an air- and oxygen-free atmosphere) of metal-catalysed CO<sub>2</sub> reduction protocols. The proposed reaction mechanism, based on experimental and spectroscopic evidence, is based on the initial formation of a NHC-CO<sub>2</sub> adduct. Computational and experimental studies performed

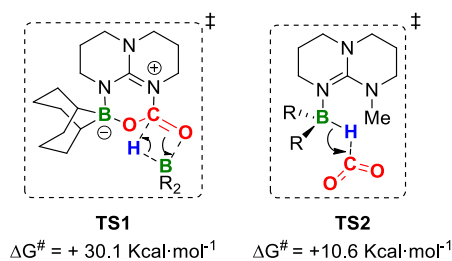
independently by different research groups led to distinct conclusions: Wang and co-workers postulated that the catalytic cycle starts with an initial attack of the silane generating a pentavalent silicon species able to deliver a highly nucleophilic hydride to CO<sub>2</sub>,<sup>134</sup> while a computational study by Zhang *et al.* supports an initial formation of an IMes-CO<sub>2</sub> adduct followed by a rate-determining [1,5] H-shift to give the corresponding formylsilane by hydrosilylation,<sup>135</sup> in agreement with the mechanism proposed initially.<sup>40</sup>



**Scheme 16** Proposed NHC-catalysed CO<sub>2</sub> hydrosilylation intermediates.

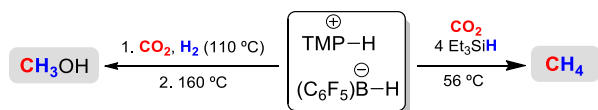
Another class of organocatalysts active for the reduction of CO<sub>2</sub> to methoxysilanes and methoxyboranes (and thus, to methanol) are guanidine-based organic superbases (TBD and MTBD; see Figure 2). In an effort to broaden the range of compounds available from CO<sub>2</sub> reduction, Cantat *et al.* combined both reduction of CO<sub>2</sub> and formation of C-C, C-N, and C-O bonds reporting on the organocatalysed synthesis of formamide derivatives starting from CO<sub>2</sub>, trialkylsilane as reducing agents and *N*-based nucleophiles: with this approach they were able to synthesize different formamide derivatives of amines, anilines, imines, hydrazines, hydrazones and *N*-heterocycles (Scheme 2 for an example).<sup>55,66</sup> 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<sub>2</sub> being a by-product from all combustion processes involving organic matter and polymethylhydrosilane (PMHS).<sup>23</sup>

It has been recently demonstrated that rather mild (ambient) conditions can be used for organocatalytic CO<sub>2</sub> conversions. TBD or MTBD catalysts (0.025 mol%) have shown to be active towards CO<sub>2</sub> 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<sup>-1</sup>, respectively.<sup>56</sup> Although for both guanidine based catalysts the reduction of CO<sub>2</sub> with R<sub>2</sub>BH 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<sub>2</sub> through direct activation of the hydroborane reagent and formation of ion pairs, while TBD is converted into an FLP that first activates CO<sub>2</sub> 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<sub>2</sub> with 9-BBN using (M)TBD as a catalyst precursor: CO<sub>2</sub> activation based mechanism (TBD, left) and hydroborane activation mechanism (MTBD, right).

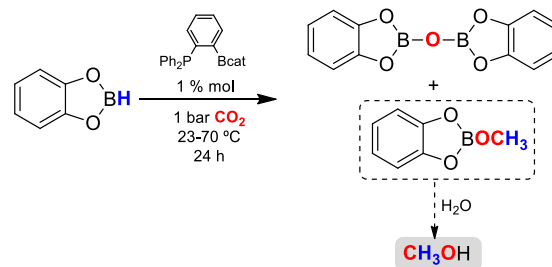
In both cases formate type (HCOOBR<sub>2</sub>) and acetal-like H<sub>2</sub>C(OBR<sub>2</sub>)<sub>2</sub> derivatives were identified as reaction intermediates. In addition, stoichiometric and catalytic reductions of CO<sub>2</sub> have been reported which utilise frustrated Lewis pairs (FLPs) for CO<sub>2</sub> activation and dihydrogen, silanes, or boranes as the hydrogen source.<sup>98</sup> The first evidence of FLPs catalysing CO<sub>2</sub> reduction was reported by O'Hare *et al.* in 2009: when heated at 110 °C at 1–2 bar of H<sub>2</sub> pressure, B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> and TMP (TMP = 2,2,6,6-tetramethylpiperidine) were shown to bind CO<sub>2</sub> stoichiometrically and generate a formate-borate product. Extended heating at 160 °C for several days yielded, after isolation by distillation, methanol as the sole C<sub>1</sub> product (Scheme 18, left).<sup>61</sup> 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<sub>2</sub> to methane (Scheme 18, right).<sup>99</sup> The reaction could be monitored spectroscopically (NMR), allowing the authors to propose a stepwise hydrosilylation process that was later supported computationally.<sup>136</sup> Unfortunately, the calculated turnover numbers are still far from those reached with transition metal-based systems based on, for instance, iridium.<sup>132,137-139</sup>



**Scheme 18** FLP catalyzed stoichiometric reduction of CO<sub>2</sub>: to methanol with H<sub>2</sub> 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-catecholboranyl-2-diphenylphosphinobenzene was reported and these kinds of FLP compounds catalyse the hydroboration of CO<sub>2</sub> 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.<sup>96</sup> The reaction was performed under mild conditions ( $p(\text{CO}_2) = 1 \text{ bar}$ ,  $T_{\text{max}} = 70 \text{ °C}$ ) observing a maximum TOF of 973 h<sup>-1</sup> (TONs up to 2950 using BH<sub>3</sub>·SMe<sub>2</sub> as

hydrogen source) reaching similar rates to the ones reported for transition-metal based catalysts.<sup>140,141</sup>



**Scheme 19** CO<sub>2</sub> reduction with catecholborane catalysed by an FLP organocatalyst.

This transformation was proposed to occur through simultaneous nucleophilic activation of the borane and electrophilic “fixation” of CO<sub>2</sub>. It was postulated that the reduction process occurs through a stepwise process: initial CO<sub>2</sub> 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<sub>2</sub> based on a relatively non-nucleophilic proton sponge [= 1,8-bis(dimethylamino)naphthalene].<sup>142</sup> In the presence of stoichiometric quantities of a BH<sub>3</sub>·SMe<sub>2</sub> reductant, at 80 °C and 1 bar of CO<sub>2</sub> this system reached a TOF value of 64 h<sup>-1</sup>. Here the postulated mechanism relies on the activation of BH<sub>3</sub>·SMe<sub>2</sub> and converting it into a boronium–borohydride ion pair which, in the presence of CO<sub>2</sub>, can evolve into a formate derivative. Final BH<sub>2</sub><sup>+</sup> abstraction from another FLP borane-proton sponge complex leads to elimination of the methoxyborane product.

The organocatalyzed *N*-methylation of amines using CO<sub>2</sub> and suitable reducing agents (hydroboranes) has recently emerged as another attractive catalysis route towards CO<sub>2</sub> valorisation. Contributions from Cantat *et al.*<sup>143</sup> and Dyson and co-workers<sup>144</sup> have set the stage for new conversions mediated by proazaphosphatane superbases and NHC based organocatalysts. The results highlight the versatile catalytic use of NHCs towards the conversion of CO<sub>2</sub> 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<sub>2</sub> transformations.

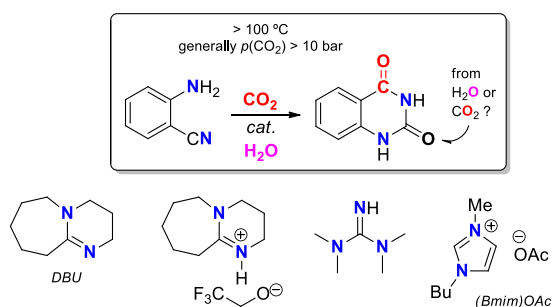
## 5. Other reactions

The use of organocatalysis for other types of CO<sub>2</sub> conversion reactions is briefly discussed. Beside the formation of organic carbonates and products derived from reductive couplings, the formation of quinazoline-2,4(1*H*,3*H*)-diones (see Figure 1, Scheme 20) has also drawn considerable attention. Similar to organic carbonate formation, the formal oxidation state of the C(CO<sub>2</sub>) carbon centre does not change, however, mechanistic proposals<sup>145</sup> seem to indicate that water may play a role in the



formation mechanism involving  $\text{H}_2\text{CO}_3$  or bicarbonate. Though suggested by DFT analysis of the mechanism, it remains an open question whether the  $\text{CO}_2$  is fully incorporated into the substrate.

Whereas metal based systems are known to catalyse the efficient formation of these heterocyclic structures from  $\text{CO}_2$  generally using 2-amino-benzonitriles as reaction partners,<sup>11,146</sup> organocatalytic methods have been investigated successfully providing green alternatives. Quinazoline-2,4(1*H*,3*H*)-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  $\text{CO}_2$  have been reported including IL based systems,<sup>147-150</sup> amine-based heterocycles<sup>151,152</sup> and carbonate bases/base impregnated clay minerals.<sup>153,154</sup> The use of water as a medium has been proposed for the non-catalytic formation of quinazoline-2,4(1*H*,3*H*)-diones.<sup>155</sup> In this latter case, the crucial role of the formation of  $\text{H}_2\text{CO}_3$  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(1*H*,3*H*)-diones starting from 2-amino-benzonitriles and  $\text{CO}_2$ .

## 6. Summary and outlook

In the last five to ten years, the field of  $\text{CO}_2$  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  $\text{CO}_2$  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  $\text{CO}_2$  couplings. However, the chemistry of other organocatalyst structures (including azaphosphatane 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  $\text{CO}_2$  conversion catalysis, and this review will hopefully spur the catalysis community to develop new methodology of common interest to academic and industrial experts.

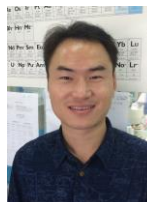
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## Notes and references

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