Top Organomet Chem (2016) 53: 143–170
DOI: 10.1007/3418_2015_97

Transition Metal-Free Incorporation of CO_2

Shuai Zhang, Ran Ma, and Liang-Nian He

Abstract Carbon dioxide can be regarded as an ideal C_1 chemical feedstock in both academic and pharmaceutical laboratories owing to its abundance, low cost, non-toxicity, and nonflammability. However, due to CO_2 inherent thermodynamic stability and kinetic inertness, it is difficult to convert CO_2 to value-added chemicals under mild conditions. In order to overcome such barriers, numerous useful synthetic methodologies by strategically using highly active catalysts have been developed for the incorporation of CO_2 to organic compounds. Transition metal-free compounds are proved to be promising efficacious catalysts able to activate CO_2 molecule for efficient transformation of CO_2 on the basis of mechanistic understanding at the molecular level. This chapter features recent advances at methodologies for catalytic transformation of CO_2 promoted by organocatalysts (e.g., *N*-heterocyclic carbenes, frustrated Lewis pairs and superbases), ionic liquids, and main group metal to produce value-added chemicals such as linear or cyclic carbonates, quinazoline-2,4(1*H*,3*H*)-diones, alkylidene cyclic carbonates, amino acids, and so on.

Keywords Carbon dioxide · Catalysis · Ionic liquid · Organocatalyst · Sustainable chemistry · Transition metal-free process

Contents

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1 Introduction

From a standpoint of C_1 chemistry and green chemistry, incorporation of CO_2 has become one of the most important subjects for the synthesis of valuable organic chemicals/materials in synthetic organic chemistry [1–3]. Much effort has been devoted to this promising subject, and numerous reactions and catalytic systems have been developed for CO_2 utilization. However, the inherent thermodynamic stability and kinetic inertness of CO_2 hinder CO_2 conversion under mild conditions. Accordingly, practical transformation of CO_2 would inevitably rely on its activation via either metal coordination or weak interaction between the active species and CO_2 molecule. Various transition metal complexes have been developed as efficient catalysts, which are usually applied in the carboxylation reactions and hydrogenations reactions. CO_2 as a ligand is able to coordinate with a transition metal center and is thus activated and subsequently converted into carboxylic acids, esters, formic acid, and methanol. On the other hand, transition metal-free compounds are also promising catalysts capable of activating CO_2 for upgrading CO_2 into organics with the advantages of low cost, easy preparation, non-sensitivity to air or moisture, and relative hypotoxicity to the environment. Furthermore, the characteristics of transition metal-free catalysts, such as nucleophilicity, basicity, ease of introducing functionalized groups, and so on, could be applied to activate both CO_2 and substrates, furnishing further transformation of CO_2. In this chapter, efficient transition metal-free catalysts for the transformation of CO_2 including organocatalysts, ionic liquids, and main group metals are summarized. Various valuable chemicals such as carbonates, carbamates, quinazoline-diones, amino acids, etc., could be synthesized with transition metal-free catalysis under mild conditions.

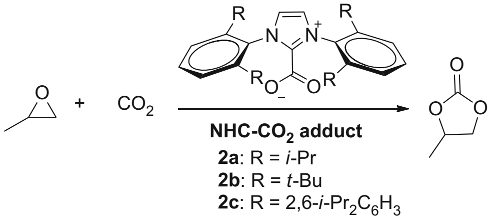
2 Organocatalysts

2.1 N-*Heterocyclic Carbenes and* N-*Heterocyclic Olefins*

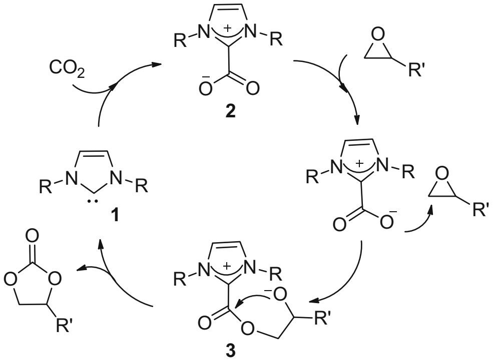
N-Heterocyclic carbenes (NHCs) are usually generated through deprotonation of the corresponding imidazolium salts by strong bases and have been extensively employed as versatile ligands for the formation of a large variety of organometallic complexes [4–7]. Inspiringly, NHCs are able to react with CO_2 to form NHC-CO_2 adducts (*N*,*N*′-disubstituted imidazolinium-2-carboxylates), in which a bent geometry with a O–C–O angle of 129–131° has been determined by X-ray single-crystal study [8, 9]. From a structural point of view, NHC-CO_2 adducts are considered to be zwitterionic compounds formed via NHC's nucleophilic attack at the weak electrophilic carbon center of the CO_2 molecule. Furthermore, NHC-CO_2 adducts show high catalytic activity for carboxylative cyclization with CO_2 because of the strong nucleophilic nature [9–11]. As depicted in Scheme 1, IPr-CO_2 adduct **2a** exhibits the highest catalytic activity for the coupling reaction of CO_2 and epoxides; 100% yield of propylene carbonate is attained from propylene oxide and CO_2 at 120°C, 2 MPa CO_2 pressure. The mechanism of the NHC-CO_2-catalyzed cycloaddition reaction is shown in Scheme 2. The zwitterionic compounds NHC-CO_2 adducts (**2**) are able to go through nucleophilic attack at the epoxide, leading to generation of the zwitterion (**3**). Then, the intramolecular cyclization produces cyclic carbonate along with the release of free NHC. The formation of NHC-CO_2 adduct **2** allows next catalytic cycle to begin. Indeed, the CO_2 adducts (MCM-41-IPr-CO_2) from mesoporous material-supported NHC (MCM-41-IPr) and CO_2 are efficient heterogeneous catalysts for the cycloaddition of CO_2 with epoxides or aziridines under 2.0 MPa CO_2 pressure at 120°C (Scheme 3) [12]. Moreover, the catalyst could easily be recovered by a simple filtration and reused multiple times without obvious loss in activity.

Furthermore, the isolable NHC-CO_2 catalyst provides access to a variety of five-membered α-alkylidene cyclic carbonates from propargyl alcohols [10, 11]. 73% yield of 4-methyl-5-methylene-4-phenyl-1,3-dioxolan-2-one is obtained from the corresponding propargyl alcohol and CO_2 with **2b** as the catalyst (catalyst loading 7.7%) under 6 MPa CO_2, 100°C. The cyclic carbonate formation can be explained by the mechanism involving the nucleophilic addition of the imidazolium-2-carboxylate at either the C–C bond and subsequent intramolecular cyclization of the alkoxide intermediate as depicted in Scheme 4.

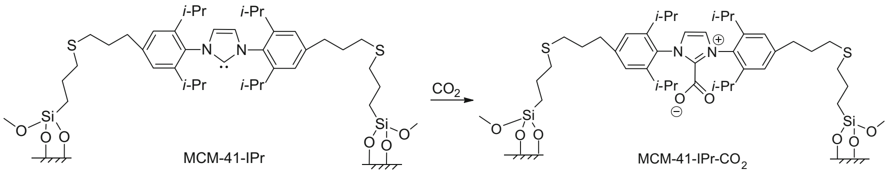
N-Heterocyclic olefins (NHOs) with high electronegativity at the terminal carbon atom are found to show a strong tendency for CO_2 sequestration, affording the NHO-CO_2 adducts. Notably, the NHO-CO_2 adducts are found to be highly active in promoting the carboxylative cyclization of propargylic alcohols with CO_2 at 60°C, 2 MPa CO_2 pressure (even at ambient temperature and 1 atm CO_2 pressure), giving α-alkylidene cyclic carbonates in excellent yields [13]. Based on deuterium-labeling experiments, two reaction paths regarding the hydrogen at the alkenyl position of cyclic carbonates coming from substrate (path A) or both substrate and



Scheme 1 The NHC-CO_2 adduct-catalyzed cycloaddition reaction of epoxide and CO_2 [9, 10]

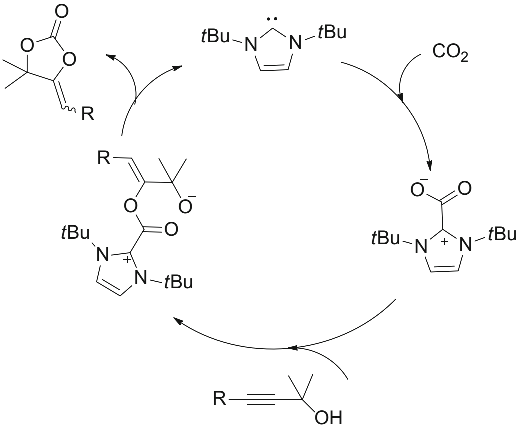


Scheme 2 Possible mechanism for the coupling reaction of CO_2 with epoxides catalyzed by NHC-CO_2 adduct [9, 10]

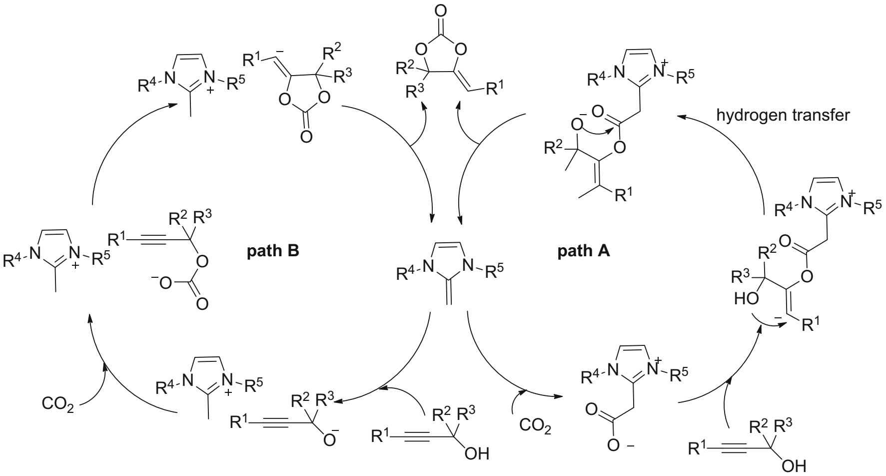


Scheme 3 The formation of MCM-41-IPr-CO_2 [12]

catalyst (path B) are proposed as shown in Scheme 5. At the identical reaction conditions, NHO-CO_2 adducts show much higher catalytic activity than that of the corresponding NHC-CO_2 adducts. The high activity of the NHO-CO_2 adducts is tentatively ascribed to its low stability for easily releasing CO_2 moiety and/or the desired product, a possible rate-determining step in the catalytic cycle.



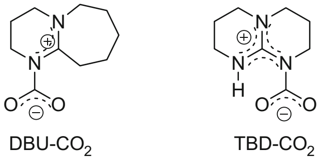
Scheme 4 Plausible mechanism for the NHC-CO_2 adduct-catalyzed carboxylative cyclization of propargylic alcohol with CO_2 [10, 11]



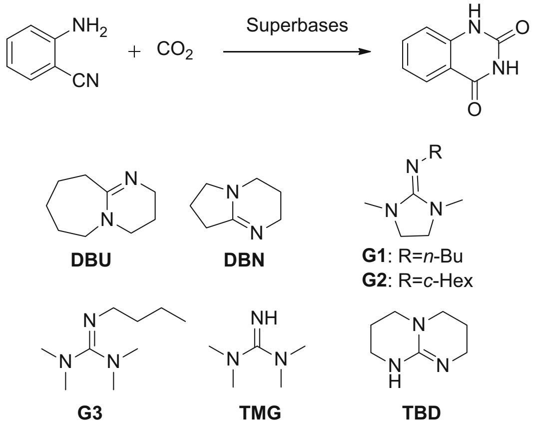
Scheme 5 Plausible mechanism for carboxylative cyclization of propargyl alcohols with CO_2 catalyzed by the NHO-CO_2 adduct [13]

2.2 Superbase

Superbases, such as amidines and guanidines, have been found in many applications in CO_2 capture and conversion because of their characteristic of nucleophilicity and basicity. For example, a mixture of superbase and alcohol could effectively capture equimolar CO_2 and has been proven to be efficient catalysts in the synthesis of organic carbonates and urethanes via the respective reactions of



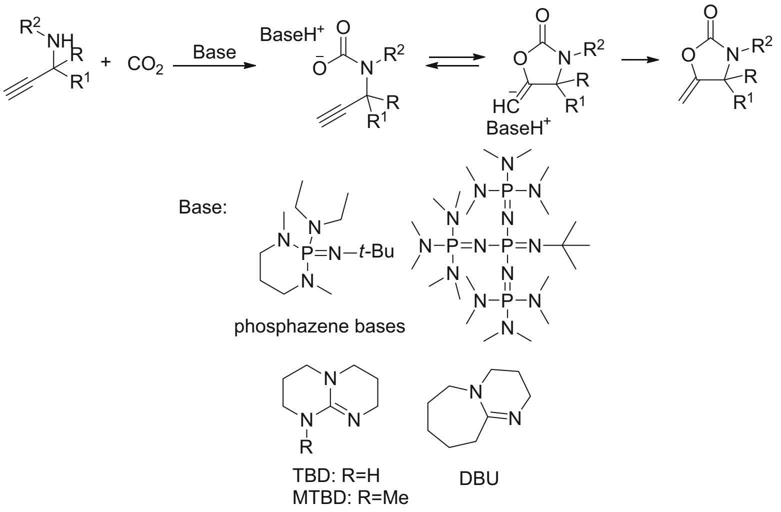
Scheme 6 The structure of DBU-CO_2 and TBD-CO_2 adducts [16–21]



Scheme 7 Guanidine-catalyzed cyclization reaction of 2-aminobenzonitrile and CO_2 [23]

CO_2 with epoxides and amines, respectively [14–18]. 1,8-Diazabicyclo[5.4.0]undec-7-ene (DBU) or 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD) performs nucleophilic attack at the weakly electrophilic carbon center of CO_2 molecule leading to the formation of zwitterionic adducts DBU-CO_2 and TBD-CO_2, respectively (Scheme 6), just like NHC and NHO [16–21]. Recently, the existence of such adducts has been clearly confirmed by X-ray single-crystal diffraction [22] and ^{11}C-labeling [14]. In addition, these DBU-CO_2 and TBD-CO_2 adducts could promote cycloaddition reaction of epoxides and CO_2 through nucleophilic attack at the ring of the epoxide.

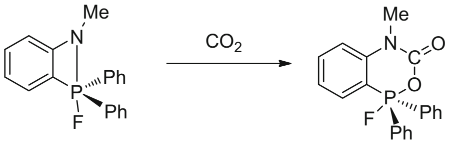
The strong basicity enables those superbases to find application in the base-catalyzed CO_2 conversion. For example, superbases are efficient catalysts for the chemical fixation of CO_2 with 2-aminobenzonitriles for the synthesis of quinazoline-2,4(1*H*,3*H*)-diones under solvent-free conditions as depicted in Scheme 7 [23, 24]. A variety of 2-aminobenzonitriles bearing electron-withdrawing or electron-donating substitutes give the corresponding quinazoline-2,4(1*H*,3*H*)-diones in moderate to excellent isolated yields (60–95%) catalyzed by low-loading TMG under 10 MPa CO_2 pressure at 120°C within 4 h. As shown in Scheme 8, superbases could also catalyze the carboxylative cyclization reactions of propargylamines or propargyl alcohols with CO_2, affording α-methylene cyclic carbonates and oxazolidinones, respectively [25, 26].



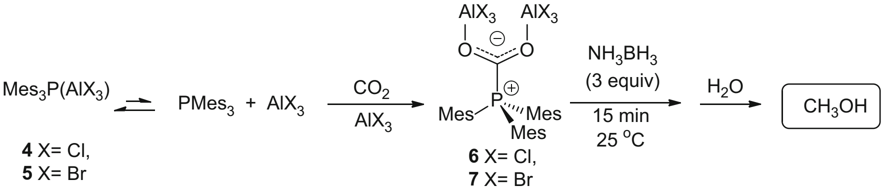
Scheme 8 Superbase-catalyzed carboxylative cyclization of propargylamines with CO_2 [25, 26]

2.3 Frustrated Lewis Pair

Frustrated Lewis pairs (FLPs) consist of sterically hindered Lewis donors and acceptors. The steric demands preclude the formation of simple Lewis acid–base adducts, allowing for subsequent reactions of both Lewis acids and bases with other potential molecules. Recently, FLPs have become a fundamentally unique strategy for activating a variety of small molecules [27, 28]. Especially, FLP amidophosphoranes [29] could rapidly capture one equivalent of CO_2 with simultaneous activation as shown in Scheme 9. Furthermore, B/P-, B/N-, P/N-, and Al/P-based FLPs have been shown to have the ability to convert CO_2 into carbonic acid derivatives, methanol, methane, or CO by the groups of Stephan [30–32], O'Hare [33], and Piers [34]. For example, Al/P-based FLPs $Mes_3P(AlX_3)$ (Mes = 2,4,6-$C_6H_2Me_3$ X = Cl **4**; Br **5**), a 1:2 mixture of $PMes_3$ with AlX_3, could irreversibly capture CO_2 with the formation of species **6** and **7** ($Mes_3P(CO_2)(AlX_3)_2$ X = Cl **6**; Br **7**) (Scheme 10). Furthermore, the species **6** and **7** could react rapidly with excess ammonia borane at room temperature to give CH_3OH upon quenching with water [30]. The structure of species **6** or **7** has been identified by X-ray single-crystal diffraction, in which phosphine is bound to the C atom of CO_2, while AlX_3 units are bonded to each of the O atoms. The P–C bond lengths in **6** and **7** are found to be 1.927(8) and 1.918(5) Å, respectively, while the O–Al distances are 1.807(5) and 1.808(6) Å in **6** and 1.829(4) and 1.803(3) Å in **7**. The C–O bond lengths are determined to be 1.233(8) and 1.251(8) Å in **6** and equivalent at 1.248(6) Å in **7**. The O–C–O angles are 126.6(7)°and 125.8(4)° in **6** and **7**, respectively, while the C–O–Al angles differ substantially from each other being 141.3(5)° and 165.2(6)° and 140.0(3)° and 178.7(4)° in **6** and **7**, respectively.



Scheme 9 Equimolar CO_2 capture by amidophosphoranes [29]



Scheme 10 Stoichiometric reduction of CO_2 to CH_3OH promoted by Al/P-based FLPs [30]

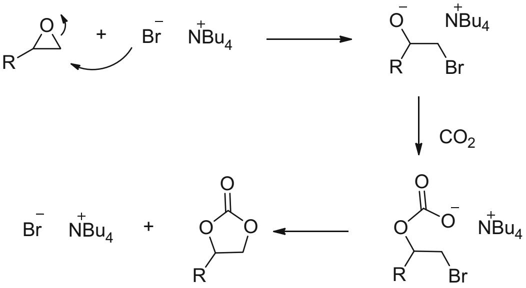
3 Ionic Liquid

Ionic liquids (ILs) being composed of organic cations and inorganic/organic anions have some very attractive properties, such as nonvolatile, nonflammable, high thermal stability, and excellent solubility. In addition, the functions of ILs can be designed for different processes by changing the structures of their cations or anions. ILs, especially task-specific ILs (TSILs) with various functionalized groups, have great potential applications in chemical reactions, material synthesis, separation, and fractionation [35, 36]. Encouragingly, by introducing corresponding functionalized groups, TSILs could activate CO_2 molecule or substrates for further transformation. Therefore, TSILs display superior performance for CO_2 capture and conversion such as hydrogenation of CO_2 to formic acid [37], preparation of 5-aryl-2-oxazolidinones from aziridines and CO_2 [38], synthesis of disubstituted urea from amines and CO_2 [39], synthesis of quinazoline-2,4(1*H*,3*H*)-diones from CO_2 and 2-aminobenzonitrile, and so on.

3.1 Homogeneous Ionic Liquid

One of the most attractive synthetic protocols utilizing CO_2 is the coupling reaction of epoxides and CO_2 to afford the five-membered cyclic carbonates such as ethylene carbonate (EC) and propylene carbonate (PC) which could serve as excellent polar aprotic solvents, intermediates in the production of pharmaceuticals, and electrolytic elements of lithium secondary batteries [40–42]. ILs, for instance, tetrabutylammonium bromide (TBAB) or tetrabutylammonium iodide (TBAI) [43], 1-octyl-3-methylimidazolium tetrafluoroborate ($[C_8MIm][BF_4]$) [44], and Lewis

Scheme 11 Proposed mechanism of propylene carbonate synthesis catalyzed by TBAB [43]

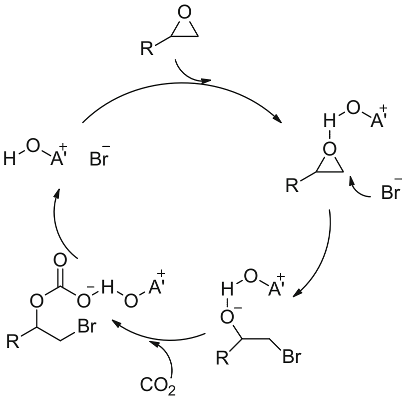


basic ILs [45] are effective catalysts for the cycloaddition reaction of epoxide and CO_2. Taking TBAB as an example, a plausible mechanism for the cycloaddition reaction is shown in Scheme 11. The epoxide ring is opened by nucleophilic attack of the bromide anion, which could lead to generation of an oxy anion species, then affording the corresponding cyclic carbonate after CO_2 insertion.

Under supercritical CO_2 ($scCO_2$) conditions, ILs usually show relatively high activity for the cycloaddition reaction due to complete miscibility of CO_2 in the ILs under high pressure conditions. With 1-octyl-3-methylimidazolium tetrafluoroborate ($[C_8MIm][BF_4]$) as the catalyst under supercritical conditions (14 MPa CO_2) at 110°C, the cycloaddition of CO_2 and propylene oxide could complete within 5 min with TOF of 516 h^{-1} [44].

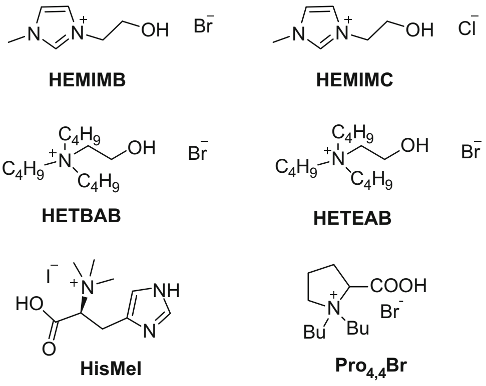
The introduction of hydroxyl group or carboxylic acid group could highly increase the catalytic activity of ILs. As depicted in Scheme 12, the interaction of the H atom with the O atom of epoxide through a hydrogen bond results in the polarization of C–O bond, so the ring of the epoxide could be opened easily. A series of hydroxyl-functionalized ILs [46, 47] and carboxyl-functionalized ILs [48–50] have been proven to be efficient catalysts for the coupling of epoxide and CO_2 (Scheme 13). In the presence of 1-(2-hydroxyl-ethyl)-3-methylimidazolium bromide (HEMIMB), 99% yield of propylene carbonate with >99% selectivity is obtained. The excellent catalytic activity is obtained because of the synergistic interaction of the hydrogen-bonding groups with the nucleophile in these ILs as shown in Scheme 12. Even the existence of water in ILs could also accelerate the reaction due to the formation of hydrogen bonds [51], which is quite similar to the role of hydroxyl group.

Poly(ethylene glycol)s (PEGs) are a family of water-soluble linear polymers which could be regarded as a kind of CO_2-philic materials. In other words, "CO_2-expansion" effect could lead to changes in the physical properties of the liquid phase mixture including lowered viscosity and increased gas/liquid diffusion rates [52]. PEG-functionalized ILs, $BrBu_3NPEG_{6000}NBu_3Br$ [53, 54], $BrBu_3PPEG_{6000}PBu_3Br$ [55], $PEG_{6000}(GBr)_2$ [56], and $BrTBDPEG_{150}TBDBr$ [57] as listed in Scheme 14, could be utilized as highly active homogeneous catalysts for CO_2 transformation. For example, the cycloaddition reaction of PO with CO_2 in the presence of 0.5 mol% $BrBu_3NPEG_{6000}NBu_3Br$ affords PC in 98% yield together with 99% selectivity at 120°C, 8 MPa CO_2, in 6 h. Furthermore, the



[A'-OH]Br: hydroxl or carboxyl-functionalized ILs

Scheme 12 Proposed mechanism for the cycloaddition reaction promoted by hydrogen bonding

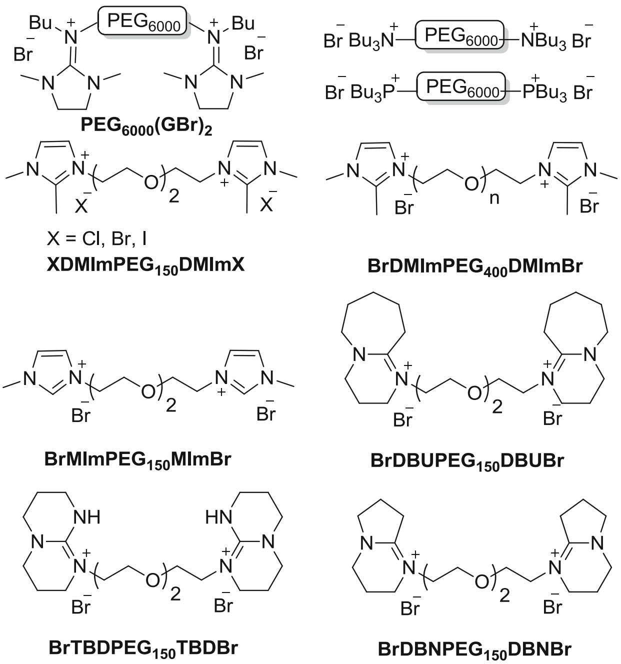


Scheme 13 Several kinds of hydroxyl-functionalized and carboxyl-functionalized ILs [46–50]

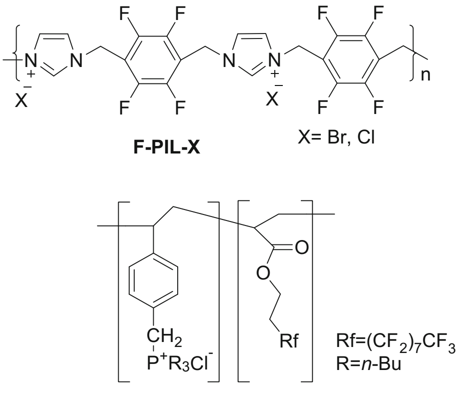
PEG_{6000}-supported catalyst can be readily recovered by simple filtration and reused without appreciable loss of activity.

Attachment of fluorinated chains to chelating agents and surfactants could generally enhances the solubility of such compounds in $scCO_2$. Fluorine-containing ILs and polymer [58–60] as illustrated in Scheme 15 have been proven to be efficient and recyclable homogeneous CO_2-soluble catalysts for solvent-free synthesis of cyclic carbonates from epoxides and CO_2 under $scCO_2$ conditions. Furthermore, these catalysts can be easily recovered after reaction and reused with retention of high activity and selectivity. For example, the catalyst F-PIL-Br is easily recovered through centrifugation, dried, and then used directly for the next run without any further purification. As for catalyst **8**, simple filtration can get the catalyst recovered because it precipitates upon venting CO_2.

Zwitterionic compounds have been used as halogen-free bifunctional catalysts for the cycloaddition of epoxides with CO_2. A range of aromatic zwitterions bearing an ammonium betaine able to activate CO_2 molecule proved to be efficient catalysts for the production of cyclic carbonates under metal-free, solvent-free



Scheme 14 PEG-functionalized ionic liquids for the synthesis of cyclic carbonates [53–57]



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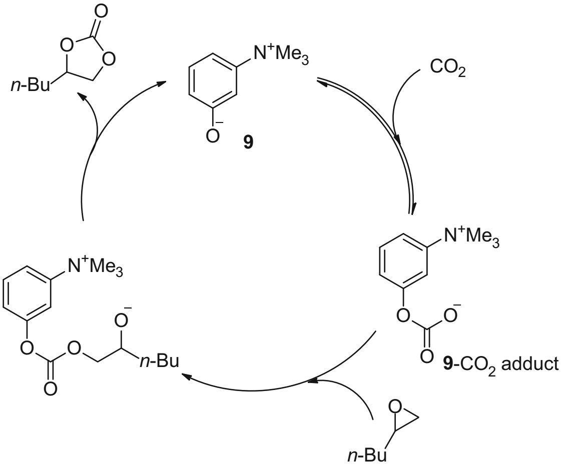
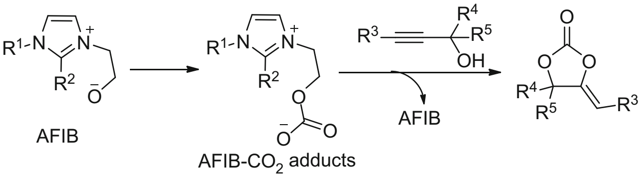
Scheme 15 Fluoro-functionalized polymeric ionic liquids [58–60]

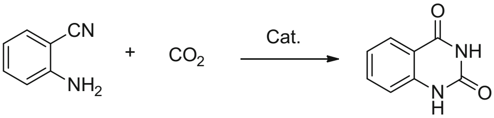
conditions [61]. Interestingly, the **9**-CO_2 adduct as shown in Scheme 16 was characterized and used as a synthon to prepare cyclic carbonates. Very recently, Lu and his coworkers reported that the alkoxide-functionalized imidazolium betaines (AFIBs) bearing an alkoxide anion and an imidazolium cation show strong tendencies for CO_2 capture, affording a CO_2 adduct (AFIB-CO_2) [62]. Furthermore,



Scheme 16 The synthesis of cyclic carbonates catalyzed by aromatic zwitterions [61]



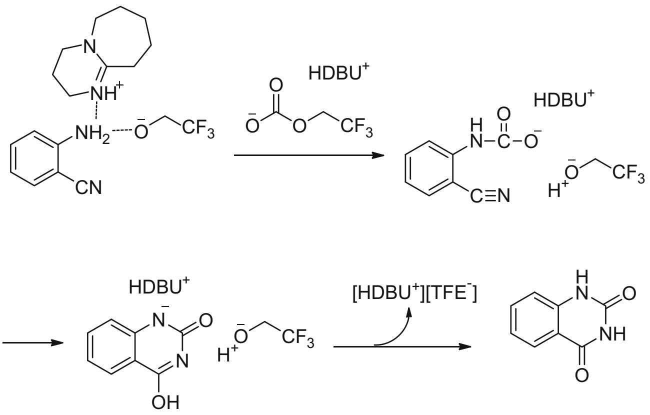
Scheme 17 AFIB-CO_2 adducts catalyzed carboxylative cyclization of propargylic alcohols with CO_2 [62]



Scheme 18 Reaction of CO_2 and 2-aminobenzonitrile to quinazoline-2,4(1*H*,3*H*)-dione

AFIB-CO_2 adducts could effectively catalyze the coupling reaction of propargylic alcohols with CO_2 under solvent-free reaction conditions, selectively affording alkylene cyclic carbonates, as depicted in Scheme 17.

ILs could act as both solvent and catalyst for the synthesis of quinazoline-2,4 (1*H*,3*H*)-dione derivatives through incorporation of CO_2 into aminobenzonitriles as delineated in Scheme 18. Excellent results are attained by using 1-butyl-3-methyl imidazolium hydroxide ([Bmim]OH) [63] and 1-butyl-3-methylimidazolium acetate ([Bmim]Ac) [64]. With [Bmim]Ac as catalysts, 92% yield of quinazoline-2,4(1*H*,3*H*)-dione is attained at 1 atm CO_2, 90°C in 10 h. Moreover,



Scheme 19 Possible dual-activation role of $[HDBU^{+}][TFE^{-}]$ [66]

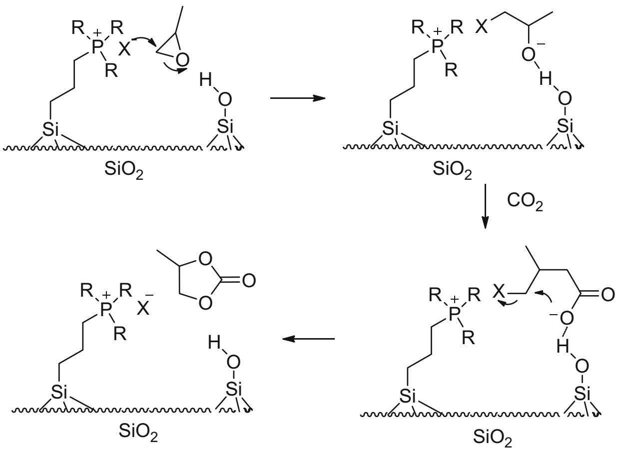
recovery of such ILs is easily performed by simple filtration. The catalyst could be reused at least five times without considerable loss in catalytic activity.

The synthesis of quinazoline-2,4(1*H*,3*H*)-dione could be regarded as a kind of base-catalyzed reactions; superbases, such as TMG, could be applied as catalysts for this transformation [65]. Furthermore, superbase-derived protic IL, e.g., $[HDBU^{+}][TFE^{-}]$, has been found to activate CO_2 and 2-aminobenzonitriles simultaneously to produce quinazoline-2,4(1*H*,3*H*)-diones under 1 atm CO_2 and room temperature as shown in Scheme 19 [66]. 97% yield of quinazoline-2,4(1*H*,3*H*)-dione is attained with $[HDBU^{+}][TFE^{-}]$ (3% catalyst loading) at 30°C, 1 atm CO_2 in 24 h. A new signal that appears at $\delta = 167.7$ ppm in the ^{13}C-NMR spectrum of $[HDBU^{+}][TFE^{-}]/CO_2$ mixture is attributed to the carbonyl carbon atom of the carbonate, suggesting that CO_2 is activated by the anion $[TFE^{-}]$, thus forming a carbonate intermediate. Simultaneously, 2-aminobenzonitriles could form hydrogen bonds with both the cation and anion of the IL, resulting in weakening the N–H bond in NH_2 group of 2-aminobenzonitrile.

3.2 Supported Ionic Liquid

Although ILs have been reported to be one of the most efficient catalysts for CO_2 fixation, application of homogeneous catalysts in industry could be limited due to the complicated separation procedure. On the other hand, proper use of heterogeneous catalysis for CO_2 conversion may offer enhancement of the reaction rate and control of selectivity, increasing catalyst lifetime and facilitating separation.

One way is to immobilize the IL onto silica. A series of silica-supported ILs including phosphonium salts [67, 68], imidazolium ILs [69–73], 4-pyrrolidinopyridinium iodide [74], aluminum(salen) complexes [75, 76], and hexa-alkylguanidinium chloride [77] exhibit high catalytic activity, selectivity,



Scheme 20 Possible acceleration mechanism for the cycloaddition reaction catalyzed by silica-supported phosphonium salts [67, 68]

and reusability in the cycloaddition of CO_2 to epoxides. An almost quantitative amount of propylene carbonate is produced using SiO_2-C_3H_6-P(*n*-Bu)$_3$I as catalyst at 100°C, 10 MPa of CO_2 in 1 h. Interestingly, the silica-supported ILs dramatically increase the catalytic activities compared to the corresponding homogeneous ILs. The cooperative catalysis originating from the silica surface and the onium part may result in the enhanced activity. In other words, the acidic surface silanol groups are able to activate epoxides, and then the ring opens via subsequent nucleophilic attack. A proposed mechanism of the coupling reaction catalyzed by silica-supported phosphonium salts [67, 68] has been proposed as shown in Scheme 20. Furthermore, these heterogeneous ILs could easily be separated and reused without considerable loss of the activity.

Besides silica, mesoporous sieves and polymeric materials are other kinds of promising supports, which could immobilize ILs. ILs immobilized on mesoporous sieves (SBA-15 [78, 79] and MCM-41 [80–82]) and polymeric materials [83, 84] could act as efficient catalysts for the transformation of CO_2 into cyclic carbonates with high yield and excellent selectivity under relatively mild conditions. High activity is displayed when ILs immobilized on carboxymethyl cellulose (CMC) and chitosan (CS) are applied as heterogeneous catalysts for cycloaddition of epoxides with CO_2, since CMC or CS is rich in hydroxyl and carboxyl groups [85–87]. CMC and CS not only act as the supporting materials for ILs but also serve as carriers of functional groups capable of activating the nucleophilic attack via the hydroxyl and the carboxyl moieties. The synergistic function originating from the hydroxyl and carboxyl moieties in the supporter could activate epoxides through formation of hydrogen bonds, thus facilitating the ring opening of epoxides.

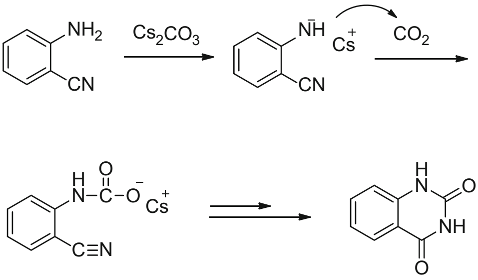
4 Main Group Metal

Main group metal compounds are an important kind of effective catalysts for CO_2 incorporation to form value-added chemicals. Unlike transition metal catalysts, which usually coordinate with CO_2 molecule leading to simultaneously activate CO_2, main group metal catalysts usually react with substrates, in situ generating nucleophiles to go through nucleophilic attack at CO_2. For example, cesium carbonate could react with 2-aminobenzonitrile, providing a nitrogen anion to perform a nucleophilic attack at CO_2. The Lewis basic cation of aluminum(III) (salen) complex could active the epoxide through interaction with the oxygen, furnishing a nucleophilic oxygen anion to react with CO_2. Fluorine salts usually react with silicon compounds, affording a carbon anion to attack at CO_2. Stannum compounds have a strong tendency to react with alcohols with the formation of Sn–O bonds, furnishing CO_2 insertion. By applying these characteristics of main metal catalysts, various valuable products are obtained in high yield and selectivity.

4.1 Main Group Metal Salts

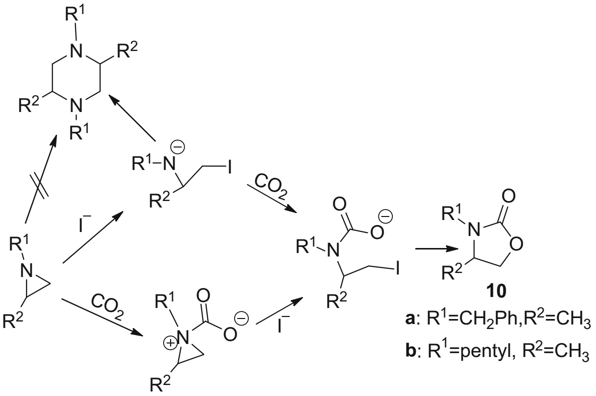
Cesium carbonate shows remarkable activity for the base-catalyzed reaction of CO_2 with 2-aminobenzonitriles [88]. Cs_2CO_3 could react with 2-aminobenzonitrile, providing a nitrogen anion due to its strong basicity. As shown in Scheme 21, the nitrogen anion could attack to CO_2, furnishing further conversion of CO_2. In the presence of 0.25 equivalent Cs_2CO_3, 94% of quinazoline-2,4(*1H*,*3H*)-diones is obtained at 1.3 MPa CO_2, 100°C in 4 h. Notably, this catalytic system is applicable to a wide variety of substituted 2-aminobenzonitriles with different steric and electronic properties. Interestingly, the reaction temperature has a pronounced positive effect on the synthesis of quinazoline-2,4(*1H*,*3H*)-diones. The reaction does not occur at 80°C, while the yield increases to 94–95% with an increase in the reaction temperature from 100 to 120°C.

Inexpensive K_2CO_3 could catalyze the formation of carbamates in $scCO_2$ with a catalytic amount of Bu_4NBr as cocatalyst [89]. The reaction efficiency in $scCO_2$ is 50–100 times higher than that attained in heptane. The amine readily forms the



Scheme 21 Cs_2CO_3-catalyzed synthesis of quinazoline-2,4(*1H*,*3H*)-diones [88]

Scheme 22 Possible mechanisms for the LiI-catalyzed cycloaddition of CO_2 with aziridine [91]



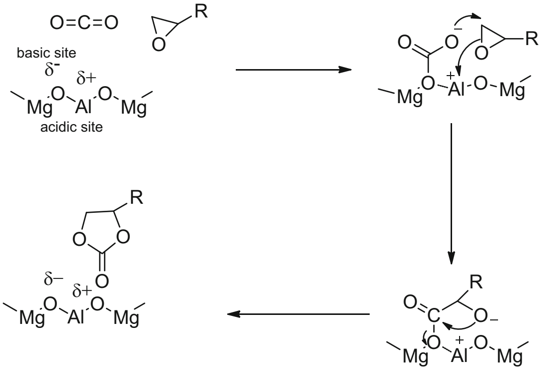
carbamic acid ammonium salt upon the introduction of liquid CO_2. As for catalytic activity among alkali metal carbonate, Cs_2CO_3 is much higher than K_2CO_3 and Na_2CO_3. Cs_2CO_3 together with tetrabutylammonium iodide (TBAI) is proven to be an efficient catalyst for the synthesis of carbamates in which Cs_2CO_3, TBAI, and alkyl halides are excessive [90]. Aliphatic, aromatic, and heterocyclic amines and reactive, unreactive, and secondary halides can be converted to the corresponding carbamates using DMF as solvent.

The conversion of the aziridine to the corresponding oxazolidinone can be performed by employing LiI as the catalyst in THF with hexamethylphosphoramide (HMPA, a lithium-complexing agent) as a cosolvent which is used to facilitate the ion pair separation of the LiI and strengthen the S_N2 character of the reaction (Scheme 22) [91]. Only one isomer oxazolidinone (**10a** 97% yield or **10b** 95% yield) can be obtained. Nucleophilic attack of the I^- at the less substituted carbon leads to the ring-opened structure of aziridine, which then reacts with CO_2 to further form oxazolidinones by intramolecular ring closure, and the catalyst is regenerated.

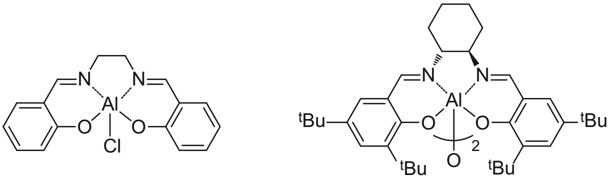
Mg–Al-mixed oxide and magnesium oxide possess both acid and base surface sites and could activate both epoxides and CO_2. With magnesium oxide or Mg–Al-mixed oxide as catalysts, the reaction of CO_2 with epoxides gives organic carbonates in excellent yields [92, 93]. As depicted in Scheme 23, the basic and acidic sites located in Mg–Al-mixed oxide could activate CO_2 molecule and substrates, respectively, which greatly increases the catalytic activity. Especially, the Lewis basic sites could absorb CO_2 onto the surfaces to form the carbonate species, which promotes the ring opening of epoxides by a nucleophilic attack. Besides Mg–Al oxide, basic zeolites [94–96] are also effective catalysts for the cycloaddition of CO_2 with epoxides.

4.2 Aluminum(Salen) Complex

Salen ligands are commonly prepared through the condensation of a salicylaldehyde and a diamine. The ease of synthesis and modification has promoted more and more interest in using salen as a ligand for many different catalytic



Scheme 23 The interaction of Mg–Al-mixed oxide with epoxide and CO_2 [93]



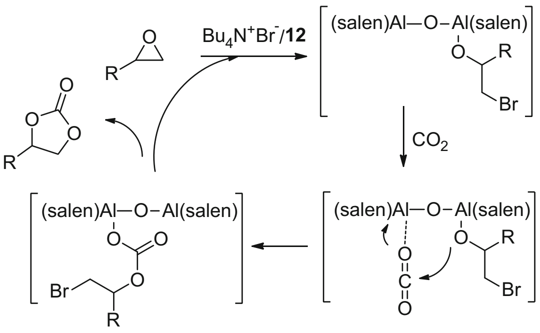
11 **12**

Scheme 24 Al(III)(salen)Cl complex **11** [97] and dimeric Al(salen) complex **12** [98]

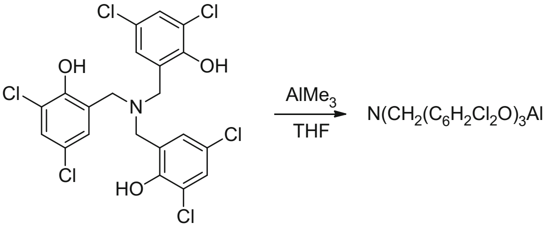
reactions. Salen complexes with a number of transition metals and main group metals have been found to catalyze the cycloaddition of CO_2 to epoxides. Aluminum(III)(salen) complexes are promising main group metal catalysts for the cycloaddition reaction. For example, Al(III)(salen)Cl complex **11** (Scheme 24) is reported to be effective catalysts for the synthesis of ethylene carbonate in the presence of TBAB as cocatalyst [97–101]. Quantitative yield is obtained under 16 MPa CO_2, 110°C, with a TOF of 2,200 h^{-1}. In the absence of onium cocatalysts, complex **11** shows a more moderate activity (TOF 174 h^{-1}) under the otherwise identical reaction conditions.

Dimeric aluminum(salen) complexes (**12**, Scheme 25) with TBAB as cocatalyst have shown exceptionally high catalytic activity for the synthesis of cyclic carbonates at ambient temperature and pressure [98]. 3-Phenylpropylene oxide, 1,2-hexene oxide, and 1,2-decene oxide are transformed into the corresponding cyclic carbonates with the yields of 99% (after 24 h), 88% (after 3 h), and 64% (after 3 h), respectively. As depicted in Scheme 19, both aluminum ions of the complex play a role in activating the epoxide and CO_2, resulting in the excellent catalytic activity. Furthermore, the catalyst **12** could be reused over 60 times without loss of catalytic activity, although periodic addition of TBAB is necessary.

An aluminum complex based on an amino triphenolate ligand scaffold as shown in Scheme 26 has been demonstrated to be a highly active and versatile catalyst for



Scheme 25 Possible mechanism to explain the catalytic activity of dimeric Al(salen) complex **12** [98]



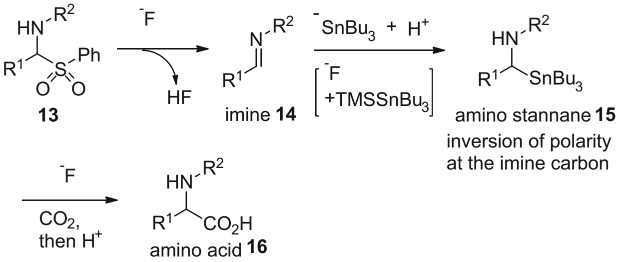
Scheme 26 Synthesis of aluminum complex based on an amino triphenolate [99]

organic carbonate formation [99]. Unprecedented activity (initial TOFs up to 36,000 h^{-1} and TONs exceeding 118,000) is attained during catalysis for the cycloaddition of CO_2 to epoxides, with a wide substrate scope and functionality tolerance [102].

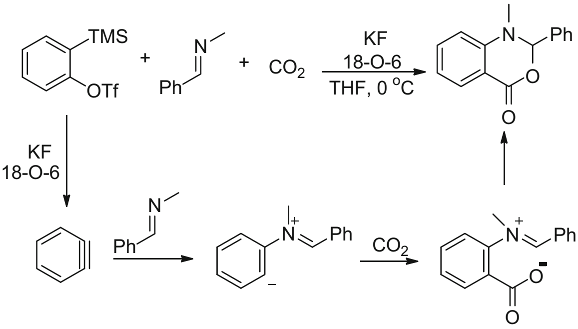
4.3 *Fluorine Salts*

Fluorine anion has a strong tendency to react with compounds containing silicon atoms, affording silicon fluoride compounds and a carbon anion. This unique characteristic is applicable to the synthesis of amino acids by using gaseous CO_2 as carboxylating reagent. Arylglycine derivatives are prepared from the imine equivalents (*N*-Boc-R-amido sulfones **13**) using a combination of TMS-$SnBu_3$ and CsF under CO_2 atmosphere as illustrated in Scheme 27 [103–106]. Reversal of polarity on the imino carbon atom is a key to the success of the proposed transformation, which could be accessed via α-metalation of alkylamine derivatives. A plausible pathway of the reaction is proposed as shown in Scheme 27. Firstly, by treatment with CsF, imine **14** could be generated in situ from a readily available synthetic precursor of imines, amino sulfone **13**. Subsequently, imine **14** is converted into amino stannane **15** by attack of tributylstannyl anion. Finally, the fluoride ion further activates α-amino stannane **15** by attack at the tin atom to improve nucleophilicity of the carbon atom, thus leading to CO_2 insertion into the C–Sn bond and affording α-amino acid derivative **16**.

Arynes are highly unstable species with salient electrophilic nature that could undergo nucleophilic addition with a variety of neutral nucleophiles, and the



Scheme 27 One-pot synthesis of α-amino acids with the aid of fluorine anion [103]

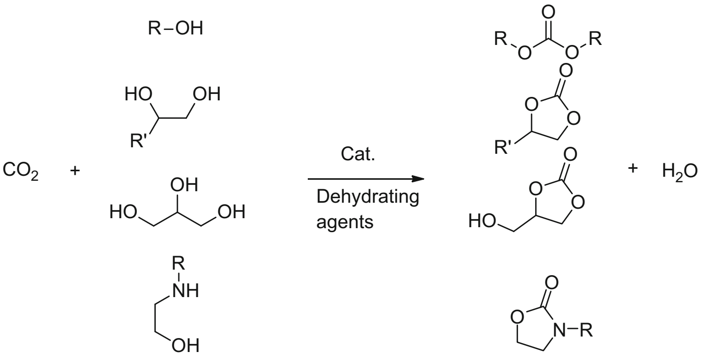


Scheme 28 Three-component coupling of benzyne, imine, and CO_2 [107]

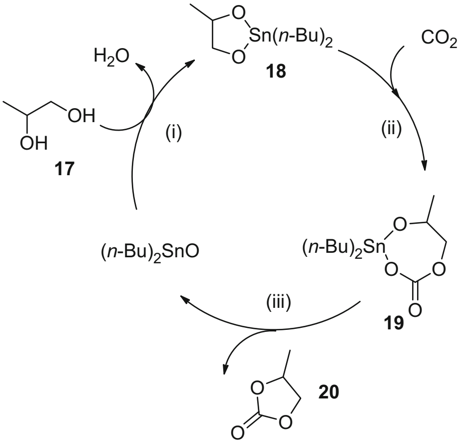
resulting reactive zwitterions are readily trapped by various carbon electrophiles such as aldehydes or sulfonylimines. In 2006, Yoshida and coworkers disclosed that CO_2 could be used as a carbon electrophile for the aryl anion intermediate which is generated from nucleophilic attack of imines at arynes [107]. A plausible mechanism is proposed as depicted in Scheme 28. Benzyne, which is formed by fluoride-induced 1,2-elimination of *o*-trimethylsilylphenyl triflate, undergoes nucleophilic addition with an imine. The resulting zwitterion is readily trapped by CO_2, and a subsequent intramolecular cyclization affords six-membered heterocycles, benzoxazinone derivatives. After that, amines or isocyanides have been used as nucleophilic partners for CO_2 incorporation into arynes, giving anthranilic acid derivatives and *N*-substituted phthalimides, respectively, under mild reaction conditions [108, 109].

4.4 Stannum Compounds

Sn compounds are remarkable catalysts for the synthesis of organic carbonates, such as dimethyl carbonate (DMC), and cyclic carbonates from methanol, glycol, and glycerol with CO_2 as raw materials as depicted in Scheme 29.



Scheme 29 Incorporation of CO_2 promoted by dehydrating agents



Scheme 30 A postulated mechanism for PC synthesis from PG and CO_2 catalyzed by Bu_2SnO [112]

Sn compounds, such as dibutyltin oxide (Bu_2SnO) and dibutyltin dimethoxide ($Bu_2Sn(OMe)_2$), have been reported to be efficient catalysts for the carboxylation of methanol [110, 111], glycol [112], glycerol [113], and 1,2-aminoalcohols into carbonates and 2-oxazolidinones, respectively. Taking the carboxylation of propylene glycol with CO_2 as an example, a plausible catalytic cycle is proposed as illustrated in Scheme 30. It involves three steps: (1) the reaction of Bu_2SnO and propylene glycol gives 2,2-dibutyl-1,3,2-dioxastannolan **18** [114]; (2) since Sn–O bond is known to be susceptible to CO_2 insertion [115], a cyclic tin carbonate **19** is formed through the insertion of CO_2 to **17**; (3) subsequent intramolecular nucleophilic attack of alkoxy group at the carbonyl group may cause the production of propylene carbonate along with regenerating dibutyltin oxide. The removal of water is a crucial issue for the reaction by shifting the equilibrium to carbonates. In the presence of a catalytic amount of Bu_2SnO or $Bu_2Sn(OMe)_2$ with molecular sieve as the dehydrating agent, the yield of propylene carbonate reaches nearly 50% at 180°C for 72 h.

5 Conclusion and Prospective

Over the past decade, CO_2 chemistry has been developed greatly. Catalytic CO_2 incorporation into valuable organic molecules has become an essential subject in synthetic organic chemistry. This chapter highlights many promising transition metal-free catalysts, including organocatalysts, ionic liquids, and main group metal, which are proven to be efficient catalysts for the transformation of CO_2. Compared to transition metal-based catalysts, catalysts outlined in this chapter possess many significant advantages of low cost, easy preparation, non-sensitivity to air or moisture, and relative hypotoxicity to the environment. Many important progresses on transition metal-free incorporation of CO_2 have been made resulting in the production of various valuable chemicals such as linear or cyclic carbonates, quinazoline-2,4(1*H*,3*H*)-diones, alkylidene cyclic carbonates, and amino acids.

Although great progresses have been made on chemical transformation of CO_2 by transition metal-free catalysts, CO_2 incorporation at milder reaction conditions and more efficient catalysts are still highly desired. Especially, it is highly wishful to perform CO_2 conversion at low pressure (<1 MPa), even at 1 atm CO_2 pressure. Therefore, more efficient transition metal-free catalysts on the basis of activation of CO_2 or substrates should be further designed to improve the catalytic efficiency. We hope this presentation will stimulate further interest in the development of more effective transition metal-free catalysts for chemical transformation of CO_2 in academic research and industrial utilization.

Acknowledgments We are grateful to the National Natural Sciences Foundation of China, the Specialized Research Fund for the Doctoral Program of Higher Education (20130031110013), the MOE Innovation Team (IRT13022) of China, and the "111" Project of Ministry of Education of China (project no. B06005) for financial support.

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