Organic synthesis using carbon dioxide as phosgene-free carbonyl reagent*

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Abstract: CO_2 is very attractive as a typical renewable feedstock for manufacturing commodity chemicals, fuel, and materials since it is an abundant, nontoxic, nonflammable, and easily available C1 resource. The development of greener chemical methodologies for replacing the utility of hazardous and environmentally undesirable phosgene largely relies on ingenious activation and incorporation of CO_2 into valuable compounds, which is of paramount importance from a standpoint of green chemistry and sustainable development. Great efforts have been devoted to constructing C–C, C–O, and C–N bond on the basis of CO_2 activation through molecular catalysis owing to its kinetic and thermodynamic stability. The aim of this article is to demonstrate the versatile use of CO_2 in organic synthesis as the alternative carbonyl source of phosgene, with the main focus on utilization of CO_2 as phosgene replacement for the synthesis of value-added compounds such as cyclic carbonates, oxazolidinones, ureas, isocyanates, and polymers, affording greener pathways for future chemical processes.

Keywords: atom economy; aziridines; carbon dioxide; carbonylation; catalysis; green chemistry; ionic liquids; organic carbonate; phosgene-free process; urea.

INTRODUCTION

CO_2 as an abundant, nontoxic, easily available, and typical renewable C1 source as well as an important "greenhouse" gas has been drawing more and more attention in line with the need for development of green chemistry and a sustainable society. Obviously, CO_2 capture and storage looks particularly effective for temporarily preserving large volumes of CO_2 from fossil fuel combustion and industrial gaseous emission [1]. Significant progress has been achieved in the chemical utilization of CO_2 as an alternative to phosgene in organic synthesis. Major drawbacks of the conventional phosgene processes would be environmental and safety problems involved with using copious amounts of chloride-based solvent, which is largely excessive compared with the total weight of target products. Above all, the utility of highly toxic phosgene would also cause easy corrosion of reaction equipment as a result of commonly coproduced hydrochloric acid and alkali chloride salts. With the increasing demands for safer and cleaner chemical processes, the hazardous phosgene route has to be improved or essentially replaced by eco-friendly technologies with CO_2 as the alternative C1 starting material. There have been many struggles to conquer the environmental and ecological disadvantages of the phosgene process by using CO_2, but these efforts have confronted significant technological obstacles in replacing phosgene,

both for effectively catalytic activation of CO_2, probably owing to its inherent thermodynamic stability and kinetic inertness, and for a cleaner reaction environment to effectively manufacture value-added products. In this regard, the formation of an active species-CO_2 adduct via direct coordination is one of the most powerful ways to induce the inert CO_2 molecule to undergo chemical reactions. However, only weak interactions between CO_2 and the active catalytic center can be sufficient to bring about catalytic reactions involving the insertion of CO_2 in some cases. Accordingly, only if we understand the underlying principles of CO_2 activation can the goal of using CO_2 as an environmentally friendly and economically feasible C1 source for the replacement of phosgene be achieved.

Nowadays, cyclic carbonates, oxazolidinones, ureas, and isocyanates are all valuable chemicals [2], and the synthetic methodology for the above-mentioned chemicals by incorporation of CO_2 is one of the most promising and eco-friendly methods. Contemporarily, polycarbonates are the most extensively used engineering plastics, and the current annual production of polycarbonates amounts to 2 million tons worldwide [3]. In addition, polyurethanes from aziridines also exhibit potential utility for industrial materials [4]. Hence, in this context, we would like to illustrate potential applications of CO_2 in the synthesis of a series of heterocyclic compounds and industrial useful chemicals as the alternative carbonyl source instead of phosgene or CO. Scheme 1 shows examples of the applications of this concept. Those findings summarized herein would open synthetic pathways for the selective synthesis of industrially important compounds from CO_2 and demonstrate that such CO_2 functionalization could be the ideal substitute for the traditional phosgene process. We believe that partial results of CO_2 chemistry disclosed herein will stimulate further interest in scientific exploration that may lead to the development of CO_2 as a new source for a wide set of value-added organic compounds such as solvents, fuels, fine/bulk chemicals, pharmaceuticals, and polymers.
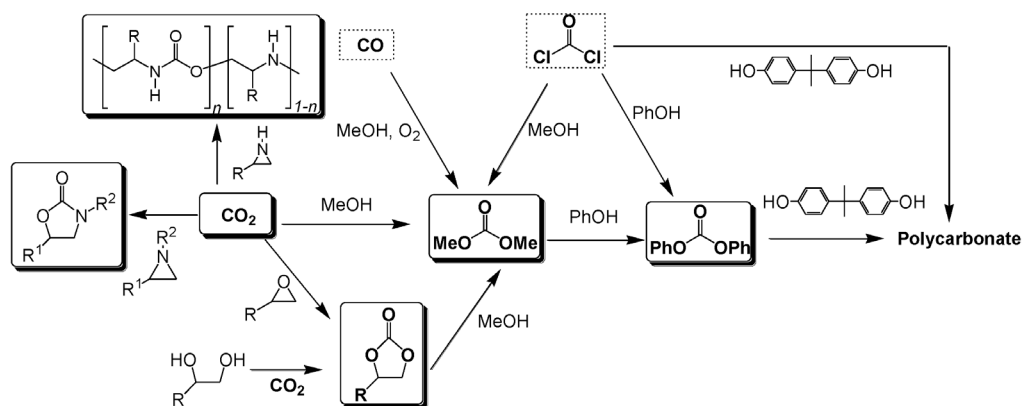
Scheme 1 Organic carbonate synthesis using CO_2 as phosgene replacement.

SYNTHESIS OF CYCLIC CARBONATES

Currently, organic carbonates are valuable products with wide applications in industry. In particular, five-membered cyclic carbonates, as one of the most important classes of heterocycles starting from CO_2, have found wide applications such as electrolytic elements of lithium secondary batteries, polar aprotic solvents, monomers for synthesizing biodegradable polycarbonate, chemical ingredients for preparing pharmaceutical or agricultural chemicals, and alkylating agents [5]. The cycloaddition of epoxides with CO_2 (Scheme 2) is one of the most promising and eco-friendly phosgene-free methods for the manufacture of cyclic carbonates since this would be a highly efficient and full atom-efficiency process with high selectivity. Although phosgene is known to be an extraordinary reactive and easily
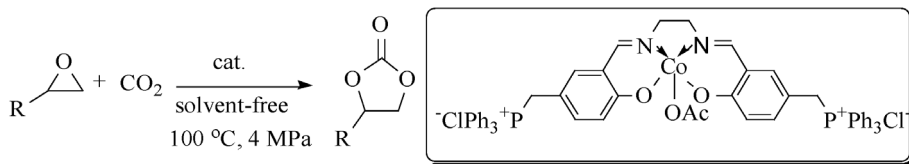
Scheme 2 A Co catalyst with no need of co-catalyst for the cycloaddition reaction of CO$_2$ and epoxide.

available reagent for industrial-scale production of cyclic carbonates [6], the greener substitute for phosgene is still highly desired owing to its toxic and corrosive nature, and the potential employment as chemical weapons. During the past several years, great efforts have been devoted to producing cyclic carbonates by using CO$_2$ as the surrogate of conventional phosgene route. The significance and advancement of this research topic could also be detailed by the recent reviews on the preparation and applications of five-membered cyclic carbonates [2,7].

Various kinds of catalysts have been developed for this reaction, particularly aiming at pursuing milder reaction conditions, recovering and reusing the catalyst, and accomplishing asymmetric reactions. On the basis of getting insight into the reaction mechanism at the molecular level, the ideal catalysts would be a kind of bifunctional one with both Lewis acid and Lewis base sites in one molecule. In the case of homogeneous catalysis, the cycloaddition reaction can proceed smoothly by using aforementioned kind of catalysts, including amines and phosphines [8], alkali metal halides and onium salts [9], organometallic compounds [10], CO$_2$ adducts of *N*-heterocyclic carbenes [11], and ionic liquids (ILs) [12].

In general, an additive is commonly required to achieve high efficiency by employing metal(salen) catalysts. A bifunctional cobalt-salen complex containing a Lewis acidic metal center and a quaternary phosphonium salt unit anchored on the ligand have been found to effectively catalyze the synthesis of cyclic carbonates from CO$_2$ and epoxides under mild conditions without the need of additional organic solvents or additives as depicted in Scheme 2 [13]. The effects of various reaction variables on the catalytic performance are studied in detail, indicating optimized reaction conditions with 100 °C and around 4 MPa of CO$_2$ pressure. Furthermore, the reaction proceeds smoothly even at a pressure as low as 2 MPa. The catalyst can be applicable to a variety of epoxides, producing the corresponding cyclic carbonates in excellent yields in most cases. In addition, the catalyst can be easily recovered and reused several times without significant loss of its catalytic activity. This process thus represents a greener pathway for the environmentally benign chemical fixation of CO$_2$ to produce cyclic carbonates. Further development of metal(salen) catalysts results in the synthesis of cyclic carbonates under atmospheric pressure of CO$_2$ and room temperature [14].

It is practical to use chiral metal-salen catalysts for producing optically active cyclic carbonates from the racemic epoxides with CO$_2$. Following the first report by Lu and co-workers of a convenient route to optically active cyclic carbonates through a catalytic kinetic resolution process catalyzed by simple and highly efficient chiral salenCo-(III)/quaternary ammonium halide systems under solvent-free and extremely mild conditions [15], there are still only a few reports available on this research topic in the literature [16]. Recently, a novel catalytic system comprising salen-Co(OAc)/CIL (CIL: chiral ionic liquid) has been developed for the asymmetric cycloaddition of CO$_2$ to epoxide under very mild conditions (Scheme 3) [17]. Several ILs based on TBAX (tetrabutyl ammonium salt, X = amino acidic anions, tartaric acidic anions, lactic acidic anion) have been synthesized and tested for the reaction. Moreover, it has been found that the chiral catalyst salen-Co(OAc) and chiral co-catalyst of CIL work together in a synergistic manner. The same absolute configurations would induce a higher ee value of chiral propylene carbonate (PC); whereas the opposite absolute configurations result in a lower ee of chiral PC. In addition, chiral polymers of BINOL-salen-cobalt (III) salt complexes have also been applied to the direct fabrication of chiral PC from racemic propylene oxide (PO) with the aid of TBAF
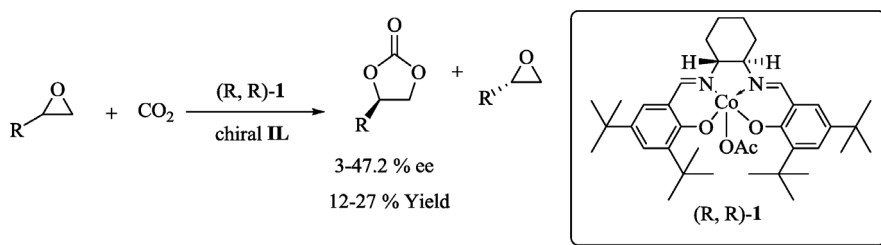
Scheme 3 Chiral Co-salen induced asymmetric version of the cycloaddition from racemic epoxides with CO_2.
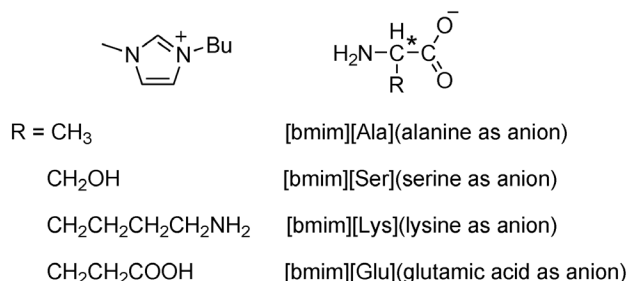
(tetrabutyl fluoride), which could be recovered and reused more than 10 times without loss of activity and enantioselectivity [18]. A single-component bifunctional catalyst incorporating salen-cobalt (III) and a quaternary onium salt are also found to be active in kinetic resolution of racemic epoxides with CO_2 to generate chiral cyclic carbonates with moderate enantioselectivity [19].

A series of easily prepared Lewis basic ILs have been developed for cyclic carbonate synthesis from epoxide and CO_2 at low pressure without utilization of any organic solvents or additives (Scheme 4) [20a]. Notably, quantitative yield together with excellent selectivity are attained while 1,8-diazabicyclo[5.4.0]undec-7-enium chloride ([HDBU]Cl) is used as a catalyst, and [C$_4$DABCO]OH is found to be effective as well. Furthermore, the catalyst could be recycled over five times without appreciable loss of catalytic activity. The effects of the catalyst structure and various reaction parameters on the catalytic performance are investigated in detail on the basis of activity examination among 17 kinds of basic ILs. This protocol is found to be applicable to a variety of epoxides, producing the corresponding cyclic carbonates in high yields and selectivity. Besides the inherent merits of good solvating ability, negligible vapor pressure, variable polarity, and ease of work-up, ILs used in this approach are represented as air stable, high temperature tolerable, easily synthesized, cheap, extremely robust, and environmentally benign catalysts for catalytic conversion of CO_2 into valuable compounds and materials.
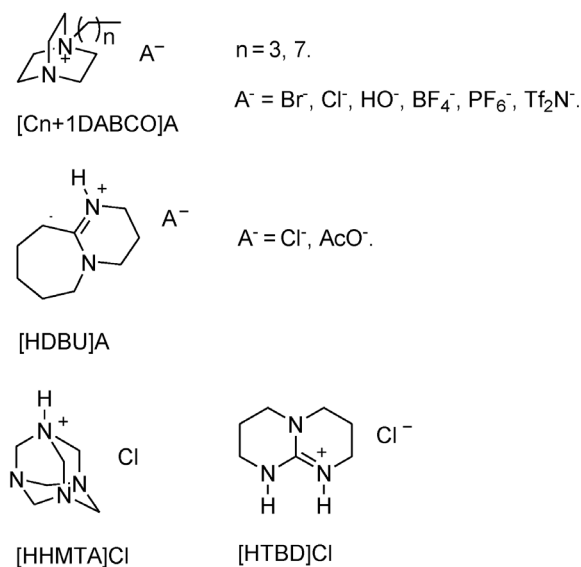
Scheme 4 Lewis basic ILs used in cycloaddition of CO_2 to epoxide.

Natural α-amino acid-derived ionic liquids (AAILs) comprising 1-butyl-3-methylimidazolium cation and amino acid anion, i.e., AAILs, are also proved to be effective catalysts for the coupling of various epoxides and CO_2 to produce cyclic carbonates in good yields and selectivity, which requires no additional organic solvent. To the uppermost point, this protocol avoids any halogen, which meets the newly risen concept of non-halogen synthesis (Scheme 5) [20b]. [Bmim][Ala] is chosen as a model catalyst for the cycloaddition as it gives excellent fluidity and moderate activity among the AAILs with a different side chain used in this study. Beyond the general characteristics of ILs, AAILs possess unique properties such as containing multifunctional groups, chirality, high thermal stability, low cost, biodegradable and biocompatible properties, and a strong hydrogen-bonding ability.

R = CH₃   [bmim][Ala](alanine as anion)

      CH₂OH   [bmim][Ser](serine as anion)

      CH₂CH₂CH₂CH₂NH₂   [bmim][Lys](lysine as anion)

      CH₂CH₂COOH   [bmim][Glu](glutamic acid as anion)

Scheme 5 AAILs used in synthesis of cyclic carbonates from CO_2 and epoxide.

The homogeneous catalysts employed by current cycloaddition processes, such as salen and ILs, could easily dissolve in a product phase, which is undesirable in industry and academia. Thus, it is often necessary to separate the catalyst from the product through a purification process such as distillation after the reaction, inevitably resulting in complicated post-processing procedures, and the possibility of catalyst decomposition or by-products formation during the separation step could not be ignored, too. In order to facilitate the catalyst separation process, several tactful solutions have been successfully applied to the cycloaddition sequence.

One strategy is heterogenization of homogeneous catalysts. Chemically or physically attaching the active species, such as ammonium salts or ILs, onto a polymer [21], silica [22], zeolite [23] and MOF-5 (metal-organic framework) [24], and other materials [25] is regarded as an effective methodology to prepare solid catalysts for this reaction. It is noteworthy that using silica-supported onium salts or imidazolium-based ILs not only provides ease of catalyst separation but also offers improved catalytic activity. Binding onium salts with silica through covalent bond is more effective than physically mixing both the catalytic species and the support. The synergistic effect stemming from the silanol group of silica would presumably account for the catalytic activity enhancement of the heterogenized catalysts in terms of the reaction mechanistic consideration at the molecule level [22].

Our previous work shows that one type of polystyryl-supported catalysts containing ammonium salt or amino group [21c], silica-supported ammonium salts, and silica-supported imidazolium-based ILs [22c] as well as a functionalized biopolymer chitosan-supported quaternary ammonium salt (abbreviated as $CS-N^+R_3X^-$) [21f], are efficient and reusable heterogeneous catalysts for the synthesis of PC from PO and CO_2 under supercritical CO_2 (scCO_2) conditions without any additional organic solvent (Scheme 6). The almost quantitative yield together with excellent selectivity is obtained. The purity of product directly separated out by filtration from the reaction mixture in a batch reactor reaches more than 99.3 %. The catalyst is then recovered and reused in subsequent cycles. The process represents a simple, ecologically safer, cost-effective approach to cyclic carbonates from epoxides and CO_2.
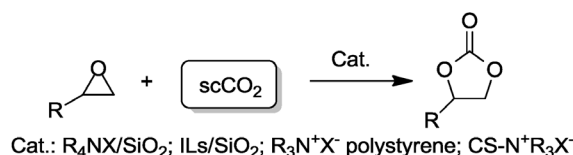
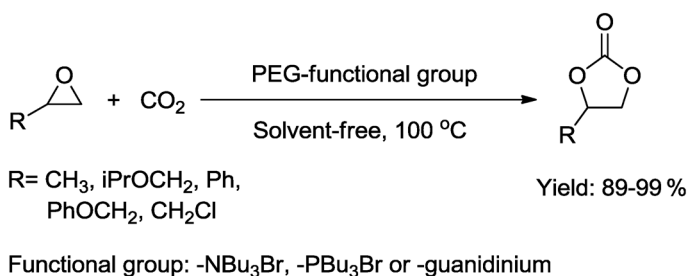**Scheme 6** Cyclic carbonate synthesis catalyzed by the supported catalysts.

Very recently, Cheng and co-workers [26] disclosed an impressive method for catalyst separation by magnetic force. The magnetic nanoparticle-supported IL catalysts demonstrate high activity at lower CO_2 pressure, which is comparable to that of the IL itself. Furthermore, the catalyst could be easily recovered using a magnetic force and reused up to 11 times with essentially no loss of activity. In general, heterogeneous catalyst possesses the merit of easy separation, but the catalyst performance may drop off in most cases. Consequently, developing a new process to reserve the benefits of a homogeneous catalyst while co-opting the primary benefits of a heterogeneous catalyst is highly desirable and of particular significance.

Sakakura and co-workers [27] developed an efficient procedure for recycling homogeneous catalyst, typically, an appealing methodology so-called "homogeneous reaction, heterogeneous separation" process. The $scCO_2$-soluble polyfluoroalkyl phosphonium iodides Rf_3RPI (Rf = $C_4F_9C_2H_4$, $C_6F_{13}C_2H_4$, $C_8F_{17}C_2H_4$; R = Me, Rf)-catalyzed PC synthesis from PO and CO_2 under $scCO_2$ conditions, where PC is spontaneously separated out from the $scCO_2$ phase under pressure. The Rf_3RPI catalyst could be recycled with maintaining a high CO_2 pressure and temperature by separating the PC from the bottom of the reactor followed by supplying PO and CO_2 to the upper $scCO_2$ phase in which the Rf_3RPI remained, as depicted in Fig. 1.
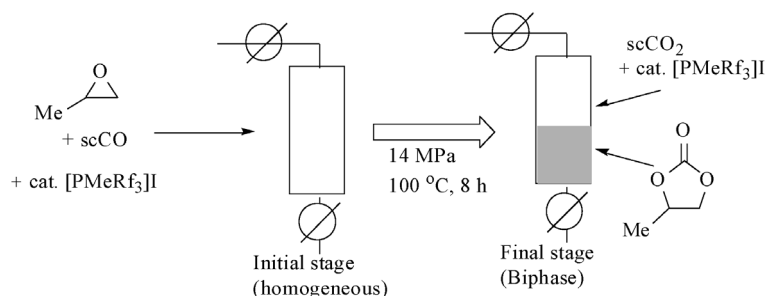
Fig. 1 Homogeneous catalyst recycling by using CO_2-soluble catalyst.

One kind of PEG (polyethylene glycol)-based CO_2-philic polymer is adopted by our group as a support to design the CO_2-expandable polymer-supported catalysts, on the basis of its high solubility and expandability in $scCO_2$ during the reaction conditions, and the subsequently separable property by simple procedure as well [21e,h,i]. PEG and its derivatives are known to be inexpensive, relatively thermally stable, recoverable, almost negligible vapor pressure, toxicologically innocuous, and environmentally benign media for chemical reactions. They are considered to be the right candidates for CO_2-philic supports. Several kinds of onium or guanidinium bromide functionalized-PEG are synthesized and prove to be a highly effective catalysts for the eco-friendly synthesis of cyclic carbonates from CO_2 and epoxides under mild conditions (Scheme 7), which requires no additional organic solvents or co-catalyst. Notably, it has been found that there is a pronounced cooperative effect between the catalyst part and the support. The enhancement of catalyst performance by grafting active molecular catalyst on soluble PEG is presumably attributed to the benefits from changes in the physical properties of

Scheme 7 Synthesis of cyclic carbonates catalyzed by the functionalized-PEG.

the reaction mixture, such as lowered melting points and viscosity, high diffusion rates, and increased solubility for PO and CO_2 through "CO_2-expansion of a liquid" effect. Indeed, as judged by visual inspection through a window-equipped high-pressure reactor, PEG and its derivatives are shown to be expandable with CO_2. Moreover, the catalyst is able to be reused with retention of high catalytic activity and selectivity. This process looks promising as a strategy for homogeneous catalyst recycling.

SYNTHESIS OF OXAZOLIDINONES

Oxazolidinones are important compounds in synthetic chemistry and medicinal chemistry, which can be widely used as chiral auxiliaries, intermediates in organic synthesis, and building blocks for biologically active pharmaceutical agents [28]. Aziridine, as a nitrogen analogue of epoxide, could incorporate with CO_2 through [2 + 3] cycloaddition to afford the corresponding oxazolidinones instead of the ever-existent carbonylation of amino alcohols using phosgene as a highly toxic and corrosive carbonyl source (Scheme 8) [29]. As this kind of CO_2 transformation represents a theoretical 100 % atom efficiency approach, great attention has been attracted from chemical industries. Numerous catalyst systems have been developed in the past decades, such as a dual-component system, viz., (salen)-Cr(III)/DMAP (dimethylamino pyridine) [30] or phenol/DMAP [31], alkali metal halide or tetraalkylammonium halide system [32], iodine [33], quaternary ammonium bromide-functionalized PEG or polystyrene-supported amines [34], zirconyl chloride [35], naturally occurring amino acids [36], ILs [37], and *N*-heterocyclic carbenes [11b].
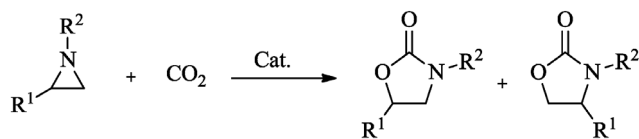

Scheme 8 Aziridine route for synthesis of oxazolidinones from CO_2.

Based on the concept of Lewis acid/base-catalyzed mechanism, many catalysts for the cycloaddition of epoxides and CO_2 can also be developed for this reaction. For example, phenol/DMAP, (salen)-Cr(III)/DMAP, and ammonium salt are similarly active for the carboxylation of aziridines with CO_2. The electrochemical approach involving nickel-catalyzed CO_2 incorporation into aziridines can also work well under mild reaction conditions (1 atm of CO_2 pressure, 20 °C) [38].

In the framework of our continuous effort on the synthesis of value-added chemicals from CO_2, an efficient process for the synthesis of 5-aryl-2-oxazolidinones by employing 1,4-diazabicyclo [2.2.2] octane (DABCO)-based Lewis basic ILs as efficient and recyclable catalysts has been developed as further expandedness of the ILs-catalyzed synthesis of organic carbonate [37]. Interest in those ILs stems

from their facile preparation from commercially available and relatively inexpensive starting materials, gratifyingly thermal behavior, and air/water stability. [C$_4$DABCO]Br displays high catalytic activity for this reaction under 6 MPa of CO_2 and 90 °C even in the absence of any additional organic solvent or additive. To the best of our knowledge, this is the first example where an IL is used to efficiently catalyze the reaction of aziridines with CO_2. Importantly, the catalyst could be stable during the reaction and can be reused for over four successive cycles without loss of efficiency. More importantly, the insight details of reaction mechanism are also investigated by means of in situ IR technique under CO_2 pressure; and the direct observation of CO_2 activation by the tertiary amino site of the catalyst provides, for the first time, the evidence of interaction of IL catalyst and CO_2, as depicted in Fig. 2.
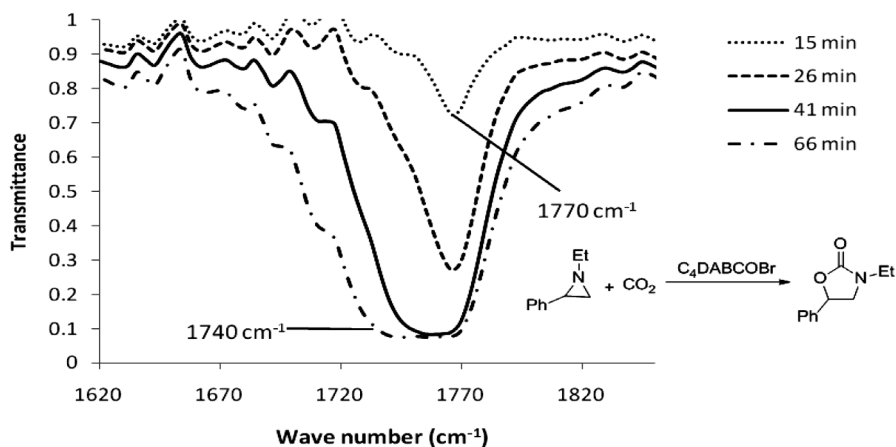
Fig. 2 Results of in situ IR spectroscopy under CO_2 pressure monitoring at various reaction time (min). Reaction conditions: 1-ethyl-2-phenylaziridine (5 mmol), [C$_4$DABCO]Br (1 mmol), 90 °C, CO_2 (6 MPa). 1770 cm^{-1} corresponds to peak for carbonyl group of [aziridine-CO_2]/[C$_4$DABCO-CO_2] carbamic salt, respectively. 1740 cm^{-1} can be assigned to absorption of carbonyl group of oxazolidines.

On the basis of previous reports [32] and the experiment results in this study, a possible mechanism for the [C$_4$DABCO]Br-catalyzed cycloaddition of CO_2 with aziridine is proposed as shown in Scheme 9. Firstly, the tertiary nitrogen atom coordinates reversibly with CO_2 to afford the carbamate salt, which could be an activated form of CO_2. Simultaneously, aziridine itself could likely coordinate with CO_2 to form a positive charge center, which is detected by in situ Fourier transform-infrared (FT-IR) method under CO_2 pressure. Subsequently, the nucleophilic attack of bromide anion leads to
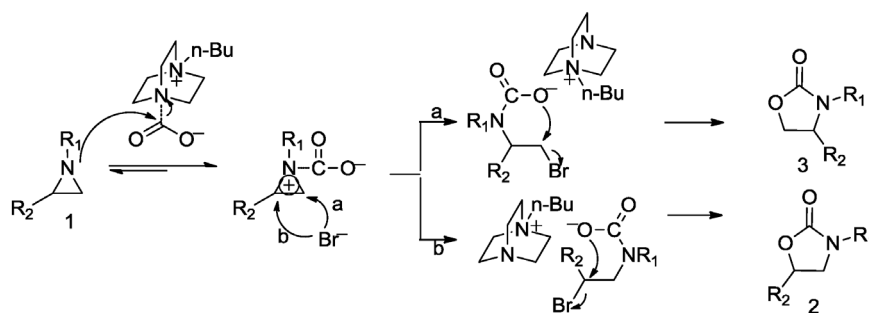
Scheme 9 Proposed mechanism for [C$_4$DABCO]Br-catalyzed synthesis of oxazolidinones.

ring opening of the aziridine through two different pathways as represented by paths *a* and *b*. The obtained carbamate salt could be stabilized by the cation of [C₄DABCO]Br. Finally, oxazolidinone is formed by subsequent intra-molecular ring closure and the catalyst is regenerated. The main product **2** could originate from ring opening of the aziridine at the most substituted carbon.

Although various catalysts have been found for this process, the development of high efficiency, eco-friendly single-component catalyst is still very attractive. Meanwhile, catalyst recovery is also an important issue to be addressed. We have developed an efficient and recyclable PEG-supported ammonium bromide as a catalyst for high selective synthesis of 5-substituted oxazolidinones from CO_2 and various aziridines without any added organic solvent or co-catalyst [34a]. It is also found that selective formation of 5-substituted oxazolidinone or 4-substituted isomer relies on substituent at the carbon of the substrate. One of the salient features of this protocol would be that the catalyst can be readily recovered by centrifugation and reused with retention of high catalytic activity and both chemo- and regioselectivities.

Zirconyl chloride as an efficient, simple, and environmentally friendly solid catalyst has been evaluated for the synthesis of 5-aryl-2-oxazolidinones without any solvent and additive [35d]. Furthermore, the catalyst could be easily separated by filtration and reused for at least five times. The catalytic system offers salient advantages and features: (1) it requires no organic solvent; (2) the catalyst is very effective under mild conditions; (3) the catalyst is moisture-stable, inexpensive, low toxic, easily handled, and readily available; (4) excellent yields and regio- and stereoselectivities toward the target products are attained; (5) simple work-up procedure; (6) the utility of this method is proven as evidenced from synthesizing various 5-aryl-2-oxazolidinones.

We have also developed a green process for the synthesis of a series of oxazolidinones by utilizing natural occuring α-amino acids as the eco-friendly and recyclable catalysts, which requires no additional organic solvent or co-catalyst and represents a halogen-/phosgene-free approach [36a]. Proline shows the highest catalytic activity among the 12 kinds of investigated amino acids, and the proline catalyst could be easily precipitated by addition of ether after the reaction completion, and recovered by a simple filtration, and reused for the next run by charging the fresh substrate, which makes this process look promising as a strategy for homogeneous catalyst recycling.

Upon our continuous pursuit of easy catalyst separation, we have found that basic ion-exchange resins, one kind of polystyryl-supported tertiary amines such as D301R, could act as the highly efficient and recyclable catalysts for the fixation of CO_2 with aziridines under mild conditions, leading to formation of 5-aryl-2-oxazolidinone with excellent regioselectivities (Scheme 10) [34b]. Notably, neither
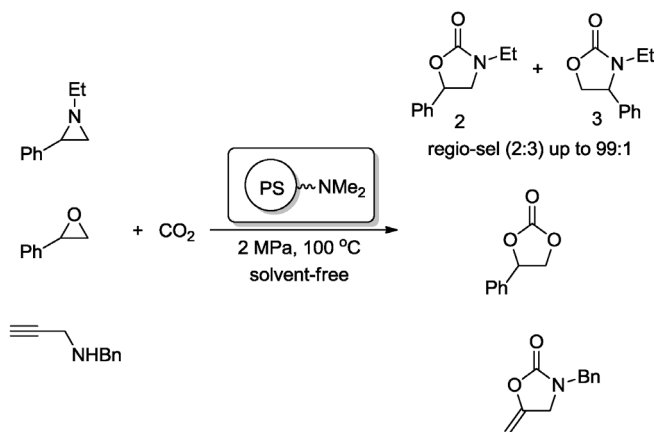
Scheme 10 Carboxylation of aziridine/epoxide/propargyl amine with CO_2.

solvent nor any additive is required, and the catalyst can be recovered by simply filtration and directly reused at least five times without significant loss of catalytic activity and selectivity. To be delighted, the present protocol is successfully applied to reactions of epoxides/propargyl amines with CO_2/CS_2 (Scheme 10). In general, this solvent-free process thus represents environmentally friendly catalytic conversion of CO_2 into value-added chemicals and has great potential to be applied in various continuous flow reactors in industry.

By way of exploring more concise and clean synthesis, we would like to introduce a simple and straightforward approach for selective synthesis of 5-aryl-2-oxazolidinones via self-catalyzed carboxylation of a series of aziridines with CO_2 by elaborately tuning pressure of CO_2 or reaction temperature in the absence of any catalyst and organic solvent [39]. The reaction outcome is found to be tuned by subtly adjusting CO_2 pressure, oxazolidinone yield increases as CO_2 pressure rising from 3.5 to 9 MPa, and reaches the maximum value of 68 % at 9 MPa. A further increase in CO_2 pressure results in a drop in the yield. This is reasonable because near-critical CO_2 may facilitate the formation of the zwitterionic adduct of aziridine with CO_2, which can be monitored by in situ FT-IR method, thereby leading to improving the reaction, The adduct formed in situ from aziridine and CO_2 is assumed to act as a self-catalyst in this reaction. A hypothetic reaction mechanism for this self-catalysis is also proposed, as depicted in Scheme 11. It mainly comprises three steps: firstly, coordination of CO_2 as a Lewis acid with an aziridine to the zwitterionic adduct in situ generated which is detected by in situ FT-IR under high pressure (step I); then ring opening through a nucleophilic attack by the partially anionic oxygen of another adduct, assisted by the pseudo-carbocation scattered on the three-membered ring (step II); and, finally, cyclization via an intramolecular nucleophilic attack, leading to the product as well as regeneration of the adduct (step III). The coordination of CO_2 to aziridine would be the rate-dominating step, which can explain the R_1 and R_2 group effect on the activity and selectivity. The branched substituted group at N atom makes the formation of the adduct (step I) more difficult and thus shows lower activity. Furthermore, an aryl or electron-withdrawing group would make the coordination between
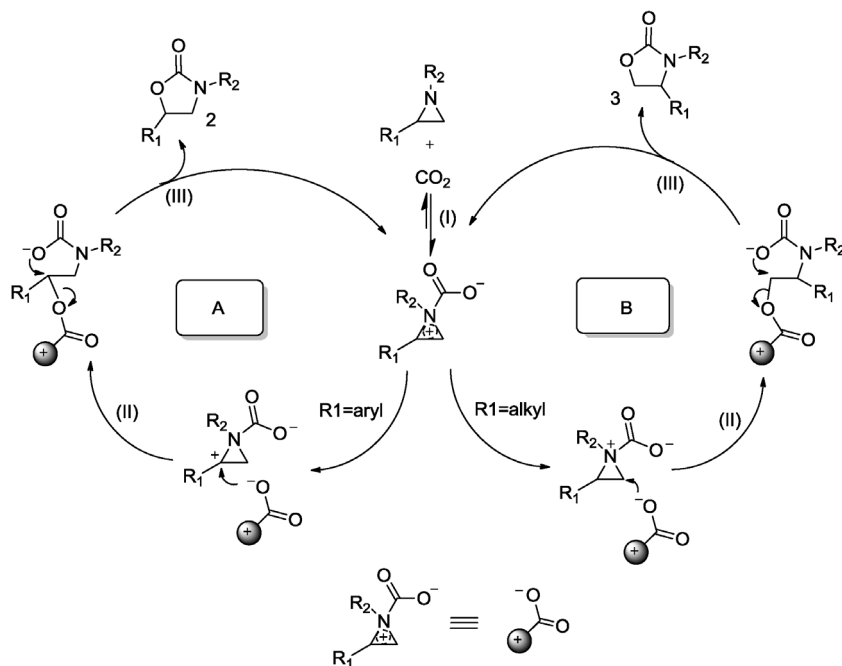
Scheme 11 Proposed mechanism for self-catalyzed carboxylation of aziridine by CO_2.

aziridine and CO_2 impossible, presumably owing to the low electron density at the N atom. Two possible cycles (A or B) exist in this self-catalytic cycle depending on the nature of R_1. When R_1 is aryl group, cycle A would be favorable, leading to preferential formation of 5-substituted product **2**; while if R_1 is alkyl, cycle B could be predominant, thus resulting in dominantly generating **3**.

Finally, a binary catalyst system composed of $^nBu_4NBr_3/^nBu_4NBr$ is developed for facile synthesis of 5-substituted-2-oxazolidinone with perfect regioselectivity in a single operation directly from olefin, chloramine-T, and CO_2 (Scheme 12) [40]. As the cycloaddition synthetic pathway generally involves the initial synthesis of aziridine from olefin and a nitrogen source, which inevitably needs a two-step manipulation, it is more desirable to synthesize an oxazolidinone through a one-pot process. A variety of alkenes including aliphatic and aromatic could be transformed into *N*-tosyl-oxazolidinones in moderate to good yields under supercritical conditions, along with N-Ts-aziridine **1** and its hydrolysate **3** as by-products. This protocol would show an additional example for efficiently utilizing CO_2 as the carbonyl source in the field of green chemistry and catalysis.
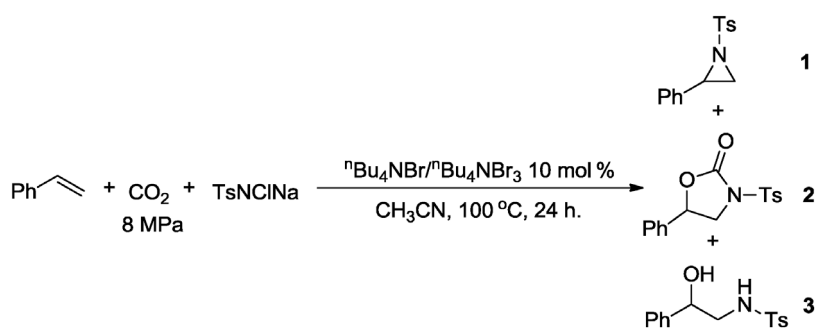

Scheme 12 One-pot synthesis of oxazolidinone via a coupling of styrene, chloramine-T, and CO_2.

SYNTHESIS OF UREAS

Urea derivatives are an important class of carbonyl compounds and useful chemical intermediates in the synthesis of pharmaceuticals, agricultural chemicals, and dyes; they can be also used as antioxidants in gasoline and additives in plastics [41]. On the other hand, conventionally preparative methodologies of urea derivatives are based on the use of dangerous reagents such as phosgene [42]. Nowadays, replacement of these hazardous reagents in chemical processes would be one of the main goals of green chemistry. Therefore, the synthesis of ureas starting from CO_2 has been drawing much attention because CO_2 is a renewable, abundant, inexpensive, and nontoxic source of functional carbon unit. In this aspect, successful routes to urea derivatives directly from CO_2 and amines have also been reported [43]; however, a stoichiometric or excessive dehydrating agent such as diorganophosphite, carbodiimide, propargyl alcohol, and P_4S_{10} is required to promote the reaction. Accordingly, it is desirable to develop simple and environmentally benign processes for the synthesis of substituted ureas from CO_2 without the need of dehydrating agent [44].

We have developed a simple process for synthesis of symmetrical ureas from amines and CO_2 without using any dehydrating agents (Scheme 13) [45]. Notably, inorganic base/PEG1000 is proved to be an efficient and recyclable catalyst. PEG1000 as support could enhance the reaction. Interestingly, the catalyst can be recovered after a simple separation procedure and reused over five times with retention of high activity. This process presented here could show much potential application in industry owing to its simplicity and ease of catalyst recycling. The reaction involves two steps, i.e., formation of the ammonium carbamate (exothermic step) and dehydration to the urea (endothermic step).
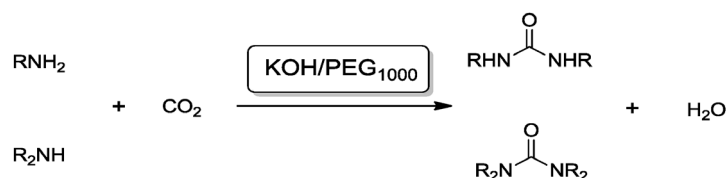
Scheme 13 KOH/PEG-catalyzed synthesis of urea from amine and CO_2.

In this reaction, PEG could form $[R_2NH_2 \cdot PEG]^+ [R_2NCO_2]^-$, and thus could increase the thermodynamic stability of $[R_2NH_2]^+$ [46]. Indeed, ^{1}H NMR measurement also supports the complexation of PEG with ammonium cation. An increase in basicity of the base in aid of PEG could also facilitate formation of the ammonium carbamate salt [47]. On the other hand, PEG can act as a physical dehydrating agent since PEG is strongly hygroscopic.

This base/PEG reaction system can be further employed for the carbamate synthesis from amine, CO_2, and alkyl halide, with K_2CO_3 as the superior surrogate of KOH (Scheme 14) [48]. An efficient and environmentally benign process for the synthesis of organic carbamate has been developed in such concise reaction system under ambient conditions (atmospheric pressure and room temperature). PEG can be presumably considered to play the crucial role as the reaction solvent and phase-transfer catalyst (PTC), which could also retard the side-reaction of alkylation of both the amine and the carbamate, thus resulting in enhanced selectivity toward the target carbamate.
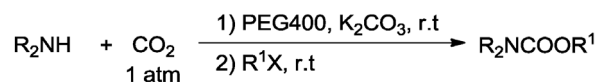
Scheme 14 K_2CO_3/PEG-catalyzed synthesis of carbamate from amine, CO_2, and alkyl halide.

Recently, a mild and efficient DBU-catalyzed one-pot stepwise synthesis of unsymmetrical ureas through the sequentially in situ formed carbamic acids and isocyanate species has been developed by Peterson and co-workers (Scheme 15) [49]. Carbamic acids derived from primary amines and CO_2 can react with Mitsunobu reagent, viz. triphenylphosphine and diethyl azodicarboxylate (DEAD), to the isocyanate intermediate in situ generated via dehydration step, which is then condensed with another amino-component to afford the desired asymmetric urea. Similarly, carbamic acids generated in situ from secondary amines could also react with alcohols under the same conditions to form carbamates. Various unsymmetrical di- and trisubstituted ureas as well as carbamates derived from primary and secondary alcohols are constructed through the stepwise synthesis. This easy-to-handle approach offers the predictably coupling reactions from amines, CO_2, and alcohols to produce unsymmetrical ureas and
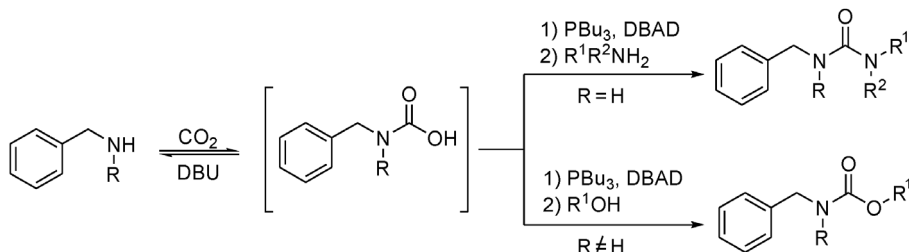
Scheme 15 DBU-catalyzed synthesis of urea and carbamate from amine and CO_2.

carbamates, which would outline a useful technique for the library construction of amide-containing compounds.

Finally, a neat and effective noncatalyzed symmetrical urea synthesis system is proposed by Feng-Yu Zhao et al. [50]. It is found that the reaction is sensitive to several reaction parameters, especially the concentration of the reactant amines, as urea yield increases drastically and then reaches a plateau slightly with increasing of the concentration of amines across approximately 1.0 mmol mL^{-1}. After the optimization of the experimental variables, including temperature, pressure, the concentration of amine, and reaction time, ureas are obtained in mild to good yield from the reactions of a series of primary aliphatic amines under the condition of 180 °C and 10 MPa CO_2 in the absence of any catalysts, organic solvents, or other additives. The preliminary investigation of the reaction mechanism shows that alkyl ammonium alkyl carbamate, which is characterized by solid-state CP/MAS ^{13}C NMR, is quickly formed as the intermediate, and then the final product is attained by the intramolecular dehydration (Scheme 16). Two possible dehydrating steps are proposed, intermolecular route A and intramolecular route B through the intermediates **3** or **4**. As a green and facile route to the synthesis of symmetrical urea derivates, this noncatalyzed system could certainly find its great potential for industrial application.
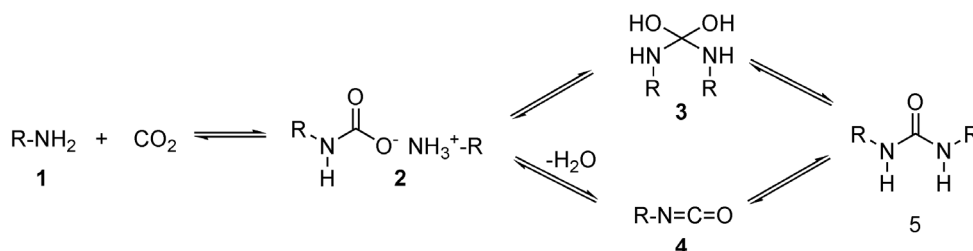
Scheme 16 Proposed reaction mechanism for synthesis of urea from amine and CO_2 in the absence of catalyst.
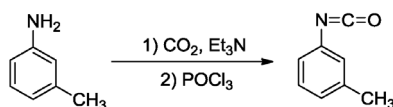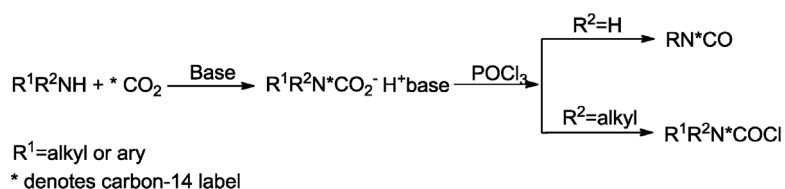
SYNTHESIS OF ISOCYANATES

Isocyanates are important synthetic intermediates in the manufacturing of industrially useful chemicals. The largest use of isocyanates in industry involves the production of polymers to fabricate foams, paints, lacquers, and electrical insulation materials. Ureas and isocyanides could also be obtained by further derivatization of isocyanates. Consequently, isocyanates have been found wide application in pharmacy, agriculture, the plastics and paint industry, leather and wood modification, and even in areas of transportation.

There were two traditional synthetic approaches to isocyanates by using either CO or phosgene [51] as the carbonyl source, respectively. Early in 1968, Bennet and Hardy reported that phenylisocyanate could be obtained by the reaction of the nitrene, which was in situ formed from an azide compound, with gaseous CO at the 160–180 °C and 200–300 atm [52]. The similar synthesis of isocyanates from azides and CO in the presence of iridium complexes was also reported nearly at the same time [53]. Under the similar conditions, carbon-11 labeled cyclic ureas and carbamates could be synthesized in good yields under high-pressure conditions from carbon-11 labeled CO and amines using selenium catalysts via the isocyanate intermediates, which represent the versatile derivatization of isocyanates [54]. Carbon-11 labeled isocyanates could also have been prepared by reaction of carbon-11 labeled phosgene with amines in the presence of stoichiometric amounts of base with a low isocyanate selectivity owing to the formation of undesired urea by-products [55]. This problem was overcome later by utilizing *N*-sulfinylamines, leading to the efficient production of a variety of simple isocyanates in high chemoselectivity [56].
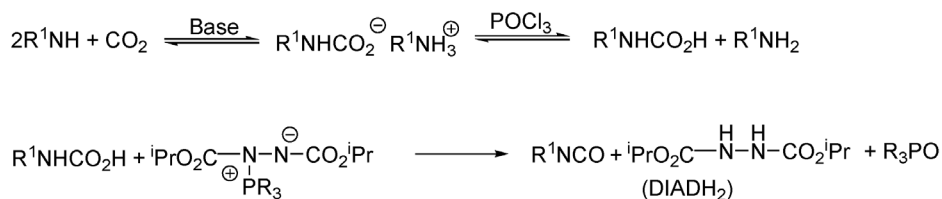
As is easily seen, either CO or phosgene route to synthesis of isocyanates could be harmful to humanity and the environment. From the green chemistry and sustainable development point of view, the direct utilization of CO_2 as the carbonyl source for isocyanate synthesis is an attractive approach. CO_2 was employed as the environmentally benign carbonyl source by Molina and co-workers in the early 1980s. In such a reaction system, isocyanates could be obtained by reaction of alkyl- and aryl-iminophosphoranes with CO_2 [57].

The ternary base, such as triethylamine, is reported to promote the reaction of primary or secondary amines with carbon-14 labeled CO_2 to form the tagged isocyanates. This protocol works well for a wide variety of alkyl and aromatic amines to afford the products in the yields from 45 to 75 % (Scheme 17) [58]. The reaction proceeds via a dehydrative pathway of the in situ formed carbamate salt, and phosphorus oxychloride and thionyl chloride are proved to be the efficient dehydrating agents.

$$R^1R^2NH + *CO_2 \xrightarrow{\text{Base}} R^1R^2N*CO_2^- H^+base \xrightarrow{POCl_3} \begin{cases} \xrightarrow{R^2=H} RN*CO \\ \xrightarrow{R^2=alkyl} R^1R^2N*COCl \end{cases}$$

R^1=alkyl or ary
* denotes carbon-14 label

Scheme 17 Synthesis of isocyanates from amine and CO_2.

Mitsunobu technology is used for the preparation of alkyl and hindered aryl isocyanates from primary amines and CO_2 under mild conditions, and this is proved to be a feasible reaction system (Scheme 18) [59]. In the first step, the reaction of primary aliphatic or hindered aromatic amines in dichloromethane with CO_2 occurs at –5 to –10 °C to form the carbamate salts, and the subsequent treatment with $POCl_3$ could furnish the carbamic acid species. Finally, the presynthesized Mitsunobu zwitterion, which is obtained by adding diisopropylazodicarboxylate (DIAD) to a solution of either tri-*n*-butylphosphine (Bu_3P) or triphenylphosphine (Ph_3P) in dichloromethane, is introduced into the reaction system; and thus isocyanate is formed in the sequential dehydration process.

$$2R^1NH + CO_2 \underset{\text{}}{\overset{\text{Base}}{\rightleftharpoons}} R^1NHCO_2^{\ominus} R^1NH_3^{\oplus} \underset{\text{}}{\overset{POCl_3}{\rightleftharpoons}} R^1NHCO_2H + R^1NH_2$$

$$R^1NHCO_2H + {}^iPrO_2C\overset{\ominus}{\underset{\oplus PR_3}{-N-N}}-CO_2{}^iPr \longrightarrow R^1NCO + {}^iPrO_2C\overset{H\ H}{-N-N}-CO_2{}^iPr + R_3PO$$

$$(DIADH_2)$$

R=Bu, Ph

Scheme 18 Synthesis of isocyanates from amine and CO_2 with diisopropylazodicarboxylate (DIAD).

A general method for synthesis of *C*-amino-*C*-carboxy derivatives proceeds through nucleophilic reaction of the intermediate *C*-isocyanates starting from amino acids [60] and even disaccharides [61]. Cyclodextrin urea derivatives including the cyclodextrin isocyanates have also been synthesized from CO_2 by one-pot phosphinimine reaction with a polymer-bound triphenylphosphine [62]. Remarkably, $scCO_2$ as both a solvent and a reagent is successfully introduced to the one-pot reaction system, resulting in the good yields of desired urea cyclodextrin derivatives within reasonable reaction time [63]. A series of novel C-functionalized β-carbonylsilanes with a silacyclohexane skeleton are also synthesized from azide compounds reacting with PPh_3 and CO_2 [64]. Besides the above-mentioned metallic catalysts, a new catalyst named titanium-imide zwitterion works well for the preparation of aryl isocyanates, carbodiimide, and isocyanide from CO_2 under mild conditions [65].

Based on those explorative initial findings, Azhayev's group has reported their study on straightforward carbamoylation employing various organic azides and phosphines, as well as different nucleophilic compounds and solvents with moderate to high yields (Scheme 19). The carbonyl source could be gaseous CO_2 or aqueous trialkylammonium hydrogen carbonate buffer as an alternative source of CO_2 to perform carbamoylation via the formation of an isocyanate. This procedure could feature as a non-metallic and phosgene-free synthesis route of isocyanates [66].
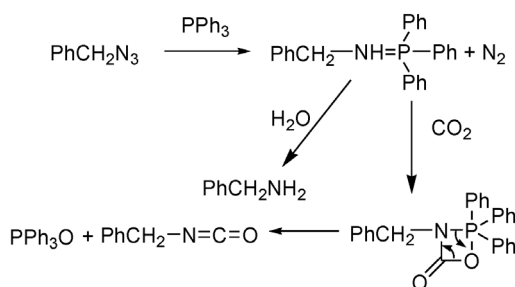
Scheme 19 Proposed mechanism.

Lately, a new reaction system for the synthesis of carbon-labeled carbamates and ureas via isocyanate intermediates has been developed, as illuminated in Scheme 20. In this system, CO_2 is trapped in a solution of benzylamine in acetonitrile containing 2-*tert*-butylimino-2-diethylamino-1,3-dimethylper-hydro-1,3,2-dia-zaphosphorine (BEMP), $POCl_3$ in acetonitrile is added to dehydratively


* denotes carbon-11 label
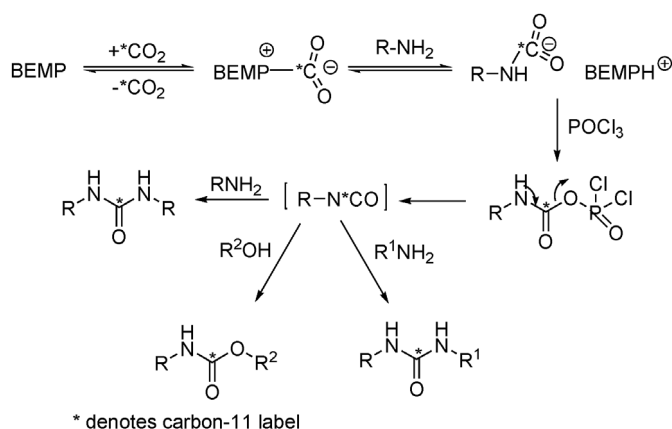
Scheme 20 Proposed mechanism for reaction sequence.

form the isocyanate intermediate. The consequent introduction of amines or alcohols as the nucleophile results in the desired carbamates or ureas. BEMP here could serve as CO_2 fixation agent. Thus, this mild reaction system has enabled the rapid, one-pot, efficient production of isocyanates, in turn, the radiosynthesis of a variety of carbonyl-^{11}C labeled carbamates and unsymmetrical ureas [67,68].

SYNTHESIS OF POLYCARBONATES AND POLYURETHANES

To date, many kinds of copolymers can be synthesized by the sequential copolymerization of CO_2 and typical three-membered heterocycles, among which the most commonly known are highly strained epoxides and aziridines (Scheme 21) [69]. The real large-scale industrial application of CO_2 potentially lies in the manufacture of the biodegradable thermoplastics, represented by polypropylene carbonate and polycyclohexene carbonate, and the current annual production of polycarbonates totals 2 million tons world-wide. The process for copolymerization of epoxides and CO_2 to produce polycarbonates has been widely studied since the late 1960s. Currently, the largest future application of CO_2 as C1 source would just rely on the surrogating of phosgene in the syntheses of polycarbonates and polyurethanes, as the total 80–90 % of polycarbonates are currently being produced through the phosgene process [70]. The major drawbacks of the phosgene processes involve the intrinsic high toxicity of phosgene itself, which was employed as the chemical weapon during World War I, and also the disposal of the potential coproduced hydrogen chloride and alkali metal chloride. From the point of view of green chemistry and sustainable development, substituting phosgene with CO_2 would be highly desired for the consequent drastically reduced environmental concerns.
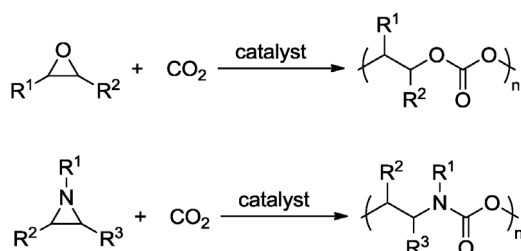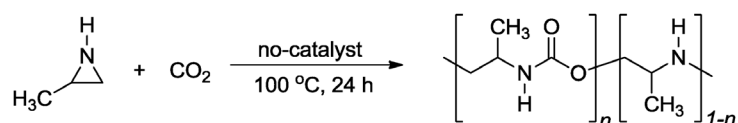

Scheme 21 Copolymerization of CO_2 with epoxides or aziridines.

The real development of this polymerization reaction has been initiated by Inoue et al., who developed the first generation of zinc catalyst ($ZnEt_2$ and water) to copolymerize CO_2 and PO, resulting in a small quantity of polymeric material [71]. The catalytic performance of the early-stage system is unsatisfactory as a result of low reaction efficiency, large quantity of by-products (cyclic carbonates and etheric oligomers), as well as irregular structures. Then various zinc-based metal complexes were later proposed [72], among which the iminate complexes have been the most intensively studied, and bulky substituents in the backbone would promote the catalytic activity. Metal complexes other than zinc complexes have also been developed; salen and porphyrin complex derived from cobalt [73] and chromium [74] is proven to be a promising class of catalysts that produce the optical active polycabonate with high degrees of carbonate linkages under mild conditions around room temperature, and even in atmospheric pressure. It is noteworthy that the cobalt salen complexes could effectively perform the copolymerization of CO_2 with epoxides derived from acyclic alkenes such as POs, which essentially expands the polymer product diversity. Catalysts based on lanthanide [75], manganese [76], cadmium [77], aluminum [78], and iron [79] complexes have also been available in the literature. Although in most systems, a co-catalyst such as the quaternary ammonium salts or phosphonium salts will still be needed, recent developments have circumvented this problem by the preparation of a series of Cr(III)

or Co(III) salen complexes as single-component catalyst, which incorporated the co-catalyst into its salen backbone via a saturated linking group [80].

Polyurethanes, as a kind of analogous polymeric materials of polycarbonates, could also be obtained by copolymerization of aziridine and scCO$_2$ under catalyst-free conditions (Scheme 22) [81]. A series of polymeric parameters, including the molecular weight, the content of urethane linkages are controllable simply by vibration of CO$_2$ pressure, as the increase of which would dramatically cause a marked improvement in the yield and urethane segment content. And more importantly, the copolymerization products of 2-methylaziridine and CO$_2$ exhibits unique thermally induced reversible phase transitions in water around the lower critical solution temperatures (LCSTs). This unique temperature-sensitive thermal property of the title polymer in water has attracted increasing attention in the fields of drug-delivery systems, protein–ligand recognition, tissue-engineering applications, separation, and catalysis, offering a bright future for CO$_2$-derived urethane polymer.

Scheme 22 Copolymerization of CO$_2$ with 2-methylaziridine.

CONCLUSIONS

Synthesis of a series of value-added chemicals, including cyclic carbonates, oxazolidinones, ureas, isocyanates, polycarbonates, and polyurethanes, via the incorporation of CO$_2$ is summarized toward the goal of non-phosgene process in this article. The findings summarized here clearly indicate that CO$_2$ can be regarded as an abundant and readily accessible atmospheric gas that could, in principle, become a useful synthon for organic compounds instead of phosgene, which is highly toxic, corrosive, and environmentally hazardous though extremely synthetic active. The development of the above-mentioned phosgene-free approaches is in accord with the principles of green chemistry, namely, low impact on human and environmental health, and could simultaneously meet the need of sustainable society by using CO$_2$ as the renewable environmentally friendly C1 building block for making bulk chemicals, fuels, and materials besides the natural biological process. Although many methodologies have been developed for utilization of CO$_2$ as carbonyl source in organic synthesis, its inherent thermodynamic stability and kinetic inertness hinder the further development of highly effective catalysts that achieve CO$_2$ activation by comparably matching the high reactivity of phosgene. So many opportunities remain to be explored further on the topic of CO$_2$ activation and subsequent transformation, particularly in terms of functionalization of CO$_2$ through smartly devising catalyst with high efficiency. We hope this presentation will stimulate further interest in academic research and industrial development that may lead to the development of CO$_2$ as a green C1 synthon for organic synthesis.

REFERENCES

1. C. Chen, S. T. Yang, W. S. Ahn, R. Ryoo. *Chem. Commun*. 3627 (2009).
2. (a) T. Sakakura, J. C. Choi, H. Yasuda. *Chem. Rev*. **107**, 2365 (2007); (b) L.-N. He, Z.-Z. Yang, A.-H. Liu, J. Gao. In *Advances in CO₂ Conversion and Utilization*, Y. H. Hu (Ed.), ACS Symposium Series No. 1056, pp. 77–101, American Chemical Society, Washington, DC (2010); (c) J. L. Wang, C. X. Miao, X. Y. Dou, J. Gao, L. N. He. *Curr. Org. Chem.* **15**, 621 (2011).
3. S. Fukuoka, M. Kawamura, K. Komiya, M. Tojo, H. Hachiya, K. Hasegawa, M. Aminaka, H. Okamoto, I. Fukawa, S. Konno. *Green Chem*. **5**, 497 (2003).
4. K. Soga, W. Y. Chiang, S. Ikeda. *J. Polym. Sci., Polym. Chem. Ed.* **12**, 121 (1974).
5. (a) A. G. Shaikh, S. Sivaram. *Chem. Rev*. **96**, 951 (1996); (b) J. H. Clements. *Ind. Eng. Chem. Res.* **42**, 663 (2003); (c) M. North, R. Pasquale, C. Young. *Green Chem.* **12**, 1514 (2010).
6. J. J. McKetta, W. A. Cunningham (Eds.). *Encyclopedia of Chemical Processing and Design*, Vol. 20, p. 177, Marcel Dekker, New York (1984).
7. (a) M. Aresta, A. Dibenedetto. *Dalton Trans.* **28**, 2975 (2007); (b) T. Sakakura, K. Kohno. *Chem. Commun.* 1312 (2009); (c) L. N. He, J. Q. Wang, J. L. Wang. *Pure Appl. Chem*. **81**, 2069 (2009).
8. (a) H. Kawanami, Y. Ikushimaab. *Chem. Commun*. 2089 (2000); (b) Y. M. Shen, M. Shi. *Adv. Synth. Catal.* **345**, 337 (2003); (c) L. N. He, H. Yasuda, T. Sakakura. *Green Chem.* **5**, 92 (2003); (d) J. W. Huang, M. Shi. *J. Org. Chem.* **68**, 6705 (2003); (e) J. L. Song, Z. F. Zhang, S. Q. Hu, T. B. Wu, T. Jiang, B. X. Han. *Green Chem.* **11**, 1031 (2009); (f) Y. B. Xiong, H. Wang, R. M. Wang, Y. F. Yan, B. Zheng, Y. P. Wang. *Chem. Commun*. **46**, 3399 (2010); (g) Y. Tsutsumi, K. Yamakawa, M. Yoshida, T. Ema, T. Sakai. *Org. Lett*. **12**, 5728 (2010).
9. (a) N. Kihara, N. Hara, T. Endo. *J. Org. Chem*. **58**, 6198 (1993); (b) V. Calo, A. Nacci, A. Monopoli, A. Fanizzi. *Org. Lett*. **4**, 2561 (2002); (c) K. Kossev, N. Koseva, K. Troev. *J. Mol. Catal. A: Chem.* **194**, 29 (2003); (d) A. Sibaouih, T. Repo. *Appl. Catal. A* **365**, 194 (2009).
10. (a) W. J. Kruper, D. V. Dellar. *J. Org. Chem.* **60**, 725 (1995); (b) R. L. Paddock, S. T. Nguyen. *J. Am. Chem. Soc.* **123**, 11498 (2001); (c) X. B. Lu, H. Wang, R. He. *J. Mol. Catal. A: Chem*. **186**, 33 (2002); (d) F. W. Li, C. G. Xia, L. W. Xu, W. Sun, G. X. Chen. *Chem. Commun.* 2042 (2003); (e) A. Barbarini, R. Maggi, A. Mazzacani, G. Mori, G. Sartori, R. Sartorio. *Tetrahedron Lett.* **44**, 2931 (2003); (f) Y. Du, D. L. Kong, H. Y. Wang, F. Cai, J. S. Tian, J. Q. Wang, L. N. He. *J. Mol. Catal. A: Chem*. **241**, 233 (2005); (g) F. Jutz, J. D. Grunwaldt, A. Baiker. *J. Mol. Catal. A: Chem.* **279**, 94 (2008); (h) J. Melendez, M. North. *Chem. Commun.* 2577 (2009); (i) W. Kleist, A. Baiker. *Eur. J. Inorg. Chem.* 3552 (2009); (j) A. Sibaouih, T. Repo. *J. Mol. Catal. A: Chem.* **312**, 87 (2009).
11. (a) H. Zhou, X. B. Lu. *J. Org. Chem* **73**, 8039 (2008); (b) S. L. Zhang, Y. Z. Huang, H. W. Jing, W. X. Yao, P. Yan. *Green Chem.* **11**, 935 (2009); (c) K. Motokura, S. Itagaki. *Green Chem.* **11**, 1876 (2009); (d) H. L. Shim, S. Udayakumar. *Catal. Today* **148**, 350 (2009); (e) S. Udayakumar, V. Raman. *Appl. Catal. A: Gen*. **368**, 97 (2009); (f) Y. Xie, K. L. Ding, Z. M. Liu, J. J. Li, G. M. An, R. T. Tao, Z. Y. Sun, Z. Z. Yang. *Chem.—Eur. J.* **16**, 6687 (2010); (g) H. Zhou, Y. M. Wang, W. Z. Zhang, J. P. Qu, X. B. Lu. *Green Chem*. **13**, 644 (2011); (h) H. C. Cho, H. S. Lee, J. Chun, S. M. Lee, H. J. Kim, S. U. Son. *Chem. Commun*. **47**, 917 (2011).
12. (a) J. J. Peng, Y. Q. Deng. *New J. Chem*. **25**, 639 (2001); (b) H. S. Kim, J. J. Kim, H. Kim, H. G. Jang. *J. Catal.* **220**, 44 (2003); (c) H. Kawanami, A. Sasaki, K. Matsui, Y. Ikushima. *Chem. Commun.* 896 (2003); (d) J. M. Sun, S. I. Fujita, F. Y. Zhao, M. Arai. *Green Chem.* **6**, 613 (2004); (e) F. W. Li, L. F. Xiao, C. G. Xia, B. Hu. *Tetrahedron Lett*. **45**, 8307 (2004); (f) J. Palgunadi, H. S. Kim. *Catal. Today* **98**, 511 (2004); (g) Y. J. Kim, R. S. Varma. *J. Org. Chem*. **70**, 7882 (2005); (h) J. Sun, S. J. Zhang. *Tetrahedron Lett.* **49**, 3588 (2008); (i) Y. X. Zhou, S. Q. Hu, X. M. Ma, S. G. Liang, T. Jiang, B. X. Han. *J. Mol. Catal. A: Chem*. **284**, 52 (2008); (j) J. Sun, J. Y. Ren, S. J. Zhang, W. G. Cheng. *Tetrahedron Lett*. **50**, 423 (2009); (k) W. L. Dai, S. F. Yin, C. T. Au. *Appl. Catal. A: Gen.* **366**, 2 (2009).

13. C. X. Miao, J. Q. Wang, Y. Wu, Y. Du, L. N. He. *ChemSusChem* **1**, 236 (2008).

14. J. Mélendez, M. North, P. Villuendas. *Chem. Commun.* 2577 (2009).

15. X. B. Lu, B. Liang, X. B. Zhang, Y. Z. Tian, Y. M. Wang, C. X. Bai, H. Wang, R. Zhang. *J. Am. Chem. Soc*. **126**, 3732 (2004).

16. A. Berkessel, M. Brandenburg. *Org. Lett.* **8**, 4401 (2006).

17. S. L. Zhang, Y. Z. Huang, H. W. Jing, W. X. Yao, P. Yan. *Green Chem.* **11**, 935 (2009).

18. P. Yan, H. W. Jing. *Adv. Synth. Catal.* **351**, 1325 (2009).

19. T. Chang, L. L. Jin, H. Jing. *ChemCatChem.* **1**, 379 (2009).

20. (a) Z. Z. Yang, L. N. He, C. X. Miao, S. Chanfreaua. *Adv. Synth. Catal.* **352**, 2233 (2010); (b) F. Wu, X. Y. Dou, L. N. He, C. X. Miao. *Lett. Org. Chem.* **7**, 73 (2010).

21. (a) T. Nishikubo, A. Kameyama, J. Yamashita, M. Tomoi, W. Fukuda. *J. Polym. Sci., Part A: Polym. Chem.* **31**, 939 (1993); (b) H. S. Kim, J. J. Kim, H. N. Kwon, M. J. Chung, B. G. Lee, H. G. Jang. *J. Catal.* **205**, 226 (2002); (c) Y. Du, F. Cai, D. L. Kong, L. N. He. *Green Chem.* **7**, 518 (2005); (d) L. F. Xiao, F. W. Li, C. G. Xia. *Appl. Catal. A: Gen*. **279**, 125 (2005); (e) Y. Du, J. Q. Wang, J. Y. Chen, F. Cai, J. S. Tian, D. L. Kong, L.-N. He. *Tetrahedron Lett.* **47**, 1271 (2006); (f) Y. Zhao, L. N. He. *J. Mol. Catal. A: Chem.* **271**, 284 (2007); (g) Y. Xie, B. X. Han. *Angew. Chem., Int. Ed.* **46**, 7255 (2007); (h) X. Y. Dou, J. Q. Wang, Y. Du, E. Wang, L. N. He. *Synlett* **19**, 3058 (2007); (i) J. S. Tian, F. Cai, J. Q. Wang, Y. Du, L. N. He. *Phosphorus Sulfur Silicon Relat. Elem.* **183**, 494 (2008).

22. (a) A. Barbarini, G. Sartori. *Tetrahedron Lett.* **44**, 2931 (2003); (b) H. B. Xie, H. F. Duan, S. H. Li, S. B. Zhang. *New J. Chem.* **29**, 1199 (2005); (c) J. Q. Wang, D. L. Kong, J. Y. Chen, F. Cai, L. N. He. *J. Mol. Catal. A: Chem.* **249**, 143 (2006); (d) L. F. Xiao, C. G. Xia. *J. Mol. Catal. A: Chem.* **253**, 265 (2006); (e) T. Takahashi, T. Watahiki, S. Kitazume, H. Yasuda, T. Sakakura. *Chem. Commun.* 1664 (2006); (f) J. Q. Wang, X. D. Yue, F. Cai, L. N. He. *Catal. Commun.* **8**, 167 (2007); (g) T. Sakai, Y. Tsutsumi. *Green Chem*. **10**, 337 (2008); (h) K. Motokura, S. Itagaki. *Green Chem.* **11**, 1876 (2009).

23. R. Srivastava, D. Srinivas, P. Ratnasamy. *Appl. Catal. A: Gen.* **289**, 128 (2005).

24. J. Song, B. X. Han. *Green Chem.* **11**, 1031 (2009).

25. R. Srivastava, D. Srinivas, P. Ratnasamy. *J. Catal.* **233**, 1 (2005).

26. X. X. Zheng, S. Z. Luo, J. P. Cheng. *Green Chem.* **11**, 455 (2009).

27. L. N. He, H. Yasuda, T. Sakakura. *Green Chem.* **5**, 92 (2003).

28. (a) C. W. Phoon, C. Abell. *Tetrahedron Lett.* **39**, 2655 (1998); (b) R. J. Watson, D. Batty, A. D. Baxter, D. R. Hannah, D. A. Owen, J. G. Montana. *Tetrahedron Lett.* **43**, 683 (2002); (c) M. R. Barbachyn, C. W. Ford. *Angew. Chem., Int. Ed.* **42**, 2010 (2003).

29. D. Ben-Ishai. *J. Am. Chem. Soc*. **78**, 4962 (1956).

30. A. W. Miller, S. T. Nguyen. *Org. Lett*. **6**, 2301 (2004).

31. (a) Y. M. Shen, W. L. Duan, M. Shi. *Eur. J. Org. Chem.* 3080 (2004); (b) C. Phung, A. R. Pinhas. *Tetrahedron Lett.* **51**, 4552 (2010).

32. (a) M. T. Hancock, A. R. Pinhas. *Tetrahedron Lett.* **44**, 5457 (2003); (b) A. Sudo, Y. Morioka, E. Koizumi, F. Sanda, T. Endo. *Tetrahedron Lett.* **44**, 7889 (2003); (c) T. Sudo, Y. Morioka, F. Sanda, T. Endo. *Tetrahedron Lett.* **45**, 1363 (2004).

33. (a) H. Kawanami, Y. Ikushima. *Tetrahedron Lett.* **43**, 3841 (2002); (b) H. Kawanami, H. Matsumoto, Y. Ikushima. *Chem. Lett.* **34**, 60 (2005).

34. (a) Y. Du, Y. Wu, A. H. Liu, L. N. He. *J. Org. Chem.* **73**, 4709 (2008); (b) A. H. Liu, L. N. He, S. Y. Peng, Z. D. Pan, J. L. Wang, J. Gao. *Sci. China Chem.* **53**, 1578 (2010).

35. Y. Wu, L.-N. He, Y. Du, J. Q. Wang, C. X. Miao, W. Li. *Tetrahedron.* **65**, 6204 (2009).

36. (a) X. Y. Dou, L. N. He, Z. Z. Yang. *Synth. Commun.* (2011) doi:10.1080/00397911.2010.521903; (b) H. F. Jiang, J. W. Ye, C. R. Qi, L. B. Huang. *Tetrahedron Lett.* **51**, 928 (2010).

37. Z. Z. Yang, L. N. He, S. Y. Peng, A. H. Liu. *Green Chem.* **12**, 1850 (2010).

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Pure Appl. Chem., Vol. 84, No. 3, pp. 581–602, 2012

38. P. Tascedda, E. Dunach. *Chem. Commun*. **6**, 449 (2000).

39. X. Y. Dou, L. N. He, Z. Z. Yang, J. L. Wang. *Synlett* **14**, 2159 (2010).

40. D. L. Kong, L. N. He, J. Q. Wang. *Catal. Commun*. **11**, 992 (2010).

41. (a) K. Matsuda. *Med. Res. Rev*. **14**, 271 (1994); (b) F. Bigi, R. Maggi, G. Sartori. *Green Chem*. **2**, 140 (2000); (c) G. Bartolo, G. Salerno, R. Mancuso, M. Costa. *J. Org. Chem*. **69**, 4741 (2004); (d) A. Estevez-Souza, K. Pissinate, M. G. Nascimento, N. F. Grynberg, A. Echevaria. *Bioorg. Med. Chem.* **14**, 492 (2006).

42. (a) R. L. Shriner, W. H. Horne, R. F. B. Cox. *Org. Synth*. **2**, 453 (1943); (b) J. S. Nowick, N. A. Powell, T. M. Nguyen, G. Noronha. *J. Org. Chem*. **57**, 7364 (1992).

43. (a) N. Yamazaki, F. Higashi, T. Iguchi. *Tetrahedron Lett.* **15**, 1191 (1974); (b) H. Ogura, K. Takeda, R. Tokue, T. Kobayashi. *Synthesis* 394 (1978); (c) R. Nomura, M. Yamamoto, H. Matsuda. *Ind. Eng. Chem. Res*. **26**, 1056 (1987); (d) J. Fournier, C. Bruneau, P. H. Dixneuf, S. Lgcolier. *J. Org. Chem.* **56**, 4456 (1991); (e) R. Nomura, Y. Hasegawa, M. Ishimoto, T. Toyosaki, H. Matsuda. *J. Org. Chem*. **57**, 7339 (1992); (f) C.-C. Tai, M. J. Huck, E. P. McKoon, T. Woo, P. G. Jessop. *J. Org. Chem*. **67**, 9070 (2002); (g) S. Porwanski, S. Menuel, X. Marsura, A. Marsura. *Tetrahedron Lett.* **45**, 5027 (2004).

44. (a) F. Shi, Y. Deng, Y. Ma, J. Peng, Y. Gu, B. Qiao. *Angew. Chem., Int. Ed.* **42**, 3257 (2003); (b) P. Munshi, D. J. Heldebrant, E. P. McKoon, P. A. Kelly, C. C. Tai, P. G. Jessop. *Tetrahedron Lett.* **44**, 2725 (2003); (c) F. Shi, Q. Zhang, Y. Ma, Y. He, Y. Deng. *J. Am. Chem. Soc*. **127**, 4182 (2005); (d) A. Ion, V. Parvulescu, P. Jacobs. *Green Chem*. **9**, 158 (2007); (e) T. Jiang, X. Ma, Y. Zhou, S. Liang, J. Zhang, B. Han. *Green Chem*. **10**, 465 (2008).

45. D. L. Kong, L. N. He, J. Q. Wang. *Synlett* 1276 (2010).

46. M. Aresta, E. Quaranta. *Tetrahedron* **48**, 1515 (1992).

47. B. Abribat, Y. L. Bigot, A. Gaset. *Synth. Commun*. **24**, 2091 (1994).

48. D. L. Kong, L. N. He, J. Q. Wang. *Synth. Commun*. **41**, 3298 (2011).

49. S. L. Peterson, S. M. Stucka, C. J. Dinsmore. *Org. Lett*. **12**, 1340 (2010).

50. C. Y. Wu, H. Y. Cheng, R. X. Liu, Q. Wang, Y. F. Hao, Y. C. Yu, F. Y. Zhao. *Green Chem*. **12**, 1811 (2010).

51. P. Landais, C. Crouzel. *Appl. Radiat. Isot*. **38**, 297 (1987).

52. R. P. Bennet, W. B. Hardy. *J. Am. Chem. Soc*. **90**, 3295 (1968).

53. (a) J. P. Collman, M. Kubota, J. W. Hoskins. *J. Am. Chem. Soc*. **89**, 4809 (1967); (b) J. P. Collman, M. Kubota, F. D. Vastine, J. Y. Sun, J. W. Kang. *J. Am. Chem. Soc*. **90**, 5430 (1968).

54. T. Kihlberg, F. Karimi, B. Langstrom. *J. Org. Chem*. **67**, 3687 (2002).

55. (a) T. Conway, M. Diksic. *Appl. Radiat. Isot*. **42**, 441 (1991); (b) G. Brown, S. Luthra, C. Brock, M. Stevens, P. Price, F. Brady. *J. Med. Chem*. **45**, 5448 (2002); (c) C. Crouzel, F. Hinnen, E. Maitre. *Appl. Radiat. Isot*. **46**, 167 (1995); (d) L. Lemoucheux, J. Rouden, M. Ibazizene, F. Sobrio, M. Lasne. *J. Org. Chem*. **68**, 8742 (2003).

56. G. Brown, D. Henderson, C. Steel, S. Luthra, P. Price, F. Brady. *Nucl. Med. Biol*. **28**, 991 (2001).

57. P. Molina, M. Alajarin, A. Arques. *Synthesis* 596 (1982).

58. D. C. Dean, M. A. Wallace, T. M. Marks, D. G. Melillo. *Tetrahedron Lett*. **38**, 919 (1997).

59. (a) M. J. Horvath, D. Saylik, P. S. Elmes, W. R. Jackson, C. G. Lovel, K. Moody. *Tetrahedron Lett.* **40**, 363 (1999); (b) D. Saylik, M. J. Horvath, P. S. Elmes, W. R. Jackson. *J. Org. Chem*. **64**, 3940 (1999).

60. R. A. Kasar, G. M. Knudsen, S. B. Kahl. *Inorg. Chem*. **38**, 2936 (1999).

61. S. Menuel, S. Porwanski, A. Marsura. *New J. Chem*. **30**, 603 (2006).

62. S. Porwanski, B. Kryczka, A. Marsura. *Tetrahedron Lett*. **43**, 8441 (2002).

63. S. Menuel, M. Wagner, D. Barth, A. Marsura. *Tetrahedron Lett*. **46**, 3307 (2005).

64. J. O. Daiß, C. Burschka, R. Tacke. *J. Organomet. Chem.* **690**, 678 (2005).

65. U. J. Kilgore, F. Basuli, J. C. Huffman, D. J. Mindiola. *Inorg. Chem*. **45**, 487 (2006).

66. A. Yagodkin, K. Löschcke, J. Weisell, A. Azhayev. *Tetrahedron* **66**, 2210 (2010).

67. A. A. Wilson, A. Garcia, S. Houle, O. Sadovski, N. Vasdev. *Chem.—Eur. J.* **17**, 259 (2011).
68. (a) J. M. Hooker, A. T. Reibel, S. M. Hill, M. J. Schueller, J. S. Fowler. *Angew. Chem., Int. Ed.* **48**, 3482 (2009); (b) A. A. Wilson, A. Garcia, S. Houle, N. Vasdev. *Org. Biomol. Chem.* **8**, 428 (2010).
69. (a) K. Soga, W. Chiang, S. Ikeda. *J. Polym. Sci., Part A: Polym. Chem.* **12**, 121 (1974); (b) D. J. Darensbourg, M. W. Holtcamp. *Coord. Chem. Rev.* **153**, 155 (1996); (c) W. Kuran. *Prog. Polym. Sci.* **23**, 919 (1998); (d) K. Nozaki. *Pure Appl. Chem.* **76**, 541 (2004); (e) G. W. Coates, D. R. Moore. *Angew. Chem.* **43**, 6618 (2004); (f) D. J. Darensbourg, R. M. Mackiewicz, A. L. Phelps, D. R. Billodeaux. *Acc. Chem. Res.* **37**, 836 (2004); (g) H. Sugimoto, S. Inoue. *J. Polym. Sci., Part A: Polym. Chem.* **42**, 5561 (2004); (h) O. Ihata, Y. Kayaki, T. Ikariya. *Macromolecules* **38**, 6429 (2005); (i) D. J. Darensbourg. *Chem. Rev.* **107**, 2388 (2007); (j) M. R. Kember, A. Buchard, C. K. Williams. *Chem. Commun.* **47**, 141 (2011); (k) S. Klaus, M. W. Lehenmeier, C. E. Anderson, B. Rieger. *Coord. Chem. Rev.* **255**, 1460 (2011).
70. (a) S. Fukuoka, M. Kawamura, K. Komiya, M. Tojo, H. Hachiya, K. Hasegawa, M. Aminaka, H. Okamoto, I. Fukawa, S. Konno. *Green Chem.* **5**, 497 (2003); (b) P. Cesti, A. Bosetti, F. Mizia, M. Notari, M. Ricci, F. Rivetti, U. Romano. (ENICHEM). WO-A1 01/56977.
71. (a) S. Inoue, H. Koinuma, T. Tsuruta. *Makromol. Chem.* **130**, 210 (1969); (b) M. Kobayashi, S. Inoue, T. Tsuruta. *Macromolecules* **4**, 658 (1971).
72. (a) D. J. Darensbourg, M. W. Holtcamp. *Macromolecules* **28**, 7577 (1995); (b) D. J. Darensbourg, J. R. Wildeson, J. C. Yarbrough, J. H. Reibenspies. *J. Am. Chem. Soc.* **122**, 12487 (2000); (c) M. Cheng, D. R. Moore, J. J. Reczek, B. M. Chamberlain, E. B. Lobkovsky, G. W. Coates. *J. Am. Chem. Soc.* **123**, 8738 (2001); (c) S. D. Allen, D. R. Moore, E. B. Lobkovsky, G. W. Coates. *J. Am. Chem. Soc.* **124**, 14284 (2002); (d) D. J. Darensbourg, S. J. Lewis, J. L. Rodgers, J. C. Yarbrough. *Inorg. Chem.* **42**, 581 (2003); (e) M. Walther, K. Wermann, M. Lutsche, W. Gunther, H. Gorls, E. Anders. *J. Org. Chem.* **71**, 1399 (2006); (f) D. R. Moore, M. Cheng, E. B. Lobkovsky, G. W. Coates. *J. Am. Chem. Soc.* **125**, 11911 (2003); (g) R. Eberhardt, M. Allmendinger, G. A. Luinstra, B. Rieger. *Organometallics* **22**, 211 (2003); (h) R. Eberhardt, M. Allmendinger, M. Zintl, C. Troll, G. A. Luinstra, B. Rieger. *Macromol. Chem. Phys.* **205**, 42 (2004); (i) Y. L. Xiao, Z. Wang, K. L. Ding. *Chem.—Eur. J.* **11**, 3668 (2005); (j) W. J. van Meerendonk, R. Duchateau, C. E. Koning, G. J. M. Gruter. *Macromolecules* **38**, 7306 (2005); (k) M. Kroger, C. Folli, O. Walter, M. Doring. *Adv. Synth. Catal.* **347**, 1325 (2005); (l) B. Y. Lee, H. Y. Kwon, S. Y. Lee, S. J. Na, S. I. Han, H. S. Yun, H. Lee, Y. W. Park. *J. Am. Chem. Soc.* **127**, 3031 (2005); (m) M. R. Kember, A. J. P. White, C. K. Williams. *Inorg. Chem.* **48**, 9535 (2009); (n) M. R. Kember, P. D. Knight, P. T. R. Reung, C. K. Williams. *Angew. Chem., Int. Ed.* **48**, 931 (2009).
73. (a) Z. Q. Qin, C. M. Thomas, S. Lee, G. W. Coates. *Angew. Chem., Int. Ed.* **42**, 5484 (2003); (b) X. B. Lu, Y. Wang. *Angew. Chem., Int. Ed.* **43**, 3574 (2004); (c) R. L. Paddock, S. T. Nguyen. *Macromolecules* **38**, 6251 (2005); (d) C. T. Cohen, T. Chu, G. W. Coates. *J. Am. Chem. Soc.* **127**, 10869 (2005); (e) C. T. Cohen, C. M. Thomas, K. L. Peretti, E. B. Lobkovsky, G. W. Coates. *Dalton Trans.* 237 (2005); (f) X. B. Lu, L. Shi, Y. M. Wang, R. Zhang, Y. J. Zhang, X. J. Peng, Z. C. Zhang, B. Li. *J. Am. Chem. Soc.* **128**, 1664 (2006); (g) I. Sugimoto, K. Kuroda. *Macromolecules* **41**, 312 (2008); (h) S. S. J. K. Min, J. E. Seong, S. J. Na, B. Y. Lee. *Angew. Chem., Int. Ed.* **47**, 7306 (2008); (i) H. R. Kember, A. J. P. White, C. K. Williams. *Macromolecules* **43**, 2291 (2010); (j) G.-P. Wu, S. H. Wei, X. B. Lu, W. M. Ren, D. J. Darensbourg. *Macromolecules* **43**, 9202 (2010).

74. (a) S. Mang, A. I. Cooper, M. E. Colclough, N. Chauhan, A. B. Holmes. *Macromolecules* **33**, 303 (2000); (b) D. J. Darensbourg, M. J. Adams, J. C. Yarbrough. *Inorg. Chem.* **40**, 6543 (2001); (c) D. J. Darensbourg, J. C. Yarbrough. *J. Am. Chem. Soc.* **124**, 6335 (2002); (d) D. J. Darensbourg, R. M. Mackiewicz, J. L Rodgers, A. L. Phelps. *Inorg. Chem.* **43**, 1831 (2004); (e) D. J. Darensbourg, R. M. Mackiewicz, J. L. Rodgers, C. C. Fang, D. R. Billodeaux, J. H. Reibenspies. *Inorg. Chem.* **43**, 6024 (2004); (f) D. J. Darensbourg, R. M. Mackiewicz. *J. Am. Chem. Soc.* **127**, 14026 (2005); (g) D. J. Darensbourg, R. M. Mackiewicz, D. R. Billodeaux. *Organometallics* **24**, 144 (2005); (h) D. J. Darensbourg, A. L. Phelps. *Inorg. Chem.* **44**, 4622 (2005); (i) X. Q. Xu, C. M. Wang, H. R. Li, Y. Wang, W. L. Sun, Z. Q. Shen. *Polymer* **48**, 3921 (2007); (j) D. J. Darensbourg, P. Bottarelli, J. R. Andreatta. *Macromolecules* **40**, 7727 (2007); (k) C. Hongfa, J. H. Tian, J. Andreatta, D. J. Darensbourg, D. E. Bergbreiter. *Chem. Commun.* 975 (2008); (l) M. F. Pilz, C. Limberg, B. B. Lazarov, K. C. Hultzsch, B. Ziemer. *Organometallics* **26**, 3668 (2007); (m) D. F. J. Piesik, S. Range, S. Harder. *Organometallics* **27**, 6178 (2008); (n) K. L. Orchard, J. E. Harris, A. J. P. White, M. S. P. Shaffer, C. K. Williams. *Organometallics* **30**, 2223 (2011).

75. (a) D. V. Vitanova, F. Hampel, K. C. Hultzsch. *J. Organomet. Chem.* **690**, 5182 (2005); (b) D. M. Cui, M. Nishiura, Z. M. Hou. *Macromolecules* **38**, 4089 (2005); (c) D. V. Vitanova, F. Hampel, K. C. Hultzsch. *J. Org. Chem.* **690**, 5182 (2005); (d) B. B. Lazarov, F. Hampel, K. C. Hultzsch. *Anorg. Allg. Chem.* **633**, 2367 (2007).

76. (a) H. Sugimoto, H. Ohshima, S. Inoue. *J. Polym. Sci., Part A: Polym. Chem.* **41**, 3549 (2003); (b) D. J. Darensbourg, E. B. Frantz. *Dalton Trans.* 5031 (2008).

77. D. J. Darensbourg, S. A. Niezgoda, J. D. Draper, J. H. Reibenspies. *J. Am. Chem. Soc.* **120**, 4690 (1998).

78. (a) T. Aida, S. Inoue. *J. Am. Chem. Soc.* **107**, 1358 (1985); (b) T. Aida, M. Ishikawa, S. Inoue. *Macromolecules* **19**, 8 (1986); (c) F. Kojima, T. Aida, S. Inoue. *J. Am. Chem. Soc.* **108**, 391 (1986); (d) W. J. Kruper, D. V. Dellar. *J. Org. Chem.* **60**, 725 (1995).

79. A. Buchard, M. R. Kember, K. G. Sandeman, C. K. Williams. *Chem. Commun.* **47**, 212 (2011).

80. (a) K. Nakano, T. Kamada, K. Nozaki. *Angew. Chem., Int. Ed.* **45**, 7274 (2006); (b) E. K. Noh, S. J. Na, S. Sujith, S. W. Kim, B. Y. Lee. *J. Am. Chem. Soc.* **129**, 8082 (2007); (c) S. J. Na, S. S. A. Cyriac, B. E. Kim, J. Yoo, Y. K. Kang, S. J. Han, C. Lee, B. Y. Lee. *Inorg. Chem.* **48**, 10455 (2009); (d) W.-M. Ren, Z. W. Liu, Y. Q. Wen, R. Zhang, X. B. Lu. *J. Am. Chem. Soc.* **131**, 11509 (2009); (e) B. Li, R. Zhang, X. B. Lu. *Macromolecules* **40**, 2303 (2007); (f) D.-Y. Rao, B. Li, R. Zhang, H. Wang, X. B. Lu. *Inorg. Chem.* **48**, 2830 (2009); (g) J. Yoo, S. J. Na, H. C. Park, A. Cyriac, B. Y. Lee. *Dalton Trans.* **39**, 2622 (2010); (h) W.-M. Ren, X. Zhang, Y. Liu, J. F. Li, H. Wang, X. B. Lu. *Macromolecules* **43**, 1396 (2010).

81. O. Ihata, Y. Kayaki, T. Ikariya. *Angew. Chem., Int. Ed.* **43**, 717 (2004).