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CO_2-Mediated Formation of Chiral Fine Chemicals

Xiao-Bing Lu

Abstract The utilization of carbon dioxide as a feedstock for the synthesis of organic chemicals can contribute to a more sustainable chemical industry, since CO_2 is an abundant, inexpensive, and nontoxic renewable C_1 resource. Nevertheless, far less attention was paid to the stereochemically controlled catalytic CO_2 fixation/conversion processes. This review therefore aims to principally showcase the recent progress regarding CO_2-mediated formation of chiral fine chemicals, including enantioselective synthesis of cyclic carbonates by asymmetric ring opening of epoxides with CO_2, enantioselective synthesis of oxazolidinones by the coupling reaction of aziridines with CO_2- or base-mediated formation of oxazolidinone from ethanolamines, metal-catalyzed enantioselective synthesis of functional carboxylic acids and derivatives, and enantioselective synthesis of CO_2-based polycarbonates from epoxides.

Keywords Asymmetric catalysis · Carbon dioxide · Carboxylation · Carboxylic acid · Chiral · CO_2-based polycarbonate · Cyclic carbonate · Epoxide · Oxazolidinone · Polymerization catalysis

Contents

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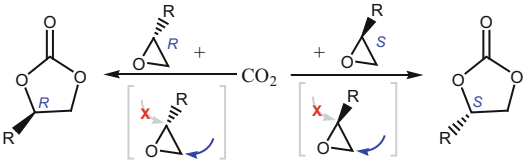
1 Introduction

The utilization of carbon dioxide as a feedstock for the synthesis of organic chemicals can contribute to a more sustainable chemical industry, since CO_2 is an abundant, inexpensive, and nontoxic renewable C_1 resource [1–3]. More than 20 reactions concerning CO_2 as a starting material have been developed in recent decades, though successful industrial processes are very limited to the syntheses of urea, inorganic carbonates, methanol, salicylic acid, and organic carbonates [4–6]. It is apparent that the quantity of CO_2 consumed in these processes is likely always to be a very small fraction of the total CO_2 generated from the emission-based human activity. However, this strategy potentially provides access to the more environmentally benign routes to producing useful chemicals otherwise made from the reagents detrimental to the environment.

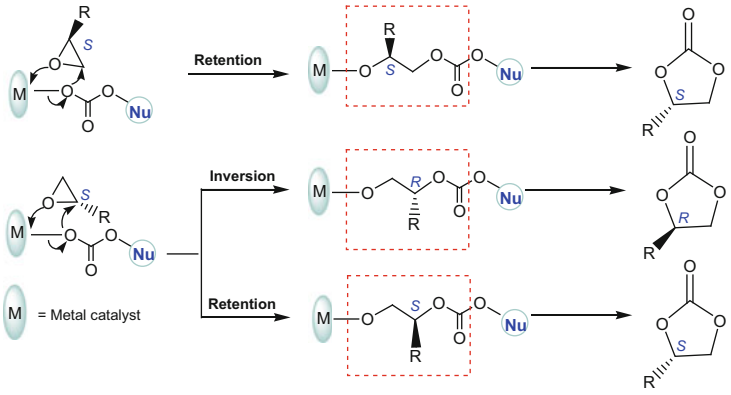
Indeed, the majority of reactions using CO_2 as a feedstock concern the preparation of relatively simple achiral chemicals, with an emphasis on CO_2 incorporation efficiency, while far less attention was paid to the stereochemically controlled catalytic CO_2 fixation/conversion processes [7, 8]. This review is intended to provide a thorough accounting of the literatures involving CO_2-mediated formation of chiral fine chemicals.

2 Enantioselective Synthesis of Cyclic Carbonates

In the early contributions, optically pure cyclic carbonates were reported to be prepared by several methods, including the cyclization of chiral diols with triphosgene [9], metal complex-catalyzed insertion of CO_2 into chiral epoxides [10], enzyme-mediated enantioselective hydrolysis of *racemic* cyclic carbonates [11, 12], and asymmetric hydrogenation of 5-methylene-1,3-dioxolan-2-ones catalyzed by chiral ruthenium complexes [13, 14]. Among them, the enantioselective coupling reaction of CO_2 and chiral terminal epoxides is the simplest route to afford enantiopure cyclic carbonates in high efficiency (Scheme 1). In this reaction process, the regioselective ring opening of a terminal epoxide at methylene C–O bond is a precondition for obtaining high enantioselectivity, since the ring opening at methine C–O bond probably results in a change in stereochemistry with configuration inversion at methine carbon (Scheme 2). Although the nucleophilic ring opening of terminal epoxides seems to typically occur at the least hindered methylene carbon, the cleavage is normally observed at both C–O bonds in the coupling reaction [15]. The regioselectivity for epoxide ring opening depends on the employed epoxide, reaction temperature, and catalyst system. Being different from propylene oxide, the nucleophilic ring opening of the terminal epoxides with an electron-withdrawing group such as styrene oxide predominantly occurs at the methine C_α–O bond rather than the methylene C_β–O bond, thereby easily causing a change in stereochemistry at the methine carbon with inversion.



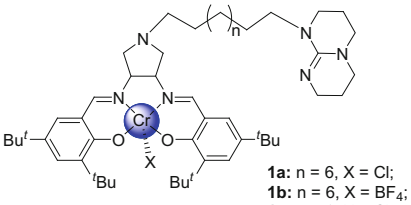
Scheme 1 Enantioselective coupling reaction of CO_2 and chiral terminal epoxides



Scheme 2 The preferential stereochemistry involved in the metal complex-mediated formation of cyclic carbonate from (*S*)-epoxide and CO_2

In 2003, Aresta and coworkers disclosed that in the use of Nb_2O_5 as catalyst for the carboxylation of (*R*) or (*S*)-configured epoxides (propylene oxide or styrene oxide) with CO_2, the resultant cyclic carbonates remained the configuration of chiral epoxide at methine carbon (>98% *ee*), while an obvious decrease in enantioselectivity (82–87% *ee*) was observed in the absence of Nb_2O_5 [16]. The high enantioselectivity was ascribed to the simultaneous interaction of the O atom of the epoxide with the Nb center, and the attack at the asymmetric carbon by the carbonate moiety formed over Nb_2O_5 might prevent any inversion at the chiral carbon of the epoxide to occur. Also, the use of DMF as a solvent played an important role for enantioselective ring opening of epoxide, in which the solvent could assist the carboxylation through a back attack at the more substituted carbon that might contribute in preventing any change of configuration at the chiral center. Recently, Lu et al. reported that an intramolecularly two-centered chromium complex **1a** bearing a sterically hindered nucleophilic center on the ligand could catalyze the reaction of CO_2 with (*S*)-propylene oxide at 80°C, giving (*S*)-propylene carbonate in 96% *ee* with retention of stereochemistry [17]. More recently, the same group demonstrated that salenAlCl bearing two appended quaternary ammonium salts **2** exhibited excellent activity (TOF, 400–5,250 h^{-1}) and unprecedented selectivity (≥99% *ee*) for catalyzing enantioselective coupling of CO_2 with various chiral epoxides in a very low catalyst loading of 0.01 mol% [18]. It was found that even performed at 120°C, the resultant cyclic carbonates from chiral

epoxides with an electron-donating group (such as propylene oxide, 1,2-butene oxide, 1,2-hexene oxide, or phenyl glycidyl ether) all had more than 99% enantioselectivity, while a significant decrease in product enantioselectivity was observed in the systems of styrene oxide or epichlorohydrin, indicating high reaction temperatures that caused the decrease in regioselective ring opening at the methylene carbon.



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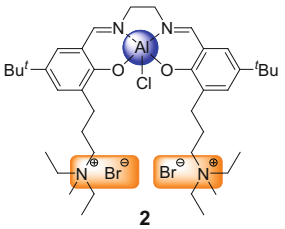
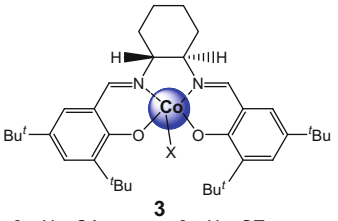


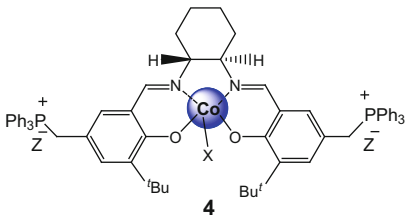
2

The most ambitious study is the enantioselective synthesis of cyclic carbonates by asymmetric ring opening of *racemic* epoxides with CO_2 via a catalytic kinetic resolution (Scheme 3). The key is to find highly efficient catalyst systems for selectively complexing and activating one enantiomer of the *racemic* epoxides. The first attempt was reported by Dibenedetto and Aresta, using homogeneous Nb (V)-catalysts based on chelating chiral ligands such as (*4S*, *5S*)-4,5-bis(diphenylphosphino-methyl)-2,2-dimethyl-1,3-dioxolane (DIOP) and 2,2-methylene-bis (*4S*)-phenyl-oxazoline (MBPO) for the coupling reaction of CO_2 with *racemic* epoxides. The highest enantioselectivity of 22% *ee* was obtained in the reaction CO_2 with racemic styrene oxide, while the same catalyst systems are inferior to the coupling with *racemic* propylene oxide [16].



3

3a: X = OAc;
3b: X = O_2CCCl_3;
3c: X = O_2CCF_3;
3d: X = Cl;
3e: X = OTs;
3f: X = BF_4;
3g: X = PF_6;
3h: X = *p*-nitrobenzoate



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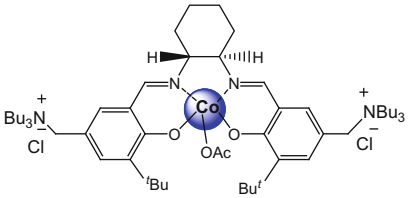
X = OAc, CCl_3CO_2, Cl, OTs, *p*-$NO_2C_6H_4CO_2$;
Z = F, Cl, Br, I



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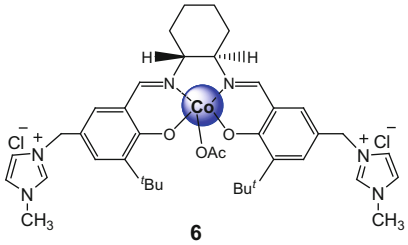

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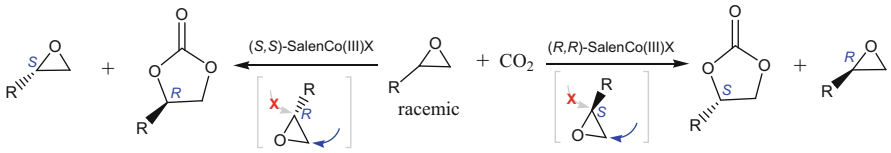
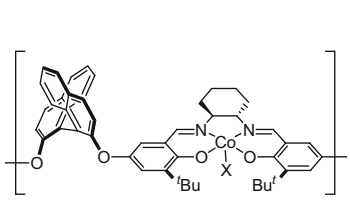


Scheme 3 Synthesis of optically active cyclic carbonate from asymmetric coupling of CO_2 and *racemic* epoxides via a catalytic kinetic resolution process

In the nucleophilic ring opening of epoxides promoted by (salen)M complexes, there is ample evidence that the epoxide is beforehand activated by the coordination to the Lewis acidic (salen)M complex [19]. Based on the possible mechanisms of epoxide ring opening catalyzed by Lewis acidic (salen)M complex and nucleophilic cocatalysts, Lu and coworkers designed a binary catalyst system for producing optically active cyclic carbonates from *racemic* epoxides [20]. Using Jacobsen's chiral (salen)Co(III) catalyst **3** in conjunction with tetrabutylammonium halides (^{n}Bu$_4$NX), the authors succeeded in preparing enantioenriched propylene carbonate from *racemic* propylene oxide through a convenient solvent-free kinetic resolution with a high rate of 245 h^{-1} under ambient temperature. It was found that both the axial X-counterion of chiral salenCo(III)X and the anion of the quaternary ammonium cocatalyst had significant effects on propylene carbonate enantiomeric purity. Although the k_{rel} (kinetic resolution coefficient) values measured in the epoxide resolution with CO_2 are below what is generally considered useful, this investigation is important because it addresses the feasibility of using CO_2 as a C_1 source in asymmetric catalysis. Almost simultaneously, Paddock and Nguyen also explored the kinetic resolution of *racemic* propylene oxide with CO_2 as reagent using chiral salenCo(III)X **3** in combination with a Lewis base [21]. The best result (with a k_{rel} of 5.6 and a TOF of 10 h^{-1}) was obtained using (*R*)-(+)-4-dimethylaminopyridinyl(pentaphenylcyclopentadienyl)iron as cocatalyst. Subsequently, Berkessel and Brandenburg investigated bis-(triphenylphosphoranylidene) ammonium halide (PPNY, Y = F, Cl) as cocatalyst in combination with chiral salenCo(III)X **3** for the production of enantiomerically enriched propylene carbonate [22]. The best selectivity with 83% *ee* for the resultant propylene carbonate, corresponding to a k_{rel} of 19, was achieved at a low temperature of −20°C.



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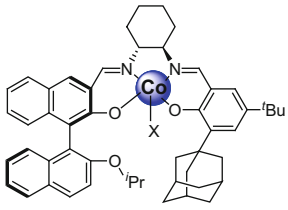
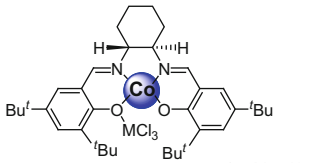


8

8a: X = 2,4-dinitrophenoxy
8b: X = BF_4

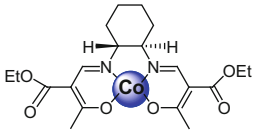
Based on the strategy of using a combination of chiral salenCo(III) complex and a nucleophilic cocatalyst for the asymmetric coupling of CO_2 and *racemic* epoxides, Jing and coworkers developed a series of bifunctional chiral catalysts **4–6**, in which a salenCo(III) complex and two quaternary ammonium or phosphonium salts are incorporated into a molecule, for the kinetic resolution of terminal epoxides with CO_2 as agent to afford optically active cyclic carbonates [23–27]. Unfortunately, no obvious improvement in product enantioselectivity and significant decrease in activity were observed. In order to improve the chiral induction environment of the catalyst, the same group designed novel polymeric binol-based cobalt(III) complex **7** bearing an auxiliary chiral site for the asymmetric coupling of CO_2 and *racemic* propylene oxide [28]. The (*R*/*S*)-polymer and (*S*/*R*)-polymer catalyst exhibited better enantioselectivity than the (*R*/*R*)-polymer and (*S*/*S*)-polymer catalyst. Nevertheless, the improvement in enantioselectivity is very limited, and the highest k_{rel} of 10.2 was achieved at 0°C. The significant progress came with the use of multichiral [(*R*,*R*,*R*)-configured] salenCo(III) complex **8** in combination with excess PPN-DNP {2,4-dinitrophenolate salt of bis-(triphenylphosphoranylidene) ammonium} cocatalyst [29]. It was found that an ammonium salt consisting of an anion with poor leaving ability and a bulky cation benefited for improving the enantioselectivity. The highest enantioselectivity of 97.1% *ee* (a k_{rel} of 75.8) was achieved for optically active propylene carbonate from *racemic* propylene oxide at –25°C. This catalyst system was found to be effective for the asymmetric coupling of CO_2 with other terminal epoxides including epichlorohydrin and glycidyl phenyl ether with k_{rel} values between 10.7 and 31.5 at 0°C.

Interestingly, in the presence of appropriate cocatalyst or additive, chiral Co(II)-salen complexes **9** and **10** could efficiently catalyze the coupling reaction of CO_2 and *racemic* terminal epoxides to afford the corresponding cyclic carbonates with moderate enantioselectivity [30, 31], comparable to the previously mentioned binary catalyst systems based on chiral salenCo(III)X **3**. For example, Yamada et al. discovered that chiral salenCo(II) **10** in combination with Et_2NSiMe_3 cocatalyst was efficient in catalyzing CO_2 and *racemic* *N*,*N*′-diphenyl-aminomethyloxirane to the corresponding cyclic carbonate [31]. The best k_{rel} of 32 was observed in the optimization conditions, in which after 49% conversion, the *ee* values of the resultant cyclic carbonate and unreacted epoxide are 86 and 87%, respectively. The high enantioselectivity should ascribe to the interaction between the cobalt atom and the oxygen atom in the epoxide as well as the heteroatom adjacent to the oxirane during the approach of the substrate to the cobalt (II) complex.



9a: M = Al
9b: M = Ga
9c: M = In

9



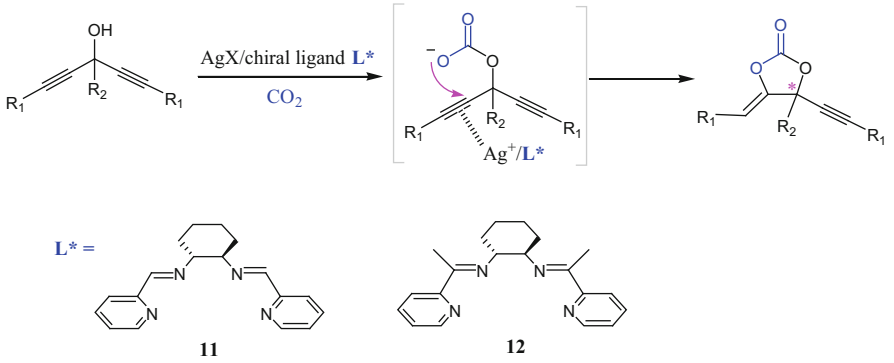
10

Recently, Yamada and coworkers reported a novel route for the synthesis of enantiopure functionalized cyclic carbonates via the asymmetric CO_2 incorporation into bispropargylic alcohols with desymmetrization catalyzed by silver acetate with a chiral Schiff base ligand (Scheme 4) [32]. Bispropargylic alcohols with various substituted groups were also good substrates that afforded the corresponding cyclic carbonates in excellent yields with good-to-high enantiomeric excesses (80–93% *ee*) regardless of the electron-donating and electron-withdrawing substituents.

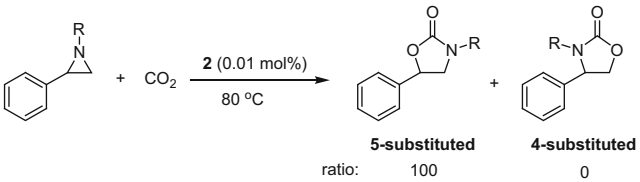
3 Enantioselective Synthesis of Oxazolidinones

Oxazolidinones, a class of heterocyclic compounds, have attracted considerable attention in medicinal chemistry as a result of their some interesting pharmacological activity, suitable for antibacterials, immunosuppressants, or monoamine oxidase inhibitors [33]. In addition, oxazolidinone heterocycles have been widely used as chiral auxiliaries in various reactions directed to the stereoselective synthesis of natural products, antibiotics, and pharmaceuticals [34]. Oxazolidinones are mainly manufactured by phosgenation of β-amino alcohols. However, the use of phosgene precludes widespread application in laboratory and industry due to phosgene's toxicity and significantly detrimental to the environment. Replacement of phosgene with CO_2 is an ideal alternative. There are four routes regarding CO_2 as a starting material for oxazolidinone synthesis, including the coupling reaction of aziridines with CO_2, base-mediated formation of oxazolidinone from ethanolamines, PPh_3-mediated synthesis of oxazolidinone from 1,2-azido alcohols, and the reaction of propargylic amines with CO_2. Among them, the former two methods were also utilized for the synthesis of enantiopure oxazolidinone by the use of chiral starting material.

In contrast with the sole product resulted from the cycloaddition of epoxides and CO_2, the coupling reaction of aziridines with CO_2 usually affords two regioisomers: 5-substituted and 4-substituted oxazolidinones. The isomeric ratio is dependent on the substituents of the aziridine and the reaction temperature. He et al. reported that polyethylene glycol-supported quaternary ammonium bromide was active for the reaction of enantiopure 1-butyl-2-phenylaziridine with CO_2 to afford the corresponding oxazolidinone with high enantioselectivity [35]. More recently, Ren and coworkers found that salenAlCl bearing appended quaternary



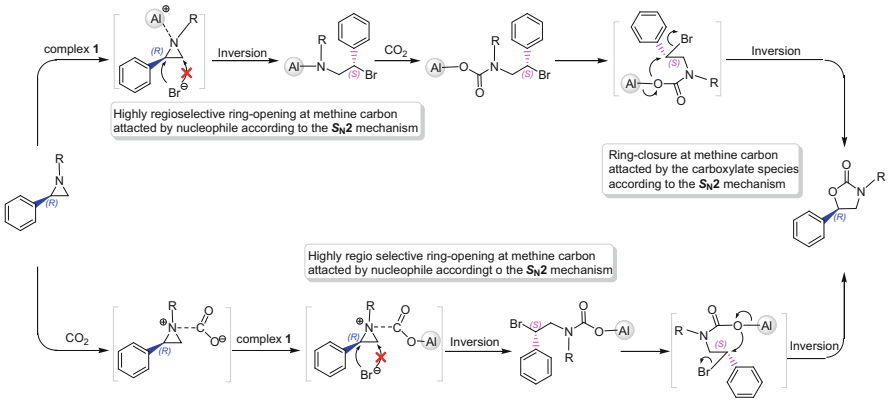
Scheme 4 Enantioselective chemical incorporation of CO_2 into bispropargylic alcohols



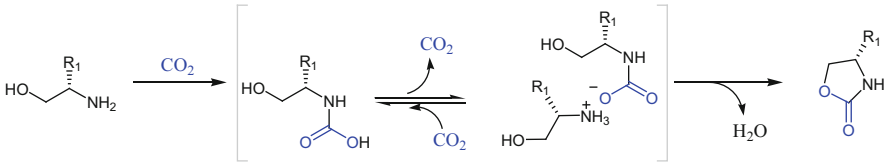
Scheme 5 The coupling reaction of aziridines with CO_2

ammonium salts **2** could catalyze the coupling reaction of CO_2 with (*R*)-1-benzyl-2-phenylaziridine or (*R*)-1-butyl-2-phenylaziridine at 80°C could afford (*R*)-5-substituted oxazolidinones with high enantiopurity up to 99% *ee* (Scheme 5). A possible mechanism involving two consecutive SN_2 processes at the same carbon was suggested (Scheme 6) [18]. The nucleophilic ring opening of *N*-substituted aziridine at methine C–N bond leads to the complete configuration inversion of the methine carbon. This is followed by the backbiting with regard to the attack of the carbamate species at methine carbon after the insertion of CO_2. This process also results in a complete inversion of the methine carbon stereochemistry. As a result, the configuration of the methine carbon of 5-substituted oxazolidinones is the same as that of the employed *N*-substituted aziridines due to double inversion. Chai et al. also illuminated that the use of an enantiopure *N*-tosyl aziridine bearing two alkyl groups in its positions 2 and 3 resulted in the selective formation of chiral oxazolidinone product with retention of configuration [36].

Classical syntheses of chiral oxazolidin-2-ones from chiral 1,2-amino alcohols or their derivatives require toxic and hazardous phosgene or its derivatives and/or drastic conditions (strong base or very high temperature). The study regarding replacement of phosgene with CO_2 was widely carried out, but usually suffered from catalyst deactivation caused by the coproduced water and limited conversion due to the thermodynamic reasons (Scheme 7) [37]. In order to overcome these drawbacks, many attempts have been made to shift the equilibrium to the product side. The most straightforward way is to use a dehydrating agent to trap the



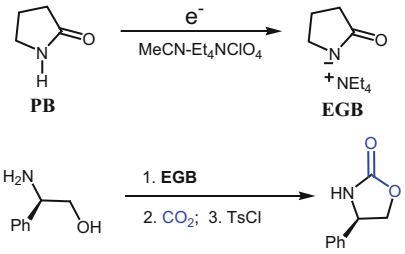
Scheme 6 Possible mechanism for the complex **2**-mediated formation of (*R*)-5-substituted oxazolidinone from the coupling reaction of CO_2 with (*R*)-1-alkyl-2-phenylaziridine



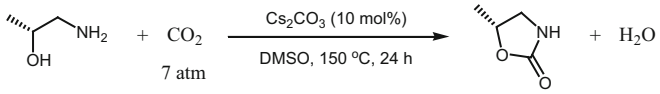
Scheme 7 Synthesis of oxazolidinone from CO_2 under atmosphere pressure

coproduced water. The significant progress came from the contribution of Feroci and Inesi laboratory [38], which involved the use of 2-pyrrolidone electrogenerated base for the synthesis of chiral oxazolidin-2-ones from *β*-amino alcohols by the reaction with CO_2 (Scheme 8), achieving the retention of the absolute configuration of all chiral atoms.

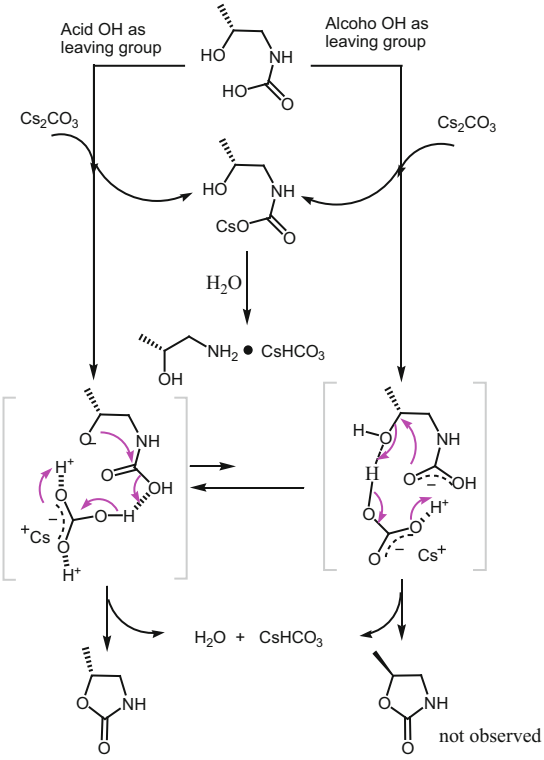
Recently, Saito and coworkers reported a chiral oxazolidinone synthesis via the incorporation of CO_2 into *β*-amino alcohols using alkali metal carbonates such as Cs_2CO_3 as catalyst (Scheme 9) [39]. It is noteworthy that 1 atm of CO_2 is enough for the reaction to proceed and no special dehydrating agent is required in this system. The preliminary mechanistic study revealed that the OH of amino alcohol acts as nucleophile and the OH at carbamic acid moiety is liberated during the cyclization process (Scheme 10). Prior to this study, Muñoz realized the preparation of various chiral oxazolidinones from *β*-amino alcohols and CO_2 in the presence of tetramethylphenylguanidine (PhTMG) as a base and a variety of phosphorus electrophiles under mild conditions [40]. Notably, the steric hindrance or the electron deficiency/richness of the substituents did not have a deleterious effect on the carbonylation reaction.



Scheme 8 Synthesis of oxazolidin-2-one from amino alcohol according to the general procedure



Scheme 9 Reaction of CO_2 with (*R*)-1-aminopropan-2-ol



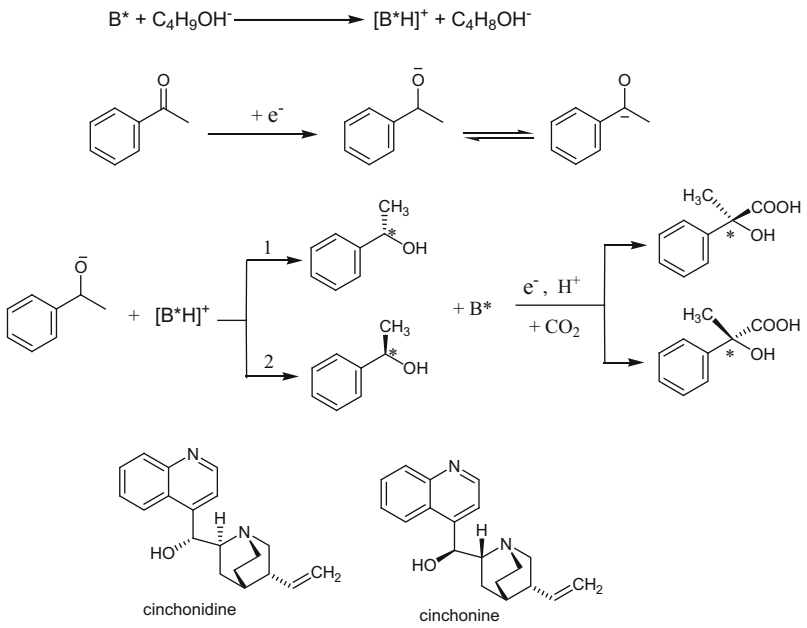
Scheme 10 Possible routes in the reaction of CO_2 with (*R*)-1-aminopropan-2-ol

4 Enantioselective Synthesis of Functional Carboxylic Acids and Derivatives

It is highly challenging to develop efficient catalytic protocols that enable carbon–carbon bond formation between CO_2 and substrates in an enantioselective manner, since the limited number of available catalytic carbon–carbon bond-forming CO_2 incorporation reactions that can be efficiently carried out under mild conditions. In a recent study, Lu and coworkers described a novel method for asymmetric electrocarboxylation of prochiral and inexpensive available acetophenone and CO_2 to provide optically active 2-hydroxy-2-phenylpropionic acid [41]. Under the optimized condition, the highest enantiomeric excess could achieve 29.8% on stainless steel cathodes by the induction of the alkaloid. Although the product enantioselectivity is not satisfactory due to the difficulty in selective fixation of the small molecule of carbon dioxide via enantioselective electron transfer, it is the first time to demonstrate asymmetric electrochemical carboxylation with CO_2 as a reagent. A plausible mechanism concerning the selective proton transfer from the chiral proton-donating alkaloid to the ketyl radical anion was proposed (Scheme 11) [42]. The crucial chiral proton-donating species was initially formed after the alkaloid obtained a proton from the cocatalyst of butanol or directly from the reaction media. Both the cinchonidine and butanol played an important role in the asymmetric electrosynthesis process for the optically active atrolactic acid. In a more recent contribution, the enantiomeric excess of 2-hydroxy-2-arylpropionic acids was further improved to 48.6% *ee* using electrocarboxylation in CO_2-saturated MeCN in the presence of cinchona alkaloids with the addition of phenol.

The exciting results were obtained by Mori group [43, 44], who developed a nickel-catalyzed highly enantioselective carbon–carbon bond-forming CO_2 incorporation reaction based on this carboxylative cyclization from bis-1,3-dienes (Scheme 12). The remarkable feature of this reaction is that the reaction proceeds under very mild conditions in a highly regio- and stereoselective manner (90–96% *ee*). Not only aromatic but also aliphatic terminal alkynes gave unsaturated carboxylic acid in high yields. The reaction was suggested to start with oxidative cycloaddition of bis-diene **1a** to a Ni(0) complex to produce bis-π-allylnickel complex **4** (Scheme 13), and subsequent insertion of CO_2 into the nickel–carbon bond afforded carboxylate **5**. The role of Et_2Zn in this reaction is probably regeneration of a Ni(0) complex via a transmetalation process. Thus, complex **5** reacted with Et_2Zn to provide complex **6**, which can then easily undergo β-hydrogen elimination to produce complex **7**. Reductive elimination from **7** reproduced the Ni(0) complex and provided carboxylate **8**, which corresponds to ester **2a**.

More recently, Zhao and coworkers developed an iridium complex-mediated enantioselective domino reaction of CO_2, amines and linear allyl chlorides, or allyl carbonate to provide the branched allyl carbamates in good yields with high regioselectivity (up to 98:2) and good to excellent levels of enantioselectivity (up to 99% *ee*) (Scheme 14) [45, 46]. The mechanistic study suggested that the



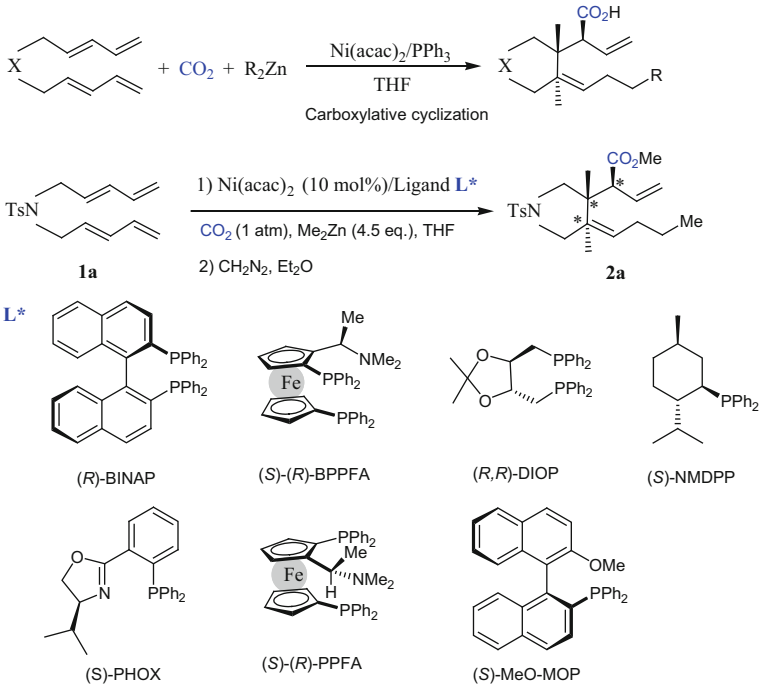
Scheme 11 Mechanism for the asymmetric electrochemical carboxylation of acetophenone by the alkaloid

reaction started by insertion of iridium into the allyl–oxygen bond to liberate an ionized π-allyl–Ir complex **A**, methoxide, and CO_2. Subsequently, an amidation reaction between CO_2 and an amine occurs to form a carbamate ion, which in turn attacks intermediate **A** to yield an allyl carbamate **B** and regenerating the catalyst. In the absence of K_3PO_4, complex **A** is directly attacked by the amine to give an extrusion product, allylamine **C** (Scheme 14).

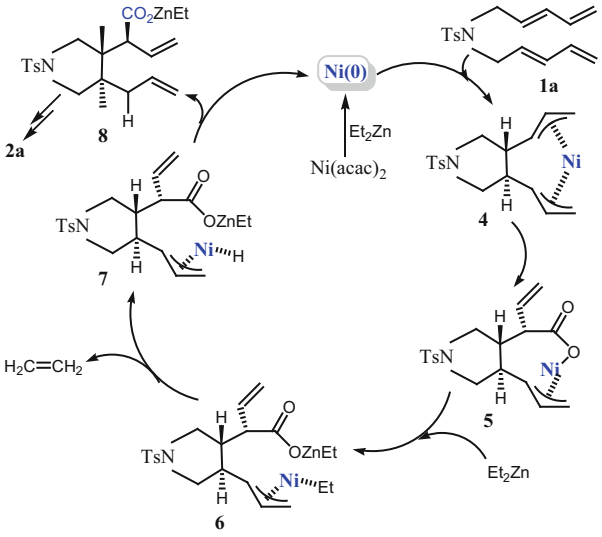
More recently, Mita and Sato reported a Cu-secondary diamine complex-catalyzed enantioselective silylation of *N-tert*-butylsulfonylimines and followed stereoretentive carboxylation under a CO_2 atmosphere (1 atm), affording the corresponding α-amino acids in a stereoretentive manner [47]. This two-step sequence provides a new synthetic protocol for optically active α-amino acids from gaseous CO_2 and imines in the presence of a catalytic amount of a chiral source.

5 Enantioselective Synthesis of CO_2-Based Polycarbonates

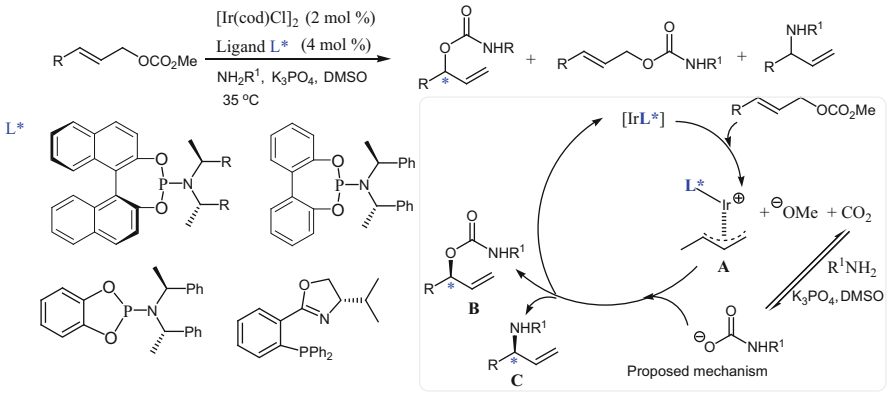
The alternating copolymerization of CO_2 with epoxides to afford degradable polycarbonates represents a green polymerization process for potential large-scale utilization of CO_2 in chemical synthesis. Although this polymerization was first demonstrated by Inoue in 1969 using $ZnEt_2/H_2O$ heterogeneously catalyzed



Scheme 12 Nickel-catalyzed enantioselective carboxylative cyclization of bis-1,3-dienes

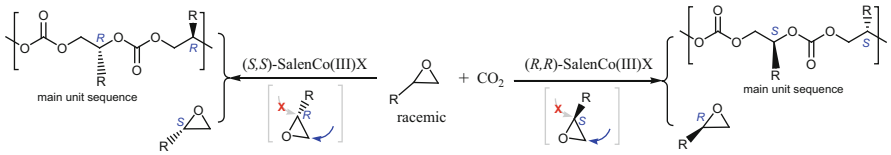


Scheme 13 Possible mechanism of Ni(0)-catalyzed enantioselective carboxylative cyclization of bis-1,3-dienes



Scheme 14 Iridium complex-mediated enantioselective domino reaction

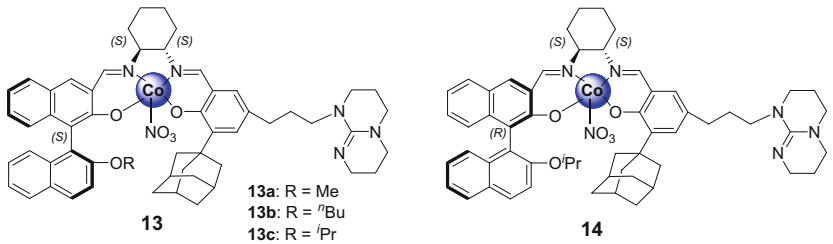
copolymerization of CO_2 and propylene oxide to give poly(propylene carbonate) with a very low reaction rate (TOF, 0.12 h^{-1}) [48], it was not until the recent decade that significant advancements were achieved by the discoveries of several highly active catalyst systems [49, 50]. Nevertheless, these atactic CO_2-based polycarbonates have limited applications because of poor physical properties. A promising approach to improving their thermal and mechanical properties is to introduce stereoregularity into the polymer main chain by enantioselective polymerization catalysis. The first attempt appeared in 2003, when Coates and coworkers reported the use of salenCo(III) complexes in selective preparation of poly(propylene carbonate) from the copolymerization of CO_2 and propylene oxide at high catalyst loadings (epoxide/catalyst = 200–500/1, molar ratio) and a very high CO_2 pressure of 5.5 MPa [51]. The resulting polymers are regioregular and highly alternating. With *racemic* propylene oxide, catalyst **3a** exhibits a k_{rel} of 2.8 and preferentially consumed (*S*)-propylene oxide via a kinetic resolution process (Scheme 15). Turnover frequencies (TOFs) extended over a range of 17–81 h^{-1}, dependent on reaction conditions and the substituent groups on the salen ligand. Surprisingly, increasing reaction temperature or reducing CO_2 pressure results in a significant loss in catalyst activity. However, soon after Lu and Wang found that the addition of a nucleophilic cocatalyst such as quaternary ammonium halide significantly enhanced the activity of (salen)Co(III)X, even at low CO_2 pressures and/or elevated temperatures, affording copolymers with >99% carbonate unit content and an increased stereochemistry control (~95% head-to-tail linkage) [52]. Systematic studies indicated that many aspects of the catalyst, including chiral diamine backbone, substituent groups on the salen ligand, and axial counterion of (salen)Co(III)X, as well as nucleophilicity, leaving ability, and coordination ability of the cocatalyst, significantly affected the catalytic activity, polymer selectivity, and enantioselectivity [53]. Binary (*R*,*R*)-(salen)Co(III)X/PPNCl (X = pentafluorobenzoate) catalyst system demonstrated a k_{rel} of 9.7 for the



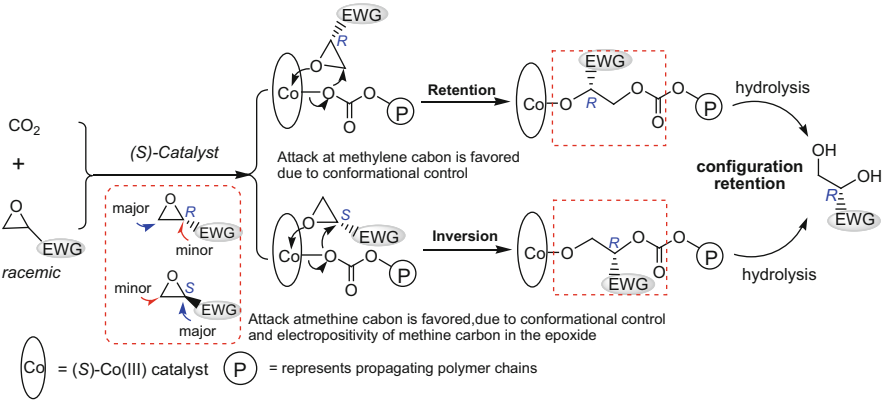
Scheme 15 Synthesis of optically active polycarbonates from asymmetric copolymerization of CO_2 and racemic epoxides via a catalytic kinetic resolution process

enchainment of (*S*)- over (*R*)-propylene oxide when the copolymerization was carried out at –20°C. The following study suggested that the nucleophilic cocatalyst played both initiator for polymer chain growth and stabilizer for preventing the active Co(III) species against decomposition to inactive Co(II) [54].

Recently, Lu and coworkers prepared multichiral (*S,S,S*)-Co(III) catalysts **8a** and **13** [55, 56]. Both the (*1S,2S*)-1,2-diaminocyclohexane backbone and S-configured 2′-isopropyloxy-1,10-binaphthyl of the ligand cooperatively provide chiral environments around the central metal ion. With complex **13c** as catalyst, the highest k_{rel} of 24.3 was obtained at −20°C [55]. Notably, epoxide ring opening occurred preferentially at the methylene carbon, resulting in the copolymer with >99% head-to-tail content. Interestingly, complex **14** with (*S,S*)-1,2-diaminocyclohexane backbone and R-configured 2′-isopropyloxy-1,1′-binaphthyl also exhibited excellent regioselectivity for epoxide ring opening with the polymeric product having 99% head-to-tail content, but the k_{rel} of only 1.4 resulted in a low copolymer enantioselectivity.



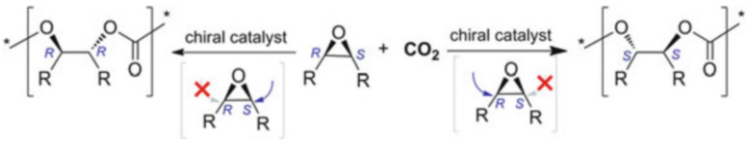
Far different from the highly regioselective ring opening of epoxides with an electron-donating group such as propylene oxide during the copolymerization with CO_2, binary catalyst systems based on salenCo(III)X **3** for epoxides with an electron-withdrawing group afforded regio-irregular copolymer, e.g., for styrene oxide case with a head-to-tail content of 51%, indicating that epoxide ring opening occurs almost equally at both C_α–O and C_β–O bonds [57]. When enantiopure (*1S,2S*)-**3** (X = 2,4-dinitrophenoxide) was used to the copolymerization of CO_2 and *racemic* styrene oxide, a kinetic resolution was observed with a k_{rel} of 1.6 at ambient temperature. The catalyst preferentially consumed (*R*)-styrene oxide over its (*S*)-configuration. Surprisingly, in comparison with the low k_{rel} value, an enhanced enantioselectivity for (*R*)-configuration carbonate unit with a selective factor of 4.3 was found in the resulting copolymer [58]. Because of the low k_{rel}, a



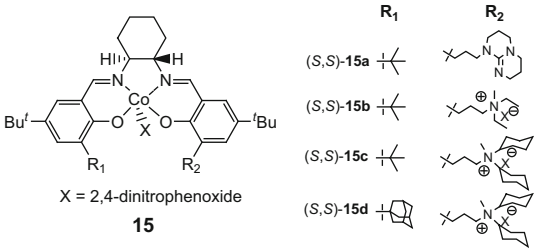
Scheme 16 Formation of optically active polycarbonates from *racemic* epoxides with a withdrawing group and CO_2 by a catalytic kinetic resolution process concerning regioselective ring opening

significant amount of (*S*)-styrene oxide should be incorporated into the polycarbonate. Therefore, the increase in poly(styrene carbonate) enantioselectivity for (*R*)-configuration was ascribed to the preferential configuration inversion occurred at the methine carbon of (*S*)-styrene oxide caused by chiral induction of (*1S,2S*)-3 (Scheme 16). To confirm this assumption, the authors also performed the chiral (*S*)-styrene oxide/CO_2 copolymerization in the presence of the same binary catalyst. The resultant copolymer has an enantioselectivity of 32% with (*R*)-configuration excess, implying that the reaction proceeded with 66% inversion at the benzyl carbon. It was found that the chiral environment around the central metal ion significantly influences the regioselectivity of epoxide ring opening. With complex (*S,S,S*)-**8a** as catalyst, a k_{rel} of 3.3 was observed in the asymmetric copolymerization of CO_2 and *racemic* styrene oxide. Upon replacing with (*R*)-styrene oxide, the resultant copolymer has an enantioselectivity of 92% with (*R*)-configuration excess, indicative of retaining 96% of the stereochemistry at the methine carbon of (*R*)-styrene oxide incorporated into the polycarbonate.

In a recent contribution, the same group reported the use of an enantiopure salenCo(III) complex **15** bearing an adamantine group and an appended bulky dicyclohexyl ionic ammonium salt as catalyst for the copolymerization of CO_2 and epichlorohydrin; a highly regioregular ring-opening step was observed with a concomitant 97% retention of configuration at the methine carbon center [59]. The resultant isotactic poly(chloropropylene carbonate) is a typical semicrystalline polymer with an enhanced T_g of 42°C and a T_m of 108°C [60]. The test of mechanical properties shows that the yield strength and tensile strength of the crystalline copolymer are about 10 and 30 times that of its amorphous counterpart, respectively.



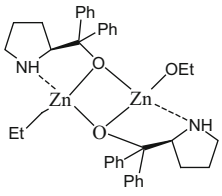
Scheme 17 Asymmetric copolymerization of CO_2 and *meso*-epoxides



It is worthwhile noting here parenthetically that salenCo(III)X **15a** bearing an appended 1,5,7-triabicyclo[4,4,0] dec-5-ene (designated as TBD, a sterically hindered organic base) is an excellent catalyst for highly regioselective ring opening of both benzyl glycidyl ether and phenyl glycidyl ether during the copolymerization with CO_2, affording the corresponding polycarbonates with >99% carbonate unit content and >99% head-to-tail linkages [61, 62]. Deprotection of the resultant copolymers from benzyl glycidyl ether afforded poly(1,2-glycerol carbonate)s with a functionalizable pendant primary hydroxyl group. Poly(1,2-glycerol carbonate) showed a remarkable increase in degradation rate compared to poly (1,3-glycerol carbonate) with a $t_{1/2} = 2$–3 days. These polymers fulfill an unmet need for a readily degradable biocompatible polycarbonate. Particularly, the isotactic CO_2-based polycarbonate from chiral phenyl glycidyl ether is a typical semicrystalline thermoplastic, which possesses a melting point of 75°C.

Indeed, in comparison with stereoregular CO_2-based polycarbonates from terminal epoxides, isotactic polycarbonates from *meso*-epoxides are easy to crystallize and usually show higher melting temperatures. It is generally known that the desymmetrization nucleophilic ring opening of *meso*-epoxides with chiral catalysts or reagents is regarded as a valuable strategy for the synthesis of enantiomerically enriched products with two contiguous stereogenic centers [63]. When such a powerful synthetic strategy is used to the alternating copolymerization of CO_2 with *meso*-epoxides, optically active polycarbonates with main-chain chirality can be produced from optically inactive *meso*-monomers (Scheme 17). Because the ring opening of a *meso*-epoxide proceeds with inversion at one of the two chiral centers, a successful asymmetric ring opening by a chiral catalyst will produce optically active polycarbonates with an (*R,R*)- or (*S,S*)-*trans*-1,2-diol unit. The first attempt of asymmetric copolymerization of CO_2 with *meso*-epoxides was disclosed by Nozaki et al. using a 1:1 Et_2Zn/(*S*)-α,α-diphenyl(pyrrolidin-2-yl)methanol mixture as catalyst, producing the corresponding polycarbonates with moderate enantioselectivity [64]. Further mechanistic studies suggested that a dimeric zinc

complex might be the active species [65]. Soon thereafter, the Coates research group reported the use of chiral hybrid imineoxazoline zinc-based catalysts for this reaction, which showed similar enantioselectivity but higher activity and controlled molecular weight [66]. Notably, they first noted the existence of the melting temperature of the resultant isotactic-enriched poly(cyclohexene carbonate), though the authors did not provide the DSC thermogram of the sample. Based on the mechanistic understanding that dimeric zinc complex was involved in the transition state of epoxide ring-opening event during CO_2/cyclohexene oxide copolymerization, Ding and coworkers described a chiral dinuclear metal catalyst **18** [67], coordinated with Trost's multidentate ligand, which exhibited moderate activity and very low enantioselectivity (8–18% *ee*) for this copolymerization. Interestingly, in a recent contribution, Wang et al. discovered that a dinuclear zinc complex of chiral ligand **19** with more rigid azetidine 4-membered ring compared with pyrrolidine cycle was efficient in catalyzing CO_2/cyclohexene oxide copolymerization at mild conditions, affording completely alternating polycarbonates in up to 93.8% *ee* [68]. It was suggested that the intramolecular dinuclear zinc structure of the catalytically active species containing azetidine ring was more rigid than pyrrolidine, which was responsible for the great improvement of the enantioselectivity. Almost simultaneously, Coates group optimized their enantioselective zinc β-diiminate (BDI) catalyst for CO_2/cyclohexene oxide copolymerization [69]. Iterative catalyst optimization yielded catalysts **20a–20c**, which show TOFs up to 190 h^{-1} at 22°C and produce polymers with repeat units of >90% *ee*. The maximum *ee* at 22°C was 92% *ee* using catalyst **20c**, and polymer with repeat units of 94% *ee* and a PDI of 1.3 was obtained using **20c** at 0°C. The presence of a bulky enantiopure ether substituent improves both the enantioselectivity and activity. Recently, Du and Abbina described the use of chiral zinc complex **21** with C_1-symmetric amido-oxazolinate ligands as catalyst for CO_2/cyclohexene oxide copolymerization [70]. Unfortunately, the asymmetric induction is generally low, with up to 71% *SS* unit in the main chain of the produced poly(cyclohexene carbonate)s. Prior to this study, optically active dinuclear aluminum complexes of β-ketoiminate or aminoalkoxide **22** [71], in conjunction with a bulky Lewis base as catalyst activator, were applied to the copolymerization of CO_2 with *meso*-epoxides, affording the corresponding polycarbonates with a moderate enantioselectivity (60–80% *ee*).



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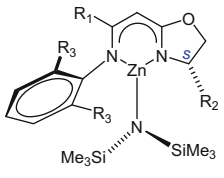
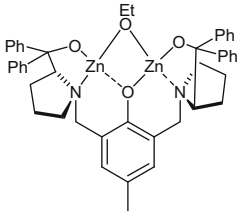


17

R_1 = Me, CF_3, ^{i}Pr
R_2 = (*R*)-Ph, (*S*)-^{i}Pr, (*S*)-^{t}Bu
R_3 = Et, ^{i}Pr



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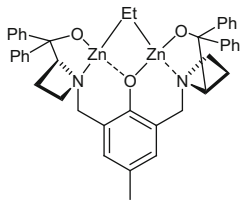

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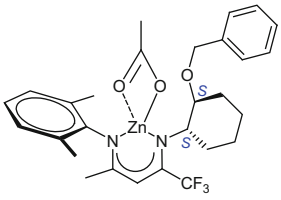
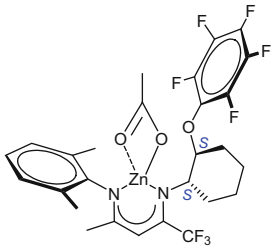
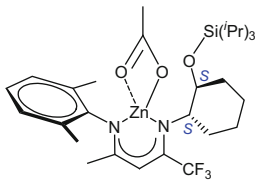


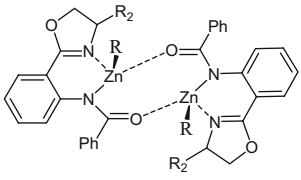
20a



20b



20c



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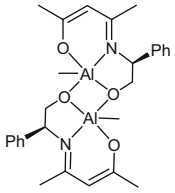

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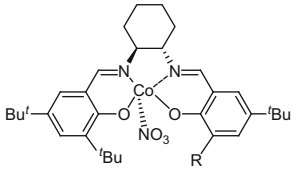


23 (*1S,2S*)-**23a**: R= CMe_2Ph
(*1S,2S*)-**23b**: R= $SiMe_2{}^tBu$
(*1S,2S*)-**23c**: R= adamyl

Stimulated by the success with chiral salenCo(III)-catalyzed asymmetric alternating copolymerization of *racemic* terminal epoxides and CO_2 [72], Lu and coworkers also applied these systems to the asymmetric copolymerization of cyclohexene oxide and CO_2 under mild conditions [73]. With binary catalyst system of enantiopure complex (*1R,2R*)-**3b** (trichloroacetate as the axial anion) and equimolar bis(triphenylphosphine)iminium chloride (PPNCl), copolymerization reaction at ambient temperature and 1.5 MPa CO_2 pressure provided isotactic-enriched poly(cyclohexene carbonate)s with a relatively low enantioselectivity of 38% *ee* for (*S,S*)-configuration. This catalyst is less selective, with an *ee* of 28%, but more active when the temperature and pressure are increased to 80°C and 2.5 MPa CO_2, respectively. The great progress came with the report from the same group. In 2012,

they reported a series of C_1-symmetric catalysts that are highly stereoselective for copolymerization of cyclohexene oxide with CO_2 [74]. Improved enantioselectivity is achieved by increasing the steric bulk of the ortho-substituent on one side of the ligand from a *tert*-butyl group to an adamantyl group. The highest selectivity (96% *ee*) is achieved by performing the polymerization with complex **23c** at −25°C in a 1:3 mixture of cyclohexene oxide and (*S*)-2-methyltetrahydrofuran as chiral induction agent. This resultant copolymer has a low M_n of 9.2 kDa and a PDI of 1.14. More importantly, they observed the isotacticity of poly(cyclohexene carbonate) has the critical influence on its crystallinity. It was found that the poly(cyclohexene carbonate)s with less than 80% isotacticity did not show any crystallization. A T_g of 122°C and a very small melting endothermic peak at 207°C with the melting enthalpy of (ΔHm) 3.92 J/g, indicating a very low degree of crystallinity, were observed in the sample (*R*)-PCHC-92 (*RR*:*SS* ratio in the polycarbonate is 92:8) (Fig. 1), while a sharp and high crystallization endothermic peak that appears at 216°C with ΔHm = 22.50 J/g was found in the highly isotactic polymer (*R*)-PCHC-98 (*RR*:*SS* = 98:2). Surprisingly, the crystallization endothermic peak of the (*R*)-PCHC-98/(*S*)-PCHC-98 (*RR*:*SS* = 2:98) blend (1/1 mass ratio) increased to 227°C with ΔHm = 29.70 J/g using the same crystallization conditions [75], indicating that the blend with two opposing configurations forms a stereocomplex with a new and distinct crystalline structure. Both WAXD (wide-angle X-ray diffraction) and AFM (atomic force microscopy) studies confirmed the formation of a stereocomplex from (*R*)-PCHC-98/(*S*)-PCHC-98 (*RR*:*SS* = 2:98) blend (1/1 mass ratio). For (*R*)-PCHC-98 sample, sharp diffraction peaks were observed at 2θ values of 12.2, 17.9, 19.0, and 20.4° (Fig. 2), while the blend of (*S*)-PCHC-98/(*R*)-PCHC-98 (1/1 mass ratio) has different diffraction peaks appearing at 2θ equal to 8.6, 17.9, and 21.5°, indicating that the stereocomplex possesses a new crystalline structure, being different from that of the sole configuration polymer. AFM observations also revealed the unique crystallization behavior. The lamellae or lamellar in (*S*)-PCHC-98 sample aggregates preferentially bend anticlockwise, while a clockwise-rotated spherulite can be clearly observed in (*R*)-PCHC-98 sample. Surprisingly, the morphological feature of the stereocomplex of (*S*)-PCHC-98/(*R*)-PCHC-98 (1/1mass ratio) changes dramatically and presents a lath-like dendritic crystal, which is very different from the bending features observed for its parent polymers (Fig. 3).

Although the binary catalyst system based on unsymmetrical chiral salenCo(III) complex **23c** exhibited the high enantioselectivity, the rigorous reaction conditions, such as a low temperature of −25°C and the use of a large amount of chiral induction agent, were prerequisites for obtaining optically active copolymer with low molecular weight in a very low rate (less than 3 h^{-1}). Additionally, this binary catalyst system was found to be inactive for the coupling of CO_2 with cyclopentene oxide (a less reactive epoxide). More recently, Lu and coworkers developed a chiral catalyst system based on enantiopure dinuclear Co(III) complexes **24** with a rigid bridging biphenyl linker, which exhibits excellent activity, unprecedented enantioselectivity, and molecular-weight control for the alternating copolymerization of CO_2 with *meso*-epoxides (both cyclopentene oxide and cyclohexene oxide) under

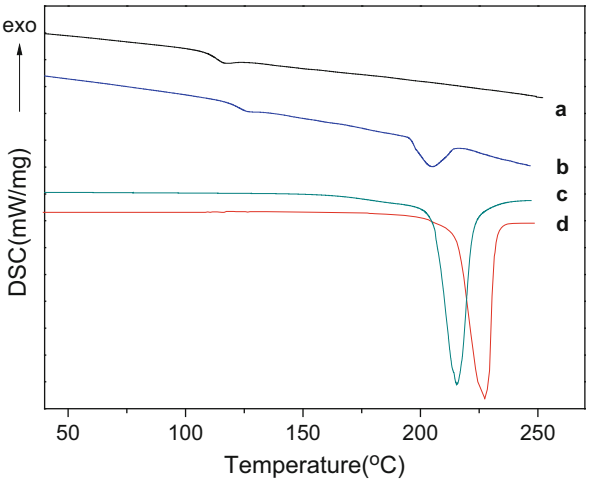


Fig. 1 DSC thermograms of various poly (cyclohexene carbonate)s. (**a**) Atactic PCHC; (**b**) (*R*)-PCHC-92; (**c**) (*R*)-PCHC-98; (**d**) (*R*)-PCHC-98/(*S*)-PCHC-98 blend, 1/1 mass ratio

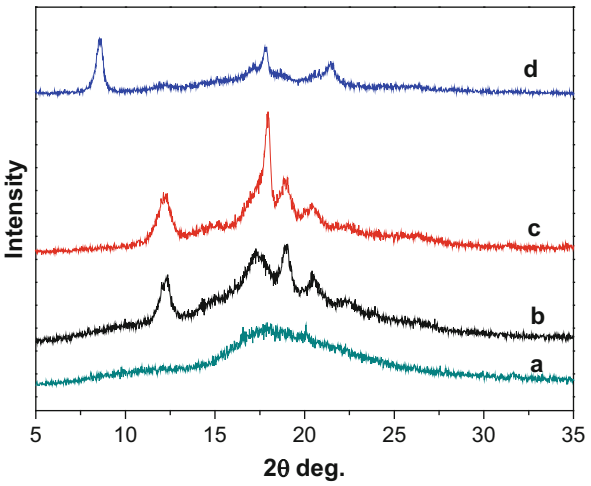


Fig. 2 WAXD profiles of various poly(cyclohexene carbonate) samples. (**a**) Atactic PCHC; (**b**) (*R*)-PCHC-92; (**c**) (*R*)-PCHC-98; (**d**) (*R*)-PCHC-98/(*S*)-PCHC-98 blend, 1/1 mass ratio

mild reaction conditions [76]. The combination of (*S*,*S*,*S*,*S*)-**24b** with a methyl group or (*S*,*S*,*S*,*S*)-**24c** without any substituents in the phenolate ortho-positions and a nucleophilic cocatalyst PPNX (X = 2,4-dinitrophenoxide) was found to be more efficient in catalyzing this asymmetric reaction, providing the copolymer with >99% carbonate linkages and an enantioselectivity of up to 99% for *S*,*S*-configuration. Notably, the biphenol-linked dinuclear Co(III) complex is a rare privileged chiral catalyst for copolymerizing CO_2 with various *meso*-epoxides, including the simplest *meso*-epoxide, *cis*-2,3-epoxybutane, showing both high reactivity and enantioselectivity for producing the corresponding polycarbonates with complete alternating structure and 99% *ee*. (Fig. 4) [77]. The TOFs are in the range of

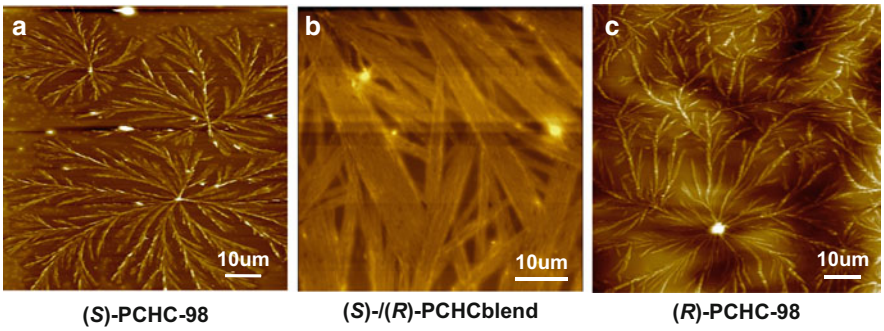


Fig. 3 AFM height images of (**a**) (*S*)-PCHC-98; (**b**) (*R*)-PCHC-98/(*S*)-PCHC-98 blend (1/1 mass ratio); (**c**) (*R*)-PCHC-98

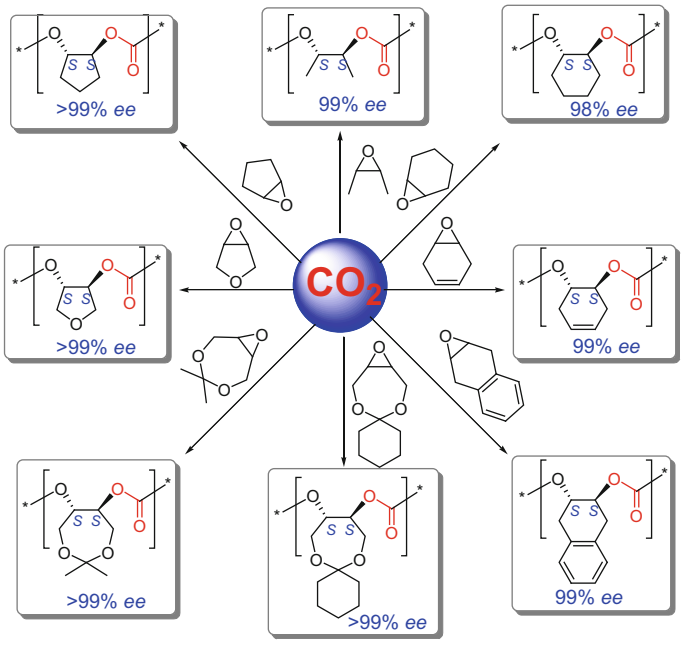
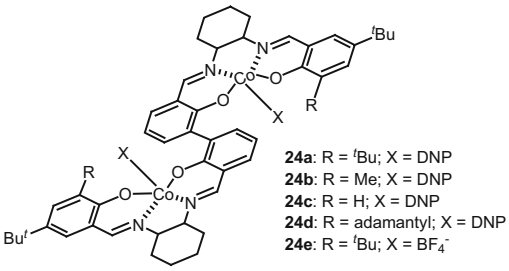


Fig. 4 Enantioselective copolymerization of CO_2 and various *meso*-epoxides mediated by dinuclear Co(III) complex (*S*,*S*,*S*,*S*)-**1b** or **1c** in combination with PPN-DNP (DNP = 2,4-dinitrophenoxide)

120–1,400 h^{-1}, dependant on the structure of *meso*-epoxides. Among them, six isotactic CO_2-based polycarbonates are crystalline, possessing T_ms of 179–257°C [78, 79].



24

DFT calculations suggested that in the two diastereoisomers, (*S*,*S*,*S*,*S*,*S*)-conformer is more effective in catalyzing CO_2/CPO copolymerization than the corresponding (*S*,*S*,*R*,*S*,*S*)-conformer (Fig. 5) [77]. The calculations also showed that the dinuclear Co(III) catalyst with a *S*,*S*,*S*,*S*,*S*-configuration predominantly resulted in the formation of polycarbonates with *S*,*S*-configuration (TS-1), which was in agreement with the experimental findings. Furthermore, on the basis of kinetic study and DFT calculations, the authors gave a comprehensive mechanism understanding on (*S*,*S*,*S*,*S*)-**24**-mediated enantioselective copolymerization of CO_2 and *meso*-epoxides. The biphenol-linked Co(III) complexes (*S*,*S*,*S*,*S*)-**24** are the mixture of two diastereoisomers with *R*- or *S*-biphenol stereochemistry, (*S*,*S*,*R*,*S*,*S*) and (*S*,*S*,*S*,*S*,*S*)-conformers, though they originate from an achiral biphenol linker. The matched configuration of (*S*,*S*,*S*,*S*,*S*) was more effective than (*S*,*S*,*R*,*S*,*S*) for enantioselectively catalyzing this asymmetric copolymerization. The initiation is triggered by one of the two nucleophilic anions of the bimetallic cobalt catalyst from the inside cleft, and chain-growth step predominantly involves an intramolecular bimetallic cooperation mechanism, wherein alternating chain growth and dissociation of propagating carboxylate species take turn between two Co(III) ions from the inside cleft of dinuclear Co(III) catalysts by the nucleophilic attack of the growing carboxylate species at one metal center toward the activated epoxide at the other (Scheme 18). Both the absolute stereochemistry of the biphenol linker and cyclohexyl diamine skeletons determine the enantiomer preference in the copolymerization. Another path for initiation and chain growth concerns a monometallic mechanism or intermolecular bimetallic mechanism that occurred in the outside cleft of the catalyst. This is similar with the mononuclear Co(III) catalyst **4a**, in which the cyclohexyl diamine skeleton determines the enantiomer preference, providing the copolymers with the opposite configuration. Since the former is predominantly responsible for the copolymer formation and the inside cleft is the more enantioselective site, it determines the product configuration and enantioselectivity.

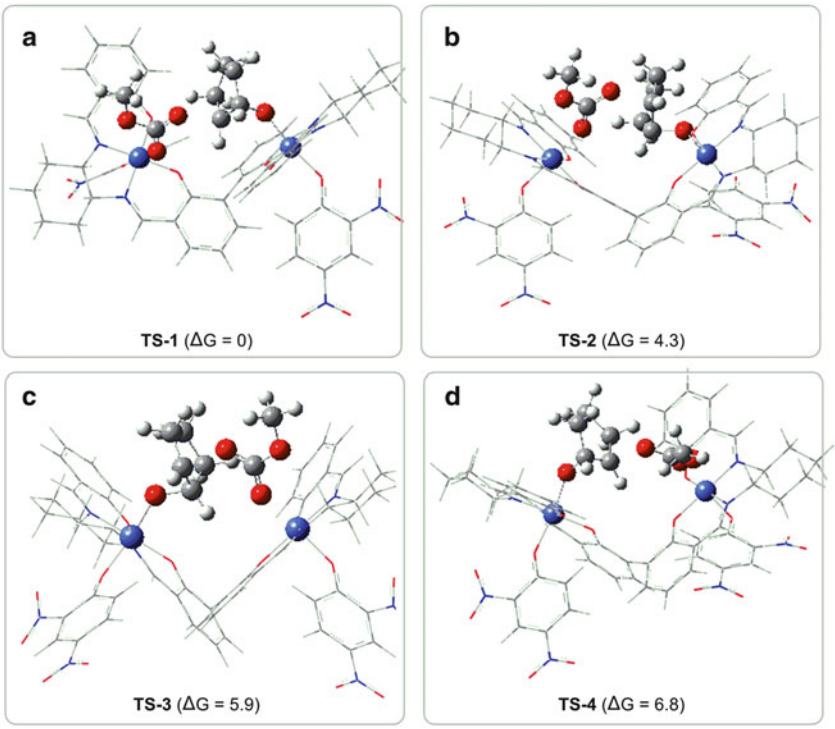
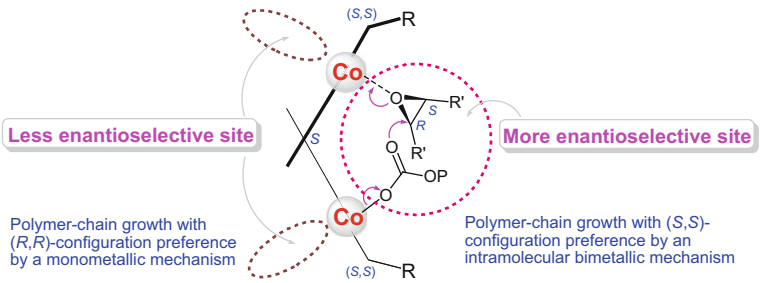


Fig. 5 Four possible transition states for the ring opening of a cyclopentene oxide (CPO) molecule by an adjacent cobalt bound carbonate group. (**a**) TS-1, ring opening at the (*R*)-C–O bond of CPO activated by (*S*,*S*,*S*,*S*,*S*)-**1f**; (**b**) TS-2, ring opening at the (*S*)-C–O bond of CPO activated by (*S*,*S*,*S*,*S*,*S*)-**1f**; (**c**) TS-3, ring opening at the (*R*)-C–O bond of CPO activated by (*S*,*S*,*R*, *S*,*S*)-**1f**; (**d**) TS-4, ring opening at the (*S*)-C–O bond of CPO activated by (*S*,*S*,*R*,*S*,*S*)-**1f**. The energy was given in kcal/mol and toluene was employed as a solvent



Scheme 18 Dinuclear Co(III) complex-mediated enantioselective polymer chain growth routes

6 Summary and Concluding Remarks

This review therefore aims to principally showcase the recent progress regarding CO_2-mediated formation of chiral fine chemicals. Although these mentioned reactions suffered from some problems, e.g., the k_{rel} values measured in the epoxide resolution with CO_2 are below what is generally considered useful, these investigations are important because they address the feasibility of using CO_2 as a C_1 source in asymmetric catalysis. To our delightsome, the discovery of the enantiopure dinuclear Co(III) catalysts for highly enantioselective copolymerization of CO_2 with various *meso*-epoxides to afford CO_2-based polycarbonates with more than 99% enantioselectivity makes this stereoselective catalysis become truly competitive. Potential applications for these isotactic semicrystalline polymers are expectant. It is hoped that further catalyst development will lead to high k_{rel} values for epoxide resolution with CO_2, deserving of significant commercial application. Clearly, it is highly desired to develop new enantioselective catalysis focusing on amplification of the organic structures one can derive from CO_2 as a molecular synthon.

Computational chemistry has contributed to our understanding of the mechanistic aspects of some organic reactions. It is anticipated that this approach will play an increasingly important role in understanding the features that account for the CO_2-mediated formation of chiral fine chemicals and thus aid in developing new privileged catalysts.

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