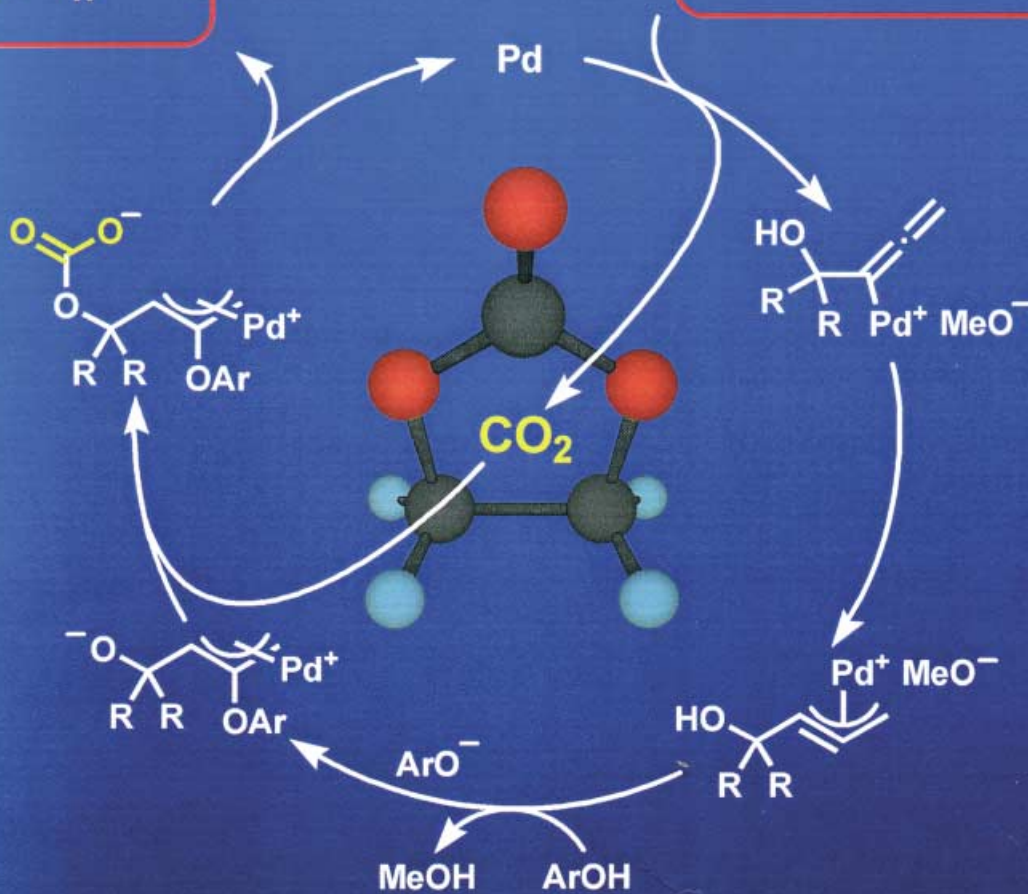
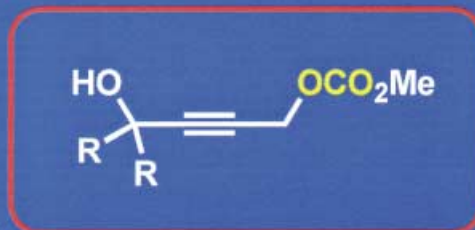
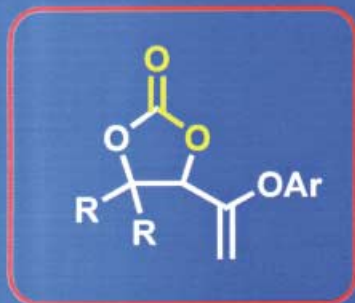


# Synthesis of Cyclic Carbonates



## Recycling of CO<sub>2</sub>

## Novel Methodologies for the Synthesis of Cyclic Carbonates

Masahiro Yoshida\* and Masataka Ihara\*[a]

**Abstract:** Cyclic carbonates are valuable compounds that have applications in a variety of chemical fields. Methodologies for the synthesis of cyclic carbonates are well investigated in recent years, and the most successful and popular procedure is the utilization of CO<sub>2</sub>. This paper presents recent progress in the synthesis of cyclic carbonates by a CO<sub>2</sub>-fixation process, which involves novel palladium-catalyzed CO<sub>2</sub>-recycling reactions.

**Keywords:** carbon dioxide fixation • cyclization • domino reactions • oxygen heterocycles • palladium

### Introduction

Cyclic carbonates are attractive and important compounds in a variety of chemical research fields. Because of their high solubility, high boiling and flash points, low odor levels and evaporation rates, low toxicities, and biodegradability, cyclic carbonates are utilized as aprotic polar solvents in degreasing, paint stripping, and cleaning.<sup>[1]</sup> Biologically active molecules that contain a cyclic carbonate component have also been isolated from various kinds of natural sources.<sup>[2]</sup> In addition, cyclic carbonates are regarded as useful and important intermediates in organic synthesis, which can be used for the protection of 1,2- and 1,3-diols<sup>[3]</sup> and the construction of structurally complex molecules.<sup>[1,4]</sup>

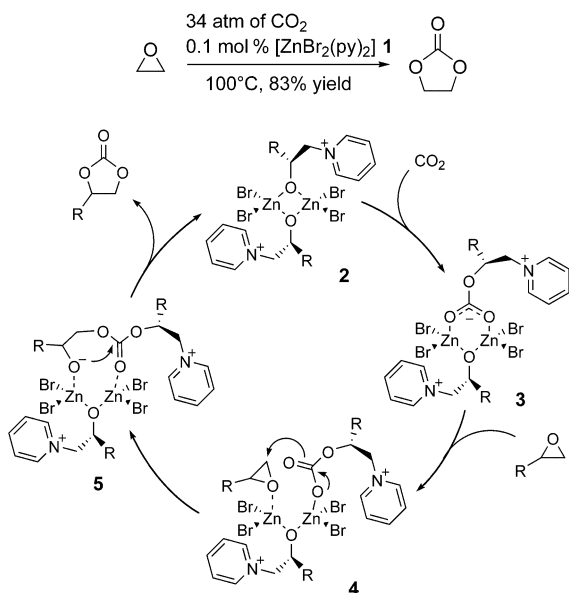
In accordance with an increase of the importance for cyclic carbonates, synthetic studies for the formation of cyclic carbonates have been thoroughly investigated.<sup>[5]</sup> One of the most successful and popular procedures for the preparation of cyclic carbonates is the utilization of CO<sub>2</sub>.<sup>[6]</sup> The chemistry of CO<sub>2</sub> has recently received much attention be-

cause of its potential use as an abundant carbon source and its indirect role as an environmental pollutant. The transformation of CO<sub>2</sub> into organic substances represents an attractive area of study in both organic and green chemistry.<sup>[7]</sup> Cyclic carbonates can be normally synthesized by the reaction of CO<sub>2</sub> with oxiranes in the presence of various activating reagents. Although the methodology was developed about fifty years ago,<sup>[8]</sup> it normally needs high pressure of CO<sub>2</sub>, high reaction temperature, and a stoichiometric amount of activating reagents. However, recent advances in chemistry have solved these problems to evolve to mild, convenient, and eco-friendly reactions. Furthermore, a new strategy for the cyclic carbonates that re-uses the CO<sub>2</sub> generated from the substrates has been discovered. Herein, we describe recent progress in the synthesis of cyclic carbonates, which includes a CO<sub>2</sub>-fixation process.

### Discussion

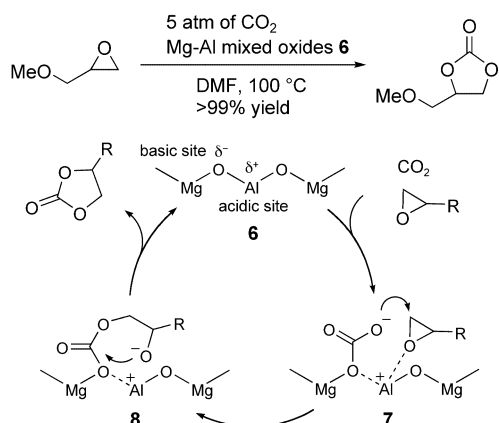
**Synthesis of cyclic carbonates by use of an external CO<sub>2</sub> source:** It is known that acid–base mixed catalysts that contain metal complexes effectively activate the CO<sub>2</sub> and epoxides to afford cyclic carbonates.<sup>[9]</sup> Recently, Kim and co-workers reported the reaction catalyzed by zinc–pyridine complex [ZnBr<sub>2</sub>(py)<sub>2</sub>] (**1**), including a detailed study on the reaction mechanism (Scheme 1).<sup>[10]</sup> The complex **1** catalyzes the reaction of ethylene oxide with CO<sub>2</sub> to give ethylene carbonate in good yield with high efficiency. An active intermediate **2** was first isolated from the stoichiometric reaction of **1** with epoxide, and NMR studies with **2** revealed a reasonable mechanism as follows. Coordination of epoxide to **1** followed by nucleophilic attack of pyridine leads to the formation of dimer **2** at first. The insertion of CO<sub>2</sub> into **2** would give the carbonate-bridged intermediate **3**, and the coordination of an additional epoxide causes nucleophilic attack of the carbonate followed by cyclization (**4** to **5**) to afford a cyclic carbonate and a re-generated complex **2**. In this reaction, zinc bromide activates an epoxide ring as a Lewis acid, and the pyridine group in complex **1** acts as both nucleophile and ligand. Complex **2** exhibits similar reactivity as **1** in catalyzing the reaction, which supports this reaction mechanism.

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Scheme 1. Synthesis of cyclic carbonates by  $[\text{ZnBr}_2(\text{py})_2]$ .

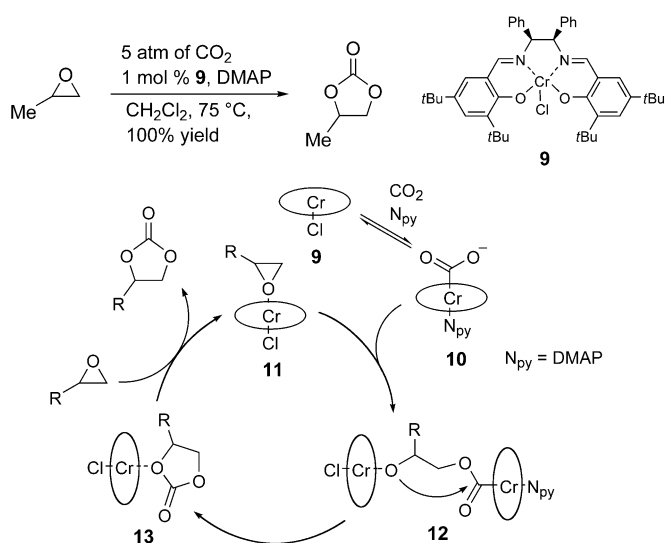
Kaneda reported a reaction with Mg–Al mixed oxides **6** as highly active acid–base catalysts (Scheme 2).<sup>[11]</sup> The catalysts **6**, which are obtained by calcination of hydrotalcites, effectively catalyze the fixation of  $\text{CO}_2$  to various epoxides to produce the corresponding cyclic carbonates. The cata-



Scheme 2. Mg–Al mixed-oxide-catalyzed reaction of epoxides with  $\text{CO}_2$ .

lysts are highly active and re-usable, and the reaction proceeds stereospecifically with retention of the configuration of epoxides. The structure of **6** is proposed to have Mg–O–Al bonds, which would bring about the formation of acidic and basic sites on the surface of mixed oxides. The reaction mechanism is considered as follows. The activation of  $\text{CO}_2$  and an epoxide is triggered by the Lewis basic oxygen sites and Lewis acidic aluminum sites to form a carbonate and coordinated epoxide species **7**. The activated epoxide in **7** causes nucleophilic attack of the carbonate species followed by cyclization of the resulting compound **8** to yield a cyclic carbonate. The reactivity of physical mixture of MgO and  $\text{Al}_2\text{O}_3$  is much less than that of catalysts **6**; this implies that the formation of the Mg–O–Al bond is important to create acid–base sites.

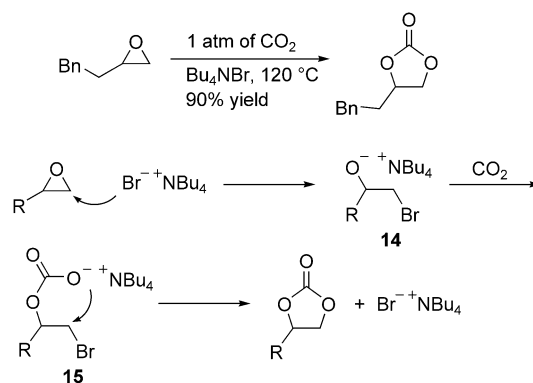
As another acid–base-catalyzed reaction, Nguyen has found that the combination of the Cr–salen complex **9** with DMAP (DMAP = 4-dimethylaminopyridine) is also effective catalyst for the synthesis of cyclic carbonates (Scheme 3).<sup>[12]</sup> The catalyst system can operate efficiently at low  $\text{CO}_2$  pres-



Scheme 3. Cr–salen catalyzed reaction of epoxides with  $\text{CO}_2$ .

sure and temperature, and the turnover number and frequency ( $\text{h}^{-1}$ ) are recorded over 900. The complex **9** or DMAP itself does not catalyze the reaction at all, indicating the parallel requirement of both Lewis acid activation of the epoxide and Lewis base activation of the  $\text{CO}_2$ . As the reaction mechanism, it is proposed that the Cr–salen complex **9** reacts with  $\text{CO}_2$  and DMAP to give the chromium carbonate **10**. Complex **10** would then attack the chromium–epoxide complex **11**, in which epoxide is activated by another molecule of **9**, followed by cyclization (**12** to **13**) to afford the cyclic carbonates.

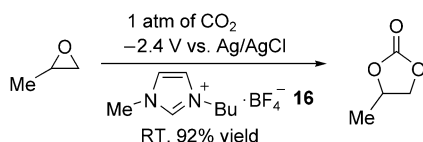
It has been recently reported by Caló that tetraalkylammonium halide is a useful reagent to synthesize cyclic carbonates (Scheme 4).<sup>[13]</sup> Various epoxides react with  $\text{CO}_2$  at an atmospheric pressure in molten tetrabutylammonium bromide to form the corresponding cyclic carbonates in high



Scheme 4. Synthesis of cyclic carbonates in tetraalkylammonium halides.

yields. The reaction product can be simply separated by distillation or extraction, which allows the recycling of the ammonium halide. A plausible mechanism is the ring opening of the epoxide by nucleophilic attack of bromide ion yielding an oxy anion species **14**. The corresponding cyclic carbonate is produced after the fixation of CO<sub>2</sub> by **14** and subsequent cyclization of the resulting compound **15**.

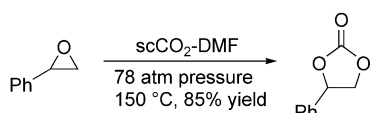
Ionic liquids are recognized as environmentally benign media for organic synthesis, and various reactions in ionic liquids have been investigated. Deng reported a synthesis of cyclic carbonates by electrochemical CO<sub>2</sub> activation in ionic liquid **16** (Scheme 5).<sup>[14]</sup> The reactive species is proposed to



Scheme 5. Fixation of CO<sub>2</sub> in electrochemical conditions.

be an anion radical of CO<sub>2</sub>, resulting from the one-electron reduction of CO<sub>2</sub>; this should react with an epoxide to afford the product. This electrochemical method can be performed by gentle bubbling of CO<sub>2</sub> at room temperature without any additional supporting electrolyte and catalyst.

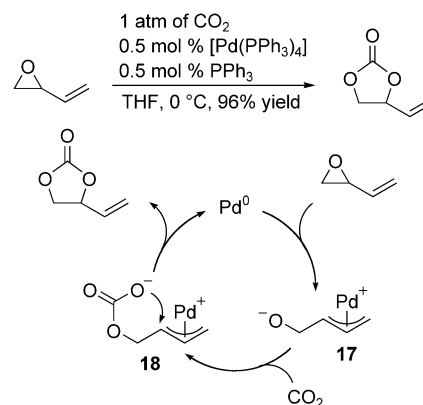
Supercritical CO<sub>2</sub> (scCO<sub>2</sub>) is considered as an economically feasible and ecologically benign reaction medium for organic reactions; it has several advantages such as no flammability, lack of toxicity, absence of a gas-liquid phase boundary, and possible simplifications in workup. Kawanami and Ikushima have reported that fixation of CO<sub>2</sub> in supercritical conditions effectively proceeds to give cyclic carbonates (Scheme 6).<sup>[15]</sup> Styrene oxide is successfully trans-



Scheme 6. Synthesis of cyclic carbonates by supercritical CO<sub>2</sub>.

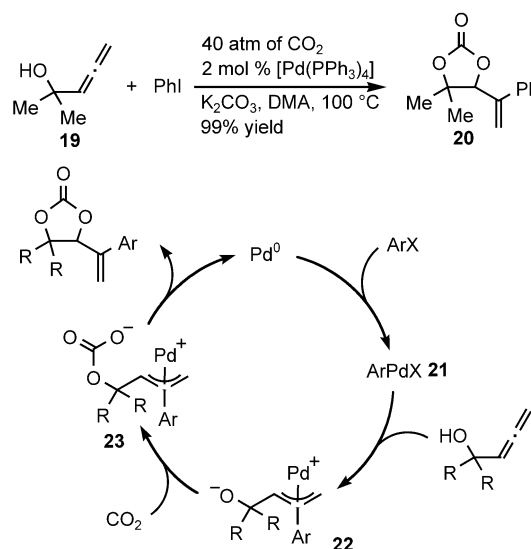
formed to the corresponding cyclic carbonate in scCO<sub>2</sub> with DMF in good yield. DMF is necessary for carrying out the reaction; this indicates that DMF itself catalyzes the fixation of CO<sub>2</sub> to epoxides. Furthermore, it has been recently found that the reaction in biphasic system of scCO<sub>2</sub> and ionic liquid dramatically increases the reactivity.<sup>[16]</sup> Various cyclic carbonates are obtained in high yields, and the reaction completes within five minutes.

Palladium-catalyzed fixation of CO<sub>2</sub> is also a useful method for the synthesis of cyclic carbonates. The first example using palladium catalyst was reported independently by Fujinami and Trost; namely vinyl-substituted epoxides react with an atmosphere of CO<sub>2</sub> at low temperature in the presence of a palladium catalyst (Scheme 7).<sup>[17]</sup> The intermediate of the reaction has been proposed as the  $\pi$ -allylpalladium intermediate **17**, which fixes CO<sub>2</sub> to give vinyl-substituted cyclic carbonates via **18**.



Scheme 7. Palladium-catalyzed reaction of vinyl epoxides with CO<sub>2</sub>.

Recently, Inoue and co-workers have reported that a palladium-catalyzed CO<sub>2</sub>-fixation reaction of allenic alcohols **19** with aryl halides affords aryl-substituted cyclic carbonates **20** (Scheme 8).<sup>[18]</sup> It has been proposed as the reaction mechanism that a  $\pi$ -allylpalladium intermediate **22** is initial-



Scheme 8. Palladium-catalyzed reaction of allenic with CO<sub>2</sub>.

ly formed by the insertion of an allene moiety into the arylpalladium species **21**. The complex **22** would be subjected to the fixation of CO<sub>2</sub> followed by cyclization of the resulting **23** to produce the cyclic carbonate. Remarkably, cyclic carbonates containing a six-membered ring, which are difficult to synthesize in comparison with the five-membered carbonates, can also be synthesized by use of this methodology. The authors also report that the similar reaction proceeds when the 1,3-dienylalcohol is subjected to the reaction.<sup>[18]</sup>

#### Synthesis of cyclic carbonates by use of internal CO<sub>2</sub> source:

As described above, all of the CO<sub>2</sub>-fixation reactions to produce cyclic carbonates have utilized an external CO<sub>2</sub> source by carrying out the reactions under high or atmospheric

pressure of CO<sub>2</sub>. However, an excess amount of CO<sub>2</sub> is required in any case; this is less efficient from a viewpoint of atom economy. As an alternative CO<sub>2</sub> source, it is expected that one could utilize CO<sub>2</sub> generated from decarboxylation reaction. Decarboxylation is a well-known reaction in which organic molecules reduce CO<sub>2</sub> by activation with heat, light and catalysts. Numerous reactions to cause decarboxylation are known, but no examples exist in which the eliminated CO<sub>2</sub> is incorporated into the product molecule. We have recently devised a new reaction, termed “recycling of CO<sub>2</sub>” (Figure 1). In this concept, a substrate bearing a CO<sub>2</sub> com-

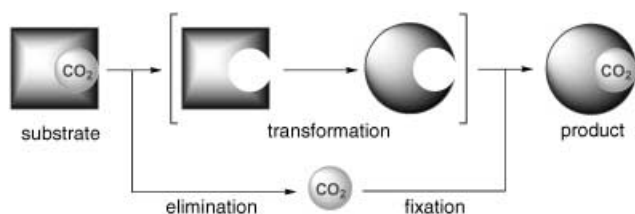
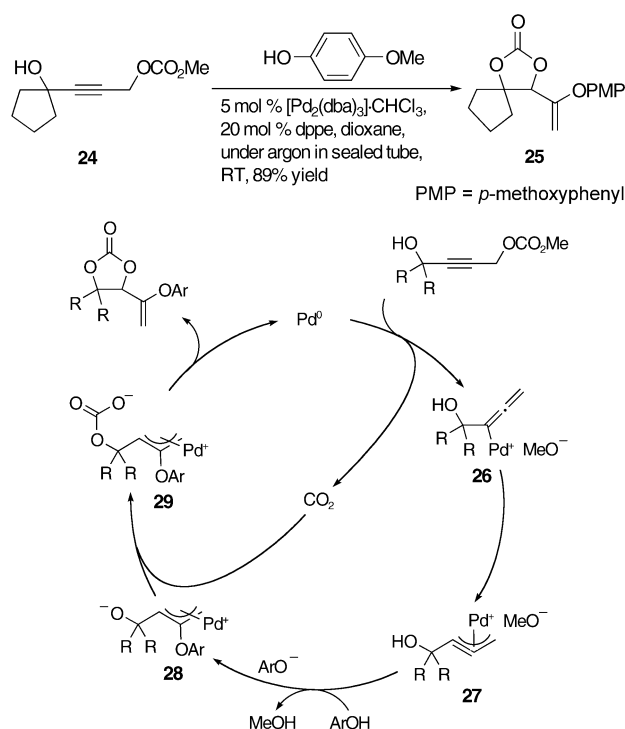


Figure 1. Concept of “recycling of CO<sub>2</sub>”.

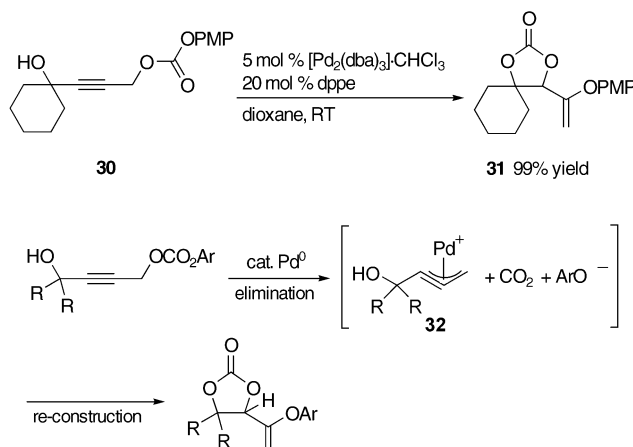
ponent initially undergoes catalyst-promoted decarboxylation to give an intermediate and CO<sub>2</sub>. Reaction of the intermediate with CO<sub>2</sub> affords a product incorporating CO<sub>2</sub>. This concept has been used to develop a new CO<sub>2</sub>-recycling process as part of a novel methodology for the synthesis of cyclic carbonates.

It is known that propargylic carbonates undergo decarboxylation with a palladium catalyst to generate allenyl/ $\pi$ -propargylpalladium complexes, which react with nucleophiles to give substitution products. On the basis of this catalytic process, we have discovered a palladium-catalyzed CO<sub>2</sub>-elimination/fixation reaction of propargylic carbonates with phenols (Scheme 9).<sup>[19,20]</sup> The reaction of 4-methoxycarbonyloxy-2-butyne-1-ol (**24**) with phenols in the presence of a palladium catalyst under an atmosphere of argon in a closed tube produces a phenoxy-substituted cyclic carbonate **25**. A plausible mechanism for the formation of cyclic carbonate is considered as follows. The palladium catalyst initially promotes decarboxylation of the substrate to generate CO<sub>2</sub> and the allenylpalladium **26**, which can be regarded as a  $\pi$ -propargylpalladium species **27**. The complex **27** undergoes nucleophilic attack by phenoxide to produce the  $\pi$ -allylpalladium intermediate **28**, which fixes CO<sub>2</sub> to afford the carbonate **29**. Subsequent cyclization of **29** gives the phenoxy-substituted cyclic carbonate. The reaction under an atmosphere of CO<sub>2</sub> increases the yield of the products, and the reaction under bubbling argon gas decreases the yield. From these results, it has been supported that the process proceeds through a pathway involving decarboxylation followed by fixation of the liberated CO<sub>2</sub>.

The methodology can be successfully applied to three-component decomposition/re-construction reactions (Scheme 10).<sup>[19,20]</sup> The substrate **30**, which contains latent nucleophilic phenolic moieties as part of the carbonate leaving groups, transforms to the corresponding cyclic carbonate **31** in the presence of a palladium catalyst. In this reaction, the



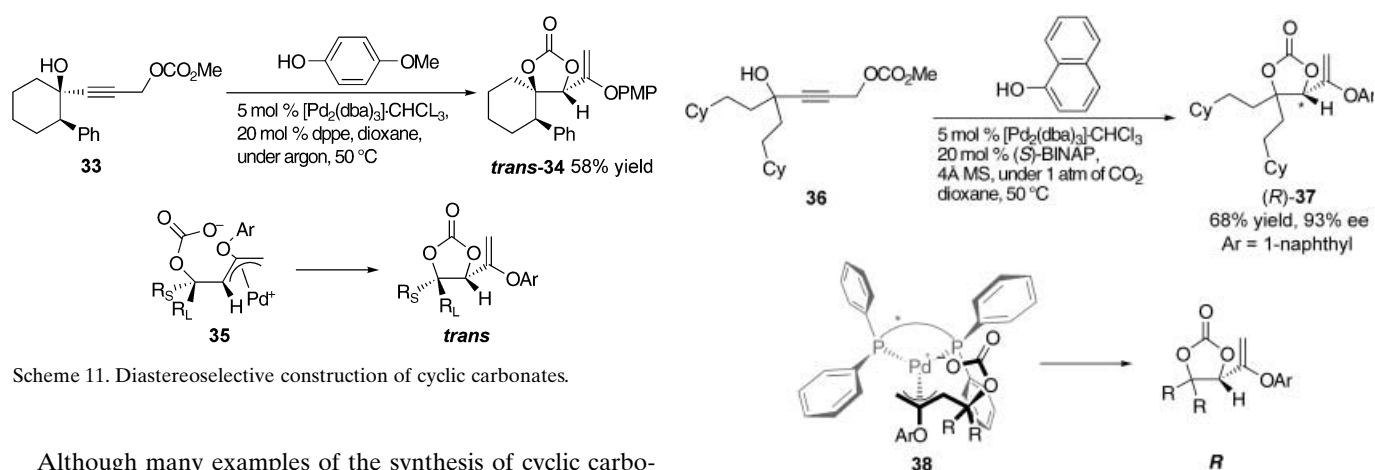
Scheme 9. Palladium-catalyzed reaction of propargylic carbonates with phenols by a CO<sub>2</sub>-elimination/fixation process.



Scheme 10. Three-component elimination/re-construction reaction of propargylic carbonate aryl esters.

substrate decomposes to yield three components,  $\pi$ -propargylpalladium **32**, phenoxide, and CO<sub>2</sub>, which then recombine to form cyclic carbonate. Crossover experiments using two kinds of substrates that have different substituent pattern reveals that the phenoxide ion completely dissociates from the propargylic moiety.

We have also found a diastereoselective version using nonsymmetrical propargylic carbonates. (Scheme 11).<sup>[20]</sup> The palladium-catalyzed reaction of the substrate **33** with *p*-methoxyphenol diastereoselectively produces the cyclic carbonate *trans*-**34**. It is expected that the transition state in the cyclization step would be the conformationally more stable  $\pi$ -allyl intermediate **35**, leading to the *trans* product.



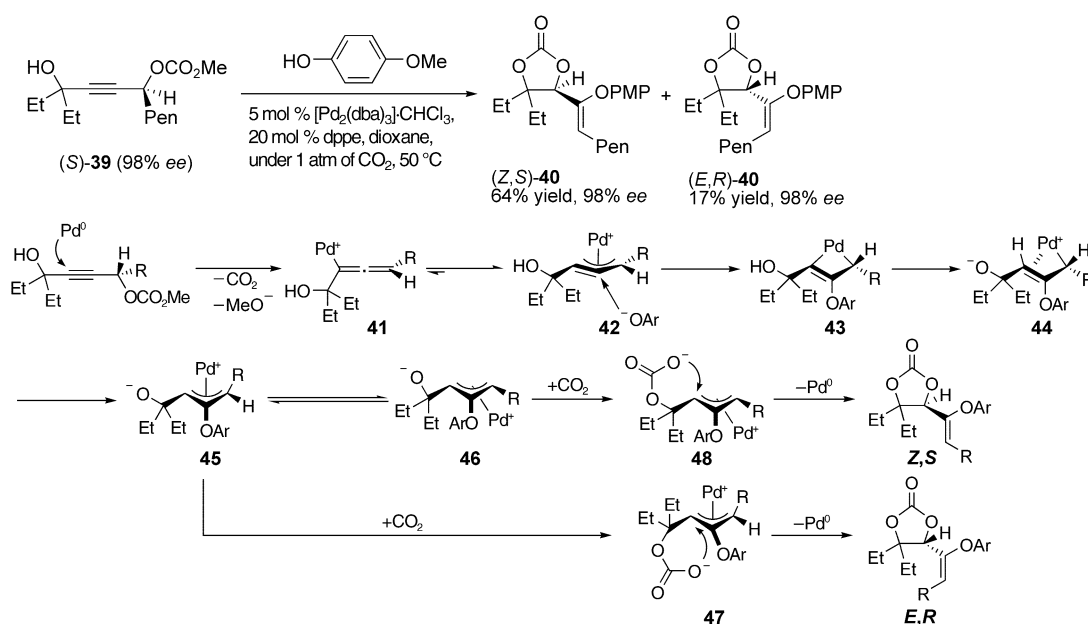
Scheme 11. Diastereoselective construction of cyclic carbonates.

Although many examples of the synthesis of cyclic carbonates have been reported, only a few examples about the application to asymmetric reaction are known.<sup>[21]</sup> We have succeeded in the enantioselective synthesis of cyclic carbonates by using chiral palladium catalysts (Scheme 12).<sup>[20]</sup> High enantioselectivities have been achieved to give chiral product (*R*)-**37** from the reaction of the substrate **36** and 1-naphthol in the presence of a palladium/(*S*)-BINAP catalyst. The presence of bulky substituents at the  $\beta$ -position of the alkyl side chain increases the enantioselectivities, and the chemical yields are increased by carrying out the reactions under an atmosphere of CO<sub>2</sub>. Absolute stereochemistry in this process would be determined in the step involving cyclization of the  $\pi$ -allylintermediate, in which the reaction takes place via the most stable transition state **38** to provide the *R* product.

We have also discovered that the reaction of chiral propargylic carbonates with phenols proceeds in a highly enantiospecific manner to give chiral cyclic carbonates by an overall cascade chirality-transfer process (Scheme 13).<sup>[22]</sup> The alkyl-substituted chiral propargylic carbonate (*S*)-**39** with 98% *ee* reacts with *p*-methoxyphenol in the presence

Scheme 12. Enantioselective reactions of propargylic carbonates with phenols catalyzed by a Pd/BINAP complex.

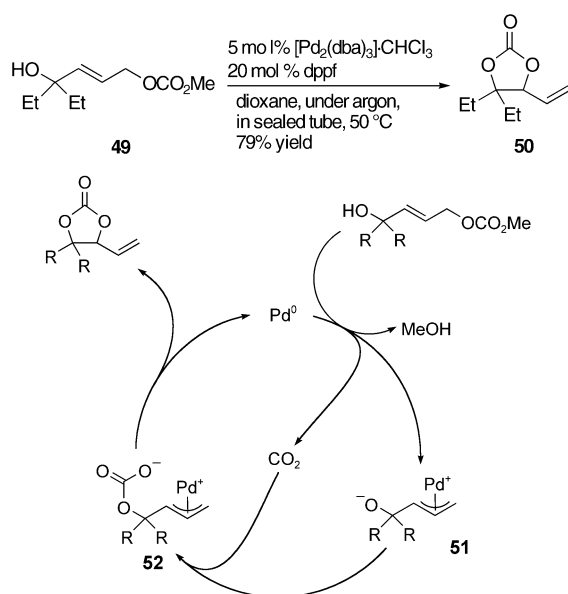
of a palladium/dppe catalyst to produce chiral cyclic carbonates (*Z,S*)- and (*E,R*)-**40** in 64% and 17% yield, respectively. The (*E*)- and (*Z*)-selectivity of the products can be controlled by choice of the phosphine ligand. It is worth noting that the optical purities of both products are 98% *ee*. A plausible mechanism for this process is shown as follows. Regio- and stereoselective anti S<sub>N</sub>2' attack of a palladium catalyst on propargylic carbonate takes place to yield the chiral  $\pi$ -propargylpalladium complex **42** via **41**, which is followed by selective addition of phenol to the central carbon of  $\pi$ -propargyl moiety to form the chiral palladacyclobutene **43**. The complex is immediately converted to the allylpalladium complex **44** by intramolecular proton transfer without loss of the chirality, and then delocalized to afford  $\pi$ -allylpalladium complexes **45** and **46**. Finally, CO<sub>2</sub> fixation followed by cyclization from these complexes via **47** and **48** produces the *E,R* and *Z,S* cyclic carbonates, respectively.



Scheme 13. Enantiospecific reaction of substituted propargylic carbonates with phenols: cascade chirality transfer.

The reaction also needs an external CO<sub>2</sub> source to give the products in high yields. This cascade chirality-transfer process can provide not only a useful synthetic method for chiral cyclic carbonates, but also important knowledge of the stereochemistry of the metal-catalyzed reactions of propargylic compounds.

Palladium-catalyzed allylic substitutions of allylic carbonates are extensively investigated reactions that invariably produce CO<sub>2</sub> as a co-product.<sup>[23]</sup> We have further developed a synthetic method for cyclic carbonates by a palladium-catalyzed reaction of allylic carbonates (Scheme 14).<sup>[24]</sup> A cyclic



Scheme 14. Palladium-catalyzed reaction of allylic carbonates including a CO<sub>2</sub>-recycling process.

carbonate **50** with a vinyl group is produced by the reaction of *trans*-4-methoxycarbonyloxy-2-buten-1-ol (**49**) in the presence of a palladium catalyst. A plausible mechanism is that a palladium catalyst initially promotes decarboxylation of allylic carbonate to generate the π-allylpalladium intermediate **51**, MeOH, and CO<sub>2</sub>. Fixation of CO<sub>2</sub> by the resulting hydroxy anion leads to the carbonate **52**, and subsequent cyclization gives a cyclic carbonate. A variety of allylic carbonates participate in the reaction giving the corresponding products in high efficiencies. Stereoselective construction of *trans*-cyclic carbonates is achieved by using nonsymmetric substrates, and an enantiospecific reaction also proceeds to afford the chiral cyclic carbonate when a chiral substrate containing a stereogenic center at allylic position is subjected to the reaction.

### Conclusion

We have summarized recent progress in the synthesis of cyclic carbonates by means of a CO<sub>2</sub> fixation process. Acid–base catalysts such as [ZnBr<sub>2</sub>(py)<sub>2</sub>], Mg–Al mixed oxides, and the Cr–salen/DMAP catalyst system exhibit high activi-

ties in the promotion of the reaction of CO<sub>2</sub> with epoxide in high efficiency. Use of tetraalkylammonium halides or ionic liquids in electrochemical means enables the reaction to be carried out under mild conditions. The synthesis of cyclic carbonates in scCO<sub>2</sub> conditions can be performed without any additional catalysts. The palladium-catalyzed reaction of unsaturated alcohols and aryl halides with CO<sub>2</sub> can lead to a variety of cyclic carbonates in addition to the formation of new carbon–carbon bond. Furthermore, we have discovered a novel synthetic method for the preparation of cyclic carbonates by palladium-catalyzed reaction of propargylic carbonates with phenols. The reaction proceeds through a CO<sub>2</sub>-elimination/fixation process, to afford various phenoxy-substituted cyclic carbonates. The reaction has been successfully applied to a three-component decomposition/re-construction reaction, and to diastereoselective, enantioselective, and enantiospecific reactions. Allylic carbonates also transform to the cyclic carbonates in the presence of palladium catalyst by means of a CO<sub>2</sub>-recycling process. We believe that these methodologies contribute not only the advances of organic and applied chemistry, but also green chemistry in the future.

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