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Activation of (salen)Col complex by phosphorane for carbon dioxide transformation at ambient temperature and pressure

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We report the activation of (salen)Col complex **3g** by a phosphorane to form a bifunctional catalyst for the reaction of carbon dioxide with terminal epoxides or aziridines at ambient temperature and 1 bar carbon dioxide pressure. Only 1.0 mol% of both (salen)Col **3g** and phosphorane **4d** are required for cyclic carbonate synthesis, and the catalyst loading could even be lowered down to 0.1 mol%. Under this condition, no polycarbonate formation is detected by NMR analysis. It is proposed that the high efficiency originates from the activation of (salen)Col by a phosphorane to form a phosphorane-salen Co(III) complex with enhanced Lewis acidity for the electrophilic activation, whilst generating an iodide anion as a Lewis base co-catalyst to facilitate the ring-opening of epoxides. Further investigation revealed that the phosphorane-(salen)Col complex could also catalyze the coupling of CO₂ with aziridines successfully under ambient conditions at a 2.5 mol% of catalyst loading.

Introduction

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The development of efficient catalytic protocols that use carbon dioxide (CO₂) as an inexpensive, nontoxic and renewable C1 feedstock for the synthesis of value-added products is of current research interest, since it provides an attractive complement to carbon capture and storage.¹ Among the known more than 20 reactions using CO₂ as starting material, the coupling reaction of epoxides and CO_2 has attracted considerable attention,² as it can be controlled to give either cyclic carbonates³ or polycarbonates⁴; both products have a range of applications.⁵ In particular, the cyclic carbonate production has been commercialized for over 50 years, because cyclic carbonates can be used as electrolytes for lithium ion batteries, polar aprotic solvents, synthons for the synthesis of value-added chemicals and monomers for polymer synthesis. However, although the synthesis of cyclic carbonates from epoxides with CO₂ is a highly exothermic reaction, all the current commercialized processes are net CO₂ emitter rather than consumer, because these commercial processes require high reaction temperatures and pressures, along with the use of highly purified CO₂.⁶ Therefore, it is important and urgent to develop efficient catalysts for the synthesis of cyclic carbonates from epoxides and CO2 under mild conditions.





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Taking advantage of such a cooperation, notable protocols are capable of performing the reaction at ambient conditions with only 2.0-2.5 mol% of both metal complex and the nucleophilic co-catalyst.⁷ However, further lowering down the catalyst loading was not successful to date in terms of epoxides conversion and substrate scope. Therefore, the development of new catalyst systems is very much in demand.

Results and discussion

Recently, we found that Jacobsen's privileged catalyst, (salen)AlCl **3a**,¹⁰ can be effectively activated by phosphorane **4a** to produce an enhanced Lewis acid for catalytic enantioselective ketone cyanosilylation.¹¹ Both electrical conductivity experiments and density functional theory calculations supported that the binding of **4a** to **3a** led to the formation of a cationic aluminum complex via the ionization of chloride, a kind of Lewis base activation of Lewis acid¹² (A, Scheme 2). Notably, the thus formed phosphorane-(salen)AlCl complex showed much higher catalytic activity, because (salen)AlCl itself was unable to catalyze the ketone cyanosilylation.

A) Ketone cyanosilylation



Scheme 2. Phosphorane-(salen)MX catalysts

Based on this mechanistic insight, along with the fact that metal salen complexes are the most widely used catalysts for the reactions of epoxides and CO₂,^{3c} we speculate that phosphorane-(salen)MX complexes might be a type of conceptually new bifunctional catalysts for this valuable transformation, for following reasons. First, while the in situ formed halide is largely a spectator in the ketone cyanosilylation, it may act as an indispensable nucleophilic cocatalyst to facilitate the ring-opening of epoxides (B, Scheme 2). Second, the enhanced Lewis acidity of the metal center resulting from the activation of the corresponding salen complex by a phosphorane is promising to inhibit the formation of undesired polycarbonates.^{3c, 4c} In addition, i_{tev} is a reasonable prepare and modify the phosphorane-salent inetal complex by varying the backbone of salen ligands and the substituent of the phosphorane. Herein, we wish to exhibit the power of such bifunctional catalysts by a highly efficient coupling reactions of CO₂ with terminal epoxides or aziridines catalyzed by phosphorane-(salen)CoI complex.

With the above hypothesis, we first examined the acceleration effect of different phosphoranes 4 in the (salen)AlCl complex 3a catalyzed coupling of epoxide 1a and CO₂, as shown in Table 1. All reactions were carried out at 25 °C under solvent-free conditions with CO2 held within a balloon to maintain a 1 atmosphere pressure, in the presence of 3a and phosphorane 4 (2.5 mol%, each). As expected, no reaction took place when (salen)AlCl 3a was used alone, in accordance to North's result¹³ (entry 1). It was found that the substituent of phosphorane 4 obviously influenced the reaction outcome (entries 2-5). While phosphorane 4a-b bearing an ester or a phenyl group had almost no acceleration effect, the addition of 4c with a smaller methyl group slightly promoted this reaction (entry 4). Therefore, we tried phosphorane 4d, and found that 27% conversion of 1a could be detected after a reaction time of 24 h (entry 5).

Table 1. The influence of phosphoranes



Entry	Phosphorane	Conv. (%) ^{<i>a</i>}	Yield (%) ^a
1	no		
2	$4a: R = CO_2Et$	Trace	
3	4b : R = Ph	Trace	
4	4c : R = Me	9	8
5	4d : R = H	27	27

^a Determined by ¹H NMR using mesitylene as internal standard.

To improve the reactivity, we next tried the merger of different metal-salen complexes with phosphorane **4d** as the cocatalyst. Since iodide was a better nucleophile and leaving group than chloride, we prepared (salen)AlI **3b** and found it was indeed more active, as the conversion of **1a** was raised to 82% (entry 1 vs 2, Table 2). On the other hand, the screening of salen complexes **3c-e** with different metals revealed that (salen)CoCl **3e** was the most active one (entry 5 vs 1, 3 and 4). Next, we tried varying axial halide ligands of cobalt-salen complexes to improve the activity. As expected, the activity of cobalt complexes **3e-g** was significantly influenced by the axial ligands, and the conversion of epoxide **1a** obviously increased with the halide ligands changing from chlorine to iodine (entries 5-7). When (salen)CoI **3g** was used, product **2a** could be obtained in 96% isolated yield (entry 7). This observation

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Table 2 The influence of metal-salen complexes

supported our hypothesis that the binding of phosphorane 4d to (salen)CoX complexes could polarize the Co-X bond to generate in situ the halide co-catalyst, and (salen)CoI 3g gave the best result simply because it gave iodide, the best cocatalyst and leaving group. It was not surprising that (salen)CoOTs 3h in combination with 4d failed to catalyze the reaction (entry 8), because p-toluenesulfonate anion was known to be an inefficient nucleophilic co-catalyst.¹⁴ These results clearly showed that both the central metal and the axial ligand of the salen-metal complexes greatly influenced the catalytic properties. With axial ligand (X⁻) of high nucleophility and leaving ability, the corresponding metal salen complex had a higher catalytic activity. Considering the substituents on the salen ligands might have a great influence on the Lewis acidity of the central metal,^{3c} we also tried some other salen ligands to further improve the activity, but in vain. For details, see supporting information, SI.

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Entry	(salen)MX complex	Y	Conv. (%) ^a	Yield (%) ^a		
1	3a: M = Al, X = Cl	2.5	27	27		
2	3b : $M = Al$, $X = I$	2.5	82	80		
3	3c: M = Mn, X = Cl	2.5	8	7		
4	3d: M = Cr, X = Cl	2.5	40	17		
5	3e : M = Co, X= Cl	2.5	50	44		
6	3f : $M = Co, X = Br$	2.5	80	77		
7	3g : M = Co, X= I	2.5	100	96		
8	3h : M = Co, X= OTs	2.5	Trace			
9	3g : M = Co, X= I	1.0	88	88		
10^{b}	3g: M = Co, X = I	1.0	97	95°		

^o Determined by ¹H NMR using mesitylene as internal standard. ^bOn a 5.0 mmol scale, 36 hours. ^c isolated yield.

Gratifyingly, if lowering the loading of **3g** and **4d** from 2.5 mol% to 1.0 mol%, the reaction could still furnish the carbonate **2a** in 88% yield (entry 9). If prolonging the reaction time to 36 h, an isolated 95% yield was obtained for product **2a** (entry10). The efficiency of **3g/4d** is comparable to North's dinuclear (salenAl)₂O complex (shown in Scheme 1), one of the most efficient catalytic systems for the coupling of CO₂ and epoxide. The combination of (salenAl)₂O with (*n*-Bu)₄NBr (1.0 mol%, each) could afford 86% conversion in 24 h.^{13, 15}

To further confirm our hypothesis, control experiments were conducted as shown in Table 3. Either 1 mol% (salen)CoI **3g** or 1 mol% phosphorane **4d** alone was unable to catalyze this reaction at 25 °C (entries 1-2). However, the merger of both could achieve a conversion of 88% after 24 h (entry 3). The use of 0.5 equiv of **4d** relative to **3g** resulted a lower conversion

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(entry 4). The use of 2.0 equivs of **4d** relative to $\mathbf{3g}_{ti}$ did not improve the reactivity (entry 5), which obviated the possibility that **4d** acted as a nucleophilic co-catalyst to facilitate the ringopening of epoxide. Furthermore, the use of 3.0 equivs of **4d** relative to **3g** almost terminated the reaction (entry 6), possibly due to the formation of the six-coordinated 1/2 complex, which has no catalytic activities as phosphorane had occupied all empty coordinating sites of cobalt center (for details, see section 3-3 of SI).

Table	3	Control	experiment.

Ph 1a (2.0 mm	+ CO ₂ nol) (1 atm)	(salen)Col 3g (X mol%) neat, 25	O Ph ₃ P 4d (Y mol%) °C, 24 h	0 - Ph 2a
Entry	Х	Y	Conv. (%) ^{<i>a</i>}	Yield $(\%)^a$
1	1.0			
2		1.0		
3	1.0	1.0	88	88
4	1.0	0.5	70	68
5	1.0	2.0	84	84
6	1.0	3.0	13	12

^a Determined by ¹H NMR using mesitylene as internal standard.

Table 4 Substrate scope of epoxides.

<u> </u>	CO2	(salen)Col	Ph ₃ P	
R		3g (1.0 mo l %)	4d (1.0 mol%)	ٽــر
1 (5.0 mmol)	(1 atm)	neat. 25 °C	C. 24-36 h	R 2

Entry	1	2	Time (h)	Conv. (%) ^a	Yield (%) ^b
1	1a : R = Ph	2a	36	97	95
2	1b : $R = 4$ -MeC ₆ H ₄	2 b	24	full	91
3	1c : $R = 4-ClC_6H_4$	2c	36	85	80
4	1d : R = Me	2d	24	98	90
5	1e : R = Et	2e	24	93	87
6	1f : $\mathbf{R} = n$ -Bu	2f	24	92	92
7	1g : $\mathbf{R} = \mathbf{PhCH}_2$	2g	36	98	91
8	1h : $R = ClCH_2$	2h	24	97	90
9	1i : $\mathbf{R} = i$ -PrOCH ₂	2i	24	97	93
10	$\mathbf{1j:} \mathbf{R} = \mathbf{BnOCH}_2$	2ј	36	full	95
11	1k : R = allylOCH ₂	2k	36	full	88
12	11: R = propargylOCH ₂	21	36	95	90
13	(S)-1a (>99% ee)	(S)-2a, 36 h, 86% yield, 93% ee			
14	(S)-1d (>99% ee)	(S)-2d, 24 h, 84% yield, >99% ee			

^a Determined by ¹H NMR. ^b Isolated yield.

In the following, the scope with respect to different epoxides was examined by running the reaction on a 5.0 mmol scale at ambient conditions (25 °C, 1 atm of CO₂), in the presence of (salen)CoI **3g** and phosphorane **4d** (1.0 mol%,

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each), as shown in Table 4. To our delight, no matter aryl epoxides **1a-c** or aliphatic substituted epoxides **1d-l**, all worked well under this mild condition, to afford the desired cyclic carbonates **2a-l** in high to excellent isolated yield (entries 1-12). In addition, different functional groups such as chloromethyl, ether, allyl and propargyl groups on the side chain of the epoxides could be tolerated. We also tried the synthesis of optically active carbonates from the enantiopure epoxides. For example, while 2-phenyloxirane (S)-**1a** (99% ee) afforded chiral product (S)-**2a** in slightly diminished 93% ee (entry 13), the aliphatic (S)-**1d** furnished (S)-**2d** in 99% ee (entry 14).

It should be noted that ¹H NMR analysis of the crude mixture of each reaction did not show the presence of polycarbonates (see SI). This exhibited the enhanced Lewis acidity of the cobalt center resulting from the activation of (salen)CoI by phosphorane was indeed effective to suppress this side copolymerization. This is impressive, because the synthesis of thermodynamically more stable cyclic carbonates was usually favored when the reactions were performed at enhanced temperatures, or in the presence of an excess of nucleophilic cocatalyst.¹⁶

To demonstrate the scalability of this protocol, a 50 mmol scale synthesis using only 0.1 mol% of **3g** and 0.1 mol% of **4d** was tried. Although the reaction proceeded slowly, the catalyst kept active during a reaction time of 15 days, giving product **2e** in 79% isolated yield.¹⁷



Now that phosphorane-(salen)CoI complex had been established as an efficient bifunctional catalyst for the coupling of CO2 with terminal epoxides at 25 °C, under 1 atm of CO2, we next tried to gain a better understanding of the reaction mechanism. In the following, electrical conductivity experiments were conducted to probe the ionization of Co-X bond resulting from the binding of phosphorane to (salen)CoI complex. According to the theory of Lewis base catalysis defined by Denmark,¹⁸ the activation of a metal complex by a Lewis base may stem from a redistribution of electron-density in the thus formed Lewis adduct, which polarizes adjacent bonds to generate a hypervalent species with enhanced Lewis acidity.¹⁹ Given a strong polarization, ionization would happen produce cationic species with greatly enhanced to electrophilicity. The electrical conductivity was measured by using a two-probe method, as we previously reported.^{11a} Although the conductivity of (salen)CoCl 3e, (salen)CoBr 3f, (salen)CoI 3g, (salen)CoOTs 3h and phosphonane 4d in CH₂Cl₂ (2 \times 10⁻³ M) were all weak, the addition of 4d to the CH₂Cl₂ solution of complexes 3e, 3f, 3g and 3h all resulted in a dramatic increase in the conductivity. When 1.0 equiv of 4d was added, the conductivity was increased by around 133, 378, 43.5 and 13.8 times, respectively. These results strongly supported that ionization process took place to form a halide or a sulfonate after the activation of (salen)CoX complexes by phosphorane 4d. Although it seemed that (salen)CoOTs 3h

could be easily activated by phosphorane as well_{iev}the_{ict} tasks why the resulting complex was impotent¹⁰tb³²tative²⁴ff coupling was simply because the in situ formed sulfonate was a weak nucleophile.¹⁴



Figure 1. Conductivity changes of (salen)CoX in response to the addition of phosphonane 4d at 25 °C. Inset: Conductivity changes of 4d.

To further confirm the generation of a halide after the activation of (salen)CoX complex by a phosphorane and to investigate whether the in situ formed halide involve in the ring-opening step, we tried to detect the intermediate resulting from the attack of a halide to epoxide 1a by GC-MS analysis. This was inspired by the successful trapping of the halogenoalcohol to confirm the role of halogen anion of the ammonium salt by the groups of Chisholm²⁰ and Ren & Lu²¹ respectively. Fortunately, when (salen)CoBr 3f in combination with phosphorane 4d (0.1 mmol, each) was stirred in 0.5 mL of styrene oxide, we could detect the signal at m/z 200, 202 (1/1), corresponding to the bromoalcohol 7 (For details, see section 3-2 of SI). Unfortunately, the reaction proceeded very slowly and was accompanied by severe hydrolysis of epoxide, so the reaction system was in a mess, difficult to clearly detect the presence of bromoalcohol 7 by NMR analysis. This result suggested the in situ generated halide facilitated the ringopening of epoxide by nucleophilic attack at the less substituted methylene carbon of oxide, as shown in Scheme 2B.



To get more information about the phosphorane-(salen)CoI complex, mass spectroscopy studies were conducted. Initially, the MALDI-TOF MS analysis of the 1:1 mixture of **3g** and **4d** detected a characteristic signal $[3g/4d - 1]^+$ at m/z 907.43, consistent with the 1/1 phosphorane-(salen)CoI complex **3g/4d**, which was further confirmed by ESI-HRMS. Further study of the 1:3 mixture of **3g** and **4d** via ESI-MS revealed that the binding of a second molecule of **4d** was also possible, but the resulting six-coordinated 1/2 complex was less stable as the CID study shown in Figure 2 and it probably had no catalytic activity as revealed in Table 3. (For details, see section 3-3 of SI)

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Figure 2. ESI-HRMS of 1/1 complex (left); Plots of $[3g/(4d)_2-i]^+$ abundance versus CID voltage (right).

We further conducted the NMR analysis to investigate the coordination fashion of the phosphonane **4d** to (salen)CoI **3g**.²² It was known that phosphorane might form various *C*-coordinated (I) and *O*-coordinated (II) metal complexes (eq 1, Figure 3).^{22c} Previously, by NMR studies, we safely arrived at a conclusion that phosphorane **4c** bound to (salen)AlCl **3a** in an *O*-coordination fashion.^{11a} However, in the case of phosphonane **4d**, the analysis was more difficult, because according to the study of Kayser and Hatt,^{22a} **4d** existed in a stable enolate ion, as a mixture of isometric forms of **4d**-*cis* and **4d**-*trans* (eq 2). Fortunately, NMR studies provided persuasive proofs to support the formation of an *O*-coordinated complex derived from phosphorane **4d** and (salen)CoI **3g** (eq 3).



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As shown in the selected part of NMR spectra, when 1,0 equiv of (salen)CoI 3g was added to a solution of 346 The CDEPA, ¹H NMR analysis showed that the quaternary H(1)-cis signal slightly shifted from 3.68 ($J_{PH} = 24.5 \text{ Hz}$) to 3.63 ppm ($J_{PH} =$ 23.0 Hz), while the H(1)-trans signal at 4.10 ppm ($J_{PH} = 19.5$ Hz) disappeared. On the other hand, 13C NMR analysis revealed that the characteristic signal of doublet C(1)-cis carbon shifted downfield from 54.87 ($J_{PC} = 99.4 \text{ Hz}$) to 63.43 ppm (J_{PC} = 99.6 Hz), and the C(1)-trans carbon signal at 56.56 ppm (J_{PC} = 109.6 Hz) disappeared. These observations implied that the binding of the cis isomeric form of phosphorane 4d to (salen)CoI 3g was favored, and the trans isomeric form of 4d readily balanced to the corresponding *cis* form for coordination. According to literature reports, the C-coordination of a phosphorane to a metal complex would result in the upfieldshift of the signal of the C1 carbon, along with the downfieldshift of the signal of phosphorous.^{22c} The current studies detected an obvious downfield-shift from 54.87 to 63.43 of the signal of C1 carbon, together with the upfield shift from 15.22 to 14.38 of that of phosphorous. Therefore, we believed that 4d coordinated to (salen)CoI 3g in a cis O-coordination, as shown in eq 3. For details of NMR analysis, see section 3-4 of SI.

Based on the aforementioned studies, we proposed a mechanism for the bifunctional phosphorane-(salen)CoI complex 3g/4d catalyzed coupling reaction of epoxide and CO2, as shown in Figure 4. The coordination of 1.0 equiv of phosphorane 4d to (salen)CoI 3g readily afforded the desired bifunctional cobalt complex. With electrophilic activation of epoxide by cobalt (III), the in situ generated nucleophilic iodide attacked the less hindered methylene carbon of the epoxide, followed by the insertion of CO₂ into the Co-O bond to form the metal carbonate. Finally, ring closure afford the desired cyclic carbonate along with the regeneration of the catalyst. However, the reaction of enantiopure epoxide (S)-1a afforded (S)-2a in only 93% ee, which indicated that the reaction did not proceed with 100% retention of the stereochemistry. In light of this, there might be other mechanism involved²³ and the nucleophilic attack at the methine carbon was also possible.



Encouraged by the successful results of the phosphorane-(salen)CoI 3g/4d complex catalyzed cycloaddition of epoxide and CO₂, we further examined the potential of phosphorane-(salen)CoI complexes for the coupling of aziridines with CO₂ under ambient conditions. It was found that under the catalysis of (salen)CoI **3g** and phosphorane **4b** (2.5 mol%, each), a variety of aryl aziridines **5** worked well with CO₂, as shown in Table 5.²⁴ Both *N*-alkyl aziridines **5a-c** and unprotected aziridine **5d** afforded the corresponding 1,3-oxazolidin-2-ones **6a-d** in moderate to high yield (entries 1-4). In addition, no matter electron-withdrawing or electron-donating substituent on the phenyl ring of the aziridines, the desired products **5e-g** were all obtained in high yield (entries 5-7). 2-Naphthyl substituted aziridine **5h** was also viable under this condition, furnishing **6h** in 40% yield (entry 8). When enantiopure (*R*)-**5a** was used, (*R*)-**6a** could be obtained in >99% ee with 82% yield (entry 9).

It is worth mentioning that as compared with the coupling of epoxides with CO₂, the corresponding coupling of aziridines is much less well studied.²⁵ A challenge is how to avoid the unselective synthesis of 4- or 5-substituted oxazolidinones.²⁶ While several elegant protocols for the selective synthesis of 5-substituted oxazolidinones have been developed by Nguyen, He and Lu groups et al.,²⁷ only very limited way could be performed at ambient conditions.^{8a, 27d, h} To the best of our knowledge, metal-catalyzed coupling of aziridines and CO₂ usually required high pressure of CO₂.^{21, 27a, b}

Table 5 Substrate scope of aziridines.

R' N 8 5 (2.0 m	+ CO ₂ mol) (1 atm)	(salen)Col P 3g (2.5 mol%) 4 neat, 25 °C,	0 h ₃ P P h (2.5 mol%) 48 h	→ R	'N∽ ^{R'} ∕ 6
Entry		5	6	Conv. (%) ^a	Yield (%) ^b
1	5a : R = Ph, R'	= Me	6a	full	84
2	5b : R = Ph, R'	= Et	6b	84	65
3	5c : $R = Ph, R' =$	= Bn	6c	58	54
4	5d : R = Ph, R'	= H	6d	full	38
5	5e : R = 4-MeC ₆	$_{5}H_{4}, R' = Me$	6e	full	83
6	5f : $\mathbf{R} = 4 - ClC_6 \mathbf{H}$	$H_4, R' = Me$	6f	full	90
7	5g: R = MeOC	$H_2C_6H_4, R' = Me$	6g	full	76
8°	5h : R = 2-Naph	thyl, R' = Me	6h	48	40
9	(R)-5a	(>99% ee)	(R)- 6a	, 82%, >9	9% ee
Determined by ¹ H NMR. ^b Isolated yield. ^c DMF (1.0 M) was used as solvent.					

Conclusions

In summary, we have demonstrated that a bifunctional phosphorane-(salen)CoI complex as a conceptually new type of efficient catalysts for the coupling reaction of CO₂ with terminal epoxides under ambient conditions (25 °C, 1 atm of CO₂), with a catalyst loading of 1.0 mol%. The key to the efficiency of the protocol is the activation of (salen)CoI complex by a phosphorane co-catalyst, which not only enhances the Lewis acidity of the Co(III) center for electrophilic activation, but also simultaneously generates an iodide to facilitate the ring-opening of the epoxide. Further investigation revealed the phosphorane-(salen)CoI complex

Importantly, the catalytic properties of such bifunctional phosphorane-(salen)MX complexes can be readily tuned by varying the axial halide ligand, the metal center and the substituent of phosphorane and salen ligands. This offers the promise for further improving catalyst properties. The current protocol using phosphorane-(salen)CoI catalyst **3g/4d** has a limitation that 1,2-disubstituted epoxides work inefficiently.²⁸ Further optimization of the catalyst structures to improve the catalytic efficiency along with the application of the catalytic system in the kinetic resolution of epoxides for the synthesis of chiral cyclic carbonates are now in progress in our laboratory²⁹.

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29 A preliminary attempt revealed that using CH_2Cl_2 as solvent, chiral cyclic carbonate **2a** could be obtained in 23% ee with 10% conversion over 15 hours, for the 1 mol% of **3g/4d** catalyzed coupling of **1a** with CO₂, which demonstrated the feasibility of the corresponding kinetic resolution reaction.

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The activation of (salen)CoI complex by phosphorane in situ formed a bifunctional catalyst for the reaction of carbon dioxide with terminal epoxides or aziridines at ambient temperature and 1 bar carbon dioxide pressure.