Enantioselective CO_2 Fixation Catalyzed by Optically Active Cobalt Complexes

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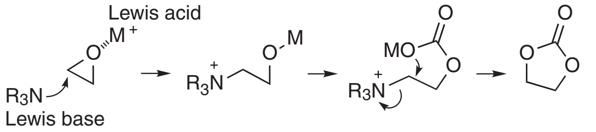
In the presence of a catalytic amount of optically active cobalt complexes and amine bases, a racemic epoxide, such as *N*,*N*-diphenylaminomethyloxirane, reacted with gaseous carbon dioxide to afford the optically active cyclic carbonate along with the optically active starting epoxide.

Carbon dioxide has drawn much attention from the viewpoint as an environmental problem.[1] In order to suppress its greenhouse effect, much effort has been devoted to the development of the effective reduction system of its exhaust from industries. Whereas it is ubiquitous, safe and abundant and could be regarded as a C_1 chemical feedstock[2] from the viewpoint of economic benefit, few synthetic processes[3] have been developed because of its thermodynamic stability. Severe reaction conditions have been applied to the chemical fixation of stable carbon dioxide with epoxides to cyclic carbonates; e.g., high-pressure,[4] high-temperature,[5] supercritical conditions,[6] and electrochemical reactions.[7] The use of well-defined complex catalysts is expected to be one of the most promising procedures for chemical fixation. Since the alternating copolymerization of carbon dioxide with epoxides to polycarbonates was reported in the 1960s,[8] various catalysis systems have been proposed to achieve remarkable catalytic activities.[9] It was reported that the optically active polycarbonates could be obtained from *meso*-epoxide using the optically active zinc complex catalysts.[10] The reaction of epoxides and carbon dioxide could also afford five-membered cyclic carbonates, which can be used as the monomer of polycarbonates and as the masked 1,2-diol[11] equivalents, etc. However concerning the enantioselective version, it was reported that the high enantioselectivity is very hard to achieve because high temperatures are required for these reactions.[5b] In this communication, we would like to report that carbon dioxide smoothly inserted into epoxides at ambient temperature under mild reaction conditions in the presence of a catalytic amount of an optically active ketoiminatocobalt complex and amine bases. As the result of kinetic resolution, the corresponding five-membered cyclic carbonate was obtained in high enantioselectivity along with the starting epoxides of high enantiomeric excess.

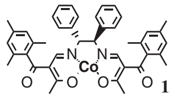
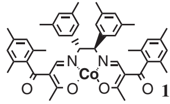
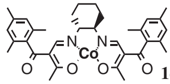
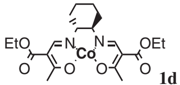
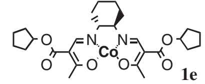
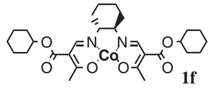
It was proposed that the chemical fixation reaction of carbon dioxide to the five-membered cyclic carbonate would be cocatalyzed by a Lewis base amine and Lewis acids.[5b] The epoxide, activated by the coordination of the Lewis acid, will react with the Lewis base to generate the alkoxide intermediate, which will capture carbon dioxide, and recyclization with the release of an amine base will afford the corresponding five-membered cyclic carbonate (Scheme 1). Consequently, amine bases are indispensable for this reaction and the optically active Lewis acid that can operate even in the presence of Lewis bases is expected to achieve the enantioselective fixation of carbon dioxide to the optically active cyclic carbonates.



Scheme 1. Chemical fixation of CO_2 cocatalyzed by Lewis acid and Lewis base.

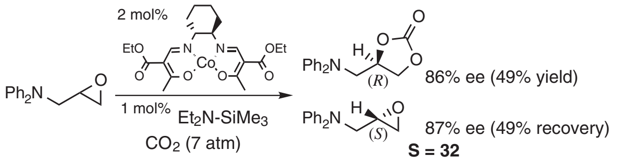
The optically active 3-oxobutylideneaminatocobalt complexes were originally developed as effective catalysts for the enantioselective borohydride reductions of carbonyl compounds.[12] They were found to also work as chiral Lewis acid catalysts for the enantioselective hetero-Diels–Alder and the enantioselective carbonyl-ene reaction.[13] Recently, it was reported that this type of cobalt complex could be successfully applied to the enantioselective 1,3-dipolar cycloaddition reactions of nitrones with an α,β-unsaturated aldehyde.[14] Therefore, they are expected to activate carbonyl compounds as an efficient chiral Lewis acid even in the presence of a strongly electron-donating compound, such as nitrones and amine bases. As *N*-methylimidazole is one of the most commonly used amine bases with transition-metal complex catalysts,[15] various effects were reported for the enantioselective aerobic epoxidation catalyzed by manganese(III) complexes,[16] the cyclopropanation reaction catalyzed by cobalt complexes,[17] and the chemical fixation of carbon dioxide.[18] While *N*-methylimidazole was adopted as a Lewis base, various optically active ketoiminatocobalt complexes were examined as a Lewis acid catalyst for the enantioselective chemical fixation of carbon dioxide with racemic *N*,*N*-diphenylaminomethyloxirane as a model substrate for glycidol derivatives (Table 1). In the presence of a 2.0 mol % cobalt complex and 1.0 mol % *N*-methylimidazole, the epoxide was treated with carbon dioxide at atmospheric pressure and 30 °C for several hours to afford the corresponding five-membered cyclic carbonate and to recover the unreacted epoxide. The selectivity of each complex was evaluated by the S value[19] calculated from the chemical yield and the optical purity of the recovered epoxide. The cobalt complex **1a** or **1c** bearing 1,2-diphenylethylenediamine or 1,2-diaminocyclohexane afforded the cyclic carbonate along with the recovered epoxide with S values of 2.7 and 2.5, respectively, while the cobalt complex **1b** with 1,2-bis(3,5- dimethylphenyl)-ethylenediamine did not catalyze the reaction. When the cobalt complexes **1d**–**1f** bearing the alkoxycarbonyl group on the side chain were employed, the S values were improved to 6.0–8.3. In the presence of complex **1d**, the carbonate of 70% ee was obtained in 18% yield and the unreacted epoxide with 54% ee was recovered in 55% yield. The Lewis base amines were examined in the reaction catalyzed by the cobalt complex **1d**. In the presence of *N*,*N*-dimethylaminopyridine and *N*-alkylimidazoles, the enantioselective CO_2 fixation reaction proceeded ranging in S value from 5.1 to 11.1. When pyridine *N*-oxides and *N*-methylmorpholine *N*-oxide were employed as Lewis bases, the S values were slightly improved to 9.0–13.2. Various *N*-alkylmorpholines

Table 1. Examination of cobalt complex catalysts for enantioselective CO_2 fixation

Entry[a]	Co(II) catalyst	Carbonate ee/%ee[b] yield/%[c]	Epoxide ee/%ee[b] recovery/%[c]	S Value[d]
1	 **1a**	41 / 8	29 / 54	2.7
2	 **1b**	No Reaction		
3	 **1c**	56 / 5	5 / 89	2.5
4	 **1d**	70 / 18	54 / 55	8.3
5	 **1e**	57 / 36	71 / 41	6.0
6	 **1f**	67 / 25	49 / 55	6.4

[a]Reaction conditions: The reaction was performed in 1 mL of dichloromethane at 30 °C using 2.0 mol% catalyst, 2.0 mmol of *N*,*N*-diphenylaminomethyloxirane and 1.0 mol% *N*-methyl imidazole under a carbon dioxide atmosphere for 80 h. [b]Enantiomeric excess was determined by HPLC (Chiralcel AD–H). [c]Isolated yield. [d]Selective value was calculated based on the recovered epoxide.

were examined. Although *N*-phenylmorpholine did not work in this reaction, it was found that the *N*-methyl, *N*-ethyl, and *N*-trialkylsilylmorpholines improved both the material balances and the S values. By the combined use of a catalytic amount of trimethylsilyldiethylamine and the cobalt complex **1d**, the racemic epoxide was reacted with carbon dioxide at atmospheric pressure and the S value reached 48.4. As a result of the kinetic resolution, the five-membered cyclic carbonate of 79% ee was obtained in 30% yield and the unreacted epoxide of 96% ee was recovered in 47% yield. After the optimization of the reaction conditions, the CO_2 incorporated carbonate was obtained in 49% yield with 86% ee and the epoxide was recovered in 49% yield with 87% ee (Scheme 2). It is noted that in the presence of a catalytic amount of an optically active cobalt complex and Lewis base amine, the enantioselective chemical CO_2 fixation was achieved with the glycidol derivative to afford the corresponding cyclic carbonate with high enantioselectivity along with the unreacted epoxide with high enantioselectivity. Further improvement of the selectivities by kinetic resolution and a detailed study of the reactive intermediate are ongoing.



Scheme 2. Enantioselective CO_2 fixation by cobalt complex.

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