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Chiral Cobalt(III) Complexes as Bifunctional Brønsted Acid–Lewis Base Catalysts for the Preparation of Cyclic Organic Carbonates

Yuri A. Rulev,[a] Vladimir A. Larionov,[a] Anastasia V. Lokutova,[a] Margarita A. Moskalenko,[a] Ol'ga L. Lependina,[a] Victor I. Maleev,[a] Michael North,*[b] and Yuri N. Belokon*[a]

Stereochemically inert cationic cobalt(III) complexes were shown to be one-component catalysts for the synthesis of cyclic carbonates from epoxides and carbon dioxide at 50 °C and 5 MPa carbon dioxide pressure. The optimal catalyst possessed an iodide counter anion and could be recycled. A catalytic cycle is proposed in which the ligand of the cobalt complexes acts as a hydrogen-bond donor, activating the epoxide towards ring opening by the halide anion and activating the carbon dioxide for subsequent reaction with the halo-alkoxide. No kinetic resolution was observed when terminal epoxides were used as substrates, but chalcone oxide underwent kinetic resolution.

Introduction

Recently, we introduced a new class of stereochemically inert coordinatively saturated chiral complexes of cobalt(III) as promoters of asymmetric carbon–carbon bond forming reactions.[1–6] The use of chiral octahedral complexes, where the metal ion is not involved in the catalytic act and only serves to position and activate organic groups of a ligand, is a fast evolving new field of research.[7–15] An efficient group of such catalysts developed by our group are cationic complexes of cobalt(III) and Schiff bases obtained from substituted salicylic aldehydes and (*R*,*R*)- or (*S*,*S*)-cyclohexane diamine (Figure 1).[5,6] The N–H bonds of the coordinated ligands were activated by the Lewis acidity of the central metal ion, becoming better Brønsted acids (so called Lewis-acid activated Brønsted catalysis[16]). The formation of strong hydrogen bonds with the counter anions was established by X-ray single crystal analysis and ^{1}H NMR spectroscopy.[5] It was this hydrogen bonding function of the NH groups that activated the substrate. Thus, the complexes became "Brønsted acids in disguise". Additionally, the counter anions of the complexes were involved in the activation of another substrate in bimolecular reactions, such as cyanosilylation of aldehydes.[17]

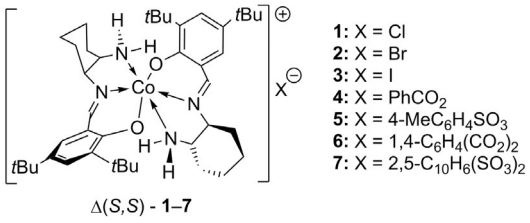


Figure 1. Δ(*S*,*S*) stereochemically inert chiral Co^{III} complexes **1**–**7**.

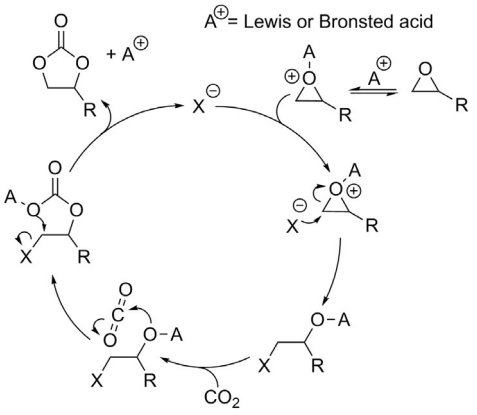
We believed that other important reactions, involving simultaneous catalysis by both nucleophilic and electrophilic groups of the catalysts, could also be efficiently promoted with our cationic complexes. Therefore, we decided to investigate the atom efficient coupling of carbon dioxide and oxiranes leading to cyclic carbonates. Cyclic carbonates have applications as solvents in organic synthesis, electrolytes for lithium-ion batteries, and as chemical intermediates for biodegradable polymer synthesis.[18–22] Catalysis of this reaction is generally believed to proceed as shown in Scheme 1, with both the nucleophilic opening of the oxirane (usually by a halide anion) and electrophilic activation of both epoxide and carbon dioxide (by strong Lewis acids or Brønsted acids) involved in the transition states.[23,24]

There are a number of catalytic systems used for producing cyclic carbonates, involving mostly Lewis acids with added ammonium halides, providing the necessary nucleophilic components.[25,26] The simplest catalysts include alkali metal salts[27–29] and quaternary ammonium or phosphonium salts.[30–33] The addition of fluorinated alcohols[34] or phenols[35] to the ammonium salts supplied an additional Brønsted acid component and improved the catalytic performance.[24,34,35]

Cationic catalysts **1**–**7** seemed to offer a convenient new bifunctional mono-component catalytic system, possessing the necessary nucleophilic and electrophilic components inside the same ionic pair. The complexes are robust and their counter anions can be easily interchanged.[5] In addition, the chirality of the complexes may provide the opportunity for the enantio-

[a] *Y. A. Rulev, Dr. V. A. Larionov, A. V. Lokutova, Dr. M. A. Moskalenko, Dr. O. L. Lependina, Dr. V. I. Maleev, Prof. Y. N. Belokon*
Nesmeyanov Institute of Organoelement Compounds
Moscow 19991 (Russia)
E-mail: yubel@ineos.ac.ru

[b] *Prof. M. North*
Green Chemistry Centre of Excellence
Department of Chemistry
University of York
Heslington, York, YO10 5DD (UK)
E-mail: Michael.North@york.ac.uk

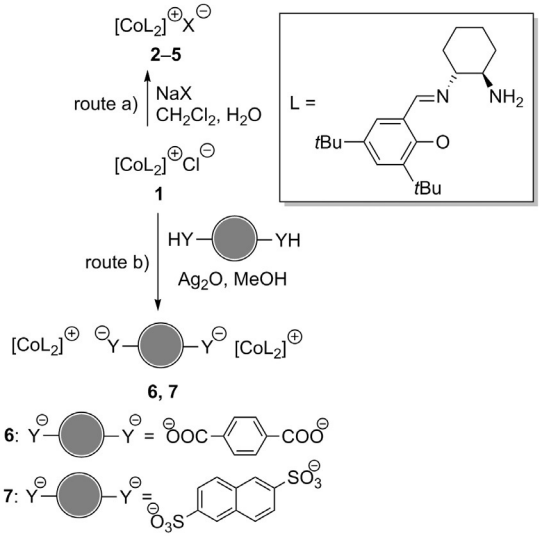


Scheme 1. Proposed mechanism of cyclic carbonate synthesis.

meric recognition of racemic oxiranes in the condensation with carbon dioxide. In this paper we report the use of the cationic stereochemically inert cobalt(III) complexes **1**–**7** as catalysts for the synthesis of cyclic carbonates.

Results and Discussion

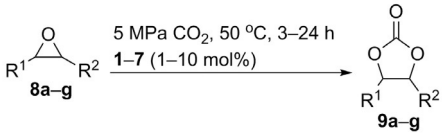
Complex **1** was prepared as described earlier.[5] The counter-anion exchange to form complexes **2**–**7** was conducted by two different routes (Scheme 2). Route a relied on a simple two phase ion-exchange experiment, as previously reported.[5] In this way a twentyfold excess of the corresponding alkali metal salt in a water solution was stirred with a dichloromethane solution of complex **1**, giving complete exchange of the chloride counter anion for bromide, iodide, benzoate, and *p*-toluenesulfonate in the organic solution of the complex. However, this approach failed in the case of doubly charged counter anions, such as terephthalate and 2,5-naphthalene disulfonate. In these cases, the appropriate di-acid was converted into the



Scheme 2. Counter-anion exchange of complex **1**.

bis-silver salt with silver oxide followed by the reaction with complex **1** in methanol, with the precipitated silver chloride being removed by filtration (route b).

Styrene oxide **8a** was used as a model substrate to test the catalytic efficiency of complexes **1**–**7** in the reaction with carbon dioxide. Preliminary results showed that to obtain good conversions using 2 mol% catalyst, reactions had to be carried out at a minimum of 50 °C and 5 MPa pressure of carbon dioxide (Scheme 3). No side reaction was observed



a: R^1 = Ph, R^2 = H; **b:** R^1 = $PhOCH_2$, R^2 = H;
c: R^1 = Me, R^2 = H; **d:** R^1 = CH_2Cl, R^2 = H;
e: R^1 = 4-ClC_6H_4, R^2 = H; **f:** R^1–R^2 = $(CH_2)_4$;
g: R^1 = Ph, R^2 = COPh.

Scheme 3. Synthesis of cyclic carbonates using catalysts **1**–**7**.

under these conditions with the conversion of styrene oxide **8a** corresponding to the formation of styrene carbonate **9a**. The results are shown in Table 1. The observed activity of the counter anions was in the order of their nucleophilicities (Cl < Br < I, Table 1, entries 1–3). On the other hand, the complexes with basic sulfonate and carboxylate counter anions had very disappointing activities (Table 1, entries 4–6). Surprisingly, complex **7** with a bis-sulfonate counter anion was twice as active as the corresponding monosulfonate complex **5** (Table 1, entries 5 and 7).

Table 1. Coupling of CO_2 and styrene oxide promoted by complexes **1**–**7**.[a]

Entry	Catalyst	Conversion	TOF[b] [h^{-1}]
1	**1**	15	0.31
2	**2**	34	0.71
3	**3**	95	1.98
4	**4**	2	0.04
5	**5**	7	0.15
6	**6**	3	0.06
7	**7**	15	0.31

[a] Reaction conditions: 2 mol% catalyst (calculated relative to Co^{III}), no solvent, 50 °C, 5 MPa CO_2, 24 h. [b] TOF = turnover frequency = (moles of product)/(moles of catalyst)×time.

The effect of tetrabutylammonium bromide (TBAB) addition to the catalytic system was next studied using 3-phenoxypropylene oxide **8b** as substrate; the results are presented in Table 2. Notably, TBAB is a better catalyst than complex **1** (Table 2, entries 1 and 2) and the catalytic effects of both promoters were almost additive (Table 2, entries 1–3). However, the introduction of more nucleophilic counter anions as in complexes **2** and **3** made TBAB inclusion in the reaction much less important (Table 2, entries 4–7). Increasing in the amount

Table 2. Coupling of CO_2 and 3-phenoxypropylene oxide promoted by complexes **1**–**3**.[a]

Entry	Catalyst	TBAB	Yield[b] [%]	TOF[c] [h^{-1}]
1	–	Yes	48	2.0
2	**1**	No	24	1.0
3	**1**	Yes	50	2.1
4	**2**	No	50	2.1
5	**2**	Yes	77	3.2
6	**3**	No	76	3.2
7	**3**	Yes	87	3.6
8[d]	**3**	No	>90	>1.9

[a] Reaction conditions: 1 mol% of the catalyst, 1 mol% of TBAB co-catalyst if added, neat 3-phenoxypropylene oxide, 50 °C, 5 MPa pressure of CO_2, 24 h. [b] Determined by weight of the isolated carbonate after purification on SiO_2. [c] TOF = turnover frequency (moles of product)/(moles of catalyst)×time. [d] 2 mol% of complex **3** used.

of complex **3** to 2 mol% gave complete conversion of epoxide **8b** to cyclic carbonate **9b** without the need for any TBAB (Table 2, entry 8). The data summarized in Tables 1 and 2 testify to the importance of the nucleophilic component in the catalysts and also proved the efficiency of the hydrogen-bond donating catalysis by the cobalt(III) moiety.

The activity pattern of the bifunctional catalysts **1**–**6** can be rationalized on the basis of the array of hydrogen bonds in the structure of **1** (Figure 2)[5] and the mechanism assumed to be

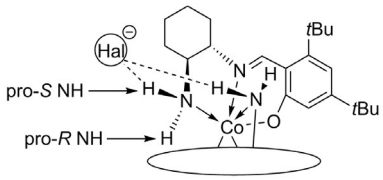
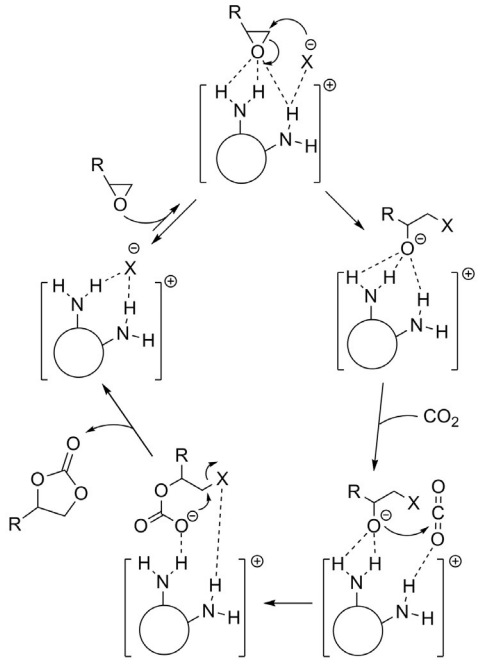


Figure 2. A schematic presentation of the array of hydrogen bonds in the ion pair of Δ(*S*,*S*)-**1**–**3** with a halide anion, as revealed by X-ray analysis.[5]

operating in a binary hydrogen bond donor (HBD)/tetralkyl ammonium halide catalytic system,[24,34] as outlined in Scheme 4. The first step of the catalytic cycle is the reversible formation of the hydrogen-bond supported adduct of the epoxide and the cobalt complex. Both the counter anion and the epoxide are combined in the single supramolecular structure with the epoxide activated towards attack by the counter anion. The pre-orientation of the two reagents is expected to compensate for the entropic penalty associated with the bimolecular reaction of the epoxide ring opening. The halohydrin anion formed by epoxide ring opening is stabilized by the same array of hydrogen bonds. The next step involves the coordination of a carbon dioxide molecule to the intermediate to form a hydrogen-bond stabilized adduct. The next and final steps of the cycle involve the intra-complex attack of the activated carbon dioxide molecule on the halohydrin anion, followed by carbon–halogen bond cleavage, most likely promoted by hydrogen bonding of the catalyst to the leaving group, and the departure of the cyclic carbonate from the complex.



Scheme 4. A plausible mechanism of CO_2 reaction with epoxides promoted by cobalt(III) complexes **1**–**7** with X^- corresponding to the counter anion of the complex.

The rate-limiting step of the reaction is, most likely, the ring opening of the epoxide by the counter anion,[34] which explains the importance of the nucleophilicity of the counter anion. The basicity of the anion, on other hand, should inhibit the reaction by competing with the substrate for the catalyst's hydrogen bonds. This explains the greater catalytic activity of **3** relative to **1**.

The catalytic cycle shown in Scheme 4 was supported by ^{1}H NMR data of complexes **1** and **3** in $CDCl_3$ before (Figure 3a and 4a) and after (Figure 3b and 4b) addition of ten equivalents of propylene oxide. The salient feature of the initial spectra was the very significant difference in the chemical shifts of the two diastereotopic hydrogens comprising the NH_2 groups of the ligands. One reason for this was a significant magnetic anisotropic screening of the pro-*R* hydrogen atom by the C=N bond of the neighboring ligand (Figure 2), moving its resonance to higher fields (around 2–3 ppm). In contrast, the pro-*S* proton is involved in the formation of hydrogen bonds with the halide anion, according to X-ray data (Figure 2).[5] The stronger the hydrogen bond, the greater the chemical shift of the proton situated in the low field region of the spectrum.[5,6] For example, for complex **1**, the signal for this NH group is situated at 6.53 ppm, whereas for complex **3** it is found at 5.55 ppm. The addition of propylene oxide had almost no effect on the spectra of complex **1** (Figure 3b), but significantly moved the signal of the pro-*S* NH proton to lower fields (from 5.55 to 5.75 ppm) for complex **3**. Almost no changes in chemical shifts were observed for the other protons of this complex. Evidently, for complex **3**, propylene oxide was able to hydrogen bond to the pro-*S* NH proton more effectively than the iodide counter anion. For complex **1**, propylene oxide could

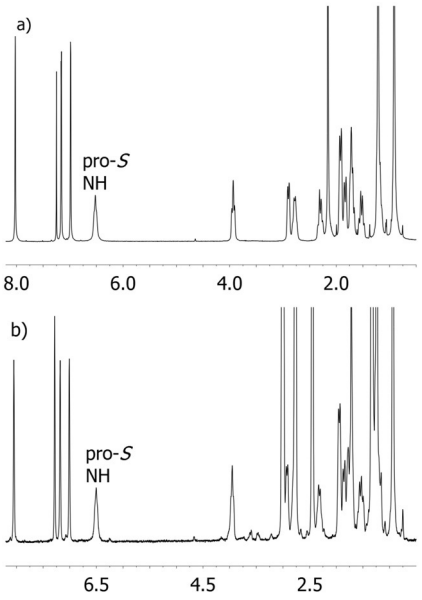


Figure 3. ^{1}H NMR spectra of complex **1** a) before and b) after addition of propylene oxide.

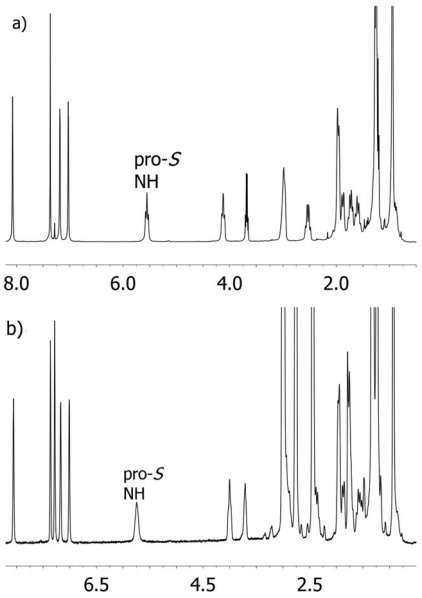


Figure 4. ^{1}H NMR spectra of complex **3** a) before and b) after addition of propylene oxide.

not compete with the strongly hydrogen-bonded chloride counter anion and hence was not activated towards nucleophilic ring opening.

The most efficient catalyst (complex **3**) exhibited a broad substrate scope. The results are summarized in Table 3. As expected, the best substrates were terminal epoxides, for which the yields of cyclic carbonate were close to 100% under the standard conditions (Table 3, entries 1–7). Propylene oxide **8c** underwent reaction even at ambient temperature and 1 MPa carbon dioxide pressure, giving a 75% yield of propylene carbonate **9c** (Table 3, entry 3). Cyclohexene oxide **8f**, as expected, was relatively unreactive, giving only 16% yield of cyclic carbonate **9f** (with *cis*-configuration) under the experimental conditions. No kinetic resolution of terminal epoxides, assessed by analyzing the enantiomeric purity of the remaining initial epoxides at the later stages of the conversion, was detected. However, in the case of the internal epoxide chalcone oxide **8g**, kinetic resolution did occur and the enantiomeric purity of the remaining epoxide **8g** was 55% (determined by chiral HPLC) at 60% conversion.[36] It may be that the positioning of the epoxide by hydrogen bonding to the chiral catalyst was more rigid than for simple epoxides owing to the presence of an additional carbonyl group, also capable of forming hydrogen bonds with the catalyst.

Table 3. Coupling of CO_2 and various epoxides promoted by complex **3**.[a]

Entry	*t* [h]	Epoxide	Yield [%]	Selectivity[b] [%]
1	3	**8c**	78[c]	>99
2	6	**8c**	69	>99
3[d]	24	**8c**	75[c]	>99
4	24	**8d**	89	>99
5	24	**8b**	76[e]	>99
6	24	**8a**	85	>99
7	24	**8e**	74	>99
8	24	**8f**	16[c]	>99
9[f]	24	**8g**	60	80

[a] Reaction conditions: neat epoxide, 2 mol% of complex **3**, 50 °C, 5 MPa CO_2, the carbonates were purified chromatographically and the yields are the isolated ones unless indicated otherwise. [b] The selectivity criteria reflect the absence of any other reaction products, including polymers and diols. [c] The yield was determined by ^{1}H NMR spectroscopy with the catalyst *tert*-butyl groups serving as the internal standard. [d] Under 1 MPa pressure of CO_2 and at room temperature. [e] Reaction conditions: neat epoxide, 1 mol% of complex **3**, 50 °C, 5 MPa CO_2. [f] In 0.1 mL toluene using 10 mol% of the catalyst.[36]

The stability complex **3** was investigated by catalyst recycling experiments using propylene oxide **8c** at 50 °C and 5 MPa carbon dioxide pressure with a reaction time of 24 h, as this was required for some other epoxides. After the first 24 h period, the yield of cyclic carbonate **9c** was determined by ^{1}H NMR spectroscopy, and then another portion of propylene oxide was added to the reaction mixture. This procedure was repeated four times and the catalyst survived for 4 days with only a small loss of its catalytic activity in the final run (Table 4, entries 1–4). After the fourth cycle the propylene carbonate was distilled under reduced pressure and the remaining catalyst again reused with no loss of its catalytic activity (compare Table 3 entry 1 and Table 4 entry 5). The ^{1}H NMR spectrum of complex **3** recovered after this fifth cycle was identical to that of the initial complex. It was also possible to recover the catalyst chromatographically on SiO_2 and reuse it. To further illustrate the stability of the catalyst, two reactions were carried out at the higher temperature of 100 °C (Table 4, entries 6 and 7). Even at this temperature the catalyst could be recovered unchanged (as determined by ^{1}H NMR analysis) and reused without loss of activity.

Table 4. Recyclability of catalyst **3**.[a]

Entry	Cycle	Catalyst concentration [M]	T [°C]	Yield [%]
1	1	0.284	50	100
2	2	0.142	50	100
3	3	0.094	50	100
4	4	0.071	50	85
5	5[b]	0.28	50	75
6	1	0.142	100	100
7	2[c]	0.142	100	100

[a] Reaction conditions: neat **8c** (50 mg, 0.06 mL, 0.86 mmol), 5 MPa CO_2, 24 h, 2 mol% of complex **3** for reactions carried out at 50 °C and 1 mol% of catalyst **3** for reactions carried out at 100 °C. The second and subsequent cycles included the addition of a fresh 50 mg portion of **8c** to the reaction mixture after each 24 h reaction period. [b] Reaction conditions: neat **8c** (50 mg, 0.06 mL, 0.86 mmol), complex **3** recovered from the experiment of entry 4 following distillation of **9c**, 5 MPa CO_2, 3 h. [c] Reaction conditions: neat **8c** (50 mg, 0.06 mL, 0.86 mmol), complex **3** recovered from the experiment of entry 6 following distillation of **9c**, 5 MPa CO_2, 24 h.

Conclusions

The stereochemically inert cationic complexes **1**–**7** were found to be catalytically active in cyclic carbonate synthesis starting from carbon dioxide and epoxides. The activity of the one component bifunctional system originated from the hydrogen-bond donating ability of the coordinated ligand and nucleophilic participation of the counter anion. The complexes are robust, simple to prepare, and easy to recycle.

Experimental Section

Commercial reagents were used as received unless stated otherwise. Column chromatography was performed using Silica Gel Kieselgel 60 (Merck). ^{1}H NMR and ^{13}C NMR spectra were recorded on Bruker Avance 300 and Bruker Avance III-400 (operating at 300 and 400 MHz for protons, respectively) spectrometers. Optical rotations were measured on a PerkinElmer 341 polarimeter in a 5 cm cell. Elemental analysis was performed by the Laboratory of Elemental Analysis INEOS RAS. X-ray fluorescence data was measured on a VRA-30 spectrometer.

Complex 1: Prepared as reported in the literature.[5] ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.03 (s, 2H), 7.17 (d, J = 2.4 Hz, 2H), 7.00 (d, J = 2.5 Hz, 2H), 6.49 (s, 2H), 3.94 (t, J = 9.8 Hz, 2H), 2.91 (d, J = 11.1 Hz, 2H), 2.78 (s, 2H), 2.28 (d, J = 9.8 Hz, 2H), 1.93 (d, J = 11.3 Hz, 4H), 1.84 (d, J = 13.1 Hz, 2H), 1.77–1.64 (m, 4H), 1.63–1.46 (m, 2H), 1.24 (s, 20H), 0.93 ppm (s, 18H); $[\alpha]_D$ = 2304 (c = 0.00067, MeOH).

Complex 2: A solution of **1** (100 mg, 0.133 mmol) in CH_2Cl_2 (5 mL) was added to a solution of KBr (316 mg, 2.66 mmol) in water (5 mL). The mixture was stirred for 4 h, then the organic layer was separated, dried ($MgSO_4$), and evaporated under reduced pressure to leave complex **2** (92 mg, 87%) as a brown powder. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.02 (s, 2H), 7.15 (s, 2H), 6.98 (s, 2H), 6.13 (s, 2H), 3.99 (s, 2H), 2.90 (d, J = 10.6 Hz, 4H), 2.41 (d, J = 12.0 Hz, 2H), 2.01–1.51 (m, 12H), 1.21 (s, 22H), 0.91 ppm (s, 18H); ^{13}C NMR (101 MHz, $CDCl_3$): δ = 162.37, 161.89, 142.20, 136.32, 129.84, 128.55, 117.94, 70.29, 58.27, 35.07, 33.74, 31.45, 31.31, 30.67, 29.48, 25.36, 23.65 ppm; X-ray fluorescence data: Co/Br = 1/1, no Cl was detected; $[\alpha]_D$ = 1630 (c = 0.00063, MeOH).

Complex 3: A solution of **1** (100 mg, 0.133 mmol) in CH_2Cl_2 (5 mL) was added to a solution of KI (440 mg, 2.66 mmol) in water (5 mL). The mixture was stirred for 4 h, then the organic layer was separated, dried ($MgSO_4$), and evaporated under reduced pressure to leave complex **3** (97 mg, 90%) as a brown powder. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.07 (s, 2H), 7.18 (d, J = 2.0 Hz, 2H), 7.03 (d, J = 1.9 Hz, 2H), 5.55 (t, J = 10.2 Hz, 2H), 4.12 (t, J = 9.5 Hz, 2H), 2.98 (s, 4H), 2.53 (d, J = 12.3 Hz, 2H), 2.06–1.49 (m, 10H), 1.25 (s, 22H), 0.94 ppm (s, 18H); ^{13}C NMR (101 MHz, $CDCl_3$): δ = 162.59, 161.74, 142.14, 136.32, 129.83, 128.60, 117.98, 70.35, 58.39, 35.06, 33.75, 31.40, 31.33, 30.80, 29.51, 25.44, 23.64 ppm; X-ray fluorescence data: Co/I = 1/1, no Cl was detected; $[\alpha]_D$ = 1940 (c = 0.0063, MeOH);

Complex 4: A solution of **1** (100 mg, 0.133 mmol) in CH_2Cl_2 (5 mL) was added to a solution of benzoic acid (324 mg, 2.66 mmol) and Na_2CO_3 (140 mg, 1.33 mmol). The mixture was stirred for 4 h, then the organic layer was separated, dried ($MgSO_4$), and evaporated under reduced pressure to leave complex **4** (75 mg, 67%) as a brown powder. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.01 (s, 4H), 7.40 (t, J = 18.8 Hz, 5H), 7.15 (d, J = 2.3 Hz, 2H), 6.98 (d, J = 2.3 Hz, 2H), 4.10 (t, J = 10.0 Hz, 2H), 2.87 (d, J = 9.6 Hz, 2H), 2.80–2.62 (m, 2H), 1.78 (m, 9H), 1.46–1.38 (m, 3H), 1.23 (s, 22H), 0.93 ppm (s, 18H); ^{13}C NMR (101 MHz, $CDCl_3$): δ = 157.54, 157.22, 137.28, 130.99, 125.33, 124.55, 124.65, 123.75, 122.98, 113.50, 65.61, 53.54, 30.34, 28.98, 26.84, 26.61, 25.74, 24.72, 20.61, 19.01 ppm; X-ray fluorescence data: no Cl was detected; $[\alpha]_D$ = 1992 (c = 0.00059, MeOH).

Complex 5: A solution of **1** (100 mg, 0.133 mmol) in CH_2Cl_2 (5 mL) was added to a solution of *p*-toluene sulfonic acid (456 mg, 2.66 mmol) and Na_2CO_3 (140 mg, 1.33 mmol). The mixture was stirred for 4 h, then the organic layer was separated, dried ($MgSO_4$), and evaporated under reduced pressure to leave complex **5** (92 mg, 78%) as a brown powder. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.04 (s, 2H), 7.79 (d, J = 7.8 Hz, 2H), 7.20 (d, J = 7.5 Hz, 4H), 7.01 (s, 2H), 5.53 (d, J = 9.7 Hz, 2H), 3.91 (t, J = 9.4 Hz, 2H), 2.93 (d, J = 9.7 Hz, 2H), 2.78 (d, J = 10.6 Hz, 2H), 2.38 (s, 3H), 2.14–1.60 (m, 10H), 1.51 (d, J = 12.9 Hz, 2H), 1.27 (d, J = 10.0 Hz, 22H), 0.95 ppm (s, 18H); X-ray fluorescence data: Co/S = 1/1, no Cl was detected; $[\alpha]_D$ = 1674 (c = 0.00037, MeOH).

Complex 6: A solution of **1** (100 mg, 0.133 mmol) in MeOH (5 mL) was added to a solution of terephthalic acid (11 mg, 0.065 mmol) and silver(I) oxide (15 mg, 0.065 mmol) in MeOH (5 mL). The solution was stirred for 4 h, then precipitate was filtered and the filtrate was evaporated under reduced pressure to leave complex **6** (62 mg, 58%) as a brown powder. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.04 (s, 4H), 7.18 (s, 4H), 7.01 (s, 2H), 4.08 (s, 2H), 2.83 (m, 2H), 2.73 (s, 1H), 2.04–1.56 (m, 14H), 1.47 (d, J = 11.8 Hz, 2H), 1.25 (s, 20H), 0.96 ppm (s, 18H); ^{13}C NMR (101 MHz, $CDCl_3$): δ = 162.20, 162.04, 142.05, 135.84, 129.47, 128.50, 118.19, 70.35, 58.25, 35.08, 33.72, 31.62, 31.35, 30.49, 29.47, 25.34, 23.73 ppm; X-ray fluorescence data: no Cl was detected; $[\alpha]_D$ = 2034 (c = 0.000625, MeOH); Calculated for $C_{92}H_{136}Co_2N_8O_8.3H_2O$: C, 66.81; H. 8.65; N, 6.77%; Found: C, 66.88; H, 8.88; N, 6.60.

Complex 7: A solution of **1** (100 mg, 0.133 mmol) in MeOH (5 mL) was added to a solution of 2,5-naphthalenedisulfonic acid (19 mg, 0.065 mmol) and silver(I) oxide (15 mg, 0.065 mmol) in methanol (5 mL). The solution was stirred for 4 h, then precipitate was filtered and the filtrate was evaporated under reduced pressure to leave complex **7** (73 mg, 64%) as a brown powder. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.43 (s, 1H), 8.04 (s, 2H), 8.00 (d, J = 8.5 Hz, 1H), 7.91 (d, J = 8.3 Hz, 1H), 7.18 (s, 2H), 7.01 (s, 2H), 5.37 (s, 2H), 3.87 (s, 2H), 2.95–2.69 (m, 4H), 2.04–1.33 (m, 16H), 1.25 (s, 18H),

0.94 ppm (s, 18H); ^{13}C NMR (101 MHz, $CDCl_3$): δ = 162.40, 161.90, 142.18, 136.27, 132.99, 129.79, 129.04, 128.53, 125.34, 124.12, 118.00, 118.00, 70.34, 58.15, 35.06, 33.74, 31.49, 31.32, 30.61, 29.48, 25.27, 23.58 ppm; X-ray fluorescence data: Co/S = 1/1, no Cl was detected; $[\alpha]_D$ = 1567 (c = 0.00059, MeOH); Calculated for $C_{94}H_{138}Co_2N_8O_{10}S_2.5H_2O$: C, 62.30; H. 8.23; N, 6.18%; Found: C, 62.34; H, 7.69; N, 6.21.

Synthesis of cyclic carbonates: All reactions were carried out in autoclaves using the conditions specified in Tables 1–4. After completion of the experiment, the reaction mixture was analyzed by ^{1}H NMR spectroscopy and passed through a pad of silica to separate the catalyst. Column chromatography (SiO_2, first hexane, then EtOAc/hexane, 1:4) was used to separate the starting material and product. For substrate screening, the yield was determined by ^{1}H NMR spectroscopy with the catalyst *tert*-butyl groups (δ = 0.94 ppm) serving as the internal standard. For the catalyst recyclability study, each new portion of propylene oxide was added to the reaction mixture after finishing the reaction (without any additional purification). For the catalyst recyclability study with styrene oxide column chromatography (SiO_2, first hexane, then EtOAc/hexane 1:4, then methanol) was used to separate the catalyst from cyclic carbonate.

Styrene carbonate **9a**:[38] ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.44–7.32 (m, 5H), 5.66 (t, J = 8.0 Hz, 1H), 4.82–4.73 (m, 1H), 4.37–4.26 ppm (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$): δ = 155.00, 135.88, 129.80, 129.31, 126.00, 78.11, 71.28 ppm.

3-Phenoxypropylene carbonate **9b**:[38] ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.37–6.84 (m, 5H), 5.08–4.94 (m, 1H), 4.63–4.46 (m, 2H), 4.30–4.06 ppm (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$): δ = 157.83, 154.76, 129.78, 122.08, 114.69, 74.20, 66.95, 66.32 ppm.

Propylene carbonate **9c**:[38] ^{1}H NMR (400 MHz, $CDCl_3$): δ = 4.87 (dd, J = 13.7, 7.3 Hz, 1H), 4.57 (t, J = 8.1 Hz, 1H), 4.04 (dd, J = 8.3, 7.3 Hz, 1H), 1.50 ppm (d, J = 6.3 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ = 155.22, 73.74, 70.78, 19.45 ppm.

3-Chloropropylene carbonate **9d**:[38] ^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.04–4.95 (m, 1H), 4.62 (t J 8.6 Hz, 1H), 4.41 (dd J 8.9, 5.7 Hz, 1H), 3.82–3.67 ppm (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$): δ = 154.49, 74.48, 67.06, 44.03 ppm.

4-Chlorostyrene carbonate **9e**:[38] ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.40 (d, J = 8.5 Hz, 2H), 7.31 (d, J = 8.5 Hz, 2H), 5.68 (t, J = 8.0 Hz, 1H), 4.81 (t, J = 8.4 Hz, 1H), 4.29 ppm (dd, J = 8.6, 7.9 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$): δ = 154.65, 135.85, 134.35, 129.59, 127.37, 77.34, 71.10 ppm.

Cyclohexene carbonate **9f** (cis-isomer):[37] ^{1}H NMR (400 MHz, $CDCl_3$): δ = 4.56–4.53 (m, 2H), 1.91–2.03 (m, 4H), 1.57–1.70 (m, 2H), 1.32 ppm (m, 2H).

Experimental procedure for cyclic carbonate 9g: The autoclave was charged with 0.1 equivalent of catalyst **3** and 1.0 equivalenth of epoxide **8g** dissolved in acetonitrile or toluene (0.1 mL). The reactor was pressurized with CO_2 to 5 MPa, heated to 50 °C, and stirred for 24 h. Subsequently, the reactor was cooled to ambient temperature and CO_2 was released slowly. The reaction mixture was filtered over SiO_2 (CH_2Cl_2), and the volatiles were removed under reduced pressure. HPLC was used to determine the enantiomeric excess of the starting epoxide after the reaction.

4-Benzoyl-5-phenyl-1,3-dioxolan-2-one **9g** (trans-isomer):[36] ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.96 (d, J = 7.5 Hz, 2H), 7.66 (t, J = 7.5 Hz, 1H), 7.55–7.43 (m, 7H), 5.98 (d, J = 6.2 Hz, 1H), 5.60 ppm (d, J = 6.2 Hz, 1H).

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