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Enantioselective Aldol Reactions in Water by a Proline-Derived Cryptand and Fixation of CO_2 by Its Exocyclic Co(II) Complex

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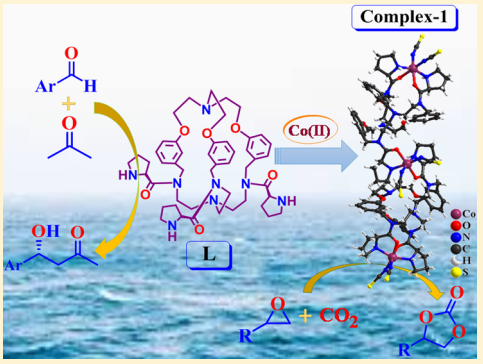
Supporting Information

ABSTRACT: The secondary amine donors present in the bridges of a laterally nonsymmetric oxa-aza cryptand have been derivatized with L-proline to obtain the chiral cryptand **L**. The cryptand **L** efficiently catalyzed aldol reactions in water with up to 75% ee. On reacting with Co(II) perchlorate in the presence of KSCN, **L** readily formed the trinuclear complex $\{[Co_3(\mathbf{L})_2(NCS)_6]\cdot(15CH_3CN)(5acetone)(6H_2O)\}$ (**1**). The complex **1** in combination with the cocatalyst tetrabutylammonium bromide (TBAB) formed an efficient catalytic system in the synthesis of cyclic carbonates from CO_2 and epoxides at room temperature and atmospheric pressure.



INTRODUCTION

Macrobicyclic cryptands have received steady attention from researchers during the past few decades due to their ability of selective and efficient ion binding.[1] Additionally, cryptands have such structural features that render them important components in supramolecular chemistry with a wide range of applications in chemical, biological, and material sciences.[2] Laterally nonsymmetric oxa-aza cryptands incorporating secondary amines in the bridges constitute an important class of cryptands.[3] The secondary amines present in the bridges can be easily derivatized with different groups forming new compounds endowed with various properties.[4] The employment of a chiral functional group in the cryptand to transform it to a chiral cryptand is quite fascinating and expands its scope for several new applications such as asymmetric organic transformations, chiral recognition, and so on. Herein, we present the synthesis of the tris-L-proline derivative (**L**; Scheme 1) of an oxa-aza cryptand. L-Proline is a naturally occurring inexpensive chiral amino acid and can catalyze many organic reactions.[5] The direct intermolecular aldol reaction is an important carbon−carbon bond forming reaction with highly efficient atom economy. Following the lead provided by List[6] and Barbas,[7] L-proline and its derivatives have been used by several groups[8−11] for enantioselective intermolecular aldol reactions. A number of L-prolinamides[12] have also been used for the purpose. However, it should be emphasized that low loading of the catalyst and a wide range of substrates for enantioselective aldol reactions in aqueous medium present an important synthetic challenge. In this study, we demonstrate the scope of the tris-proline derivative **L** in asymmetric intermolecular aldol reactions in water.

Furthermore, cryptand **L** reacts with Co(II) in the presence of KSCN at room temperature to form a trinuclear complex, $\{[Co_3(\mathbf{L})_2(NCS)_6]\cdot(15CH_3CN)(5acetone)(6H_2O)\}$ (**1**; Scheme 1).

Complex **1** has been used to catalyze the reaction between epoxides and CO_2 gas at atmospheric pressure and room temperature in solvent-free condition, to generate cyclic carbonates. This process not only removes CO_2 from the atmosphere but also produces cyclic carbonates that are key intermediates in the synthesis of a variety of compounds of pharmaceutical relevance. Besides, they are useful as polar aprotic solvents, electrolytes for lithium ion batteries, and so on.[13,14] Cyclic carbonates are also used as constituents of oils and paints and as monomers for the synthesis of polycarbonates[15] and polyurethanes[16] since they can undergo ring-opening polymerization. Our approach benefits from eliminating the commonly used highly toxic carbonylation reagent phosgene and is 100% atom economical, making it a highly desirable transformation. To date, there are several catalysts reported for the coupling of CO_2 with epoxides, comprising simple alkali metal salts, phosphines, main group metal complexes, transition metal complexes, porous metal oxides, and MOFs.[17−29] However, most of them suffer from low catalyst stability/reactivity, air sensitivity, the need for cosolvent, or the requirement of high pressure and/or high temperature. However, several salen-Co/Al complexes have been identified as homogeneous catalysts in the formation of cyclic carbonate from CO_2 and epoxides at relatively low temperatures and pressures.[30−33] If the utilization of cyclic carbonates is to be substantially increased, then new commercially viable catalysts and processes which operate at

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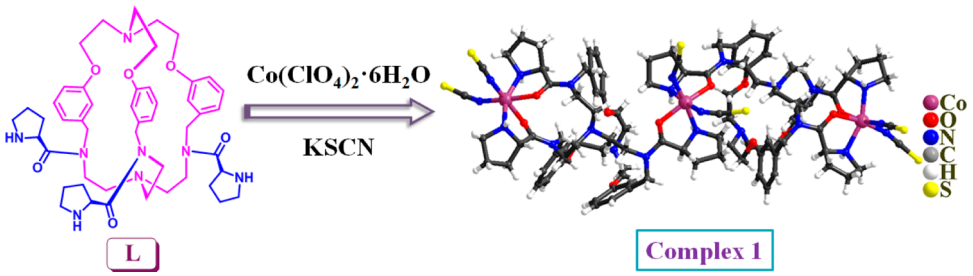
Scheme 1. Synthesis of Complex 1 from the Tris-Proline Derivative L



close to atmospheric pressure and near room temperature are required.

RESULTS AND DISCUSSION

Structural Characterization. The compound **L** was synthesized via the reaction of *N*-(*tert*-butoxycarbonyl)-L-proline with the cryptand. Also, the complex **1** could be synthesized readily by reacting Co(II) perchlorate and **L** in the presence of KSCN. Single-crystal X-ray structure determination revealed that **1** crystallized in the trigonal chiral space group $P3_221$ (Table S1). The asymmetric unit consisted of one **L**, one Co(II) with full occupancy, and another Co(II) with half occupancy, besides three thiocyanate anions and lattice solvent molecules. The lattice solvent molecules were highly disordered, and their content was established from thermogravimetric weight-loss analysis (TGA), IR spectra, and elemental analysis. The values are in good agreement with the PLATON-calculated[34] solvent-accessible void volume, which is found to be 39% of the unit-cell volume. The structure showed two **L** and three Co(II) ions (Figure 1) where

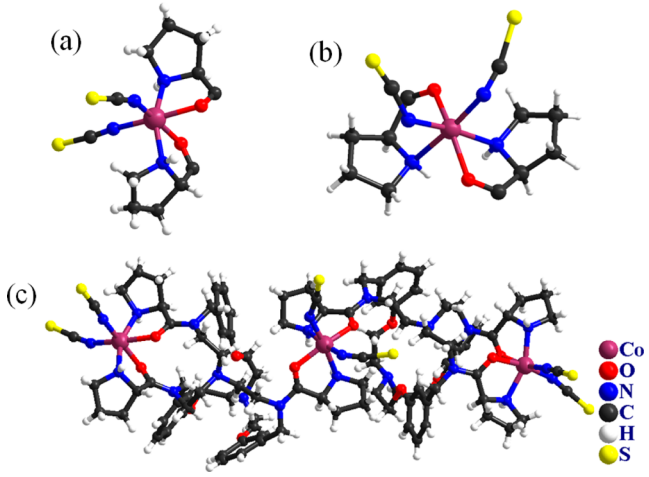


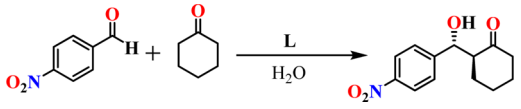
Figure 1. Coordination environment around (a) each terminal Co(II) and (b) the middle Co(II) ion. (c) Overall structure of the complex **1**.

each Co(II) ion exhibited distorted octahedral geometry. The two terminal metal ions had ligation from two proline groups attached to the same cryptand moiety (Figure 1a) and additionally two N atoms of two SCN^- ions.

The middle Co(II) ion was bonded to two such cryptand units through the third proline group besides two N-bonded SCN^- anions (Figure 1b). The Co−N and Co−O bond distances (Table S2) were found to be within normal ranges.[35,36] The UV−vis spectrum (Figure S1) of the complex **1** in MeCN shows three ligand field bands at 620, 535, and 495 nm consistent with octahedral Co(II) complex with the CoN_4O_2 chromophore.[37,38] The CD spectrum (Figure S2) of **L** in CH_3CN showed negative Cotton effect at 280 nm and positive Cotton effect at 275 nm while the complex **1** showed negative Cotton effect at 295 nm and positive Cotton effect at 272 nm and also a monosignate CD signal at 494 nm.

Aldol Reactions Catalyzed by L. The enantioselective aldol reaction is an important C−C bond forming reaction. Most of the prior studies on this reaction were done with large amounts of (10.0 mol %) catalyst loading. Thus, there is a demand for efficient catalysts, which can function at a lower loading without affecting much of the enantiopurity and the duration of reaction. On the other hand, due to increasing environmental awareness, water should be the ideal alternative medium for this reaction. It was found that **L** acted as a very efficient organocatalyst for enantioselective aldol reactions in an aqueous medium. Initially, the aldol reaction of cyclohexanone (0.3 mmol) with 4-nitrobenzaldehyde (0.2 mmol) was studied by using different loading of the catalyst **L** (5.0−0.2 mol %) in 1 mL of water (Table 1). It was observed that, with 5.0 mol %

Table 1. Optimization of Reaction Conditions[a]



entry	catalyst loading (mol %)	temp (°C)	time (h)	% yield[b]	*anti*/*syn*[c]	% ee[d]
1	5.0	rt	2	94	62:38	75
2	2.0	rt	2	89	59:41	72
3	1.0	rt	2	87	66:33	72
4	0.5	rt	4	86	57:43	69
5	0.2	rt	5	84	52:48	68
6	0.2	0	8	78	68:32	63
7	0.0	rt	24	trace		

[a]Reaction conditions: aldehyde (0.2 mmol), cyclohexanone (0.3 mmol) in 1 mL of H_2O. [b]Yields of isolated products after silica gel column chromatography. [c]Diastereoselectivities were determined by ^1H NMR analysis of the crude rection mixture. [d]The ee's were determined by HPLC using chiral columns.

of the catalyst in water at room temperature, the reaction was almost complete in 2 h and the product was obtained in 94% yield with 75% ee (Table 1, entry 1). Upon gradually reducing the catalyst loading up to 0.2 mol %, the reaction proceeded smoothly but required a little longer time for completion (5 h,Table 1, entry 5). In this particular case, we could get the corresponding product with only up to 68% ee. Further, on lowering the temperature to 0 °C it was observed that the enantioselectivity was slighty reduced to 63% (Table 1, entry 6). Finally, the use of a higher loading of catalyst in the reaction

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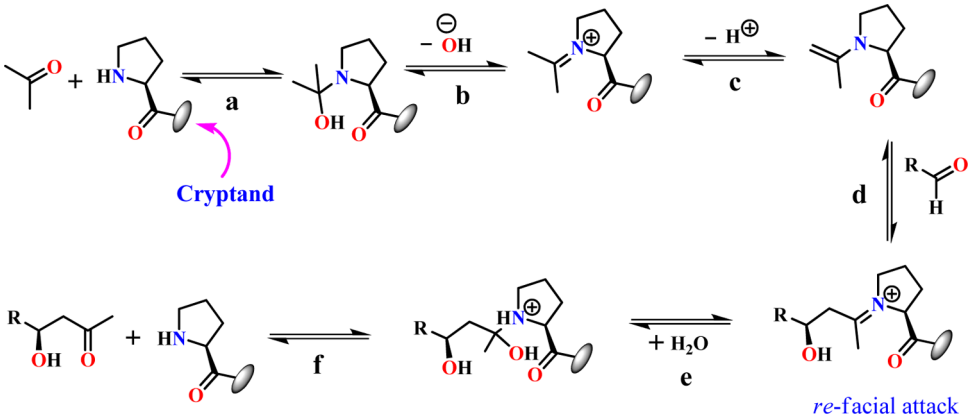
Table 2. Aldol Reaction of Various Substrates Using Organocatalyst L

Entry	Catalyst[e]	ArCHO	Ketone/Aldehyde	% Yield[f]	% ee[g]	*anti/syn*[h]
1	L	4-$NO_2C_6H_4$		87	72(*anti*); 32(*syn*)	66:33
2	L	3-$NO_2C_6H_4$		83	28 (*anti*); ND (*syn*)[i]	93:07
3	L	2-$NO_2C_6H_4$		75	63 (*anti*); 98 (*syn*)	69:31
4	L	4-FC_6H_4		77	30 (*anti*); 15 (*syn*)	96:4
5	L	Ph		65	25 (*anti*)	90:10
6	L	4-$NO_2C_6H_4$		85	17	-
7	L	4-$NO_2C_6H_4$		88	15 (*anti*); 98 (*syn*)	29:71
8	L	4-$NO_2C_6H_4$		35	-	-
9	L-Proline	4-$NO_2C_6H_4$		81	44 (*anti*)	53:47

[e]Catalyst 1.0 mol %, water medium. [f]Isolated yields after silica gel chromatography. [g]The ee's were determined by HPLC using chiral columns. [h]Diastereoselectivities were determined by ^{1}H NMR analysis of thecrude reaction mixture. [i]Enantiomeric excess could not be determined by chiral HPLC analysis.

Scheme 2. Proposed Enamine Mechanism of the L Catalyzed Asymmetric Aldol Reaction



with 4-nitrobenzaldehyde with a large excess of cyclohexanone (3 equiv) led to the formation of the final product quantitatively.

Using the optimized reaction conditions, it was extended to other substrates using 1.0 mol % of the catalyst, **L**. A variety of aromatic aldehydes were tested for the aldol reactions (Table 2). For the electon-deficient aromatic aldehydes, the reaction proceeded smoothly (Table 2, entries 1–4). For the neutral aromatic aldehyde, the reaction needed a longer time (12 h), and lower isolated yield was obtained (Table 2, entry 5). Reactions were not successful with electon-rich aromatic aldehydes. For most of the substrates, the aldol products were formed as the major product with excellent yields. Other ketones were also used under the same conditions, and the aldol products were obtained in good yields (Table 2, entries 6–8). In the case of acetaldehyde (Table 2, entry 8),the yield was lowest (35%) because the enamine intermediate might attack the carbonyl group of acetaldehyde in addition to that of 4-nitrobenzaldehyde. In this particular case, the aldol-dehydratation product was major. The desired aldol products were confirmed by the ^{1}H and ^{13}C NMR, IR, and ESI-MS analyses (Figures S3–S42).

We assumed that the asymmetric aldol reactions occurred via an enamine mechanism[6] (Scheme 2). This catalyst might facilitate each individual step, including the nucleophilic attack of the amino group (a), the dehydroxylation of the carbinol amine intermediate (b), the deprotonation of the iminium species (c), the carbon–carbon bond forming step (d), and both steps of the hydrolysis of the iminium–aldol intermediate (e and f).

Low catalyst loading, less reaction time, and water as reaction medium are the key aspects of the catalyst, **L**. Though the L-proline derived chiral catalysts reported by Wang et al.,[39] Wu et al.,[8] and Zhao et al.[40] showed high catalytic activity, they suffer from the use of higher loading of the catalyst (>10 mol %) with longer reaction time (>24 h). Several other groups also showed the same reaction using a catalyst loading of as high as 20 or 30 mol % to achieve a good isolated yield of the aldol product.[6,41−45]

Synthesis of Cyclic Carbonates from Epoxides and CO_2. There is considerable current interest to develop novel technologies that allow the synthesis of cyclic carbonates from CO_2 and reactive epoxides under more economic conditions, thus reducing both the cost and greenhouse gas emissions. In this context, complex **1** was tested as a catalyst for the

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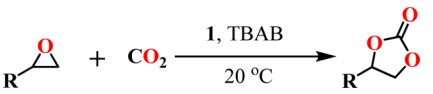
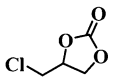
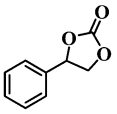
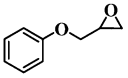
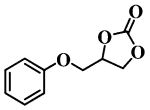
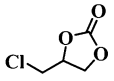
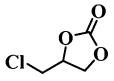
Table 3. Coupling of Various Epoxides with CO_2 at Atmospheric Pressure Using 1[j]



Entry	Epoxide	Catalyst	Co-catalyst	Time (h)	Cyclic Carbonate[k]	Yield (%)[l]
1		1	TBAB	24		48
2		1	TBAB	12		43[m]
3		1	TBAB	24		32
4		1	TBAB	24		49
5		1	None	48		6
6		None	TBAB	48		11

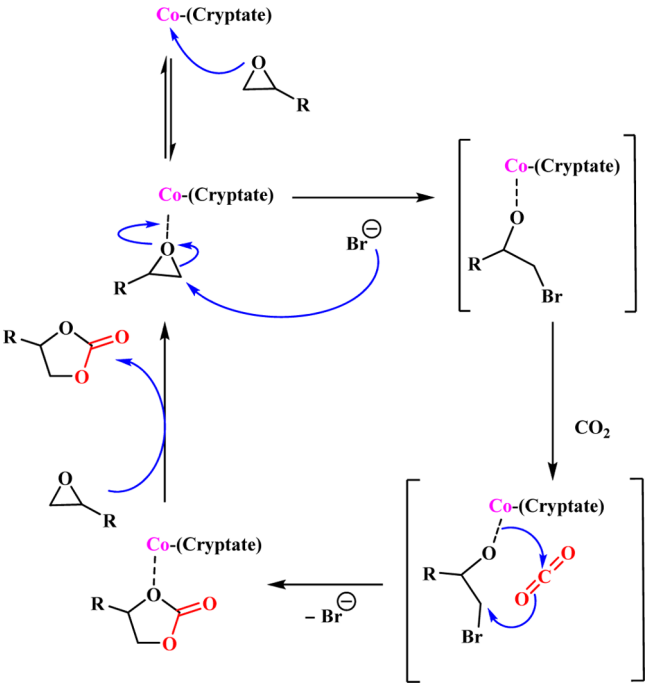
[j]Reactions were carried out in a 10 mL two-necked round-bottom flask at room temperature with CO_2 bubbling. Epoxide (1.0 mL, 1 equiv), complex **1** (0.0005 equiv), TBAB (0.05 equiv). No solvent was added. [k]Selectivity for cyclic carbonate in all systems is 100% based on ^{1}H NMR spectroscopic analysis. [l]Yield of the isolated product obtained after column chromatography. [m]To avoid the loss of volatile propylene oxide caused by CO_2 flow, the reaction was carried out at 0 °C with sluggish CO_2 flow.

cycloaddition of various epoxides and CO_2 under mild conditions to yield cyclic carbonates. A combination of **1** and TBAB showed the superior catalytic activity for the cycloaddition reaction of CO_2 to epichlorohydrin to yield the corresponding cyclic carbonate in good yields (48%) under 1 atm of CO_2 at room temperature, within 24 h (Table 3, entry 1). Furthermore, in the absence of **1**, the same reaction catalyzed by the cocatalyst TBAB alone gave 11% yield (Table 3, entry 6). Yet, when the catalyst **1** and cocatalyst TBAB were combined together, a facile reaction occurred (Table 3, entry 1). This result is notably better than the results already described by Lu et al.[46] (41% yield), Jing et al.[47] (16.9% conversion), and Brandenburg et al.[48] (up to 40% yield using propylene oxide as substrate) under similar experimental conditions using multichiral Co(III) complexes.

Using the same reaction conditions, a series of epoxides could be converted to the corresponding cyclic carbonates with good yields (Table 3). In case of phenyl glycidyl ether (Table 3, entry 4), 1.0 mL of ethyl acetate was added to prevent the solidification of the cyclic carbonate. The desired carbonates were confirmed by the ^{1}H and ^{13}C NMR, IR, and ESI-MS analyses (Figures S43−S62). Notably, the products were nearly racemic (Figures S55, S56, S61, and S62), indicating the influence of the chirality of complex **1** to be minimal.

The plausible mechanism (Scheme 3) for this chemical fixation reaction was similar to those by the salen Co(III)X complexes as catalysts and quaternary ammonium salts as cocatalysts.[49] The complex **1** promoted the ring-opening of the

Scheme 3. Proposed Mechanism for the Complex 1 Catalyzed Carbon Dioxide Fixation into Epoxide in the Presence of TBAB



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epoxide with the help of Bu_4NBr to afford a cobalt-bound alkoxide in an S_N2-type reaction. The subsequent addition of CO_2 to the ring-opened epoxide was preferred by the presence of Bu_4NBr, which stabilized the polarized intermediate resulting in a metal carbonate capable of cyclization to form cyclic carbonate with the regeneration of the catalyst.

CONCLUSIONS

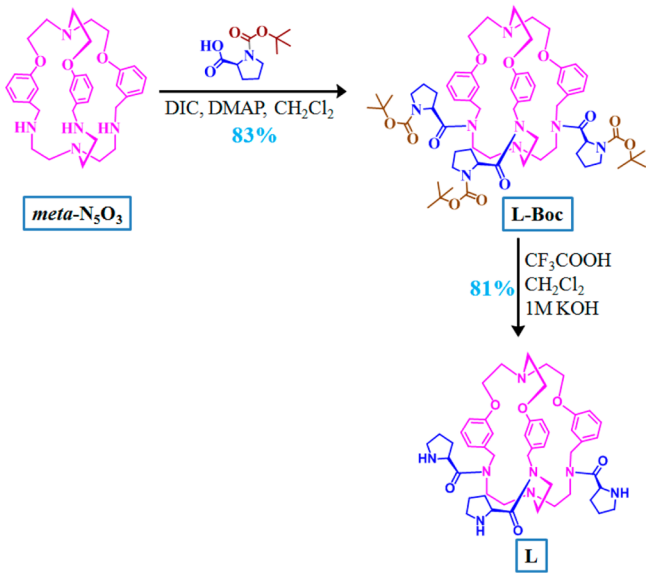
We have constructed a chiral aza-oxa cryptand derivatized with L-proline. The metal free cryptand **L** acts as a chiral organocatalyst and efficiently catalyzed the direct aldol reaction between aldehydes and carbonyl compounds in water in good yields. The Co(II) complex of the cryptand **L** in combination with the cocatalyst Bu_4NBr acts as a highly efficient catalytic system for the synthesis of cyclic carbonates from CO_2 and epoxides under mild reaction conditions. In view of the global industrial and academic interest in this reaction, it is likely that further significant developments in catalyst and process design will occur in the next few years, thus allowing cyclic carbonate synthesis as one of the technologies which can be used to help to limit global CO_2 emissions.

EXPERIMENTAL SECTION

The details of materials, instruments, and single-crystal X-ray study are given in the Supporting Information.

Synthesis of L. The *meta*-N_5O_3 cryptand was synthesized following a well-established procedure in our laboratory.[50] Synthesis of the tris-proline derivative (**L**) was carried out following the procedure shown in Scheme 4.

Scheme 4. Synthetic Scheme for L



Synthesis of L-Boc. *N*-(*tert*-Butoxycarbonyl)-L-proline (1.5 g, 6.98 mmol), 1,3-diisopropylcarbodiimide (DIC; 1.4 mL, 8.93 mmol), and 4-dimethylaminopyridine (DMAP; 100.0 mg) were dissolved in CH_2Cl_2 (50.0 mL) and then added dropwise to a stirred solution of the cryptand (1.0 g, 1.78 mmol) dissolved in CH_2Cl_2 (50.0 mL) at 5 °C. After complete addition, the reaction mixture was stirred at 45 °C for 48 h. The reaction mixture was then evaporated to dryness and purified by column chromatography (elution with 5% methanol in $CHCl_3$) using silica gel (200 mesh) to obtain **L-Boc** as a white solid (yield: 1.7 g, 83%); mp 84−85 °C. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, $Si(CH_3)_4$): δ = 7.17−6.49 (m, 12H), 4.63−4.40 (m, 8H), 4.01−3.93 (m, 6H), 3.54−3.42 (m, 9H), 3.15−3.05 (m, 7H), 2.80−2.33 (m, 11H), 2.09−1.66 (m, 9H), 1.41 (s, 27H) ppm (Figure S63). ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C, $Si(CH_3)_4$): δ = 23.5, 23.7, 24.4, 28.5, 28.6, 28.7, 29.8, 30.3, 30.9, 31.5, 46.4, 46.9, 47.1, 56.2, 56.6, 59.1, 59.4, 68.1, 79.4, 79.5, 79.8, 80.1, 81.4, 113.9, 129.9, 154.4, 154.5, 158.8, 159.8, 172.9, 173.3, 173.5 ppm (Figure S64). ESI-MS (m/z): 1151 (97%) [M + H], 526 (100%) [M/2 + H] (Figure S65). Anal. Calcd for $C_{63}H_{90}N_8O_{12}$: C, 65.72; H, 7.88; N, 9.73%. Found: C, 65.97; H, 8.04; N, 9.79%.

Synthesis of L. L-Boc (1.5 g, 1.30 mmol) was suspended in CH_2Cl_2 (50.0 mL) and cooled in an ice bath with stirring. Exactly 15.0 mL of TFA was added, and the mixture was stirred for 30 min. After warming up to room temperature, the stirring continued for 24 h. All of the solvent was removed *in vacuo*, the mixture cooled in an ice bath, and 1 M KOH was added to maintain a pH of 7−8. The product was extracted with CH_2Cl_2 and washed with water. The organic layer, after drying over anhydrous Na_2SO_4, was completely dried in a rotary evaporator and then under high vacuum to obtain **L** as gray solid (yield: 900 mg, 81%); mp 77−78 °C. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, $Si(CH_3)_4$): δ = 7.17−7.10 (m, 3H), 6.75−6.50 (m, 9H), 4.48−4.24 (m, 3H), 4.03−3.84 (m, 8H), 3.15−3.05 (m, 20H), 2.85−2.77 (m, 6H), 2.41−2.30 (m, 4H), 2.01−1.56 (m, 9H), 1.22 (br s, 4H) ppm (Figure S66). ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C, $Si(CH_3)_4$): δ = 26.6, 26.7, 29.8, 31.3, 31.4, 44.9, 45.4, 47.6, 47.7, 51.4, 51.7, 52.3, 52.4, 56.9, 58.1, 58.4, 68.5, 68.7, 68.9, 113.1, 113.3, 113.9, 114.1, 114.6, 114.9, 118.7, 119.3, 129.9, 130.0, 137.8, 157.1, 159.6, 159.7, 174.1 ppm (Figure S67). ESI-MS (m/z): 851 (32%) [M + H], 426 (68%) [M/2 + H] (Figure S68). FT-IR (KBr pellets, cm^{-1}): 3425 (broad), 2924 (s), 2853 (s), 1639 (s), 1602 (s), 1446 (s), 1263 (s), 1156 (s), 1043 (s), 782 (s) (Figure S69). Anal. Calcd for $C_{48}H_{66}N_8O_6$: C, 67.74; H, 7.82; N, 13.17%. Found: C, 67.92; H, 7.98; N, 13.24%.

Synthesis of {[Co_3(L)$_2$(NCS)$_6$]·(15CH_3CN)(5acetone)(6H_2O)} (1). To a solution of **L** (850.0 mg, 0.1 mmol) in 5.0 mL of MeOH was added Co(II) perchlorate (370.0 mg, 0.1 mmol) in 5.0 mL of MeOH. A light pink solid precipitated immediately and was collected by filtration, washed with MeOH, and air-dried. It was taken in 4.0 mL of MeCN and 1.0 mL of acetone and treated with KSCN (100.0 mg, 0.1 mmol). Upon addition of KSCN, the color of the solution changed to dark pink. This solution was filtered, and the filtrate was allowed to evaporate slowly at room temperature. After 2 days, pink crystals appeared. Yield: 68%. FT-IR (KBr pellets, cm^{-1}): 3453 (broad), 2928 (s), 2872 (s), 2067 (s), 1602 (s), 1489 (s), 1445 (s), 1267 (s), 1157 (s), 1042 (s), 749 (s) (Figure S69). Anal. Calcd for $C_{147}H_{219}Co_3N_{37}O_{23}S_6$: C, 54.46; H, 6.81; N, 15.99%. Found: C, 54.85; H, 6.97; N, 16.13%. A similar result was obtained when Co(II) picrate was used in place of the perchlorate salt.

Caution! *The perchlorate/picrate salts must be handled with care as they are potential explosives in the presence of organic compounds.*

General Procedure for the Aldol Condensation Reaction. An aldehyde (0.2 mmol) was added to a mixture of ketone (0.3 mmol) and the organocatalyst **L** (1.0 mol %) in water (1.0 mL) at room temperature and stirred. Progress of the reaction was monitored by TLC. After the reaction was over, the reaction mixture was purified by silica gel column chromatography. The enantiomeric excess (ee) of the aldol products was determined by chiral HPLC analysis. Relative and absolute configurations of the products were determined by comparison with the known ^{1}H NMR, chiral HPLC analysis, and optical rotation values. The HPLC data and ^{1}H and ^{13}C NMR, IR, and ESI-MS analyses of all the compounds are given in the Supporting Information (Figures S3−S42).

General Procedure for the Coupling of Epoxides with CO_2. Reactions were carried out in a 10 mL two-necked round-bottom flask at room temperature under CO_2 atmosphere at 1 bar. A mixture of complex **1** (0.0005 equiv), cocatalyst TBAB (0.05 equiv), and an epoxide (1.0 mL, 1 equiv) was stirred. The reaction was allowed to go for a fixed time decided empirically. All cyclic carbonates were isolated by column chromatography and analyzed through ^{1}H and ^{13}C NMR, IR, and ESI-MS spectroscopy (Figures S43−S62).

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■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorgchem.7b02007.

Materials and methods, X-ray structural studies, ESI-MS, IR, CD, and NMR spectra, and HPLC analysis (PDF)

Accession Codes

CCDC 1551085 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

The authors declare no competing financial interest.

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