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Chiral metal-containing ionic liquid: Synthesis and applications in the enantioselective cycloaddition of carbon dioxide to epoxides

SONG YingYing, JIN QianRu, ZHANG SuLing,
JING HuanWang* & ZHU QianQian

State Key Laboratory of Applied Organic Chemistry; College of Chemistry and Chemical Engineering, Lanzhou University, Lanzhou 730000, China

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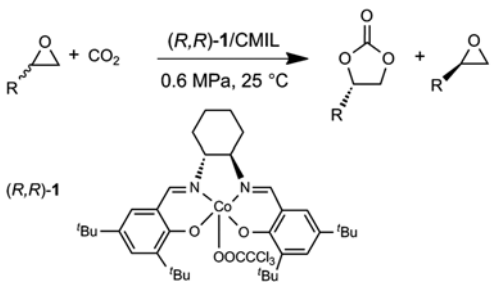
A series of novel chiral metal-containing ionic liquids (CMILs) consisting of the cation of crown ether-chelated potassium/sodium and the anion of chiral amino acids were designed and synthesized. These new CMILs were used to catalyze the enantioselective cycloaddition of epoxides and carbon dioxide incorporating with the salenCo($OOCCCl_3$) to generate corresponding chiral cyclic carbonates under mild conditions. These new catalysts can be recycled at least five times without significant loss of activity and enantioselectivity.

chiral metal-containing ionic liquids, epoxides, carbon dioxide, enantioselective cycloaddition, chiral cyclic carbonates

1 Introduction

Ionic liquids have attracted increasing interests in both academy and industry in view of their particular properties such as excellent thermal and chemical stability, lower vapor pressure and good tunable solubility [1–10]. Their applications have significantly increased in the last decade exemplifying in material synthesis, separation sciences, and reaction media, etc. [5]. Especially, they can be used as catalysts in organic synthesis [11–16]. Even though some ionic liquids have been used as catalysts in the coupling of CO_2 and epoxides [17–21], chiral ionic liquids (CIL) used in enantioselective cycloaddition reactions was only reported once by our group [22]. Due to the fact that few literatures reported enantiomerically pure cyclic carbonates [22–31], new methodologies for the enantioselective cycloaddition of CO_2 to epoxides are still desired in terms of the atom economy and environmentally benign characteristics of this reaction.

Recently, we have designed and synthesized a series of novel chiral salts consisting of natural amino acid anions and crown ether-chelated alkali metal cations. Because the metal-containing ionic liquids (MILs) are different from the classical ionic liquids, we defined MILs as the type of salts with melting points lower than 200 °C. As continuation of our efforts for the synthesis of chiral cyclic carbonates, we report, herein, a new efficient catalyst system of (salen)Co($OOCCCl_3$) and chiral metal-containing ionic liquid (CMIL) for the enantioselective cycloaddition reaction of CO_2 to terminal epoxides (Scheme 1).



Scheme 1 Enantioselective cycloaddition of CO_2 to terminal epoxides.

*Corresponding author (email: hwjing@lzu.edu.cn)

2 Experimental

2.1 Materials

Propylene oxide (PO) was distilled from CaH_2. Other epoxides were purchased from Aldrich and used without further purification. Enantiomeric excess of the resulting cyclic carbonates was determined by chiral GC analysis (Supeclo-DEX series (225) chiral column; injection temperature = 250 °C; detection temperature = 250 °C; 180 °C isothermal) using a Varian CP-3800 gas chromatograph with N_2 as the carry gas. Elemental analyses were carried out on Carioel elemental analyzer.

2.2 Preparation of chiral metal-containing ionic liquids

The preparation of CMILs is a simple reaction. [18-C-6K][L-Thr] was chosen as model to illustrate the preparation procedure. The synthesis of [18-C-6K][L-Thr] was carried out by mixing the 1.1:1:1 molar ratio of L-Threonine, KOH and 18-C-6 in water. The reaction mixture was stirred at room temperature for 24 h and then concentrated under reduced pressure to afford a mixture of ionic liquid and superabundant L-threonine. The mixture was then dispensed into ethanol to precipitate out the unreacted L-threonine. The filtrate was concentrated and dried under vacuum at 80 °C to obtain the desired chiral MIL [18-C-6K][L-Thr] as a white solid. All remaining CMILs were performed employing a procedure analogous to that used to synthesize [18-C-6K][L-Thr].

Characterization of CMILs

[18-C-6K][L-amino acid anion] HRMS (ESI): *m/z*: calcd for [18-C-6K] 303.1204; found: 303.1209. [15-C-5Na][L-amino acid anion] HRMS (ESI): *m/z*: calcd for [15-C-5Na] 243.1203; found: 243.1200.

[18-C-6K][L-Thr]·2.5H_2O

^{1}H NMR (300 MHz, D_2O) δ 1.25 (d, 3H, J = 6.6 Hz, CH_3), 3.17 (d, 1H, J = 6.0 Hz, $NH_2C\underline{H}$), 3.72 (s, 24H, 6 × (CH_2CH_2O)), 4.00 (m, 1H, C<u>H</u>OH) ppm. ^{13}C NMR (100 MHz, D_2O) δ 19.3, 61.9, 69.4, 69.9, 180.1 ppm. Elemental Anal. calcd (%): C 41.19, H 7.99, N 3.00; found: C 41.19, H 7.57, N 2.99.

[15-C-5Na][L-Thr]

^{1}H NMR (300 MHz, D_2O) δ 1.17 (d, 3H, J = 6.3 Hz, CH_3), 3.08 (d, 1H, J = 5.1 Hz, $NH_2C\underline{H}$), 3.64 (s, 20H, 5 × (CH_2CH_2O)), 3.92 (m, 1H, C<u>H</u>OH) ppm. ^{13}C NMR (75 MHz, D_2O) δ 19.4, 61.8, 69.0, 179.4 ppm. Elemental Anal. calcd (%): C 46.53, H 7.81, N 3.88; found: C 46.65, H 7.94, N 3.80.

[18-C-6K]$_2$[L-Asp]·4H_2O

^{1}H NMR (300 MHz, D_2O) δ 2.65 (dd, 1H, J = 8.7 Hz, COOCH(H)), 2.83 (dd, 1H, J = 3.3 Hz, COOCH(H)), 3.68 (s, 48H, 6 × (CH_2CH_2O)), 3.88 (dd, 1H, J = 4.2, 3.6 Hz, $NH_2C\underline{H}$) ppm. ^{13}C NMR (100 MHz, D_2O) δ 36.9, 52.5, 69.9, 174.3, 177.5 ppm. Elemental Anal. calcd (%): C 42.26, H 7.51, N 1.73; found: C 42.34, H 7.24, N 2.03.

[15-C-5Na]$_2$[L-Asp]·H_2O

^{1}H NMR (300 MHz, D_2O) δ 2.60 (dd, 1H, J = 9.0, 9.3 Hz, COOCH(H)), 2.82 (dd, 1H, J = 3.6 Hz, COOCH(H)), 3.73 (s, 40H, 5 × (CH_2CH_2O)), 3.85 (dd, 1H, J = 3.9 Hz, $NH_2C\underline{H}$) ppm. ^{13}C NMR (75 MHz, D_2O) δ 35.3, 51.3 69.5, 173.3, 177.0 ppm. Elemental Anal. calcd (%): C 45.35, H 7.45, N 2.20; found: C 45.24, H 7.18, N 2.03.

[18-C-6K][L-Val]·0.5H_2O

^{1}H NMR (300 MHz, D_2O) δ 0.82 (d, 3H, J = 8.4 Hz, CH_3), 0.92 (d, 3H, J = 6.9 Hz, CH_3), 1.94 (m, 1H, C<u>H</u>(CH_3)$_2$), 3.09 (d, 1H, J = 5.1 Hz, $NH_2C\underline{H}$), 3.65 (s, 24H, 6 × (CH_2CH_2O)) ppm. ^{13}C NMR (100 MHz, D_2O) δ 17.1, 19.2, 31.6, 61.9, 70.0, 182.1 ppm. Elemental Anal. calcd (%): C 47.64, H 8.23, N 3.27; found: C 47.49, H 7.93, N 3.25.

[15-C-5Na][L-Val]·0.8H_2O

^{1}H NMR (300 MHz, D_2O) δ 0.89 (m, 3H, CH_3), 0.97 (m, 3H, CH_3), 1.96 (m, 1H, C<u>H</u>(CH_3)$_2$), 3.10 (d, 1H, J = 8.1 Hz, $NH_2C\underline{H}$), 3.75 (s, 20H, 5 × (CH_2CH_2O)) ppm. ^{13}C NMR (75 MHz, D_2O) δ 16.8, 19.0, 31.3, 61.6, 69.1, 181.4 ppm. Elemental Anal. calcd (%): C 48.20, H 8.52, N 3.75; found: C 47.95, H 8.43, N 3.61.

[18-C-6K]$_2$[L-Cys]·4H_2O

^{1}H NMR (300 MHz, D_2O) δ 2.94 (dd, 1H, J = 7.8, 7.5 Hz, SCH(H)), 3.17 (dd, 1H, J = 4.8 Hz, SCH(H)), 3.62 (dd, 1H, J = 4.5 Hz, NHC<u>H</u>), 3.72 (s, 24H, 6 × (CH_2CH_2O)) ppm. ^{13}C NMR (100 MHz, D_2O) δ 43.6, 55.0, 69.9, 180.6 ppm. Elemental Anal. calcd (%): C 39.29, H 7.25, N 3.05; found: C 39.39, H 7.43, N 3.28.

[15-C-5Na]$_2$[L-Cys]·2.5H_2O

^{1}H NMR (300 MHz, D_2O) δ 2.93 (dd, 1H, J = 7.5, 7.8 Hz, SCH(H)), 3.15 (dd, 1H, J = 4.5, 4.2 Hz, SCH(H)), 3.62 (dd, 1H, J = 4.8, 4.5 Hz, NHC<u>H</u>), 3.73 (s, 20H, 6 × (CH_2CH_2O)) ppm. ^{13}C NMR (75 MHz, D_2O) δ 42.1, 54.6, 69.2, 178.9 ppm. Elemental Anal. calcd (%): C 36.49, H 6.70, N 5.32; found: C 36.55, H 6.81, N 5.42.

[18-C-6K][L-Ala]·H_2O

^{1}H NMR (300 MHz, D_2O) δ 1.25 (d, 3H, J = 6.9 Hz, CH_3), 3.62 (m, 1H, CH), 3.67 (s, 24H, 6 × (CH_2CH_2O)) ppm. ^{13}C NMR (100 MHz, D_2O) δ 17.1, 51.6, 70.0, 183.7 ppm. Elemental Anal. calcd (%): C 43.99, H 7.88, N 3.42; found: 43.99, H 7.51, N 3.22.

[15-C-5Na][L-Ala]

^{1}H NMR (300 MHz, D_2O) δ 1.27 (d, 3H, J = 6.9 Hz, CH_3),

3.37 (dd, 1H, J = 7.2, 5.7 Hz, CH), 3.72 (s, 20H, 5 × (CH_2-CH_2O)) ppm. ^{13}C NMR (75 MHz, D_2O) δ 16.7, 50.6, 69.3, 176.8 ppm. Elemental Anal. calcd (%): C 47.12, H 7.91, N 4.23; found: C 47.09, H 7.79, N 4.33.

[18-C-6K][L-Lys]·0.6H_2O

^{1}H NMR (300 MHz, D_2O) δ 1.40 (m, 2H, CH(NH_2)CH_2-C$\underline{H}_2$), 1.64 (m, 4H, CH(NH_2)C$\underline{H}_2$$CH_2C\underline{H}_2$), 2.89 (t, 2H, J = 7.2, 7.5 Hz, C$\underline{H}_2$-NH_2), 3.30 (t, 1H, J = 6.9 Hz, NH_2C$\underline{H}$), 3.71 (s, 24H, 6 × (CH_2CH_2O)) ppm. ^{13}C NMR (100 MHz, D_2O) δ 22.2, 28.6, 33.9, 39.78, 55.8, 69.9, 182.8 ppm. Elemental Anal. calcd (%): C 47.06, H 8.38, N 6.10; found: C 46.98, H 8.35, N 6.17.

[15-C-5Na][L-Lys]·0.5H_2O

^{1}H NMR (300 MHz, D_2O) δ 1.39 (m, 2H, CH(NH_2)CH_2-C$\underline{H}_2$), 1.62 (m, 4H, CH(NH_2)C$\underline{H}_2$$CH_2C\underline{H}_2$), 2.88 (t, 2H, J = 6.9, 7.2 Hz, NH_2C$\underline{H}_2$), 3.30 (t, 1H, J = 6.3 Hz, NH_2C$\underline{H}$), 3.72 (s, 20H, 5 × (CH_2CH_2O) ppm. ^{13}C NMR (75 MHz, D_2O) δ 22.0, 27.3, 33.07, 39.4, 55.5, 69.4, 181.3 ppm. Elemental Anal. calcd (%): C 48.35, H 8.62, N 7.05; found: C 48.07, H 8.77, N 6.89.

[18-C-6K]$_2$[L-Glu]·0.5H_2O

^{1}H NMR (300 MHz, D_2O) δ 2.05 (m, 2H, CH(NH_2)C$\underline{H}_2$), 2.33 (t, 2H, J = 7.5 Hz, COO-CH_2), 3.67 (m, 1H, NH_2C$\underline{H}$), 3.74 (s, 48H, 6 × (CH_2CH_2O)) ppm. ^{13}C NMR (100 MHz, D_2O) δ 27.2, 33.6, 54.8, 69.8, 174.7, 181.2 ppm. Elemental Anal. calcd (%): C 45.77, H 7.42, N 1.84; found: C 45.94, H 7.44, N 2.00.

[15-C-5Na]$_2$[L-Glu]·0.5H_2O

^{1}H NMR (300 MHz, D_2O) δ 2.08 (m, 2H, CH(NH_2)C$\underline{H}_2$), 2.33 (t, 2H, J = 7.5, 7.2 Hz, $COOCH_2$), 3.62 (m, 1H, NH_2C$\underline{H}$), 3.70 (s, 40H, 5 × (CH_2CH_2O)) ppm. ^{13}C NMR (75 MHz, D_2O) δ 27.4, 33.6, 54.8, 69.0, 175.3, 181.5 ppm. Elemental Anal. calcd (%): C 46.87, H 7.55, N 2.19; found: C 46.76, H 7.47, N 2.39.

[18-C-6K][L-Met]·1.8H_2O

^{1}H NMR (300 MHz, D_2O) δ 1.89 (m, 2H, CH(NH_2)C$\underline{H}_2$), 2.14 (s, 3H, CH_3), 2.58 (t, 2H, J = 7.5, 8.1 Hz, SCH_2), 3.36 (dd, 1H, J = 6.0, 5.1 Hz, NH_2C$\underline{H}$), 3.70 (s, 24H, 6 × (CH_2-CH_2O)) ppm. ^{13}C NMR (100 MHz, D_2O) δ 14.2, 29.8, 33.9, 55.3, 69.8, 182.1 ppm. Elemental Anal. calcd (%): C 42.18, H 7.83, N 2.89; found: C 42.20, H 7.64, N 2.74.

[15-C-5Na][L-Met]·H_2O

^{1}H NMR (300 MHz, D_2O) δ 1.89 (m, 2H, CH(NH_2)C$\underline{H}_2$), 2.14 (s, 3H, CH_3), 2.86 (t, 2H, J = 7.5, 8.1 Hz, SCH_2), 3.37 (dd, 1H, J = 5.7, 5.4 Hz, NH_2C$\underline{H}$), 3.72 (s, 20H, 5 × (CH_2CH_2O)) ppm. ^{13}C NMR (75 MHz, D_2O) δ 14.1, 29.6, 33.2, 55.0, 69.2, 181.2 ppm. Elemental Anal. calcd (%): C 44.00, H 7.88, N 3.42; found: C 43.69, H 7.67, N 3.65.

[18-C-6K][L-Trp]

^{1}H NMR (300 MHz, D_2O) δ 3.01 (dd, 1H, J = 7.8, 7.5 Hz, CH(NH_2)C$\underline{H}$($\underline{H}$)), 3.23 (dd, 1H, J = 4.8 Hz, CH(NH_2)C$\underline{H}$($\underline{H}$)), 3.56 (s, 24H, 6 × (CH_2CH_2O)), 3.64 (1H, NH_2C$\underline{H}$), 7.59 (m, 3H, Ar$\underline{H}$, α-H), 7.45 (d, 1H, J = 8.1 Hz, ArH), 7.68 (d, 1H, J = 9.0 Hz, ArH) ppm. ^{13}C NMR (100 MHz, D_2O) δ 29.6, 56.3, 69.7, 110.0, 111.8, 118.8, 119.2, 121.8, 124.4, 127.3, 136.3, 180.8 ppm. Elemental Anal. calcd (%): C 54.53, H 6.96, N 5.53; found: C 54.49, H 6.74, N 5.57.

[15-C-5Na][L-Trp]

^{1}H NMR (300 MHz, D_2O) δ 3.07 (dd, 1H, J = 7.5 Hz, CH(NH_2)C$\underline{H}$($\underline{H}$)), 3.25 (dd, 1H, J = 4.8 Hz, CH(NH_2)-C$\underline{H}$($\underline{H}$)), 3.69 (s, 20H, 5 × (CH_2CH_2O)), 3.71 (1H, NH_2C$\underline{H}$), 7.21 (m, 3H, ArH, α-H), 7.51 (d, 1H, J = 8.4 Hz, ArH), 7.73 (d, 1H, J = 8.1 Hz, ArH) ppm. ^{13}C NMR (100 MHz, D_2O) δ 29.6, 56.2, 69.4, 110.0, 111.8, 118.7, 119.2, 121.9, 124.4, 127.3, 136.3, 180.8 ppm. Elemental Anal. calcd (%): C 56.49, H 7.00, N 6.27; found: C 56.12, *H* 6.87, N 6.43.

[18-C-6K][L-Leu]·1.5H_2O

^{1}H NMR (300 MHz, D_2O) δ 0.92 (m, 6H, CH(C$\underline{H}_3$)C$\underline{H}_3$), 1.46 (m, 2H, CH(NH_2)C$\underline{H}_2$), 1.68 (m, 1H, C$\underline{H}$(CH_3)CH_3), 3.29 (dd, 1H, J = 6.0, 5.7 Hz, NH_2C$\underline{H}$), 3.71 (s, 24H, 6 × (CH_2CH_2O)) ppm. ^{13}C NMR (100 MHz, D_2O) δ 21.6, 22.7, 24.6, 44.1, 54.7, 69.9, 183.8 ppm. Elemental Anal. calcd (%): C 46.94, H 8.53, N 3.04; found: C 46.94, H 8.41, N 2.66.

[15-C-5Na][L-Leu]·1.2H_2O

^{1}H NMR (300 MHz, D_2O) δ 0.95 (m, 6H, CH(C$\underline{H}_3$)C$\underline{H}_3$), 1.45 (m, 2H, CH(NH_2)C$\underline{H}_2$), 1.69 (m, 1H, C$\underline{H}$(CH_3)CH_3), 3.32 (dd, 1H, J = 5.7, 6.0 Hz, NH_2C$\underline{H}$), 3.74 (s, 20H, 5 × (CH_2CH_2O)) ppm. ^{13}C NMR (100 MHz, D_2O) δ 21.4, 22.5, 24.5, 43.8, 54.5, 69.1, 183.5 ppm. Elemental Anal. calcd (%): C 48.65, H 8.78, N 3.55; found: C 48.47, H 8.56, N 3.40.

[18-C-6K][L-Phe]·0.8H_2O

^{1}H NMR (300 MHz, D_2O) δ 2.90 (dd, 1H, J = 7.2, 7.5 Hz, CH(NH_2)C$\underline{H}$($\underline{H}$)), 3.07 (dd, 1H, J = 5.1, 5.4 Hz, CH(NH_2)-C$\underline{H}$($\underline{H}$)), 3.58 (t, 1H, J = 5.7, 5.4 Hz, NH_2C$\underline{H}$), 3.69 (s, 24H, 6 × (CH_2CH_2O)), 7.36 (m, 5H, ArH) ppm. ^{13}C NMR (100 MHz, D_2O) δ 40.5, 57.5, 69.9, 126.9, 128.8, 129.6, 138.2, 181.4 ppm. Elemental Anal. calcd (%): C 52.33, H 7.44, N 2.91; found: C 52.12, H 7.21, N 3.05.

[15-C-5Na][L-Phe]·H_2O

^{1}H NMR (300 MHz, D_2O) δ 2.84 (dd, 1H, J = 7.2 Hz, CH(NH_2)C$\underline{H}$($\underline{H}$)), 2.98 (dd, 1H, CH(NH_2)C$\underline{H}$($\underline{H}$)), 3.52 (t, 1H, J = 5.7, 6.6 Hz, NH_2C$\underline{H}$), 3.66 (s, 20H, 5 × (CH_2CH_2O)), 7.28 (m, 5H, ArH) ppm. ^{13}C NMR (100 MHz, D_2O) δ 40.0, 57.3, 69.2, 126.9, 128.9, 129.5, 138.1, 181.1 ppm. Elemental Anal. calcd (%): C 53.64, H 7.58, N 3.29; found: C 53.99, H

7.29, N 3.58.

[18-C-6K][L-His]

^{1}H NMR (300 MHz, D_2O) δ 2.79 (dd, 1H, J = 8.4 Hz, CH(NH_2)C<u>H</u>(<u>H</u>)), 2.94 (dd, 1H, J = 5.1, 5.4 Hz, CH(NH_2)-C<u>H</u>(<u>H</u>)), 3.48 (dd, 1H, J = 5.1, 5.4 Hz Hz, NH_2C<u>H</u>), 3.64 (s, 24H, 6 × (CH_2CH_2O)), 6.89 (s, 1H, 5-<u>H</u>), 7.64 (s, 1H, 2-H) ppm. ^{13}C NMR (100 MHz, D_2O) δ 31.9, 56.1, 69.8, 118.1, 133.4, 135.9, 181.7 ppm. Elemental Anal. calcd (%): C 47.25, H 7.05, N 9.18; found: C 47.10, H 7.20, N 9.40.

[15-C-5Na][L-His]

^{1}H NMR (300 MHz, D_2O) δ 2.90 (dd, 1H, J = 7.5, 7.8 Hz, CH(NH_2)C<u>H</u>(<u>H</u>)), 3.04 (dd, 1H, J = 5.4 Hz, CH(NH_2)-C<u>H</u>(<u>H</u>)), 3.60 (dd, 1H, J = 5.1, 5.4 Hz, NH_2C<u>H</u>), 3.75 (s, 20H, 5 × (CH_2CH_2O)), 6.98 (s, 1H, 5-<u>H</u>), 7.72 (s, 1H, 2-H) ppm. ^{13}C NMR (100 MHz, D_2O) δ 31.0, 55.8, 69.1, 117.7, 133.2, 136.0, 179.9 ppm. Elemental Anal. calcd (%): C 46.26, H 7.28, N 10.12; found: C 46.39, H 7.57, N 10.25.

[18-C-6K][L-Ser]

^{1}H NMR (300 MHz, D_2O) δ 3.46 (t, 1H, J = 4.8 Hz NH_2C<u>H</u>), 3.69 (s, 24H, 6 × (CH_2CH_2O)), 3.77 (m, 2H, C<u>H</u>$_2$OH) ppm. ^{13}C NMR (100 MHz, D_2O) δ 57.2, 62.9, 69.9, 177.1 ppm. Elemental Anal. calcd (%): C 44.21, H 7.42, N 3.44; found: C 44.61, H 7.26, N 3.57.

[15-C-5Na][L-Ser]

^{1}H NMR (300 MHz, D_2O) δ 3.45 (t, 1H, J = 4.5, 5.4 Hz, NH_2C<u>H</u>), 3.64 (m, 1H, CH(H)OH), 3.70 (s, 20H, 5 × (CH_2-CH_2O)), 3.76 (m, 1H, C<u>H</u>(<u>H</u>)OH) ppm. ^{13}C NMR (100 MHz, D_2O) δ 56.6, 60.2, 69.2, 173.4 ppm. Elemental Anal. calcd (%): C 43.82, H 7.64, N 3.93; found: C 43.70, H 7.32, N 3.77.

[18-C-6K][L-Pro]

^{1}H NMR (300 MHz, D_2O) δ 1.89 (m, 3H, 3-H, 4-H), 2.22 (m, 1H, 3-H), 3.05 (m, 1H, 5-H), 3.23 (m, 1H, 5-H), 3.68 (s, 24H, 6 × (CH_2CH_2O)), 3.81 (m, 1H, 2-H) ppm. ^{13}C NMR (100 MHz, D_2O) δ 24.5, 29.9, 46.1, 61.4, 69.5, 178.4 ppm. Elemental Anal. calcd (%): C 48.90, H 7.72, N 3.35; found: C 48.97, H 7.79, N 3.63.

[15-C-5Na][L-Pro]·H_2O

^{1}H NMR (300 MHz, D_2O) δ 1.87 (m, 3H, 3-H, 4-H), 2.22 (m, 1H, 3-H), 3.04 ((m, 1H, 5-H), 3.24 (m, 1H, 5-H), 3.70 (s, 20H, 5 × (CH_2CH_2O)), 3.80 (m, 1H, 2-H) ppm. ^{13}C NMR (100 MHz, D_2O) δ 24.7, 30.2, 46.1, 61.5, 69.1, 179.7 ppm. Elemental Anal. calcd (%): C 47.99, H 8.06, N 3.73; found: C 47.75, H 8.05, N 3.88.

2.3 Enantioselective cycloaddition of CO_2 to epoxides

All coupling reactions were performed in a 100 mL stainless autoclave equipped with a magnetic stir bar and pressurized with CO_2 to 0.6 MPa. The autoclave was charged with propylene oxide (100 mmol), salenCo(OOCCCl_3) catalyst (0.1 mmol) and CMIL (0.1 mmol). After a proper reaction time, CO_2 was released to terminate the reaction. The remaining mixture was fractionally distilled under reduced pressure or recrystallized in ethanol to obtain a pure chiral cyclic carbonate.

3 Results and discussion

3.1 Properties of chiral metal-containing ionic liquids

The obtained CMILs have high purity and give sharp melting points (Table 1). They have demonstrated good thermal stabilities as measured by TG-DTA. Their colors range from white to orange. Two of them are ILs at room temperature (entries 4, 25). The rest are solids, in which

Table 1 The properties of chiral metal-containing ionic liquids (CMILs)

Entry	Ionic liquid [a]	Color	mp [b] °C	T_d [c] °C	$[a]_D^{20}$ [d]
1	[18-C-6K][L-Thr]·2.5H_2O	white	138	174	–5°
2	[15-C-5Na][L-Thr]	white	125	172	–5°
3	[18-C-6K]$_2$[L-Asp]·4H_2O	orange	100	173	–4°
4	[15-C-5Na]$_2$[L-Asp]·H_2O	yellow	-48	138	–1°
5	[18-C-6K][L-Val]·0.5H_2O	yellow	130	188	+4°
6	[15-C-5Na][L-Val]·0.8H_2O	white	133	142	+3°
7	[18-C-6K]$_2$[L-Cys]·4H_2O	orange	127	160	–43°
8	[15-C-5Na]$_2$[L-Cys]·2.5H_2O	orange	152	152	–44°
9	[18-C-6K]$_2$[L-Glu]·0.5H_2O	yellow	85	189	–1°
10	[15-C-5Na]$_2$[L-Glu]·0.5H_2O	yellow	157	157	+1°
11	[18-C-6K][L-Lys]·0.6H_2O	orange	76	183	+3°
12	[15-C-5Na][L-Lys]·0.5H_2O	orange	56	162	+2°
13	[18-C-6K][L-Leu]·1.5H_2O	yellow	94	192	+1°
14	[15-C-5Na][L-Leu]·1.2H_2O	white	150	183	+1°
15	[18-C-6K][L-Trp]	brown	95	189	–15°
16	[15-C-5Na][L-Trp]	brown	115	148	–14°
17	[18-C-6K][L-His]	yellow	66	194	–5°
18	[15-C-5Na][L-His]	yellow	113	172	–5°
19	[18-C-6K][L-Ser]	yellow	55	197	–3°
20	[15-C-5Na][L-Ser]	yellow	80	222	–4°
21	[18-C-6K][L-Pro]	yelow	95	182	–37°
22	[15-C-5Na][L-Pro]·H_2O	yellow	69	154	–36°
23	[18-C-6K][L-Phe]·0.8H_2O	orange	68	179	–6°
24	[15-C-5Na][L-Phe]·H_2O	orange	37	157	–7°
25	[18-C-6K][L-Met]·1.8H_2O	yellow	26	194	–1°
26	[15-C-5Na][L-Met]·H_2O	orange	38	143	–2°
27	[18-C-6K][L-Ala]·H_2O	yellow	130	196	–1°
28	[15-C-5Na][L-Ala]	yellow	115	177	–2°

a) The chemical compositions were confirmed by elemental analysis. b) Melting points were determined on an XT-4 melting point apparatus without calibration. c) Decomposition temperature (T_d) was determined by TG-DTA heating at 10 °C min^{-1} under nitrogen. d) Solution in H_2O and c = 1.0.

almost half of them have melting point lower than 100 °C and the rest have melting points higher than 100 °C but lower than 160 °C. The CMILs obtained are thermally stable up to 135 to 225 °C. Their specific rotations were also determined.

3.2 The effect of CMIL on the coupling of CO_2 and PO

Our initial investigation showed that salenCo(OOCCCl$_3$) can successfully catalyze the coupling reaction of CO_2 and racemic PO in the presence of the CMILs such as [18-C-6K][L-amino acid anion] or [15-C-5Na][L-amino acid anion] to form the pure chiral propylene carbonate without any by-products. That is to say the conversion of PO equals to the yield of propylene carbonate (PC). According to our previous study [32], the salts that consist of two parts: cation (Lewis acid, electrophile) and anion (Lewis base, nucleophile), have catalytic activity under a generally harsh condition. The metal-containing ionic liquid (MIL) is a good catalyst since its cation can act as a Lewis acid center and its amino acid anion can acts as a Lewis base center In the catalyst systems, salenCo(OOCCCl$_3$), which gives the chiral Lewis acid center and works as the main catalyst, activates the epoxides, while the chiral anion of CMILs which supplies the chiral Lewis base center for the coupling reaction and functions as the co-catalyst, attacks the activated epoxides to produce intermediates for the insertion of CO_2 to lead to cyclic carbonates

The results revealed that the ee values of chiral PC were significantly enhanced compared to the ee values produced by chiral catalyst (*R*, *R*)-**1** combined with TBAB as the co-catalyst (Table 2, entries 1, 5, 7–18 vs. 19). According to Table 2, the most efficient catalytic system was salenCo (OOCCCl$_3$)/[18-C-6K][L-Val]·0.5H$_2$O, which gave the highest ee value of (*S*)-PC (53.8%) (entry 1). When the reaction was carried out at 0 °C, the ee value of (*S*)-PC augmented to 64.0% (entry 3). Other catalyst systems of salenCo (OOCCCl$_3$)/[18-C-6K][L-amino acid anion] were also effective (Table 2, entries 5, 7–18). When the catalyst system was switched from (*R*,*R*)-**1** to (*S*,*S*)-**1**, the enantioselectvity was decreased (entries 1, 2, 5, 6). The significant synergistic effects between chiral catalysts and cocatalysts were revealed: the cocatalyst with *R*,*R* chirality increased the ee values of (*S*)-PC catalyzed by (*R*,*R*)-**1** and it decreased the ee values of (*R*)-PC catalyzed by (*S*,*S*)-**1**, which are consistent with our previous report [22]. Higher yields could be obtained when the reaction times were increased (entries 1, 8, 10, 14, 15, 18). It is worth noting that when chiral MIL of [18-C-6K][L-Val]·0.5H$_2$O was used alone as catalyst, the reaction could also induce the chiral PC with 5.4% ee (entry 4) which is higher than that of 1% ee obtained by chiral IL [22].

When the cocatalyst was switched from [18-C-6K][L-amino acid anion] to [15-C-5Na][L-amino acid anion], similar results were obtained (Table 3). The highest ee value of (*S*)-PC (58.5%) was achieved with [15-C-5Na][L-Pro]·H$_2$O as the chiral cocatalyst (entry 10). In contrast to [18-C-6K][L-amino acid anion], the coupling reaction catalyzed by [15-C-5Na][L-amino acid anion] needs a longer period of reaction time (Table 3 vs. Table 2). For the enantioselective cycloaddition of CO_2 to PO catalyzed by [18-C-6K][L-amino acid anion] or [15-C-5Na][L-amino acid anion], higher yields and shorter reaction times were presented when the amount of catalyst and cocatalyst was doubled (Table 2, entry 12; Table 3, entries 1, 2, 11, 14).

Table 2 The effect of [18-C-6K][L-amino acid anion] in the coupling reaction of CO_2 and propylene oxide [a)]

Entry	Co-catalyst	Time (h)	Yield (%)	PC ee (%)	K_{rel} [b)]
1	[18-C-6K][L-Val]·0.5H$_2$O	5.5	43.6	53.8(*S*)	4.9
		7.0	49.0	48.2(*S*)	4.4
		8.0	50.5	46.8(*S*)	4.3
2 [c)]	[18-C-6K][L-Val]·0.5H$_2$O	9.5	40.3	48.2(*R*)	3.9
3 [d)]	[18-C-6K][L-Val]·0.5H$_2$O	21	27.2	64.0(*S*)	5.7
4 [e)]	[18-C-6K][L-Val]·0.5H$_2$O	72	3.1	5.4(*S*)	1.1
5	[18-C-6K]$_2$[L-Glu]·0.5H$_2$O	6.5	42.4	51.1(*S*)	4.4
6 [c)]	[18-C-6K]$_2$[L-Glu]·0.5H$_2$O	12	41.3	48.0(*R*)	3.9
7	[18-C-6K][L-His]	14	37.8	50.7(*S*)	4.1
8	[18-C-6K][L-Lys]·0.6H$_2$O	11	48.1	46.2(*S*)	4.1
		12	50.1	45.0(*S*)	4.4
9	[18-C-6K][L-Trp]	11	32.4	53.4(*S*)	4.2
10	[18-C-6K][L-Ser]	10	46.4	48.1(*S*)	4.2
		12	52.5	46.1(*S*)	4.3
11	[18-C-6K][L-Thr]·2.5H$_2$O	14	35.3	54.9(*S*)	4.6
12	[18-C-6K][L-Phe]·0.8H$_2$O	11	32.5	52.5(*S*)	4.1
		5.5 [f)]	51.0	45.1(*S*)	4.1
13	[18-C-6K][L-Leu]·1.5H$_2$O	5.5	35.8	51.1(*S*)	4.0
14	[18-C-6K][L-Ala]·H$_2$O	11	44.1	49.1(*S*)	4.2
		12	48.6	47.7(*S*)	4.3
15	[18-C-6K][L-Pro]	11	46.8	49.2(*S*)	4.4
		12	49.0	47.9(*S*)	4.3
16	[18-C-6K][L-Met]·1.8H$_2$O	13	35.9	53.3(*S*)	4.4
17	[18-C-6K]$_2$[L-Cys]·4H$_2$O	14	34.5	52.5(*S*)	4.2
18	[18-C-6K]$_2$[L-Asp]·4H$_2$O	10	48.1	51.0(*S*)	4.8
		12	50.9	48.8(*S*)	4.7
19	TBAB	1.3	40.8	33.7(*S*)	2.5

a) Reaction conditions: PO 100 mmol; catalyst: (*R*,*R*)-**1** 0.1 mmol; co-catalyst 0.1 mmol; CO_2: 0.6 MPa, T = 25 °C. b) $K_{rel} = \ln[1-c(1+ee)/\ln[1-c(1-ee)]$, where c is the yield and ee% is the enantiomeric excess of the resulting propylene carbonate. c) Catalyst: (*S*, *S*)-**1**. d) T = 0 °C. e) Catalyst: [18-C-6K][L-Val]·0.5H$_2$O 1.0 g. f] PO 50 mmol.

3.3 Cycloaddition of CO_2 to epoxides catalyzed by salenCo(OOCCCl$_3$)/[18-C-6K][L-Val]·0.5H$_2$O

To further extend the reaction scope, various epoxides were utilized as substrates in this coupling reaction using [18-C-6K][L-Val]·0.5H$_2$O as a chiral cocatalyst (Table 4). As can be seen, the catalyst was effective for the cycloaddition of 1,2-epoxybutane to yield the corresponding chiral cyclic carbonate (CC) with a good enantioselectivity (entry 1).

Table 3 The effect of [15-C-5Na][L-amino acid anion] in the coupling reaction of CO_2 and propylene oxide [a)]

Entry	Co-catalyst	Time (h)	Yield (%)	PC ee (%)	K_{rel}
1	[15-C-5Na][L-His]	72	37.1	49.8(*S*)	3.9
		28 [b)]	48.2	41.2(*S*)	3.4
2	[15-C-5Na][L-Val]·0.8H_2O	72	30.7	55.3(*S*)	4.4
		24 [b)]	50.2	46.3(*S*)	4.2
3	[15-C-5Na][L-Lys]·0.5H_2O	80	35.3	50.0(*S*)	3.9
4	[15-C-5Na][L-Trp]	86	32.8	51.7(*S*)	4.0
5	[15-C-5Na][L-Ser]	100	34.2	52.7(*S*)	4.2
6	[15-C-5Na][L-Thr]	72	37.0	50.4(*S*)	4.8
7	[15-C-5Na][L-Phe]·H_2O	67	33.4	50.9(*S*)	3.9
8	[15-C-5Na][L-Leu]·1.2H_2O	85	33.4	54.9(*S*)	4.5
9	[15-C-5Na][L-Ala]	91	35.3	53.1(*S*)	4.3
10	[15-C-5Na][L-Pro]·H_2O	72	29.4	58.5(*S*)	4.8
11	[15-C-5Na][L-Met]·H_2O	62	41.3	44.5(*S*)	3.5
		22 [b)]	48.9	41.6(*S*)	3.4
12	[15-C-5Na]$_2$[L-Glu]·0.5H_2O	88	35.9	53.2(*S*)	4.3
13	[15-C-5Na]$_2$[L-Cys]·2.5H_2O	95	35.3	50.5(*S*)	3.9
14	[15-C-5Na]$_2$[L-Asp]·H_2O	46	36.6	49.5(*S*)	3.9
		19 [b)]	49.9	43.1(*S*)	3.7

a) Reaction conditions: PO 100 mmol; catalyst: (*R*,*R*)-**1**, 0.1 mmol; cocatalyst 0.1 mmol; CO_2: 0.6 MPa, T = 25 °C. b) PO 50 mmol.

Table 4 Coupling of CO_2 and various epoxides catalyzed by salenCo-($OOCCCl_3$)/[18-C-6K][L-Val]·0.5H_2O [a)]

Entry	Epoxide	Time (h)	Yield (%)	CC ee (%)
1	1,2-epoxybutane	21	35.1	50.8(*S*)
2	epichlorohydrin	31	21.8	4.0(*R*)
3	1,2-epoxy-3-phenoxy propane	28	38.5 [b)]	3(*S*)
4	styrene oxide	48	13.5 [b)]	2(*S*)

a) Reaction conditions: epoxide 100 mmol; catalyst: (*R*,*R*)-**1**, 0.1 mmol; [18-C-6K][L-Val]·0.5H_2O 0.1 mmol; CO_2: 0.6 MPa, T = 25 °C. b) Solid product purified by recrystallization in ethanol.

Whereas, cyclic carbonates from epichlorohydrin, 1, 2-epoxy-3-phenoxypropane, and styrene oxide can be only acquired with diminishing ee values (entries 2–4) due to their larger substituted groups.

3.4 The recycle of salenCo($OOCCCl_3$)/[18-C-6K][L-Val]·0.5H_2O

Futhermore, the recycle and reuse of the catalysts were also investigated. The optimized catalyst system of salenCo ($OOCCCl_3$)/[18-C-6K][L-Val]·0.5H_2O was chosen as the model catalyst and the results are listed in Table 5. The recovery of catalysts was straightforward: the product of PC was completely distilled under vacuum and the residue was a mixture of catalyst and co-catalyst that was reoxidized under oxgen atmosphere within 1h by adding CH_2Cl_2 (5 mL) and CCl_3COOH (0.1 mmol). It can be seen that there was no significant loss of activity and enantioselectivity after five recycles.

Table 5 Recycling of catalyst salenCo($OOCCCl_3$)/[18-C-6K][L-Val]·0.5H_2O [a)]

Recycle time	Time (h)	Conv (%)	PC ee (%)	K_{rel}
Fresh	5.5	43.6	53.8(*S*)	4.9
1	5.5	42.3	54.2(*S*)	4.9
2	5.5	41.2	54.0(*S*)	4.8
3	5.5	40.0	53.5(*S*)	4.6
4	5.5	39.1	53.0(*S*)	4.5

a) Reaction conditions: PO 100 mmol; catalyst: (*R*,*R*)-**1**, 0.1 mmol; [18-C-6K][L-Val]·0.5H_2O 0.1 mmol; CO_2: 0.6 MPa, T = 25 °C

4 Conclusions

In summary, we have firstly designed and synthesized a series of novel chiral metal-containing ionic liquids (CMILs) that were used as chiral cocatalysts in the enantioselective cycloaddition of CO_2 to epoxides catalyzed by salenCo ($OOCCCl_3$). The new catalyst systems of salenCo($OOCCCl_3$)/CMIL exhibit high activity under mild reaction conditions and demonstrate the synergistic effect between the chiral catalyst and cocatalyst.

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