

Article

Cobalt carbonyl ionic liquids based on the 1,1,3,3-tetra-alkylguanidine cation: Novel, highly efficient, and reusable catalysts for the carbonylation of epoxides

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ABSTRACT

A series of novel cobalt carbonyl ionic liquids based on 1,1,3,3-tetra-alkyl-guanidine, such as $[1,1-dimethyl-3,3-diethylguanidinium][Co(CO)_4]$ (**3a**), $[1,1-dimethyl-3,3-dibutylguanidinium][Co(CO)_4]$ (**3b**), $[1,1-dimethyl-3,3-tetramethyleneguanidinium][Co(CO)_4]$ (**3c**), and $[1,1-dimethyl-3,3-pentamethyleneguanidinium][Co(CO)_4]$ (**3d**), were synthesized in good yields and were also characterized using infrared spectroscopy, ultraviolet-visible spectroscopy, ¹H nuclear magnetic resonance (NMR) spectroscopy, ¹³C NMR spectroscopy, high-resolution mass spectrometry, differential scanning calorimetry, and thermogravimetric analysis. The four compounds exhibited high thermal and chemical stability. In addition, the catalytic performance of these compounds was investigated in the carbonylation of epoxides, with **3a** exhibiting the best catalytic activity without the aid of a base as the additive. The catalyst could be reused at least six times without significant decreases of the selectivity or conversion rate. Moreover, the catalyst system exhibited good tolerance with terminal epoxides bearing alkyl, alkenyl, aryl, alkoxy, and chloromethyl functional groups.

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1. Introduction

Ionic liquids (ILs), such as organic salts consisting of an organic cation and an inorganic or organic anion, have attracted considerable attention because of their unique properties, such as negligible vapor pressure and high thermal, chemical, and electrochemical stability [1–6]. In addition, the structure and properties of ILs can be modified by varying the nature of the anions and cations [7]. Recently, among the vast research related to ILs, organometallic ILs [8–12] based on transition metals have received increasing attention, especially in catalysis [5,13], because of their potential catalytic activity and considerable reusability [11,14]. Notably, $Co(CO)_4^-$ as a widely used catalytic active species has been used in organometallic ILs [11,15–21]. For example, the compounds [bmim][Co(CO)4] (bmim = 1-butyl-3-methylimidazolium), [CnPy][Co(CO)4] (CnPy = N-CnH_{2n+1}pyridinium), [methylguanidinium][Co(CO)4] and [tetramethylguanidinium][Co(CO)4] have been investigated by researchers [11,22–26]. According to the previous reports, [CnPy][Co(CO)4] and [bmim][Co(CO)4] organometallic ILs have been applied in the carbonylation of epoxides. However, the stability and reusability of this type of catalyst could be further enhanced.

Guanidinium offers many significant and advantageous features because of its structural characteristics. The guanidinium cation can act as a hydrogen bond donor because of the pres-

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ence of substituted hydrogen of the N atom and *N*-alkyl substituents, which can somehow stabilize the $Co(CO)_{4}^{-}$ anion and activate an epoxide [22,28]. Moreover, the guanidinium cationic plane structure can be modified by the action of relatively large alkyl substituents. Therefore, the C atom connected with the three N atoms presents an electron-deficient state. Thus, the cationic part can be regarded as a Lewis acid [29], which can assist the ring-opening process of the epoxides [23,30–32]. It is expected that cobalt carbonyl ILs based on 1,1,3,3-tetraalkylguanidine can play the dual role of stabilizing $Co(CO)_{4}^{-}$ anions and activating epoxy compounds.

To verify our speculation, we designed and synthesized a series of cobalt carbonyl ILs based on 1,1,3,3-tetra-alkylguanidine (Scheme 1), which was applied in the carbonylation of epoxides. Notably, it was observed that **3a** exhibited the best catalytic activity without the aid of a base as an additive as well as perfect recyclability.

2. Experimental

2.1. General

All the organometallic manipulations were performed in a glove box or under a N2 atmosphere using standard Schlenk techniques. Unless otherwise noted, all the reagents were of analytical grade and were used as received. Tetrahydrofuran (THF), dichloromethane, ethanol, and propylene oxide were purged with argon to eliminate the dissolved oxygen and were dried to remove water. Co₂(CO)₈ was prepared by our research group according to the method described in a previous report [33]. Infrared (IR) spectra were recorded on a Bruker IFS120HR spectrophotometer. ¹H nuclear magnetic resonance (NMR) and ¹³C NMR spectra were measured on Bruker Avance III (400 MHz) spectrometers. High-resolution mass spectrometry (HRMS) analyses were performed on a Bruker Micro TOF-QII mass instrument with electrospray ionization (ESI) in the positive ionization and negative mode on samples dissolved in methanol. The glass transition temperature (T_g) was determined on a Mettler-Toledo differential scanning calorimeter (model DSC 822e) at a scan rate of 10 °C/min. The thermal decomposition temperature was characterized on a Netzsch STA449F3 thermogravimetric differential scanning calorimeter (TG-DSC) at a scan rate of 10 °C/min.

2.2. Synthesis of cobalt carbonyl ILs based on 1,1,3,3-tetra-alkylguanidine

Compound 1 (1,1,3,3-tetra-alkylguanidine) was synthesized according to the method described in the Ref. [34] using dimethyl cyanamide and diamine as the starting materials. Moreo-

ver, the structures of the products were confirmed by $^{1}H/^{13}C$ NMR.

Compound **2** was prepared *via* neutralization of 1,1,3,3-tetra-alkylguanidine with acids. In the experiment, 10.0 mL of ethanol and 1,1,3,3-tetra-alkylguanidine (10.0 mmol) were loaded into a 100-mL flask in an ice water bath at 0 °C. Then, 16.0 mmol of HCl in 8.0 mL of ethanol was slowly added into the flask under stirring, and the stirring was continued for 4 h. The reaction mixture was evaporated under reduced pressure. The concentrated mixture was then washed with ether, and the product was dried under vacuum at 50 °C for 24 h. All the products were white solids, except for **2b**, which was a colorless viscous liquid. Moreover, ¹H/¹³C NMR characterization data were obtained.

The 1,1,3,3-tetra-alkylguanidine cobalt carbonyl ILs (compounds 3a-3d) were synthesized by the reaction of KCo(CO)₄ with 1,1,3,3-tetra-alkylguanidine chloride salts. A 50-mL Schlenk flask containing milled KOH (6.0 mmol) and Co₂(CO)₈ (1.0 mmol) was placed in the glove box. Then, 6.0 mL of degassed THF was slowly dripped into the flask under stirring, and the stirring was continued for 2 h. Subsequently, the supernatant was transferred to another Schlenk flask containing 1.1 mmol 1,1,3,3-tetra-alkylguanidine chloride salt. The reaction was continued for 8 h under stirring. The THF solvent was then removed with a vacuum pump. Next, 6.0 mL CH₂Cl₂ was added into the flask under an Ar atmosphere. Afterward, the mixture was filtered under an Ar atmosphere, and the solvent was removed in vacuo to obtain the desired products 3 as light or dark-blue viscous oily liquids. The 1,1,3,3-tetra-alkylguanidine cobalt carbonyl ILs were all characterized using IR, ultraviolet-visible (UV-Vis) spectroscopy, ¹H NMR, ¹³C NMR, HRMS (ESI), TG-DSC, and DSC.

2.3. Characterization data for cobalt carbonyl ILs based on 1,1,3,3-tetra-alkylguanidine

3a 0.27 g, 86%; $T_{g:}$ -77 °C; thermal decomposition temperature: 215 °C; selected v_{max}/cm^{-1} (KBr) 1882 vs (Co(CO)₄⁻); ¹H NMR (400 MHz, DMSO-*d*₆): δ 7.93 (s, 2H), 3.27 (q, *J* = 7.1 Hz, 4H), 2.90 (s, 6H), 1.10 (t, *J* = 7.1 Hz, 6H); ¹³C NMR (100 MHz, DMSO-*d*₆): δ 160.6, 43.1, 39.4, 12.5; HRMS (ESI) positive ion: *m/z* 144.1488 (C₇H₁₈N₃+); HRMS (ESI) negative ion: *m/z* 170.9135 (Co(CO)₄⁻), 142.9199 (Co(CO)₃⁻), 114.9254 (Co(CO)₂⁻).

3b 0.30 g, 81%; T_g : -65 °C; thermal decomposition temperature: 207 °C; selected v_{max}/cm^{-1} (KBr) 1886 vs (Co(CO)₄⁻); ¹H NMR (400 MHz, DMSO-*d*₆): δ 7.96 (s, 2H), 3.20 (t, *J* = 7.0 Hz, 4H), 2.89 (s, 6H), 1.54–1.39 (m, 4H), 1.23 (dt, *J* = 14.8, 7.5 Hz, 4H), 0.87 (t, *J* = 7.3 Hz, 6H); ¹³C NMR (100 MHz, DMSO-*d*₆): δ 161.1, 48.2, 39.3, 28.8, 19.1, 13.5; HRMS (ESI) positive ion: *m/z*



Scheme 1. Synthetic routes and structures of 1,1,3,3-tetra-alkylguanidine cobalt carbonyl ILs.

200.2120 (C₁₁H₂₆N₃⁺); HRMS (ESI) negative ion: *m/z* 170.9135 (Co(CO)₄⁻), 142.9203 (Co(CO)₃⁻), 114.9254 (Co(CO)₂⁻).

3c 0.25 g, 80%; T_{g} : -60 °C; thermal decomposition temperature: 208 °C; selected v_{max}/cm^{-1} (KBr) 1882 vs (Co(CO)₄⁻); ¹H NMR (400 MHz, DMSO-*d*₆): δ 7.62 (s, 2H), 3.39 (t, *J* = 6.4 Hz, 4H), 2.91 (s, 6H), 1.86 (dd, *J* = 7.8, 5.1 Hz, 4H); ¹³C NMR (100 MHz, DMSO-*d*₆): δ 158.1, 49.2, 39.4, 24.9; HRMS (ESI) positive ion: *m*/*z* 142.1342 (C₇H₁₆N₃+); HRMS (ESI) negative ion: *m*/*z* 170.9134 (Co(CO)₄⁻), 142.9196 (Co(CO)₃⁻), 114.9249 (Co(CO)₂⁻).

3d 0.27 g, 83%; T_g : -55 °C; thermal decomposition temperature: 202 °C; selected v_{max}/cm^{-1} (KBr) 1879 vs (Co(CO)₄⁻); ¹H NMR (400 MHz, DMSO-*d*₆): δ 7.82 (s, 2H), 3.25 (d, *J* = 5.1 Hz, 4H), 2.91 (s, 6H), 1.59 (s, 6H); ¹³C NMR (100 MHz, DMSO-*d*₆): δ 160.4, 48.6, 39.3, 25.0, 23.3; HRMS (ESI) positive ion: *m/z* 156.1489 (C₈H₁₈N₃+); HRMS (ESI) negative ion: *m/z* 170.9132 (Co(CO)₄⁻), 142.9204 (Co(CO)₃⁻), 114.9253 (Co(CO)₂⁻).

2.4. Catalytic activity of cobalt carbonyl ILs based on 1,1,3,3-tetra-alkylguanidine in the carbonylation of epoxide

The catalytic activity of the cobalt carbonyl ILs based on 1,1,3,3-tetra-alkylguanidine in the reaction of ring-opening carbonylation of epoxides was investigated. In our test, we observed that the compounds **3a–3d**, especially **3a**, without the aid of a base additive, exhibited relatively good catalytic activity in the reaction of alkoxycarbonylation of epoxides (Scheme 2).

The reaction was conducted in a 50-mL stainless steel autoclave equipped with a stirring magnet. The reactor was charged with ethanol (3.0 mL), epoxide (5.0 mmol), and catalyst **3a** (3 mol%). Then, the reactor was pressurized with 6.0 MPa CO and heated to 80 °C. After completion of the reaction, the autoclave was cooled with ice water and slowly depressurized to atmospheric pressure. The product mixture underwent simple flash column chromatography to dispose of the ILs catalyst and was then analyzed using gas chromatography (GC) and GC-MS.

The structures and purities of the products were fully characterized using NMR spectroscopy. Analytical data for these compounds are listed below.

Ethyl 3-hydroxybutyrate (**4a**). This compound was prepared using the general procedure described above and purified by flash column chromatography to give a colorless oil, 0.54 g, 81% yield. ¹H NMR (400 MHz, CDCl₃): δ 4.31–4.05 (m, 3H), 2.79 (s, 1H), 2.46 (qd, *J* = 16.4, 6.1 Hz, 2H), 1.28 (t, *J* = 7.1 Hz, 3H), 1.23 (d, *J* = 6.3 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 173.0, 64.3, 60.7, 42.8, 22.4, 14.2.

Ethyl 3-hydroxyvalerate (**4b**). This compound was prepared using the general procedure described above and purified by flash column chromatography to give a colorless oil, 0.66 g, 90% yield. ¹H NMR (400 MHz, CDCl₃): δ 4.16 (q, *J* = 7.1 Hz, 2H), 4.02–3.85 (m, 1H), 2.89 (s, 1H), 2.49 (dd, *J* = 16.4, 3.1 Hz, 1H), 2.38 (dd, *J* = 16.4, 9.1 Hz, 1H), 1.62–1.39 (m, 2H), 1.26 (t, *J* = 7.1 Hz, 3H), 0.95 (t, *J* = 7.5 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃): δ



173.1, 69.3, 60.6, 40.9, 29.4, 14.2, 9.8.

Ethyl 3-hydroxyheptanoate (**4c**). This compound was prepared using the general procedure described above and purified by flash column chromatography to give a colorless oil, 0.77 g, 89% yield. ¹H NMR (400 MHz, CDCl₃): δ 4.15 (q, *J* = 7.1 Hz, 2H), 4.05–3.92 (m, 1H), 2.92 (s, 1H), 2.48 (dd, *J* = 16.4, 3.2 Hz, 1H), 2.38 (dd, *J* = 16.4, 9.0 Hz, 1H), 1.56–1.43 (m, 2H), 1.42–1.34 (m, 2H), 1.34–1.29 (m, 2H), 1.26 (dd, *J* = 8.9, 5.4 Hz, 3H), 0.92–0.86 (m, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 173.1, 68.0, 60.6, 41.3, 36.2, 29.7, 27.6, 22.6, 14.1.

3-Hydroxyhept-6-enoic acid ethyl ester (**4d**). This compound was prepared using the general procedure described above and purified by flash column chromatography to give a colorless oil, 0.69 g, 80% yield. ¹H NMR (400 MHz, CDCl₃): δ 5.91–5.67 (m, 1H), 5.12–4.92 (m, 2H), 4.23–4.07 (m, 2H), 4.07–3.92 (m, 1H), 3.04 (s, 1H), 2.55–2.35 (m, 2H), 2.28–2.01 (m, 2H), 1.72–1.41 (m, 2H), 1.30–1.21 (m, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 173.0, 138.1, 115.0, 77.4, 77.0, 76.7, 67.4, 60.7, 41.3, 35.6, 29.7, 14.2.

4-Butoxy-3-hydroxybutyric acid ethyl ester (**4e**). This compound was prepared using the general procedure described above and purified by flash column chromatography to give a colorless oil, 0.94 g, 92% yield. ¹H NMR (400 MHz, CDCl₃): *δ* 4.25–4.12 (m, 3H), 3.52–3.37 (m, 4H), 3.11 (d, *J* = 77.9 Hz, 1H), 2.53 (d, *J* = 6.3 Hz, 2H), 1.61–1.51 (m, 2H), 1.43–1.31 (m, 2H), 1.28 (t, *J* = 7.1 Hz, 3H), 0.92 (t, *J* = 7.4 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃): *δ* 172.2, 73.7, 71.3, 67.2, 60.7, 38.3, 31.7, 19.3, 14.2, 13.9.

3-Hydroxy-4-phenoxybutyric acid ethyl ester (**4f**). This compound was prepared using the general procedure described above and purified by flash column chromatography to give a colorless oil, 0.94 g, 84% yield. ¹H NMR (400 MHz, CDCl₃): δ 7.26 (s, 2H), 7.00–6.95 (m, 1H), 6.91 (dd, *J* = 11.4, 3.6 Hz, 2H), 4.48–4.37 (m, 1H), 4.23–4.16 (m, 2H), 4.00 (d, *J* = 5.3 Hz, 2H), 3.10 (d, *J* = 33.6 Hz, 1H), 2.68 (dd, *J* = 9.7, 5.5 Hz, 2H), 1.30–1.27 (m, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 172.1, 158.4, 129.5, 121.2, 114.6, 70.6, 66.8, 60.9, 38.1, 14.2.

4-Butyryloxy-3-hydroxybutyric acid ethyl ester (**4g**). This compound was prepared using the general procedure described above and purified by flash column chromatography to give a colorless oil, 0.86 g, 79% yield. ¹H NMR (400 MHz, CDCl₃): δ 4.29 (td, *J* = 11.7, 6.1 Hz, 1H), 4.24–4.16 (m, 2H), 4.17–4.03 (m, 2H), 3.36–2.80 (m, 1H), 2.74–2.45 (m, 2H), 2.40–2.27 (m, 2H), 1.73–1.62 (m, 2H), 1.32–1.25 (m, 3H), 0.96 (t, *J* = 7.4 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 173.6, 172.0, 66.9, 66.4, 61.0, 37.9, 36.0, 18.4, 14.2, 13.7.

Ethyl-4-chloro-3-hydroxybutyrate (**4h**). This compound was prepared using the general procedure described above and purified by flash column chromatography to give a colorless oil, 0.58 g, 70% yield. ¹H NMR (400 MHz, CDCl₃): δ 4.30–4.22 (m, 1H), 4.22–4.13 (m, 2H), 3.66–3.54 (m, 2H), 3.14 (s, 1H), 2.68–2.56 (m, 2H), 1.35–1.20 (m, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 171.8, 68.0, 61.0, 48.1, 38.5, 14.1.

Ethyl-3-hydroxy-3-phenyl propionate (**4i**). This compound was prepared using the general procedure described above and purified by flash column chromatography to give a colorless oil, 0.39 g, 40% yield. ¹H NMR (400 MHz, CDCl₃): δ 4.30–4.22 (m,

1H), 4.22–4.13 (m, 2H), 3.66–3.54 (m, 2H), 3.14 (s, 1H), 2.68–2.56 (m, 2H), 1.35–1.20 (m, 3H); ^{13}C NMR (100 MHz, CDCl₃): δ 172.4, 142.5, 128.6, 127.8, 125.7, 70.3, 60.9, 43.4, 14.2.

3-Hydroxy-4-phenylbutyric acid ethyl ester (**4j**). This compound was prepared using the general procedure described above and purified by flash column chromatography to give a colorless oil, 0.74 g, 71% yield. ¹H NMR (400 MHz, CDCl₃): δ 7.56–6.95 (m, 5H), 4.33–4.21 (m, 1H), 4.21–4.07 (m, 2H), 3.01 (d, *J* = 33.8 Hz, 1H), 2.87 (dd, *J* = 13.6, 7.1 Hz, 1H), 2.76 (dd, *J* = 13.6, 6.2 Hz, 1H), 2.58–2.35 (m, 2H), 1.31–1.22 (m, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 172.7, 137.7, 129.5, 128.5, 126.6, 69.1, 60.7, 43.0, 40.5, 14.2.

3. Results and discussion

3.1. Characterization of cobalt carbonyl ILs based on 1,1,3,3-tetra-alkylguanidine

3.1.1. Miscibility

The miscibilities of the four compounds **3a–3d** were qualitatively determined to be similar in several common solvents. They were all well dissolved in more polar organic solvents such as methanol, ethanol, dichloromethane, tetrahydrofuran, and acetone, whereas they were insoluble in some less polar solvents such as petroleum ether, hexane, and toluene, most likely because of the existence of the ionic bond [35]. However, none of the compounds could be dissolved in chloroform despite its polarity. In addition, all of the compounds were insoluble in water.

3.1.2. IR studies

The IR spectra of all four salts reveal a strong band at approximately 1880 cm⁻¹ for the characteristic CO absorption, also indicating the presence of the Co(CO)₄⁻ anion [36]; however, the spectra also contain minor differences. With the lengthening of the alkyl chain, the CO absorption (T₂) band shifts to lower wavenumbers, indicting the effect of so-called interionic hydrogen bonding between ion pairs [22]. The bands at ~3450 cm⁻¹ also reflect intermolecular hydrogen bands. In each infrared spectrum of the four prepared compounds, the symmetry-forbidden A₁ bands at ~2008 cm⁻¹ are observed,



Fig. 1. IR spectra of 3a-3d.

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Tabla 1

rg values of Ja-Ju .							
Compound	3a	3b	3c	3d			
T _g ∕°C	-77	-65	-60	-55			

indicating a distortion of the anion $Co(CO)_4^-$ from ideal T_d symmetry. This distortion could be caused by the hydrogen bonds [22,37–38], and the appearance of these forbidden bands provides a reliable measure to confirm the existence of these distortions in crystalline charge-transfer salts, which has been previously illustrated by Bockman et al. [37]. Moreover, the most distorted anion out of the four salts is apparent because of the close proximity of the anion/cation pairs (Fig. 1).

3.1.3. Melting point and stability

The thermal behavior of the four ILs salts **3a–3d** was analyzed using DSC and TG-DSC techniques, and the T_g data are listed in Table 1. For all four compounds, the glass transition temperature was approximately –60 °C, indicating that they are room-temperature ILs.

The thermal stability of the four compounds was also measured using thermogravimetric analysis. The TG-DSC curves (Fig. 2) reveal that the four ILs are quite robust and thermal stable, and their decomposition temperatures are high (approximately 200 °C). It is clear that the thermal stability of compounds **3a**-**3d** satisfies the requirements of most chemical reaction systems.

Because of the existence of interionic hydrogen bonding (which can be confirmed by the bands at ~3450 cm⁻¹ in the IR spectrum in Fig. 1) [22], the stability of compounds **3a-3d** is much better than that of conventional Co(CO)₄⁻ salts, such as NaCo(CO)₄ and KCo(CO)₄. After exposure to air for 24 h at room temperature, the physical appearances of compounds **3a-3d** were unchanged. The IR spectra of compound **3a** before the reaction and after 4 runs are presented in Fig. 3, and there are no obvious changes. The characteristic CO absorption band at ~1860 cm⁻¹ and symmetry-forbidden A₁ band at ~2008 cm⁻¹ can still be observed in the IR spectra of compound **3a** after 4 runs. However, the bands at 3300–3500 cm⁻¹ show slight changes, which were most likely caused by the presence of a few impurities. Therefore, this result also demonstrates the stability of catalyst **3a**.



Fig. 2. TG-DSC curves of 3a-3d.



3.1.4. NMR studies

All four salts (3a-3d) exhibited similar ¹H and ¹³C NMR chemical shifts compared with their corresponding halide precursors (2a-2d), which indicated that no major change occurred in the chemical structure of the cationic part of the compounds. Thus, the cationic part of the compounds was confirmed to exhibit the expected structure. In the ¹H NMR spectra, the peaks for the 1-H of the N atoms and 1-H of the *N*-alkyls were shifted upfield compared with those of their corresponding halide precursors because of the effect of the interionic hydrogen bonding. In addition, the carbonyl carbon atoms were still not observed under normal conditions, as previously reported [11,22], most likely because of the paramagnetism of the cobalt center.

3.1.5. UV-Vis studies

The UV-Vis absorption spectra for all four compounds **3a–3d** in the region 200–700 nm were investigated in dichloromethane. The results are presented in Table 2. Data for KCo(CO)₄ derived from the literature [22] are also listed for comparison. The spectra are clearly similar to that of KCo(CO)₄. According to the literature [22], the latter shows a major absorption band at 233 nm and a shoulder at 360 nm, which is assigned as the internal charge-transfer absorption band (> 350 nm). Compounds **3a–3d** exhibit a similar absorption band at approximately 230 nm, as observed in Table 2. The characteristic Co(CO)₄⁻ band at ~230 nm persists, indicating the presence of Co(CO)₄⁻.

3.1.6. HRMS (ESI) studies

In the HRMS (ESI) spectra, the peaks of the cations and anions are observed, which strongly confirms the structure and purity of the expected compounds, except that in some cases, the cobalt tetracarbonyl anion tends to lose one or two carbonyls to afford $Co(CO)_3^-$ or $Co(CO)_2^-$.

3.2. Catalytic performance of cobalt carbonyl ILs based on 1,1,3,3-tetra-alkylguanidine

3.2.1. Optimization of reaction conditions

The catalytic activity of cobalt carbonyl ILs based on

Table 2 UV-Vis absorption bands of KCo(CO)₄ and **3a–3d** in dichloromethane.

•	, ,
Compound	UV-Vis absorption bands (nm)
KCo(CO) ₄	233, 360(sh)
3a	229
3b	229
3c	229
3d	234

1,1,3,3-tetra-alkylguanidine in the reaction of alkoxycarbonylation of propylene oxide (PO) was investigated. In addition, the reaction conditions were optimized (Table 3). Upon treating the substrate PO with 2 mol% catalyst 3a-3d in ethanol under CO atmosphere, the desired product was obtained with little difference in conversion or selection (Table 3, entries 1-4). Compounds 3a-3d showed distinct catalytic activity, with that of 3a exhibiting the optimal activity. Moreover, good catalytic activity of 3a could be achieved when ethanol was used as both the reactant and solvent (Table 3, entries 5-7) without adding other solvents. The conversion of PO and yield of ethyl 3-hydroxybutyrate increased with increasing catalyst loading and changed slightly when the catalyst:PO ratio was greater than 3 mol% (Table 3, entries 5 and 8-10). The effect of temperature on this reaction was significant (Table 3, entries 5 and 11-13). With increasing temperature, the PO conversion greatly increased; however, the selectivity to ethyl 3-hydroxybutyrate decreased when the temperature was above 80 °C (Table 3, entries 5 and 11-13). The conversion of PO and yield of ethyl 3-hydroxybutyrate increased with increasing CO pressure and changed slightly when the CO pressure was greater than 5 MPa (Table 3, entries 12 and 14-16). In addition, the effect of time on this reaction should not be underestimated (Table 3, entries 16-18). The conversion of PO and yield of ethyl 3-hydroxybutyrate increased with increasing time. Fairly high conversion (99%) and selectivity (98%) could be obtained with optimal and relatively mild reaction conditions (Table 3, entry 19).

Moreover, the catalytic performance of **3a** for the hydroesterification of PO was compared with that of a conventional catalytic system $Co_2(CO)_8$ (Table 3, entry 20). It is apparent that the catalytic activity of **3a** was better than that of $Co_2(CO)_8$. The existence of 1,1-dimethyl-3,3-diethylguanidinium⁺ appeared to assist the ring-opening process of the PO [23,28,30–32], and the introduction of the guanidinium ILs pattern to the catalyst not only prevented catalyst leaching but also increased the stability of the catalyst.

3.2.2. Substrate scope of the terminal epoxide

The ready alkoxycarbonylation of propylene oxide with catalyst **3a** in ethanol under relatively mild reaction conditions motivated the study of the general range of this catalytic process for the synthesis of β -hydroxy esters. Thus, the scope of the substrate epoxides bearing alkyl, alkenyl, glycidyl, heteroatom, aryl, and alkyl-aryl groups for the reaction was explored. Generally, β -hydroxy esters were obtained in good yields. Terminal epoxides bearing simple alkyl and alkenyl groups reacted

Table 3
Optimization of reaction conditions a

$\bigcirc O + CO + EtOH \longrightarrow OH O OH O$								
Entry	Catalyst	Catalyst/PO (mol%)	Solvent	<i>Т/</i> °С	<i>P</i> (CO)/MPa	t/h	Conversion ^b (%)	Selectivity ^b (%)
1	3a	2	EtOH (2 mL)	60	7	24	54	95
2	3b	2	EtOH (2 mL)	60	7	24	50	91
3	3c	2	EtOH (2 mL)	60	7	24	46	86
4	3d	2	EtOH (2 mL)	60	7	24	35	85
5	3a	2	EtOH (3 mL)	60	7	24	77	90
6	3a	2	EtOH (0.5 mL), 1,4-dioxane (2.5 mL)	60	7	24	25	80
7	3a	2	EtOH (0.5 mL), THF (2.5 mL)	60	7	24	27	83
8	3a	1	EtOH (3 mL)	60	7	24	46	85
9	3a	3	EtOH (3 mL)	60	7	24	92	99
10	3a	4	EtOH (3 mL)	60	7	24	94	97
11	3a	2	EtOH (3 mL)	40	7	24	14	89
12	3a	2	EtOH (3 mL)	80	7	24	97	95
13	3a	2	EtOH (3 mL)	100	7	24	99	73
14	3a	2	EtOH (3 mL)	80	4	24	73	90
15	3a	2	EtOH (3 mL)	80	5	24	82	93
16	3a	2	EtOH (3 mL)	80	6	24	97	96
17	3a	2	EtOH (3 mL)	80	6	8	35	89
18	3a	2	EtOH (3 mL)	80	6	16	77	98
19	3a	3	EtOH (3 mL)	80	6	24	99	98
20	Co ₂ (CO) ₈	3	EtOH (3 mL)	80	6	24	78	85

^a Reaction conditions: PO (5.0 mmol). ^b Determined by GC with internal standard method.

well (Table 4, entries 1-4). In addition, various glycidol ether-functionalized epoxides also showed good reactivity (Table 4, entries 5-7). Moreover, the epoxides bearing heteroatoms such as epichlorohydrin obtained general yields (Table 4, entry 8). In addition, aryl- and alkyl-aryl-functionalized epoxides are known to react slowly, thus affording lower yields. Fortunately, 2-phenylpropylene oxide and 3-phenylbutene 1,2-oxide produced relatively good yields compared with those reported in previous studies [25,39] (Table 4, entries 9 and 10). However, the reaction of the cyclohexene oxide failed to afford the desired isolated product because of the poor reactivity (Table 4, entry 11).

3.2.3. Effect of configuration on ethoxycarbonylation of PO

The effect of the configuration on ethoxycarbonylation of PO was also studied (Table 5) with this catalytic system. We observed that the configuration of the product was consistent with the substrate without racemization.

Table 4

Substrate scope of alkoxycarbonylation of terminal epoxides to β -hydroxy esters ^a.

		R +	CO +	EtOH -	3 a	\rightarrow R O			
Entry	Epoxide	Product	Conver- sion ^b (%)	Isolated yield (%)	Entry	Epoxide	Product	Conver- sion ^b (%)	Isolated yield (%)
1	Å		99	81	7			89	79
2	\checkmark	он о о~ 4b	98	90	8	Cl		87	70
3		он о о~ 4с	95	89	9			53	40
4		OH O → → → → → → → → → → → → → → → → → → →	89	80	10			85	71
5			97	92	11	O		14	0
6			91	84			\ 4 K		

^a Reaction conditions: epoxide (5.0 mmol), 3a (0.15 mmol) in ethanol (3.0 mL) under CO 6.0 MPa at 80 °C for 24 h. ^b Determined by GC with internal standard method.

Table 5

Effect of configuration on ethoxycarbonylation of PO a.

- + CO + EtOH -	$3a \rightarrow 4$	$\sim 0^{-1}$
Conversion ^b	Selectivity ^b	ee of the
(%)	(%)	product ^c (%)
99	98	—
99	99	> 99.9
98	99	> 99.9
	Conversion b (%) 99 99 98	$\begin{array}{c ccccccccccccccccccccccccccccccccccc$

 $^{\rm a}$ Reaction conditions: PO (5.0 mmol), **3a** (0.15 mmol) in ethanol (3.0 mL) under CO 6.0 MPa at 80 °C for 24 h.

^b Determined by GC with internal standard method.

^c Determined by GC with available capillary column Chirasil-Dex CB.



Fig. 4. Recyclability of **3a** in the alkoxycarbonylation of PO. Reaction conditions: PO (5.0 mmol), **3a** (0.15 mmol) in ethanol (3.0 mL) under CO 6.0 MPa at 80 °C for 24 h.

3.2.4. Catalyst reusability

To evaluate the recyclability of the catalyst, the reusability of catalyst **3a** was examined for the ethoxycarbonylation of PO, and the results are presented in Fig. 4. The catalyst **3a** could be reused effectively at least six times with a small loss of selectivity and only a minor decrease in conversion. The catalytic system clearly exhibited good recyclability, which is considered a breakthrough that can mostly be attributed to the good stability of the catalyst.

4. Conclusions

A series of new cobalt carbonyl ILs based on 1,1,3,3-tetraalkylguanidine were designed, successfully synthesized, and characterized using various techniques. Because of the presence of interionic hydrogen bonds, compounds **3a–3d** are relatively stable when exposed to air. Moreover, the compounds exhibited remarkably good thermal stability. Notably, the catalyst **3a** exhibited quite good catalytic activity and reusability in the reaction of alkoxycarbonylation of epoxides. The catalytic system could be reused at least six times with no significant decrease in selectivity or conversion. These new discoveries are beneficial for future investigations of these novel and interesting compounds.

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Graphical Abstract

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Cobalt carbonyl ionic liquids based on the 1,1,3,3-tetra-alkylguanidine cation: Novel, highly efficient, and reusable catalysts for the carbonylation of epoxides

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A series of novel cobalt carbonyl ionic liquids based on 1,1,3,3-tetra-alkylguanidine were synthesized. The catalytic performance of these compounds was investigated in the carbonylation of epoxides, with **3a** exhibiting the best catalytic activity and recyclability.

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