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

200.2120 ($\text{C}_{11}\text{H}_{26}\text{N}_3^+$); HRMS (ESI) negative ion: m/z 170.9135 ($\text{Co}(\text{CO})_4^-$), 142.9203 ($\text{Co}(\text{CO})_3^-$), 114.9254 ($\text{Co}(\text{CO})_2^-$).

3c 0.25 g, 80%; T_g : -60°C ; thermal decomposition temperature: 208°C ; selected $\nu_{\text{max}}/\text{cm}^{-1}$ (KBr) 1882 vs ($\text{Co}(\text{CO})_4^-$); ^1H NMR (400 MHz, $\text{DMSO}-d_6$): 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); ^{13}C NMR (100 MHz, $\text{DMSO}-d_6$): δ 158.1, 49.2, 39.4, 24.9; HRMS (ESI) positive ion: m/z 142.1342 ($\text{C}_7\text{H}_{16}\text{N}_3^+$); HRMS (ESI) negative ion: m/z 170.9134 ($\text{Co}(\text{CO})_4^-$), 142.9196 ($\text{Co}(\text{CO})_3^-$), 114.9249 ($\text{Co}(\text{CO})_2^-$).

3d 0.27 g, 83%; T_g : -55°C ; thermal decomposition temperature: 202°C ; selected $\nu_{\text{max}}/\text{cm}^{-1}$ (KBr) 1879 vs ($\text{Co}(\text{CO})_4^-$); ^1H NMR (400 MHz, $\text{DMSO}-d_6$): δ 7.82 (s, 2H), 3.25 (d, $J = 5.1$ Hz, 4H), 2.91 (s, 6H), 1.59 (s, 6H); ^{13}C NMR (100 MHz, $\text{DMSO}-d_6$): δ 160.4, 48.6, 39.3, 25.0, 23.3; HRMS (ESI) positive ion: m/z 156.1489 ($\text{C}_8\text{H}_{18}\text{N}_3^+$); HRMS (ESI) negative ion: m/z 170.9132 ($\text{Co}(\text{CO})_4^-$), 142.9204 ($\text{Co}(\text{CO})_3^-$), 114.9253 ($\text{Co}(\text{CO})_2^-$).

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, CDCl_3): 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); ^{13}C NMR (100 MHz, CDCl_3): 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, CDCl_3): 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); ^{13}C NMR (100 MHz, CDCl_3): 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, CDCl_3): 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); ^{13}C NMR (100 MHz, CDCl_3): 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, CDCl_3): 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); ^{13}C NMR (100 MHz, CDCl_3): 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, CDCl_3): 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); ^{13}C NMR (100 MHz, CDCl_3): 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, CDCl_3): 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); ^{13}C NMR (100 MHz, CDCl_3): 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, CDCl_3): 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); ^{13}C NMR (100 MHz, CDCl_3): 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, CDCl_3): 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, CDCl_3): 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, CDCl_3): δ 4.30–4.22 (m,

Scheme 2. Alkoxycarbonylation of epoxides.

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, CDCl_3): 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, CDCl_3): 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); ^{13}C NMR (100 MHz, CDCl_3): 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 $\text{Co}(\text{CO})_4^-$ anion [36]; however, the spectra also contain minor differences. With the lengthening of the alkyl chain, the CO absorption (T_2) band shifts to lower wavenumbers, indicating the effect of so-called interionic hydrogen bonding between ion pairs [22]. The bands at $\sim 3450\text{ cm}^{-1}$ also reflect intermolecular hydrogen bands. In each infrared spectrum of the four prepared compounds, the symmetry-forbidden A_1 bands at $\sim 2008\text{ cm}^{-1}$ are observed,

Fig. 1. IR spectra of **3a–3d**.

Table 1

T_g values of **3a–3d**.

Compound	3a	3b	3c	3d
$T_g/^\circ\text{C}$	−77	−65	−60	−55

indicating a distortion of the anion $\text{Co}(\text{CO})_4^-$ 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 $-60\text{ }^\circ\text{C}$, 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 $200\text{ }^\circ\text{C}$). 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 $\sim 3450\text{ cm}^{-1}$ in the IR spectrum in Fig. 1) [22], the stability of compounds **3a–3d** is much better than that of conventional $\text{Co}(\text{CO})_4^-$ salts, such as $\text{NaCo}(\text{CO})_4$ and $\text{KCo}(\text{CO})_4$. 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 $\sim 1860\text{ cm}^{-1}$ and symmetry-forbidden A_1 band at $\sim 2008\text{ cm}^{-1}$ can still be observed in the IR spectra of compound **3a** after 4 runs. However, the bands at $3300\text{--}3500\text{ cm}^{-1}$ 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**.

Fig. 3. IR spectra of **3a**.

3.1.4. NMR studies

All four salts (**3a–3d**) exhibited similar ^1H and ^{13}C 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 $\text{KCo}(\text{CO})_4$ derived from the literature [22] are also listed for comparison. The spectra are clearly similar to that of $\text{KCo}(\text{CO})_4$. 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 $\text{Co}(\text{CO})_4^-$ band at ~ 230 nm persists, indicating the presence of $\text{Co}(\text{CO})_4^-$.

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 $\text{Co}(\text{CO})_3^-$ or $\text{Co}(\text{CO})_2^-$.

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 $\text{KCo}(\text{CO})_4$ and **3a–3d** in dichloromethane.

Compound	UV-Vis absorption bands (nm)
$\text{KCo}(\text{CO})_4$	233, 360(sh)
3a	229
3b	229
3c	229
3d	234

1,1,3,3-tetra-alkylguanidine in the reaction of alkoxy carbonylation 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 $\text{Co}_2(\text{CO})_8$ (Table 3, entry 20). It is apparent that the catalytic activity of **3a** was better than that of $\text{Co}_2(\text{CO})_8$. 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 alkoxy carbonylation 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 3Optimization of reaction conditions ^a.

Entry	Catalyst	Catalyst/PO (mol%)	Solvent	T/°C	P(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 4Substrate scope of alkoxy carbonylation of terminal epoxides to β -hydroxy esters ^a.

Entry	Epoxide	Product	Conversion ^b (%)	Isolated yield (%)	Entry	Epoxide	Product	Conversion ^b (%)	Isolated yield (%)
1			99	81	7			89	79
2			98	90	8			87	70
3			95	89	9			53	40
4			89	80	10			85	71
5			97	92	11			14	0
6			91	84					

^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 5Effect of configuration on ethoxycarbonylation of PO ^a.

Optical	Conversion ^b (%)	Selectivity ^b (%)	ee of the product ^c (%)
Rac (ee = 0)	99	98	—
S (> 99.9%)	99	99	> 99.9
R (> 99.9%)	98	99	> 99.9

^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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1,1,3,3-四烷基胍羰基钴离子液体: 高效可循环利用的环氧化合物 羰基化反应催化新材料

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摘要: 离子液体因其所独有的物理化学性质如蒸气压低、热稳定性好以及结构和性能的可调性等优点而备受关注。四羰基钴阴离子是多种重要均相催化反应的催化活性物种, 含有四羰基钴阴离子的金属有机离子液体有效结合了羰基金属和离子液体各自的特点和优势, 作为一类新颖而且重要的功能化离子液体, 受到国内外研究者的青睐。2001年, Dyson等首次报道了一种室温下为液态的羰基钴金属有机离子液体 [bmim][Co(CO)₄], 为四羰基钴阴离子离子液体的研究开创了先河。此后, 有关羰基钴金属有机离子液体的催化应用研究也相继报道。目前[CnPy][Co(CO)₄]以及[bmim][Co(CO)₄]在环氧化合物的羰基化反应中已有报道, 但该类催化剂的催化活性特别是循环使用性能有待进一步提高。

胍盐具有阳离子电荷分散程度高、热稳定性和化学稳定性高、三个氮原子上的基团可以调节等特点, 使得胍盐离子液体的设计、合成和应用研究受到国内外学者关注。由于其自身结构特点, 氮原子上有取代基可以和含F、O、N底物作用形成氢键, 并且氮原子上取代烷基之间作用使阳离子的平面结构发生变化, 使得与三个氮原子相连的碳原子处于缺电子状态, 使阳离子表现出Lewis酸性。所以其在环氧化合物氢酯基化反应中可起到稳定四羰基钴阴离子以及活化环氧化合物的作用。

基于此, 本文以较高收率合成了四种新型的1,1,3,3-四烷基胍羰基钴金属有机离子液体: 1,1-二甲基-3,3-二乙基胍羰基钴(**3a**), 1,1-二甲基-3,3-二正丁基胍羰基钴(**3b**), 1,1-二甲基-3,3-四亚甲基胍羰基钴(**3c**), 1,1-二甲基-3,3-五亚甲基胍羰基钴(**3d**)。通过红外光谱、紫外-可见光谱、¹H核磁共振谱、¹³C核磁共振谱、高分辨质谱、差示量热扫描仪和热重分析对该类化合物进行了结构确认及性质研究。这四种催化剂, 特别是**3a**, 在环氧化合物的氢酯基化反应中表现出优异的催化性能, 在无需任何助剂的情况下具有较好的催化活性及底物适用性。此外, 以不同构型的环氧丙烷为反应底物, 氢酯基化反应结果显示: 在该催化体系作用下, 产物的构型与底物保持一致, 没有发生消旋。尤其值得指出的是, 催化剂**3a**在环氧丙烷的氢酯基化反应中表现出了优异的循环稳定性, 在循环使用6次后依然可以获得较好的转化率(91%)和选择性(94%)。

关键词: 羰基钴离子液体; 羰基化反应; 环氧化合物; 四烷基胍; 循环稳定性

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