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Synthesis and Evaluation of Stable, Efficient, and Recyclable Carbonylation Catalysts: Polyether-Substituted Imidazolium Carbonyl Cobalt Ionic Liquids

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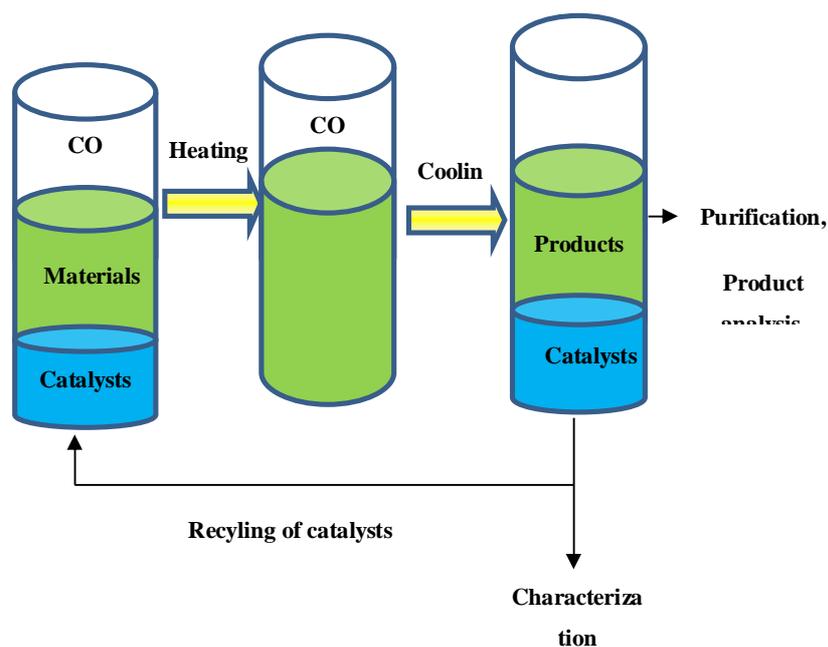
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Graphical Abstract:

Polyether-substituted imidazolium ionic liquids, representing an affirmative case of stabilizing the highly air sensitive cobalt tetracarbonyl anion, have been successfully synthesized and used in hydroesterification of 4-isobutylstyrene by thermoregulated phase-separable catalysis (TPSC) system. The TPSC system exhibits good recycling efficiency and provides a potential route for an environmentally benign carbonylation reaction.



Materials: 4-isobutylstyrene, methanol, CO

Catalysts: $[\text{H}(\text{OCH}_2\text{CH}_2)_n\text{bim}][\text{Co}(\text{CO})_4]$

Products: 2-(4-isobutylphenyl) propionic acid methyl ester

Highlights:

1. Functionalized $[\text{H}(\text{OCH}_2\text{CH}_2)_n\text{bim}][\text{Co}(\text{CO})_4]$ ILs are synthesized successfully.
2. Thermoregulated phase-separable catalysis (TPSC) system has been established.
3. The TPSC system exhibits good recycling efficiency in hydroesterification of 4-isobutylstyrene.

ABSTRACT: The synthesis and catalytic performance of stable, efficient, and recyclable multi-functionalized ionic liquid catalysts are reported for the first time. Through an optimized synthetic strategy, a series of polyether-substituted imidazolium cobalt tetracarbonyl salts, $[\text{H}(\text{OCH}_2\text{CH}_2)_n\text{bim}][\text{Co}(\text{CO})_4]$ ($n = 8, 15, \text{ and } 22$, bim = butylimidazolium), and their intermediates, were successfully synthesized and characterized by IR, UV-Vis, ^1H NMR, ^{13}C NMR, and TGA. The stability, solubility, and critical solution temperature of the ionic liquids were also determined. A thermoregulated phase-separation catalysis system for the hydroesterification of olefins has been established based on the above multi-functionalized ionic liquid catalyst. The results show that this catalysis system has a high recycling efficiency, and provides a potential method for an environmentally benign carbonylation process.

Abbreviations: Critical solution temperature (CST); thermoregulated phase-separation catalysis (TPSC); functionalized ionic liquid (FIL); butylimidazolium (bim); 1-butyl-3-methylimidazolium (bmim).

Keywords: Bifunctionalized ionic liquids; Carbonylation catalyst; Thermoregulated biphasic system; Imidazolium; Carbonyl cobalt

1. INTRODUCTION

In recent years, functionalized ionic liquids (FILs) have been paid increasing research attention because of their ability to be tailored for various chemical tasks [1,2]. Many transition metal carbonyl species have been introduced into FILs, producing organometallic ionic liquids [3-5], which, while having comparable catalytic activity to conventional organometallic catalysts, show some improvements, such as lower viscosity, better stability, improved solubility, and excellent recovery [6,7].

PEG-based ionic liquids are a new appealing group of solvents making the link between two distinct but very similar fluids: ionic liquids and poly(ethylene glycol)s. They find applications across a range of innumerable disciplines in science, technology, and engineering. In the last two years, the possibility to use these as alternative solvents for organic synthesis and catalysis has been increasingly explored [8].

The cobalt tetracarbonyl anion, $[\text{Co}(\text{CO})_4]^-$, is one of the most important active catalytic species and has been widely used in a number of catalytic reactions [9-16]. Although some ionic liquid compounds containing $[\text{Co}(\text{CO})_4]^-$ have been successfully synthesized and employed in some reactions, most of them are homogeneous catalysts, which are difficult to recycle. In addition, because it is unstable and sensitive to air, the direct use of $[\text{Co}(\text{CO})_4]^-$ is limited [5].

The search for a way to combine the advantages of homogeneous catalysis, such as ease of modulation, and heterogeneous catalysis, such as ease of recycling, is one of the most exciting challenges in modern chemistry. Indeed, various efficient immobilization methods for homogeneous catalyst have been developed in recent years through the use of methods such as liquid-liquid organometallic biphasic catalysis and heterogenization of molecular catalysts on solid supports. However, the advantages of these methods come at the expense of catalytic activity. [17]

For the purpose of the recycling of catalysts, functionalized ionic liquid methodology was tentatively applied to the ionic liquid/organic biphasic catalysis system [18]. For example, we have shown that $[\text{bmim}][\text{Co}(\text{CO})_4]$ ($\text{bmim} = 1\text{-butyl-3-methylimidazolium}$) is an efficient catalyst for the hydroesterification of ethylene oxide [14]. It was reported that introducing the polyether chain to the ligands or ionic liquids not only facilitates dispersion in the reaction system by reducing ionic liquid viscosity, but also allows catalysts to be thermoregulated [19].

In this paper, we report the convenient synthesis of a series of polyether-substituted imidazolium cobalt carbonyl ionic liquids, as well as their detailed characterization and catalytic performance in hydroesterification. Moreover, preliminary studies on the application of these functionalized ionic liquids in a thermoregulated phase-separation catalysis system (TPSC) have been performed by applying this system to the hydroesterification of 4-isobutyl styrene.

2. RESULTS AND DISCUSSION

2.01 Synthesis of the Polyether-Substituted Imidazolium Carbonyl Cobalt Ionic Liquids. The synthesis of $[\text{H}(\text{OCH}_2\text{CH}_2)_n\text{bmim}][\text{Co}(\text{CO})_4]$ **4** is shown in Scheme 1. $\text{NaCo}(\text{CO})_4$ was prepared by a method previously reported in the literature [20]. Firstly, ethylene oxide was reacted with imidazole to obtain 3-poly(ethylene glycol) imidazole **2** containing different numbers of polymerized ethylene oxide units ($n = 8, 15, \text{ and } 22$). Then, **2** was reacted with *n*-butyl chloride to produce chloro-substituted 1-butyl-3-poly(ethylene glycol) imidazole **3**, i.e. $[\text{H}(\text{OCH}_2\text{CH}_2)_n\text{bmim}]\text{Cl}$, **3**. Finally, compounds **4** were obtained by the ion exchange reaction of **3** with $\text{NaCo}(\text{CO})_4$. The resultant compounds **4** were red-brown, viscous liquids at room temperature.

2.02 Solubility. The solubilities of **4** ($n = 8, 15, \text{ and } 22$) were determined qualitatively in several common solvents. All three salts show similar solubility. They are all well dissolved in polar organic solvents, such as methanol, ethanol, acetone, and water, and are insoluble in some weakly polar solvents such as ether, cyclohexane, and *n*-hexane, most likely due to existence of the ionic bond. Moreover, the length of the polyether chain also has a significant effect on the solubility. In some solvents, such as ethyl acetate, toluene, THF and 1,4-dioxane, the solubility of **4** increases with an increase in the length of the polyether chain. According to the literature $[\text{bmim}][\text{Co}(\text{CO})_4]$ is almost insoluble in water [21]. However, all the versions of **4** are highly soluble in water because of the polyether chain, which can form hydrogen bonds with water through the alternate ether linkages and the hydroxyl terminus. This solubility in water removes the need for organic solvents, making our catalyst potentially applicable to green chemistry.

2.03 Stability. These compounds have shown comparatively better air stability than analogous conventional $[\text{Co}(\text{CO})_4]^-$ salts, such as $\text{NaCo}(\text{CO})_4$ and $\text{KCo}(\text{CO})_4$, which are easily oxidized by air because of the -1 valence of Co, due to the strong effect of the electron pair (it can be seen by IR spectrum in figure 1). In addition, their air stability significantly increases with the value of n. No obviously changes in the physical appearance and IR spectrum of $[\text{H}(\text{OCH}_2\text{CH}_2)_{22}\text{bim}][\text{Co}(\text{CO})_4]$ are observed after exposure to air for 32 h at room temperature.

2.04 Infrared Studies. In all infrared spectra of $\text{Na}[\text{Co}(\text{CO})_4]$, $\text{K}[\text{Co}(\text{CO})_4]$, and compounds **4a–4c**, the characteristic carbonyl T_2 absorption bands near 1886 cm^{-1} are found, indicating the presence of $[\text{Co}(\text{CO})_4]^-$. However, these absorption bands are slightly different for the different compounds. Generally, compared with the corresponding pyridinium compounds, the carbonyl absorption band for the imidazolium compounds is shifted to higher wave numbers [5], and with the change of polyether chain length, the carbonyl stretching band appears to be red-shifted, which usually indicates the presence of interionic hydrogen bonds between the ion pairs. In the IR spectra of compounds **4a–4c**, the appearance of the symmetry-forbidden A_1 bands near 2003 cm^{-1} indicate that $[\text{Co}(\text{CO})_4]^-$ has a certain degree of torsion deformation compared with the usual tetrahedral structure. This may be caused by the hydrogen bonding between the tetracarbonyl cobalt and the cation. In contrast, the single band at 1883 cm^{-1} for crystalline $[\text{PPN}][\text{Co}(\text{CO})_4]$ (PPN = $(\text{Ph}_3\text{P})_2\text{N}^+$) is assigned to the T_2 mode of undistorted tetrahedral $[\text{Co}(\text{CO})_4]^-$ [20]. The IR spectrum of $\text{NaCo}(\text{CO})_4$ shows a split carbonyl peak at 2014 cm^{-1} , while the T_2 bands of **4a–4c** are split in another way (Table 1), which is similar to previous observations of $\text{Q}^+[\text{Co}(\text{CO})_4]^-$ (Q = N-methyl-1-quinolinium) [23]. It has been demonstrated by Bockman and Kochi that the splitting of carbonyl peaks provides a means for the effective and accurate measurement of the degree of torsional deformation in $[\text{Co}(\text{CO})_4]^-$ compared with the standard tetrahedral shape. The occurrence of this distortion can also indicate that the substance is present as a charge-transfer salt. Edgell *et al.* [24] also reported that the splitting degree of carbonyl peaks is an effective method for measuring anionic asymmetry. These results suggest that the $[\text{Co}(\text{CO})_4]^-$ anion of compounds **4a–4c** are distorted due to the close proximity of the anion/cation pairs. Additionally, in the case of compound **4c**, the characteristic absorption band for the hydroxyl-terminus of the polyether chain is found at 3418 cm^{-1} , and the absorption bands of the methylene ($-\text{CH}_2-$) and alternate ether linkages ($-\text{C}-\text{O}-\text{C}-$) appear at 2822 cm^{-1} and 1114 cm^{-1} , respectively. These indicate the formation of a polyether structure (see Figure 1).

2.05 NMR Studies. There was almost no difference in the chemical shifts in the ^1H and ^{13}C NMR spectra of compounds **4a–4c** and their corresponding halide precursors. This suggests that the chemical structure of the cations does not change after the synthesis of the compounds. In addition, peaks at $\delta\ 2.8\text{--}3.6\text{ ppm}$ in the ^1H spectra, and $\delta\ 68\text{--}71$ in the ^{13}C spectra, indicate the existence of the polyether structure. The integral area ratio of characteristic peaks can be used to estimate the average polymerization degree in terms of the formula: $n \approx \text{Ap}/\text{At} \times \text{Bt}/4$ (Ap: Integral area of polyether unit; At: Integral area of butyl in the imidazole ring; Bt: The number of hydrogen atoms on the butyl) [27]. Taking ^1H NMR spectrum of compound **4c** for example, the result of the calculation is approximately 23.72, which is consistent with the theoretical value.

2.06 UV-Vis Studies. The UV-Vis absorption spectra were investigated in the region 200–800 nm for the two compounds **4b** (n = 15) and **4c** (n = 22). Data for $\text{NaCo}(\text{CO})_4$ and compounds **3** (n = 15 and 22) were also recorded for comparison. The results are listed in Table 2. It is clear that the spectra of compounds **4** absorption spectra of compounds **4b** and **4c** are almost consistent with those of their corresponding halide precursors in dichloromethane. In previously published papers [26,27], the absorption bands in the halogenated alkylimidazolium ionic liquids are generally found in the 200–290 nm region, while the characteristic absorption band for $[\text{Co}(\text{CO})_4]^-$ at 305 nm in this paper may be due to the imidazole ring absorption, which is red shifted by polyether chains serving as auxochrome groups. Compounds **4** exhibit a single UV-Vis absorption band because the absorption bands of the anions and cations appear at the same position.

2.07 Thermogravimetric Analysis (TGA). The thermal stability of compound **4c** has been studied by means of thermogravimetric analysis. The TGA curve (Figure 2), shows that the initial decomposition temperature of compound **4c** is $243.9\text{ }^\circ\text{C}$. This stability

meets the requirements of the majority of chemical reaction systems, especially hydroesterification reactions catalyzed by cobalt carbonyl, in which the reaction temperature is generally below 200 °C.

Melting Point and Viscosity. The melting point of the solid compound **4c** was measured with a micro-melting point instrument. The results show that the melting point is well below 50 °C, thus the salt can be classified as an ionic liquid. Compounds **4a** and **4b** are liquid at room temperature, and all three compounds are similar to conventional imidazolium ionic liquids. The viscosity of the compounds is high due to interionic hydrogen bonds between the ion pairs (see the IR) [28,29]. Deng [20] suggested that, where the cation is the same, ionic liquids containing $[\text{Co}(\text{CO})_4]^+$ generally exhibit better fluidity compared to ionic liquids containing BF_4^- , PF_6^- . These anions are two-layer structures, unlike the three-layer atomic structure of $[\text{Co}(\text{CO})_4]^+$. The larger volume of $[\text{Co}(\text{CO})_4]^+$ leads to a bigger distance between the anions and cations, resulting in weaker ionic interaction. In addition, the viscosity of compounds **4** increases with the length of the polyether chain. Possible reasons are that increasing the length of the substituents on the imidazole ring leads to a strengthening of the van der Waals forces.

2.08 Critical Solution Temperature (CST) of Compounds 4.

The CST properties of polyether-substituted nonionic phosphine ligands in nonpolar aprotic solvents have been previously reported [30,31]. The results of the solubility for compounds **4** are shown in Table 3. Compounds **4b** and **4c** exhibit good thermoregulated solubility in 2:1 and 1.5:1 v/v mixtures of THF and n-heptane. At room temperature, compound **4c** is sparingly soluble, but when the temperature rises to around 82 °C, the solubility increases markedly. Above 82 °C, the compound is completely soluble in the mixture and the whole system becomes monophasic. Therefore, compound **4c** has a CST of 82 °C in the 1.5:1 v/v mixture of THF and n-heptane.

Moreover, as the cation and thermoregulated property provider, the solubility of compounds **3** (n = 8, 15, and 22) in the 1.5:1 v/v mixture of THF and n-heptane were also investigated and are shown in Figure 3. These compounds possess a distinctive CST, at which the solubilities of the compounds in the mixture of THF and n-heptane increase dramatically. At a certain temperature, compounds **3** (n = 8, 15, and 22) are completely dissolved in the organic solvent. Additionally, at the same temperature, the solubility decreases with increasing n, suggesting that the compound **3** (n = 22) would be a better cation as a thermoregulated property provider for the recovery of carbonyl cobalt catalysts.

The CST in the mixture of THF and n-heptane enables the polyether-substituted imidazolium ionic liquid catalysts to meet the requirements of a TPSC system. The general principle of TPSC is illustrated in Figure 4. At room temperature, the ionic liquid catalysts are insoluble in organic solvent, and the system is biphasic. When heated to temperatures above the CST, the ionic liquid catalysts are completely soluble in organic solvent, and the system becomes homogeneous. After the reaction, upon cooling to a temperature below the CST, the system becomes biphasic again, accompanied by separation of the products in the organic phase from the ionic liquid catalysts. After simple decantation, the lower ionic liquid catalysts can be recycled.

2.09 General Principle of TPSC for Polyether-substituted Imidazolium Ionic Liquid Catalysts. The utilization of $\text{Co}_2(\text{CO})_8$ as a homogeneous catalyst in carbonylation reactions has been previously established [32,33]. However, this system involves serious loss of catalyst, both due to difficulties in reclamation and decomposition due to aerobic oxidation. The $\text{Co}_2(\text{CO})_8$ generates the real active species $[\text{Co}(\text{CO})_4]^+$ *in situ* [34] whereas our system directly applies the quaternary $[\text{Co}(\text{CO})_4]^+$ salt to the reaction.

The ionic liquid catalysts **4b** and **4c** have been used in the hydroesterification of 4-isobutylstyrene in a TPSC system for preparing methyl 2-(4-isobutylphenyl)propionate, which is an important intermediate in the production of ibuprofen (Scheme 2). This is, to the best of our knowledge, the first time such a reaction has been performed in this way. The results are shown in Table 4.

2.10 Hydroesterification of 4-isobutylstyrene Catalyzed by Compounds 4b and 4c. The lengthening of the polyether chain may lead to a slight reduction of catalytic activity. It should be noted that lower conversion is obtained (Table 4, entry 4) using n-heptane⁷

as the organic phase instead of a THF/heptane mixture. However, the conversion increases when using THF as solvent (Table 4, entry 5). This result implies that the homogeneous system is better. After the reaction, the organic phase is separated from the ionic liquid catalysts by simple decantation, and the ionic liquid catalysts are directly recycled by addition of fresh solvents and substrates. Table 5 shows the recycling efficiency of the catalysts **4b** and **4c** in the TPSC system, and shows that the conversion of 4-isobutylstyrene with **4b** decreases significantly after the catalyst is reused 4 times, while catalyst **4c** could be reused 8 times with little loss of selectivity and only a minor drop in conversion. The characteristic IR carbonyl absorption bands and splitting of the major T₂ band of carbonyl in catalyst **4c** after 8 uses appeared at the 1885.89 cm⁻¹ and 2003.74 cm⁻¹, respectively, indicating the strong stability of the active catalytic component [Co(CO)₄]⁻ [24].

The leaching of Co, obtained by measuring the Co content of the organic phase after catalyst recycling in the TPSC system, is also shown in Table 5. The concentration of Co was measured by inductively coupled plasma atomic emission spectroscopy. Using **4c** as the catalyst, the leaching of Co is only 1.29% and 0.15% in the first and two uses, and rises to 0.21% and 0.18% in the 7th and 8th reuse. Using **4b** as the catalyst, the leaching of Co is between 5.85% and 8.36%. This result further indicates that a longer polyether chain is conducive to the recovery of catalysts.

The reusability of catalysts in this system can be attributed to the stability of the catalyst and the distinctive properties of the TPSC system. This represents a successful and promising example of a fairly stable catalyst which directly immobilizes the versatile [Co(CO)₄]⁻ species, and a catalysis system which has the potential to solve the problems of recovery of precious metal catalysts from homogeneous reactions.

The conversion of 4-isobutylstyrene could be greatly increased by enhancing mass transfer factors such as the increase of the stirring speed or the length of blades. The optimized hydroesterification conditions catalyzed by compound **4c** are determined as follows: temperature ~150°C, reaction time ~32 h, pressure ~7.0MPa. Under above-mentioned conditions, the conversion of 4-isobutylstyrene, selectivity of A, and selectivity of B are 97.2%, 83.9%, 16.1% respectively.

2.11 Reaction Mechanism. The mechanism proposed previously mechanism suggested for the hydroesterification reaction [35] can be modified as shown in Scheme 3. It is well established that the active species in the [H(OCH₂CH₂)_nbim]Co(CO)₄ catalyzed hydroesterification of 4-isobutylstyrene is LnCo(CO)₄ complex. The olefin added to Ln-Co bond to form a mixture of isomeric alkylcobalt tetracarbonyls. then add carbon monoxide to form acylcobalt tetracarbonyls [36-40] that reacts with methanol, which also acts as a proton source. Finally, the branched-chain ester is obtained while the catalyst is reformed.

3. CONCLUSION

New polyether-substituted imidazolium ionic liquids (**4a-4c**) have been successfully synthesized and characterized. Notably, compound [H(OCH₂CH₂)₂₂bim][Co(CO)₄]⁻ (**4c**) has good stability compared with formerly reported analogues, and may be regarded as a highly stabilized form of the highly air sensitive cobalt tetracarbonyl anion. We believe that the effective stabilization of the anion is brought about by interionic bonds and the structure of the polyether chain.

Due to its solubility in water and a wide range of other strongly polar solvents, compound **4c** can be applied to various solution systems as the catalyst. Additionally, a thermoregulated phase-separable catalysis (TPSC) system has also been developed for solving the problems associated with separation and reuse of hydroesterification catalysts. This TPSC system exhibits good recycling efficiency and provide a potential method for environmentally benign carbonylation. The conversion of 4-isobutylstyrene, selectivity of A and selectivity of B are 97.2%, 83.9%, and 16.1% respectively. These new breakthroughs are important for future investigations on these and interesting metal carbonyl ionic liquids, and the TPSC systems that may be devised using them.

4. EXPERIMENTAL SECTION

4.01 Materials and Analysis of Product

All chemicals used in this work were purchased. The solvents were used after distillation and drying by standard procedures. The products of the reaction were analyzed by GC (SP6800A) equipped with a flame ionization detector, a capillary column (OV-17, 308

m × 0.25 μm × 0.25 mm). N₂ was used as the carrier gas. GC-MS measurements were performed on a 7890A-G C/5975C-MSD instrument with a 19091S-433HP-5MS column (30 m × 250 μm × 0.25 μm). Helium was used as the carrier gas. IR spectra was measured from 4000 to 500 cm⁻¹ with a Bruker TENSOR 27 FT-IR instrument. UV spectra was recorded from 900 to 200 nm with a UNICO UV-2802 UV-Vis spectrophotometer. ¹H and ¹³C NMR spectra (500 and 125 MHz, respectively) were recorded with a Bruker AV 500 MHz spectrometer. The thermogravimetric curve was measured with NETZSCH STA-449C Thermogravimetric Analyzer and N₂ was used as the protective gas. Analysis of cobalt content was performed on an ICP-AES (IRIS INTREPID II XSP).

4.02 Preparation of NaCo(CO)₄

All chemicals were chilled for 2 h at 0 °C. Excess NaOH was put in a 100 mL round-bottom flask which was placed at once on a Schlenk line. After thorough evacuation, the flask was opened to a continuous flow of N₂ and charged with Co₂(CO)₈ (1.22 g, stabilized by n-hexane). Then, THF (40 mL) was added slowly with stirring, while a gentle stream of N₂ was maintained. The solution was stirred for 1-2 h, and then formed a pinkish purple precipitate. The light yellow solution was separated from the precipitate by centrifuging for 5min at the speed of 3000r/min, and the precipitate was washed with THF 40 mL to afford NaCo(CO)₄.

4.03 Preparation of Chloro-Substituted 1-Butyl-3-poly (ethylene glycol) Imidazole

Refrigerated imidazole (1.36 g, 20 mmol) and n-hexane (15 mL) were placed into an autoclave (75 mL). Refrigerated ethylene oxide (21.5 mL, 425.6 mmol) liquid was subsequently added into the autoclave with stirring, which was then closed and flushed with N₂. The mixture in the autoclave was stirred at room temperature for 4 h, and then at 60 °C for 6 h. The reactor was then cooled to room temperature and depressurized. After removing the solvent by reduced pressure distillation, the mixture was dried under vacuum to obtain compound **2** as a dark brown viscous liquid. Cold (~0°C) Et₂O was added to wash out the unreacted imidazole. The top Et₂O layer was decanted off, and the product was repeatedly washed with fresh Et₂O, after which it was dried in vacuo for about 12h to obtain the pure compound **2** [41]. 3-poly (ethylene glycol) Imidazole (compound **2**): ¹H NMR (500MHz, CDCl₃, δ): 7.55 (s, 1H, N-CH=N), 7.38 (br s, 1H, N⁺CHCH), 7.01 (br s, 1H, N⁺CH), 4.12 (s, 1H, OH), 2.78-3.64 (br m, 47.1H, CH₂CH₂O). The average number of ethylene oxide units in the polyether chain was calculated using the increased weight of the products [42,43]. Then 1-butyl chloride (9.28 g, 100 mmol) as reactant and solvent, and compound **2** (20 mmol) were placed in an autoclave and stirred under N₂ (6.0 MPa) for 10 h at 90 °C. The reactor was then cooled to room temperature and depressurized. Unreacted materials were removed by vacuum distillation, and chloro-substituted 1-butyl-3-poly (ethylene glycol) imidazole was obtained. The mixture was used in next step, without further purification. ¹H NMR (500MHz, CDCl₃, δ): 7.61 (s, N-CH=N), 7.37 (br s, N⁺CH), 7.03 (br s, N⁺CH), 4.30 (br s, 2H, N⁺CH₂), 4.12 (s, OH), 2.78-3.64 (br m, CH₂CH₂O), 1.89 (br s, 2H, N⁺CH₂CH₂), 1.39 (br s, 2H, N⁺CH₂CH₂CH₂), 0.97 (br s, 3H, N⁺CH₂CH₂CH₂CH₃). ¹³C NMR (125.7MHz, CDCl₃, δ): 136.21, 122.76, 121.15, 71.87, 69.68, 69.46, 60.52, 48.79, 31.26, 18.62, 12.72.

4.04 Synthesis of Compounds 4a-c

All procedures were completed on a Schlenk line under a N₂ flow. NaCo(CO)₄-THF solution (60 ml, containing 5.4 mmol of [Co(CO)₄]) was placed in a 3-necked flask, and compound **3** in THF (15 ml, containing 5.4 mmol of **3**) was added with stirring at room temperature. The ion exchange reaction completed rapidly, forming a NaCl precipitate, which could be removed through filtering by sand core funnel under N₂ protection. Then the remaining solution was added to H₂O/CH₂Cl₂ biphasic system, the compound **4** and its solvent THF could preferentially enter into CH₂Cl₂ organic phase. Both NaCo(CO)₄ and by-products were then dissolved and commixed in water [25]. Therefore, after simple phase-separation, product **4** was obtained directly from organic solution. Solvent THF and CH₂Cl₂ could be removed by reduced pressure distillation, compounds 4a-c were obtained. ¹³C NMR (125.7MHz, CDCl₃, δ): 136.21, 122.76, 121.15, 71.87, 69.68, 69.46, 60.52, 48.79, 31.26, 18.62, 12.72. FT-IR (KBr): γ_{max}/cm⁻¹ 3381.33, 3142.10, 2821.85, 2003.74, 1885.89, 1660.08, 1564.74, 1454.85, 1350.71, 1297.69, 1250.22, 1108.48, 950.28, 885.60, 845.16, 754.60.

4.05 Hydroesterification of 4-isobutylstyrene Catalyzed by 4c in the TPSC System

Freshly distilled 4-isobutylstyrene (17.4 mmol) and methanol (18.5 mmol), Pyridine (2.1 mmol), catalyst **4c** (1.27 mmol), and 25 mL THF/n-heptane mixture (v/v = 1.5:1) were added to an autoclave (75 mL). The autoclave was closed, the air in the autoclave was replaced with N₂ and CO for 3 times in turn. The mixture was heated to 100~160 °C and stirred for 16~32h under the pressure⁹

of 7.0 MPa. After completion of the reaction, the mixture was cooled to room temperature. By simple decantation, the upper organic phase (containing products) was separated from the catalyst. Then, the organic phase was washed with water, and dried over MgSO_4 . The solvent was removed by atmospheric distillation to obtain the product.

4.06 The Treatment of Reaction Mixture for Measuring Cobalt Content by ICP-AES

After being fully mixed, 1 mL of reaction mixture was pipetted into a quartz crucible, and the solvent was heated to dry at low temperature. The crucible was placed in an electric furnace, and heated until no further smoke was evolved. Then, the organic components were completely combusted in a muffle furnace at $700\text{ }^\circ\text{C}$. Then 5 mL aqua regia (a 3:1 mixture of hydrochloric and nitric acids) was added to dissolve the inorganic components. The solution was transferred to 100 mL volumetric flask, and diluted with water to the mark.

ASSOCIATED CONTENT

Supporting Information

Text and figures giving synthetic procedures and characterization data (IR, UV-Vis, ^1H NMR, ^{13}C NMR, and TGA) for $[\text{H}(\text{OCH}_2\text{CH}_2)_n\text{bim}][\text{Co}(\text{CO})_4]$ ($n=8,15,22$). This material is available free of charge via the Internet at <http://pubs.acs.org>.

Notes

The authors declare no competing financial interest

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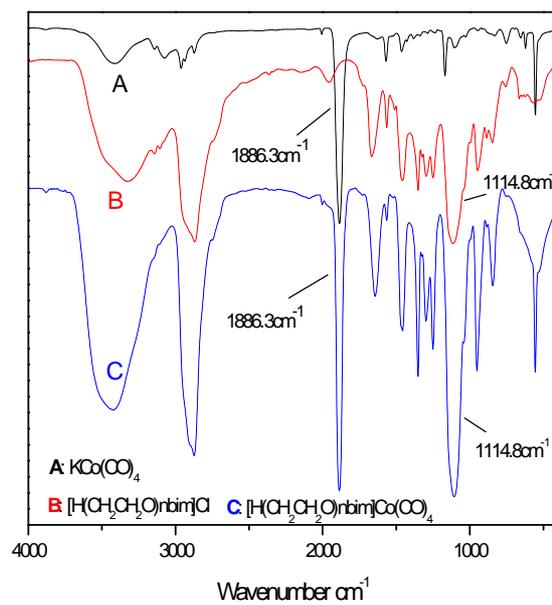


Figure 1. IR Spectra of KCo(CO)_4 , $[\text{H(OCH}_2\text{CH}_2\text{)}_{22}\text{bim}]\text{Cl}$ and $[\text{H(OCH}_2\text{CH}_2\text{)}_n\text{bim}]\text{Co(CO)}_4$.

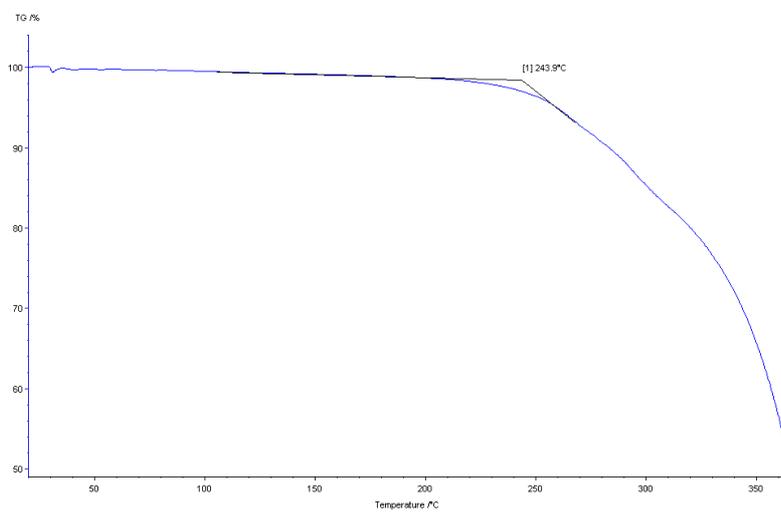


Figure 2. The TGA curve of $[\text{H(OCH}_2\text{CH}_2\text{)}_{22}\text{bim}]\text{Co(CO)}_4$.

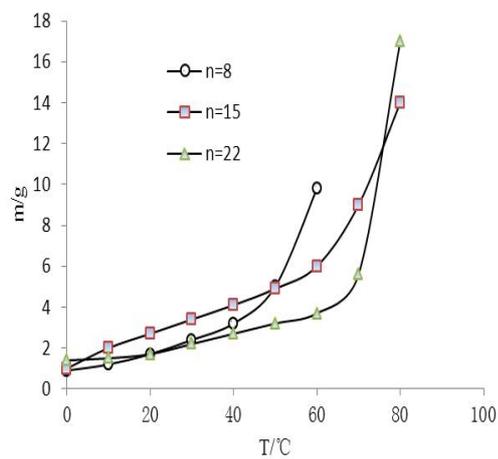
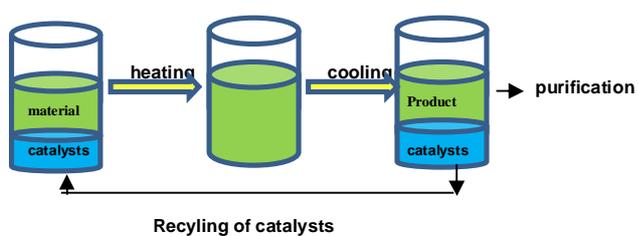


Figure 3. Solubility of compounds **3** ($n = 8, 15,$ and 22) in a mixture of THF and *n*-heptane as a function of temperature.

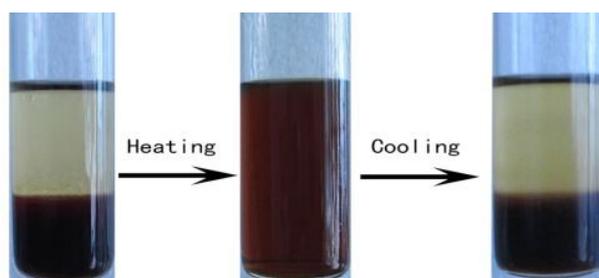


Materials: 4-isobutylstyrene, methanol, CO

Catalysts: $[\text{H}(\text{OCH}_2\text{CH}_2)_n\text{bim}][\text{Co}(\text{CO})_4]$

Products: 2-(4-isobutylphenyl) propionic acid methyl ester

Figure 4. General principle of a TPSC system.



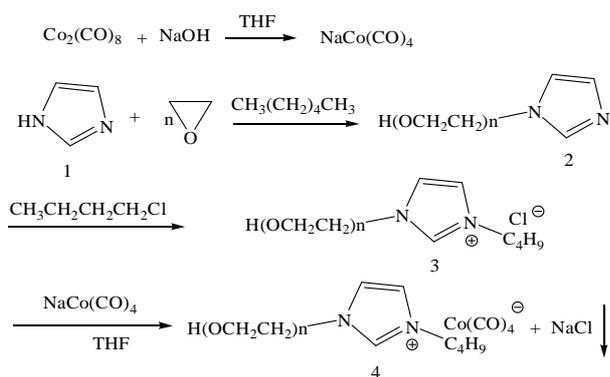
(A) (B) (C)

(A) Freshly prepared compound **4c** (lower) and the mixture of THF and n-heptane (upper) in two phases at room temperature

(B) Catalyst **4c** dissolved in the organic phase while heating to 82°C

(C) The system became two phases again while cooling to room temperature

Figure 5. TPSC of compound **4c** in a mixture of THF and n-heptane

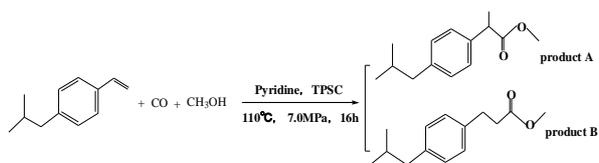


4a: [H(OCH₂CH₂)₈bim][Co(CO)₄].

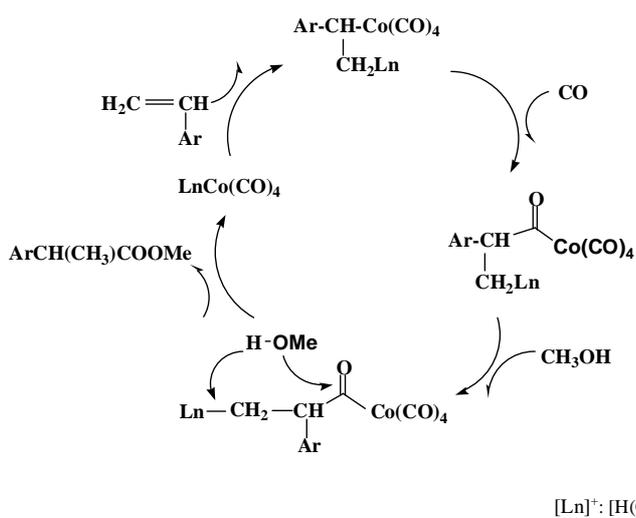
4b: [H(OCH₂CH₂)₁₅bim][Co(CO)₄].

4c: [H(OCH₂CH₂)₂₂bim][Co(CO)₄].

Scheme 1. Synthesis of polyether-substituted imidazolium carbonyl cobalt ionic liquids



Scheme 2. Hydroesterification of 4-isobutylstyrene with CO and methanol



Scheme 3. Mechanism of the hydroesterification of 4-isobutylstyrene

Table 1. IR spectra of compounds 4 and conventional salts of $[\text{Co}(\text{CO})_4]^-$

Entry	$\text{NaCo}(\text{CO})_4$	$[\text{PPN}][\text{Co}(\text{CO})_4]^*$	4a	4b	4c
T ₂	1885.76	1883.00	1885.54	1886.07	1886.48
A ₁	2013.55		2003.77	2002.57	2003.64
4a: $[\text{H}(\text{OCH}_2\text{CH}_2)_8\text{bim}][\text{Co}(\text{CO})_4]$.			4b: $[\text{H}(\text{OCH}_2\text{CH}_2)_{15}\text{bim}][\text{Co}(\text{CO})_4]$.		
4c: $[\text{H}(\text{OCH}_2\text{CH}_2)_{22}\text{bim}][\text{Co}(\text{CO})_4]$.					

Table 2. UV-Vis absorption of $\text{NaCo}(\text{CO})_4$ and compounds 3b, 3c, 4b, and 4c in two different solvents

Compound	UV-Vis absorption bands/nm (Solvent)	
$\text{NaCo}(\text{CO})_4$	305 (in THF)	
3b		313 (in CH_2Cl_2)
3c		318 (in CH_2Cl_2)
4b	307 (in THF)	315 (in CH_2Cl_2)
4c	307 (in THF)	317 (in CH_2Cl_2)

Table 3. The solubility of compounds 4 in THF/heptane (v/v)

ILC at		+/0	6/1	3/1	2/1	1.5/1
conditions						
4a	at R.T.	Soluble	Slightly soluble	Insoluble	Insoluble	Insoluble
			Soluble at 51°C	Insoluble on heating	Insoluble on heating	Insoluble on heating
4b	at R.T.	Soluble	Soluble	Slightly soluble	Insoluble	Insoluble
				Soluble at 45°C	Soluble at 75°C	Insoluble on heating
4c	at R.T.	Soluble	Soluble	Slightly soluble	Insoluble	Insoluble
				Soluble at 38°C	Soluble at 64°C	Soluble at 82°C

4a: $[\text{H}(\text{OCH}_2\text{CH}_2)_8\text{bim}][\text{Co}(\text{CO})_4]$. 4b: $[\text{H}(\text{OCH}_2\text{CH}_2)_{15}\text{bim}][\text{Co}(\text{CO})_4]$. 4c: $[\text{H}(\text{OCH}_2\text{CH}_2)_{22}\text{bim}][\text{Co}(\text{CO})_4]$

R.T.: Room Temperature

Table 4. Hydroesterification of 4-isobutylstyrene catalyzed by compounds 4b and 4c

Entry	CAT(n)	Conversion(%)	Selectivity of A(%)	Selectivity of B(%)
1	KCo(CO) ₄	38.1	68.3	31.7
2	Co ₂ (CO) ₈	39.3	61.2	38.8
3	CAT 4c(22)	43.0	82.7	17.3
4 ^[a]	CAT 4c(22)	35.5	80.2	19.8
5 ^[b]	CAT 4c(22)	46.1	78.7	21.3
6	CAT 4b(15)	44.1	83.8	16.2

[a] Using heptane as the sole upper-phase organic solvent (two-phase).

[b] Using THF as the sole upper-phase organic solvent (homogeneous).

Catalytic conditions: 110 °C, 7.0 MPa, 16 h.

Table 5. Recycling efficiency of catalyst 4 in the hydroesterification of 4-isobutylstyrene

CAT(n)	Run*	Conversion(%)	Selectivity of A(%)	Selectivity of B(%)	leaching of Co(%)
4b(15)	0	44.1	83.8	16.2	5.85
4b(15)	1	33.3	84.4	15.6	-
4b(15)	2	29.7	79.5	20.5	-
4b(15)	3	21.9	81.1	18.9	8.36
4c(22)	0	43.1	82.7	17.3	1.29
4c(22)	1	39.2	80.2	19.8	0.15
4c(22)	2	41.4	78.6	21.4	-
4c(22)	3	40.6	80.8	19.2	-
4c(22)	4	41.2	81.5	18.5	-
4c(22)	5	39.3	82.5	17.5	-
4c(22)	6	36.7	81.9	18.1	0.21
4c(22)	7	34.2	81.6	18.4	0.18

* In the next catalytic run, the reaction mixture was directly charged with another portion of substrate and solvent without any further treatment.

Catalytic conditions: 110 °C, 7.0 MPa, 16 h.