

Highly efficient and quantitative synthesis of a cyclic carbonate by iron complex catalysts



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ABSTRACT

The novel iron complexes [N,N'-bis-2-pyridinylmethylene-cyclohexane-1,2-diamine]iron(II) chloride (**1**) and [N,N'-bis-2-pyridinylmethyl-cyclohexane-1,2-diamine]iron(II) chloride (**2**) were designed, and they showed excellent activity for the coupling reaction epoxides and CO₂ to generate the corresponding cyclic carbonates. When complex **2** was used alone as a catalyst for the cycloaddition of propylene oxide (PO) and CO₂, the PO conversion was 95% at 130 °C and 4 MPa CO₂ pressure in 4 h. Once a co-catalyst like tetrabutylammonium bromide (TBAB) was added, the conversion could reach 100% with nearly 100% selectivity for propylene carbonate (PC), with a turnover number (TON) of 1000 at 100 °C and 4 MPa CO₂ pressure in 6 h, *i.e.* the quantitative synthesis of propylene carbonate can be realized. Moreover, in combination with TBAB, the iron complex can also catalyze the cycloaddition of cyclohexene oxide (CHO) and epichlorohydrin (ECH) with CO₂ to produce the corresponding cyclic carbonates, and the cyclohexene carbonate obtained was mainly the *cis*-isomer.

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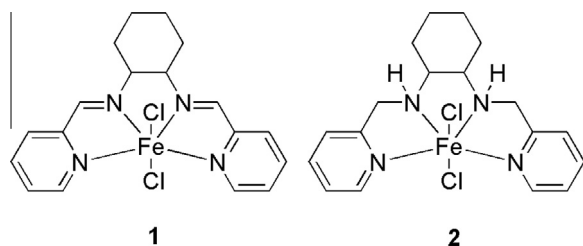
1. Introduction

Carbon dioxide is regarded as a renewable source of carbon since it is abundant, cheap and non-toxic [1,2]. Employing CO₂ as a raw material to prepare large scale chemicals may create a way to high value-added utilization of CO₂. In this regard, synthesis of cyclic carbonates via cycloaddition of CO₂ and epoxides is one of the most attractive processes (Scheme 1) [3–5]. Cyclic carbonates are widely used as green solvents, electrolytes, fuel additives and intermediates for polycarbonates [6,7]. However, a central challenge for employing CO₂ is to overcome its kinetic and thermodynamic stability. In the past decade, numerous catalyst systems have been reported to catalyze this transformation, including ionic liquids [8,9], metal oxides [10,11], transition-metal complexes [12,13], onium salts [14,15], organic bases [16,17] etc. Cycloaddition reactions catalyzed by heterogeneous catalysts, such as metal oxides, are conducted under strict conditions, moreover, both the catalytic activity and selectivity need further enhancement, although the catalysts are easily removed from the products. As far as homogeneous catalysts are concerned, onium salts exhibit low catalytic activity, unless in the presence of metal complexes [18]. Among the homogeneous catalysts, salen complexes of

chromium [12], cobalt [13,19,20], zinc [21,22] and aluminium [23,24] show high catalytic activities under mild conditions. In 2007, Jing et al. [25] reported that the combination of a cobalt salen complex and phenyltrimethylammonium tribromide (PTAT) catalyzed the cycloaddition of CO₂ and propylene oxide (PO) in high yield with a turn over frequency (TOF) of 706 h⁻¹. However, some of these metals are highly toxic, especially cobalt and chromium, and they are difficult to be completely separated from products, which limits the potential application in industry. Therefore, non-toxic central metals, like irons have received much attention. Correspondingly, work can be dated back to 1985 when Kruper found that the Fe-Zn double metal cyanides could catalyze the copolymerization of PO with CO₂ [26]. In 2009, a magnetic nanoparticle supported ionic liquid containing iron was found to catalyze the cycloaddition [27]. However, iron is not the active species of the above-mentioned catalysts. In 2011, Rieger and co-workers [28] reported a one-component iron catalyst, which can catalyze the formation of cyclic propylene carbonate, and Williams et al. designed a bimetallic iron catalyst for both polycarbonate and cyclic carbonate synthesis [29]. Recently, the Zevaco group prepared an ionic iron(III) complex that could catalyze the cycloaddition of CO₂ and PO, with a turnover number (TON) of up to 500 [30]. Up until now, despite the fact that many investigations have been carried out, the design of new catalysts for the coupling reaction of CO₂ and epoxides with improved catalytic activity as well as

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Scheme 1. Structure of the iron complexes.

selectivity is still a scientific challenge. In the present work, we report the synthesis of novel iron complexes (Scheme 1), which can be used to catalyze the cycloaddition of CO₂ and epoxides to generate the corresponding carbonates with high catalytic activity (Scheme 2). The iron complex catalyst, in combination with TBAB as a co-catalyst, can provide a quantitative synthesis of propylene carbonate with nearly 100% selectivity and 100% yield, with a TON of 1000 at 100 °C and 4 MPa CO₂ pressure in 6 h.

2. Experimental

2.1. General procedures and methods

All reactions of air- and/or moisture-sensitive complexes and product manipulations were performed in an inert atmosphere using standard Schlenk techniques or in a glove box. Methanol was refluxed over a mixture of Mg/I₂ and fractionally distilled under an inert atmosphere prior to use. Dichloromethane (DCM) and the epoxides were distilled over CaH₂ under an inert atmosphere. Other reagents with analytical purity were used as received.

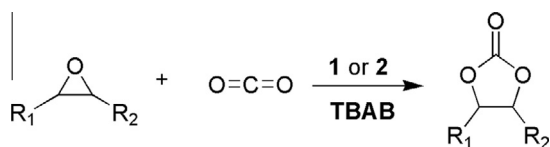
Solution NMR spectra were recorded at room temperature using a Bruker ARX300 spectrometer with TMS as the internal standard. The solvent proton shift (ppm) for CDCl₃ was 7.26 (s). Chemical shifts are reported in ppm and coupling constants are in Hz. ESI mass spectra were performed on a Waters Quattro Premier XE spectrometer using CH₂Cl₂ as the solvent. The IR spectra of the ligands were measured on a Bruker Optics Tensor 27 spectrometer using CH₂Cl₂ as the solvent, whereas KBr was used as the diluter for the IR spectra of the complexes.

2.2. Catalyst preparation and characterization

The ligands N,N'-bis-2-pyridinylmethylene-cyclohexane-1,2-diamine (L1) and N,N'-bis-2-pyridinylmethyl-cyclohexane-1,2-diamine (L2) were synthesized following the procedure reported in the literature [31,32].

2.2.1. Preparation of complex 1

N,N'-bis-2-pyridinylmethylene-cyclohexane-1,2-diamine (2.00 g, 6.84 mmol) was dissolved in DCM, and excess FeCl₂ was added. After stirring overnight at room temperature, a deep-purple solution was obtained after filtration and the complex was precipitated by addition of diethyl ether. The target product was isolated as a deep-blue powder in quantitative yield (2.87 g).



Scheme 2. Cycloaddition of CO₂ and epoxides.

MS (ESI): $m/z = 383.2 [M-Cl]^+$ (calcd. 383.1). IR (cm⁻¹): 1648 ($\nu_{C=N}$), 1595 ($\nu_{C=N}$). Elemental Anal. Calc. for C₁₈H₂₀Cl₂FeN₄: C, 51.58; H, 4.81; N, 13.37. Found: C, 51.34; H, 4.85; N, 13.22%.

2.2.2. Preparation of complex 2

N,N'-bis-2-pyridinylmethyl-cyclohexane-1,2-diamine (2.00 g, 6.84 mmol) was dissolved in DCM, and excess FeCl₂ was added. After stirring overnight at room temperature, a yellow solution was obtained after filtration, and the complex was precipitated by addition of diethyl ether. The product was isolated as a yellow powder in quantitative yield (2.86 g).

MS (ESI): $m/z = 387.3 [M-Cl]^+$ (calcd. 387.1). IR (cm⁻¹): 1603 ($\nu_{C=N}$), 1280 (ν_{C-N}). Anal. Calc. for C₁₈H₂₄Cl₂FeN₄: C, 51.09; H, 5.72; N, 13.24. Found: C, 51.56; H, 5.76; N, 13.58%.

2.3. X-ray structural study

A single crystal of **2** was obtained by the slow diffusion of *n*-hexane into a concentrated CH₂Cl₂ solution of **2**. The X-ray crystallographic analysis was performed using a crystal of **2** of the size 0.35 × 0.21 × 0.10 mm. The intensity data were collected with the ω scan mode (190 K) on a Bruker Smart APEX diffractometer with a CCD detector using Mo K α radiation ($\lambda = 0.71073$ Å). Lorentz and polarization factors were performed using the SADABS program. The crystal structures were solved using the SHELXTL program and refined using full matrix least-squares. The positions of hydrogen atoms were calculated theoretically and were included in the final cycles of refinement in a riding model along with the attached carbons.

2.4. Cycloaddition reaction

The epoxides, iron complex and/or the co-catalyst were added to a 10 mL stainless-steel autoclave with a magnetic stirrer in a glove box. CO₂ was pressurized into this mixture and the reaction was operated at the determined conditions. After the reaction, the autoclave was cooled to room temperature and the CO₂ pressure was released by opening the outlet valve. The crude reaction mixture thus obtained was used to calculate the conversion by ¹H NMR spectroscopy in deuterated chloroform.

3. Results and discussion

3.1. Synthesis and characterization of the ligands and the complexes

The procedures for the preparation of the ligands and the complexes are shown in Scheme 3. The ligand L1 was prepared by the condensation of trans-1,2-diaminocyclohexane with 2-pyridinealdehyde at room temperature in methanol, while ligand L2 was obtained by the hydrogenation of L1 with NaBH₄ in methanol. By stirring the ligand L1 in DCM with FeCl₂, complex **1** was obtained in quantitative yield as a deep-blue powder. Similarly, complex **2** was obtained in quantitative yield as a yellow powder by stirring the ligand L2 in DCM with FeCl₂.

A single crystal of complex **2** suitable for X-ray diffraction was obtained by the slow diffusion of *n*-hexane into a concentrated CH₂Cl₂ solution of **2**. Unfortunately, we failed in the attempts to obtain a single crystal of complex **1**. The ORTEP diagram of the structure is shown in Fig. 1. As is shown in Fig. 1, in the solid state, the structure of complex **2** is a six-coordinate, near-octahedral complex. However, the coordination geometry is not ideally octahedral due to the high degree of ring strain imposed by the three adjacent five-membered metallacycles and the chemically different nature of the two pairs of nitrogen donors [28,33]. The plane defined by the atoms (Fe1, N5, N8) intersects the equatorial plane

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