



Ketone synthesized cobaloxime/organocobaloxime catalysts for cyclic carbonate synthesis from CO₂ and epoxides: Characterization and electrochemistry



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ABSTRACT

Herein we report the synthesis and characterization of a new series of synthesized mono- and trinuclear cobaloxime/organocobaloximes from ketone that act as catalysts for cyclic carbonate synthesis from CO₂ and epoxides under appropriate conditions (2 h, 100 °C and 1.6 MPa pressure). These reactions were carried out with and without co-catalyst, namely, 4-dimethylaminopyridine (DMAP), pyridine (py), triethyl amine (NEt₃) or triphenyl phosphine (PPh₃). In the catalytic experiments, the 4-dimethylaminopyridine (DMAP) was used as co-catalyst, since the DMAP was a more active base with higher yield compared to other Lewis bases. In addition, various factors influencing the cycloaddition reaction, such as co-catalyst, temperature, CO₂ pressure and reaction time, were investigated. A dioxime ligand (LH₂) (**1**) was obtained in two steps from 4-methylpropiophenone as ketone. Reaction of CoCl₂·6H₂O with the dioxime ligand (LH₂) (**1**) and 4-tertbutyl pyridine afforded six-coordinate mononuclear cobaloxime or organocobaloxime (**2–3**) complexes. The mononuclear cobaloxime or organocobaloxime (**2–3**) complexes were used as precursors for building trinuclear cobaloximes or organocobaloxime (**4–11**) complexes. All compounds were fully characterized by ¹H and ¹³C NMR spectra, FT-IR spectra, UV–Vis spectra, molar conductivity measurements, melting point measurements, magnetic susceptibility measurements, and LC-MS spectroscopic studies as well as by cyclic voltammetry.

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Introduction

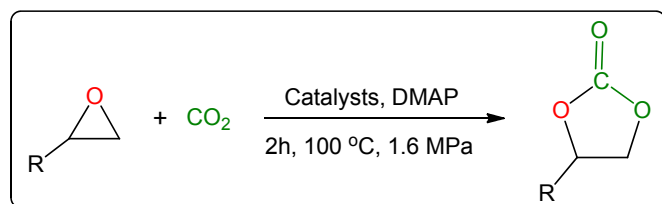
In recent years, the synthesis of cyclic carbonate from CO₂ and epoxides has received much attention because CO₂ is the most inexpensive and renewable carbon resource from the viewpoint of green chemistry and atom economy [1–4]. On the other hand, CO₂ is considered the major greenhouse gas contributing to global warming. Since the beginning of the industrial revolution in about 1850, the average atmospheric concentration of CO₂ has increased from 280 ppm to 370 ppm and as a result, the average global temperature has increased between 0.6 °C and 1 °C in the same period [5,6]. The uncontrolled CO₂ gas emission increase may contribute to sea level increases and many other problems occurring worldwide. In this context, the efficient transformation of CO₂

under mild conditions into useful chemical compounds is very attractive from both an industrial and an academic viewpoint [7]. One way for efficient transformation of CO₂, is cycloaddition of CO₂ to epoxides to produce five-membered cyclic carbonates under appropriate conditions (Scheme 1).

Synthesized cyclic carbonates such as ethylene carbonate, and propylene carbonate have been widely used for various purposes, for instance, as valuable organic synthetic intermediates, electrolytic elements of lithium secondary batteries, polar aprotic solvents, monomers for synthesizing polycarbonates and chemical ingredients for preparing medicines or agricultural chemicals, pharmaceutical or fine chemical intermediates, and are applied broadly in both industrial and academic areas [1,8–12].

For cyclic carbonate synthesis from CO₂ and epoxides, various catalytic systems have been developed including homogeneous [13–16] and heterogeneous catalysis [17–21]. In this paper, our aim is to draw attention to cyclic carbonate synthesis from CO₂ and epoxides through assistance from homogeneous catalysts. Thus, we

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Scheme 1. Synthesis of cyclic carbonates from various epoxides and CO₂.

prefer a new generation of mono- and trinuclear cobaloxime/organocobaloximes incorporating ketone synthesized dioxime ligands, which were shown to be remarkable molecular catalysts for cyclic carbonate synthesis from CO₂ and various epoxides. The synthesized cobaloxime/organocobaloxime complexes from ketone were considered to be a promising class of catalysts, because they are air-stable and can be stored for months on the bench if kept in the dark. Although cobaloxime/organocobaloximes complexes have been studied for a long time as vitamin B₁₂ models, their description, spectroscopic data, structure–property relationships, and correlation to Co–C bond lengths have been emphasized in recent years [22–24]. On the other hand, cobaloximes or organocobaloximes are not only among the best synthetic transition metal complexes known for H₂ production but are also relatively easy to synthesize, are oxygen-tolerant, are amenable for coupling to natural and artificial photosynthetic systems and rely only on earth-abundant materials [25–27].

In this paper, we described a new dioxime ligand (LH₂) (**1**) from ketone and mono- and trinuclear cobaloxime/organocobaloxime (**2–11**) complexes that were synthesized and characterized using elemental analysis, ¹H and ¹³C NMR spectra, FT-IR spectra, UV–Vis spectra, LC-MS spectra, molar conductivity measurements, melting point measurements and magnetic susceptibility measurements. Moreover, their electrochemical properties were investigated using cyclic voltammetric (CV) techniques in a DMSO solution. All of the mono- and trinuclear cobaloxime/organocobaloximes (**2–11**) complexes as homogeneous catalysts were used in direct synthesis of cyclic carbonates from carbon dioxide and epoxides. The optimal catalytic conditions were investigated by changing the epoxides, solvents, temperature, pressure, and time, consecutively.

Experimental

Materials and measurements

All reagents and solvents were purchased from Sigma Aldrich, Merck or Alfa Aesar and used without any further purification. NMR spectra were recorded in 5-mm tubes at 298 K with a Bruker Avance 300 NMR spectrometer at 300 MHz for ¹H and at 75 MHz for ¹³C; chemical shifts are expressed in ppm relative to DMSO-*d*₆. Signals are quoted relative to tetramethylsilane ($\delta = 0.00$ ppm) and coupling constants (*J*) are in hertz. Abbreviations used for the NMR resonances are: s singlet, d doublet, t triplet, m multiplet. Elemental analyses (C, H, and N) were performed on a LECO CHNS model 932 elemental analyzer. FT-IR spectra were measured in KBr on a Perkin Elmer Spectrum RXI FT-IR spectrometer (4000–400 cm⁻¹). UV–Vis spectra were obtained on a Perkin–Elmer model Lambda 25 spectrophotometer in the wavelength range from 200 to 1100 nm and in the C₂H₅OH and CH₂Cl₂ solvents. Magnetic susceptibilities were determined on a Sherwood Scientific Magnetic Susceptibility Balance (Model MK1) at room temperature (25 °C) using Hg [Co(SCN)₄] as a calibrant; diamagnetic corrections were calculated from Pascal's constants [28]. Melting points were measured in open

capillary tubes with an Electrothermal 9100 melting point apparatus and are uncorrected. Molar conductivities (Λ_M) were recorded on a Inolab Terminal 740 WTW Series. LC-MS spectra results were recorded on an Agilent LC/MSD LC-MS/MS spectrometer. CV measurements were carried out with an instrument (Princeton Applied Research Model 2263 potentiostat controlled by an external PC, using the computer program-Power CV) utilizing a three-electrode configuration at 25 °C. A platinum wire served as the counter electrode. A Ag/AgCl electrode was employed as the reference electrode. The working electrode was a platinum plate with an area of 0.2 cm². The working electrode was polished with Al₂O₃ prior to each experiment. Throughout the experiment, oxygen free-argon was bubbled through the solution for 10 min. Electrochemical grade tetrabutylammoniumperchlorate (TBAP) (0.2 mol dm⁻³) was employed as the supporting electrolyte. The Origin 7.5 graphing program was used to evaluate Power CV data, to draw voltammograms and to analyze them. Catalytic tests were performed in a PARR 4560 50 mL stainless pressure reactor. Gas chromatography was performed on a Agilent 7820A GC system with hydrogen as the carrier gas. 1,10-Phenanthroline-5,6-dione (dione) [29] was prepared according to the literature procedures.

Synthesis of the ligand (LH₂) (**1**)

The ligand (LH₂) (**1**) was synthesized following the literature procedure with some modifications [30]. Color: pale yellow, yield (%): 88, m.p.: 239 °C, Anal. Calc. for [C₁₀H₁₂N₂O₂] (F.W: 192.2 g/mol): C, 62.49; H, 6.29; N, 14.57. Found: C, 62.47; H, 6.26; N, 14.59%. LC-MS (Scan ES⁺): *m/z* (%) 191.8 (10) [M]⁺, 179.0 (50), 119.0 (100) and 101.0 (35). FT-IR (KBr pellets, $\nu_{\max}/\text{cm}^{-1}$): 3473–3095 $\nu(\text{O–H}\cdots\text{O})$, 3021 $\nu(\text{Ar–CH})$, 2964–2870 $\nu(\text{Aliph–CH})$, 1611 $\nu(\text{C=N})$, 1461–1410 $\nu(\text{C=C})$ and 1258 $\nu(\text{N–O})$. ¹H NMR (DMSO-*d*₆, TMS, 300 MHz, δ ppm): 11.45 (s, 2H, C=N–OH), 7.13 (d, 4H, *J* = 12.7 Hz, Ar–CH), 2.33 (s, 3H, Ar–CH₃) and 2.09 (s, 3H, C–CH₃). ¹³C NMR (DMSO-*d*₆, TMS, 75 MHz, δ ppm): 155.59 and 154.37 (C=N–OH), 137.31, 130.30, 129.25 and 128.43 (Ar–CH), 21.33 (Ar–CH₃) and 10.52 (C–CH₃). UV–Vis (λ_{\max} , nm, * = shoulder peak): 231, 271, 299, 315 and 372* (C₂H₅OH); 244, 292, 342, and 368* (CH₂Cl₂).

Synthesis of the mononuclear cobaloxime [ClCo(LH)₂(4-*t*-BuPy)] (**2**) complex

In a two-necked, 250 mL round-bottom flask and equipped with a blanket of nitrogen (N₂) was placed 100 mL of 96% ethanol. To this solution was added cobalt(II) chloride hexahydrate (CoCl₂·6H₂O) (1.55 g, 5.5 mmol) slowly with stirring, followed by addition of a stirred solution of dioxime ligand (LH₂) (**1**) (2.50 g, 13.0 mmol). The mixture was vigorously stirred for 30 min with occasional swirling, during which the solution turned green, and the mixture was again heated for 3 h at reflux temperature. Later the mixture was allowed to cool to room temperature and then 4-*tert*-butylpyridine (0.88 g, 6.5 mmol) was added to the mixture and a very gentle stream of air was passed through the solution for about 5 h. Then water (10 mL) was added to get the desired product and the crude product obtained was recrystallized from CH₂Cl₂/C₂H₅OH. The mixture was set aside for 2 h, after which the product was collected on sintered glass and washed successively with small amounts of water, and diethyl ether and finally air-dried. Color: brown, yield (%): 82, m.p.: 164 °C, Anal. Calc. for [C₂₉H₃₅N₅O₄ClCo] (F.W: 612.0 g/mol): C, 56.91; H, 5.76; N, 11.44. Found: C, 56.89; H, 5.75; N, 11.45%. $\Lambda_M = 13 \Omega^{-1} \text{cm}^2 \text{mol}^{-1}$, $\mu_{\text{eff}} = \text{Dia}$, LC-MS (Scan ES⁺): *m/z* (%) 611.2 (23) [M – H]⁺, 463.0 (18), 279.0 (80), 257.0 (100) and 219.1 (35). FT-IR (KBr pellets, $\nu_{\max}/\text{cm}^{-1}$): 3022 $\nu(\text{Ar–CH})$, 2964–2870 $\nu(\text{Aliph–CH})$, 1727 $\nu(\text{O–H}\cdots\text{O})$, 1619 $\nu(\text{C=N})$, 1548–1513 $\nu(\text{C=C})$, 1271 $\nu(\text{N–O})$, 508 and 501 $\nu(\text{Co–N})$. ¹H NMR (DMSO-*d*₆, TMS, 300 MHz, δ ppm):

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