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# Synthesis and characterization of novel positively charged organocobaloximes as catalysts for the fixation of $CO_2$ to cyclic carbonates

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ABSTRACT

A series of cobaloxime complexes **(1-6)** and corresponding to positively charged phosphonium linked cobaloximes (called cobaloximes-PCPL) **(1a-6a)** have been prepared in high yields and characterized by means of NMR ($^1H$, $^{13}C$, and $^{31}P$) spectra, FT-IR spectra, UV–Vis spectra, mass spectra, melting point as well as elemental analysis. Following a full characterization, the study of spectroscopic properties of these novels cobaloximes/cobaloximes-PCPL compounds was done in detail. Under optimized reaction conditions, these novel cobaloximes **(1-6)** and cobaloximes-PCPL **(1a-6a)** were applied to the as a molecular catalyst for the cycloaddition of epoxides with $CO_2$ without organic solvent. In a combination with (4-bromo butyl)triphenylphosphonium bromide **(BTP)** and cobaloxime compounds, namely cobaloximes-PCPL were identified as highly active catalysts for the formation of cyclic carbonates compared to previously reported cobaloximes catalysts by our groups. As an axial group bounding to the Co(III) center of cobaloximes-PCPL, **(BTP)** was barely revealed that it has an effect on catalyst activities. Also, a systematic investigation of reaction parameter effects such as temperature, time and pressure was done.

## 1. Introduction

It was a long time goal for numerous scientists in chemical sector to develop superior performance, high stability, reactivity, inexpensive and environmental friendly catalysts for the coupling reactions of $CO_2$ and epoxides which produce five-membered cyclic carbonates in a 100% atom economic manner, due to the fact that $CO_2$ is an abundant, cheap, renewable, nonflammability, easy accessibility and non-toxic $C_1$ feedstock [1,2]. But, the thermodynamic and kinetic stability of $CO_2$ and its negative adiabatic electron affinity and large ionization potential [3] make effective fixation and conversion of $CO_2$ into high-value chemicals under normal conditions arduous [4]. Currently, in light of those researches, many ways to solve this problem have been suggested. In this context, one of the promising and mostly preferred route is the chemical utilization of $CO_2$ to synthesize cyclic carbonates as valuable products, owing to widespread applications of cyclic carbonates as organic intermediates, monomers for polymerization, aprotic polar solvents that are used widely in chemical and pharmaceutical industries [5], electrolytes for lithium-ion batteries, precursors of polymeric materials, crude materials for plastics and fine chemicals [6]. For the formation of cyclic carbonates via cycloaddition of $CO_2$ to epoxides that are currently used as useful chemicals in numerous applications, diverse homogeneous and heterogeneous catalytic systems have been reported.

To date, numerous metal-based homogeneous catalysts, including metal-organic frameworks (MOFs) [7,8], metal-salen complexes [9–19], metalloporphyrin [20–22], metal chloride [23–26], polyoxometalate [27], metal oxide [28,29] and metal-free catalysts containing hydroxyl [30–34], carboxyl [35–37] have been used to encourage $CO_2$ conversion under ambient conditions. But, the production of the cyclic carbonates through the cycloaddition of $CO_2$ to epoxides was the factor for which the research of the effective, robust, cheap, and stable catalyst has been continued. With this in mind, one of the novel classes of catalysts are the cobaloximes and corresponding to cobaloximes-PCPL form have undoubtedly attracted much attention probably due to the intrinsic properties of various dioxime ligands such as easy-to-handle, air-stable, different structures, strong complexation ability with almost

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all metal ions, structural diversity, and tenability. To the best of our knowledge, the use of PCPL-based and, in general, the use of truly organometallic complexes (containing a C-metal bond) for the cycloaddition of $CO_2$ to epoxides is very rare. The nature of the metal center in metal complexes plays an important role in their catalytic performance and cobaloxime with corresponding to cobaloximes-PCPL are maybe one of the most efficient catalyst systems for desirable $CO_2$ transformation. Especially, the covalent linked **(BTP)** containing cobaloximes-PCPL **(1a-6a)** were identified as highly active catalysts for the formation of cyclic carbonates compared to previously reported cobaloxime catalysts by our groups [38]. To that end, we hope that the cobaloximes-PCPL continue to generate a lot of interest compared to the cobaloximes due to synergistic effects of multiple sites on epoxide activation which Lewis acidic cobalt, protonated triphenyl phosphonium able to activate epoxide and bromide anion acting as a nucleophile source. For our study, six cobaloxime complexes **(1-6)** and six corresponding to cobaloximes-PCPL **(1a-6a)** were prepared and characterized by means of NMR ($^1H$, $^{13}C$, and $^{31}P$) spectra, FT-IR spectra, UV–Vis spectra, mass spectra, melting point as well as elemental analysis and evaluated the catalytic activity for the cycloaddition between epoxides and $CO_2$.

## 2. Experimental

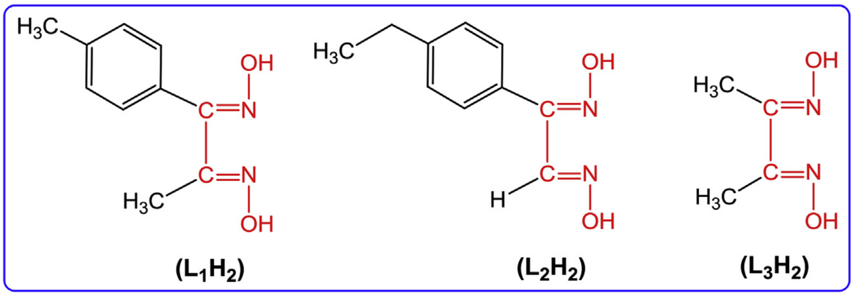
Organic solvents and chemicals with analytical and starting reagents obtained from commercial sources were used as received for this study any additional chemical process. All FT-IR measurements were acquired in the range of 4000–400 $cm^{-1}$ using the ATR accessory on a Perkin-Elmer Two UATR-FT spectrophotometer. UV–Vis spectra were recorded on a Perkin-Elmer model Lambda 25 spectrophotometer in the range of 200–1100 nm using quartz cuvettes at room temperature. The $CH_2Cl_2$ and $CH_3OH$ have been selected as solvents for electronic spectra. Elemental analyses (C, H, and N) were performed on a LECO CHNS model 932 of the elemental analyzer. The $^1H$ and $^{13}C$ NMR spectra were acquired on a Bruker 300 and 75 MHz spectrometer with DMSO-d6 as solvent referenced to 2.50 ppm, consecutively. $^{31}P$ NMR spectra were recorded at 242.9 MHz in DMSO-d6. The example was allowed to equilibrate for at least 20 min at room temperature before the $^{31}P$ NMR spectrum was obtained. The mass spectra (LC-MS) were obtained through using an Agilent LC-MS/MS spectrometer by ESI technique. Melting points of all complexes have been determined in open capillary tubes on an Electrothermal 9100 melting point apparatus and are uncorrected. Catalytic experiments were carried out in a PARR 4560 50 mL stainless steel high-pressure reactor. $CO_2$ with a purity of 99.999% was commercially available and used without further purification. GC analysis was performed on an Agilent 7820A model for conversion and selectivity of the mixture. The mixture was separated by centrifugation, and the liquid phase was subjected to GC analysis with ethylene glycol dibutyl ether as an internal standard and hydrogen as the carrier gas. ($Ph_3P^+Br^-C_4H_8Br$) **(BTP)** was synthesized according to the following procedure [39] (Scheme 2). The ligand precursors **$L_1H_2$** and **$L_2H_2$** were synthesized according to optimization of literature methods [38]. The dimethylglyoxime is preferred as ligand **$L_3H_2$** and purchased from Sigma-Aldrich Company. The preferred ligands **($L_1H_2$)**, **($L_2H_2$)**, and **($L_3H_2$)** for this study are given in the Scheme 1.

### *2.1. General procedure for the cycloaddition of epoxides to $CO_2$*

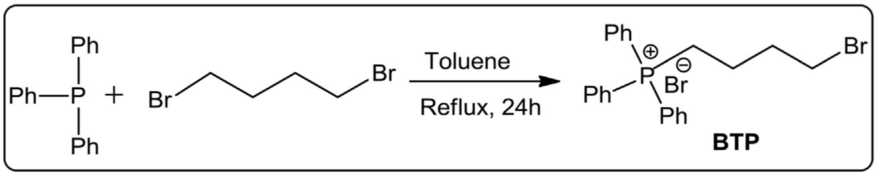
A 25 mL stainless pressure reactor was charged with cobaloximes or cobaloximes-PCPL ($4.5 \times 10^{-8}$ mmol), epoxides ($4.5 \times 10^{-5}$ mmol), Lewis base ($9 \times 10^{-8}$ mmol) and an appropriate amount of ethylene glycol dibutyl ether (as an internal standard for GC analysis). The reaction vessel was placed under a constant pressure of $CO_2$ for 2 min to allow the system to equilibrate and then the autoclave was charged with $CO_2$ to the desired pressure. The reaction mixture was heated to the desired temperature. The pressure was kept constant during the reaction. After the desired reaction time the vessel was cooled to 5-10 °C in the ice bath. The pressure was released by venting the excess gases. The yields of the corresponding cyclic carbonates were determined by using an Agilent 7820A Gas Chromatograph.

### *2.2. Synthesis of the cobaloximes $[ClCo(L_{(1-3)}H)_2(B_{1-2})]$ (1-6)*

The ligand precursors **$L_1H_2$** (1.15 g, 6.0 mmol), **$L_2H_2$** (1.15 g, 6.0 mmol), and **$L_3H_2$** (0.70 g, 6.0 mmol) with $CoCl_2.6H_2O$ (0.72 g, 3.0 mmol) were mixed in a 100 mL reaction flask for 30 min at room temperature under an $N_2$ atmosphere. The solutions turned green immediately. The green reaction mixtures were stirred for another



**Scheme 1.** The selected ligands **($L_1H_2$)**, **($L_2H_2$)**, and **($L_3H_2$)** for this study.



**Scheme 2.** The synthesis of ($Ph_3P^+Br^-C_4H_8Br$) **(BTP)** compound.