



Structurally well-characterized zinc complexes bearing imine-benzotriazole phenoxide ligands: Synthesis, photoluminescent properties and catalysis for carbon dioxide/epoxide coupling

Ting-Yi Chen^a, Chen-Yu Li^a, Chen-Yen Tsai^b, Chi-Huan Li^a, Chin-Hsiang Chang^a, Bao-Tsan Ko^{b,*}, Ching-Yao Chang^c, Chia-Her Lin^a, Hsi-Ya Huang^a

^a Department of Chemistry, Chung Yuan Christian University, Chung-Li 32023, Taiwan

^b Department of Chemistry, National Chung Hsing University, Taichung 402, Taiwan

^c Department of Biotechnology, Asia University, Wufeng, Taichung 413, Taiwan

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ABSTRACT

New imine-benzotriazole phenol ligands, $RFuIBTP-H$ were prepared from the condensation of 3-(2*H*-benzotriazol-2-yl)-2-hydroxy-5-alkyl-benzaldehyde (R = C1 for alkyl = CH₃; R = C8 for alkyl = C₈H₁₇) with 1-(2-furyl)methylamine (1.1 equiv) in diethyl ether. Air-tolerant zinc complexes of bis-**IBTP** derivatives were synthesized and structurally characterized. The monomeric and homoleptic zinc complexes ($[(C^{1Fu}IBTP)_2Zn]$ (**1**), $[(C^{8Fu}IBTP)_2Zn]$ (**2**)) resulted from treatment of $RFuIBTP-H$ (2.0 equiv) with ZnEt₂, in which the metal center is tetra-coordinated with two *N,O*-bidentate **IBTP**[−] ligands. Further reaction of **2** with 4-dimethylaminopyridine (DMAP) or 1-methylimidazole (Melm) in stoichiometric proportion furnished the penta-coordinated monomeric zinc complexes ($[(C^{8Fu}IBTP)_2Zn(DMAP)]$ (**3**), $[(C^{8Fu}IBTP)_2Zn(Melm)]$ (**4**)). Optical properties and catalysis of epoxide/carbon dioxide (CO₂) coupling of these **IBTP**-containing zinc complexes were systematically investigated. The luminescent properties showed that Zn complexes **1–4** in solution produce intense blue fluorescence with wavelength of emission maximum in a range 473–482 nm. **IBTP**-ligated zinc complex **2** is an active catalyst (TOF: 33.3 h^{−1}) for the cycloaddition of CO₂ with propylene oxide in the presence of *n*-Bu₄NBr to give propylene carbonate (PC) under mild conditions. The single-component character of Zn complex **3** that is extra-coordinated with one DMAP molecule also enabled an efficient preparation of PC without a co-catalyst.

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1. Introduction

Considerable attention has been paid to epoxide/carbon dioxide (CO₂) coupling catalyzed by metal complexes because it provides a promising and safe method to prepare important chemical compounds such as aliphatic polycarbonates and cyclic carbonates. Accordingly, various catalytic systems incorporating diverse ancillary ligands, such as porphyrin, phenoxide, β-diiminato, Schiff base, anilido-aldiminate, macrocyclic [1–7] and many others [8,9], have been shown to achieve effective activities with satisfactory turnover frequencies (TOF). The metal center in these active catalysts mainly involves an aluminum(III), cobalt(II/III), chromium(III) or zinc(II) atom. According to these authors, the most developed binary catalysts are salen-type metal complexes combined with

Lewis-base co-catalysts, which demonstrated great catalytic activities for the copolymerization or coupling of CO₂ and epoxides [10–12]. For instance, Lu et al. and Coates et al. reported that $\{[(salcy)CoX]/[PPN]Y\}$ (X, Y = halide or carboxylate) copolymerizes propylene oxide (PO) and CO₂ with not only a large TOF but also an excellent polymerization behavior such as great selectivity (>99% carbonate linkage) and regioselectivity (head-to-tail linkages > 95%) [13,14]. Furthermore, aluminum- and zinc-based complexes of salen ligands that are readily characterized with spectra (i.e. NMR) were demonstrated to be active catalysts for the cycloaddition of CO₂ with epoxides. North et al. developed bimetallic $\{[Al(salen)_2(O)]/n-Bu_4NBr\}$ catalytic systems and one-component bimetallic aluminum(salen)-based catalysts to couple CO₂ with epoxides; these systems exhibited satisfactory activity for the formation of cyclic carbonates from diverse terminal epoxides at pressure only 1 atm and near 295 K [15–18]. Kleij and co-workers reported effective, cheap and robust Zn(salphen) complexes for various carbonate syntheses in satisfactory yields; a plausible

* Corresponding author. Tel.: +886 4 22840411x715; fax: +886 4 22862547.
E-mail address: btko@dragon.nchu.edu.tw (B.-T. Ko).

mechanism of the reaction was proposed involving crystallographically characterized metallocene-epoxide structures [19]. We investigated the synthesis and catalysis of well-characterized aluminum complexes originating from benzotriazole phenoxide (BTP) derivatives (type I, Chart 1); the BTP-ligated bimetallic aluminum demonstrated great productivity and good activity to yield propylene carbonate under optimal conditions [20].

Encouraged by the efficient catalytic systems supported by BTP ligands, our current interest lies in developing aluminum, magnesium, copper, group 4 and zinc derivatives containing amino- or imine-BTP ligands and applying these complexes as catalysts for the ring-opening polymerization (ROP) of cyclic esters and CO₂/epoxide coupling. For instance, magnesium complexes bearing amine-bis(BTP) ligands were synthesized for bifunctional catalysis, showing efficient activities towards ROP of ϵ -caprolactone and cycloaddition of CO₂ with cyclohexene oxide [8]. Such amino-BTP ligands (type II, Chart 1) are readily prepared in a one-pot Mannich condensation, whereas imine-BTP ligands (type III, R₄ = alkyl or aryl, Chart 1) are obtainable with the combination of the Duff reaction and imination from commercially available BTP-H derivatives [21,22]. Although the synthetic route of the latter imine-BTP ligands required two steps to afford the final products, the purified method is simple, involving only recrystallization without a chromatographic technique. To extend the investigation of benzotriazole phenoxide metal complexes and to explore thoroughly their catalytic activity for CO₂/epoxide coupling, we have designed and synthesized new imine-BTP ligands containing the pendant arm of the furyl group (type IV, Chart 1). We envisaged that the imine group attached at the ortho-position of the phenoxy group might lead to varied bonding modes and provide better chelation to stabilize the metal center. In this article, we present the synthesis, characterization and catalytic tests of the CO₂/epoxide coupling of zinc derivatives based on imine-BTP ligands of this kind.

2. Results and discussion

2.1. Syntheses and characterization

The synthetic routes of imine-benzotriazole phenol ligands (C¹Fu¹IBTP-H and C⁸Fu¹IBTP-H) and their Zn complexes 1–4 appear in

Scheme 1. These R^{Fu}IBTP-H derivatives (R = C1 for alkyl = CH₃; R = C8 for alkyl = C₈H₁₇) were synthesized in high yield (>80%) on condensation of 3-(2H-benzotriazol-2-yl)-2-hydroxy-5-alkyl-benzaldehyde (alkyl = CH₃ and C₈H₁₇) [21] with 1-(2-furyl)methylamine (1.1 equiv) in diethyl ether (Et₂O). Such ligands were isolated as yellow solids and were characterized with spectral methods and elemental analysis. For instance, the ¹H NMR spectrum of C¹Fu¹IBTP-H displayed resonances at δ 8.49, 4.77 and 2.36 ppm for aldimine proton (N=CH), methylene protons of C=N-CH₂- and methyl protons of phenol group, respectively, with integration ratio 1:2:3, indicating the formation of the expected C¹Fu¹IBTP-H ligand. The O-H signal downfield \sim 14.2 ppm for both ligands indicates a hydrogen bond between O-H and N(imine), for which further evidence came from a X-ray structural determination. Single crystals suitable for X-ray structural characterization of C¹Fu¹IBTP-H were grown from a saturated Et₂O solution. The crystal structure of C¹Fu¹IBTP-H (electronic supplementary material, Fig. S1) exhibits an intramolecular hydrogen bond O-H...N between the phenol and aldimine groups. The distance N...H (1.665(3) Å) is much smaller than the sum (\sim 2.75 Å) of van der Waals radii of the N and H atoms, and the angle (O(1)-H(1)...N(4)) formed by the hydrogen bond is 153.6(2)°. The type of intramolecular hydrogen bond in C¹Fu¹IBTP-H is different from that in (E)-2-(2H-benzotriazol-2-yl)-4-methyl-6-(phenyliminomethyl)phenol of our previous work [22]. Alkane elimination of ZnEt₂ with C¹Fu¹IBTP-H or C⁸Fu¹IBTP-H (2.0 mol equiv) in toluene afforded a homoleptic tetra-coordinated zinc complex (1, [(C¹Fu¹IBTP)₂Zn]; 2, [(C⁸Fu¹IBTP)₂Zn]) in high yield. The formation of expected complexes 1–2 was proved by the disappearance of the O-H signal (14.2 or 14.4 ppm) of Fu¹IBTP-H and by the upfield shift of signals (δ = 8.01 or 8.10 ppm) for the aldimine proton in the ¹H NMR spectrum. The NMR spectra of bis-adduct complexes 1–2 exhibited R^{Fu}IBTP signals on one set, implying that two ligands bound to the zinc atom assumed the same coordination mode in solution. Attempts to obtain the mono-adduct zinc complex, supported by the R^{Fu}IBTP ligand, were unsuccessful. This result was verified as treatment of ZnEt₂ with C¹Fu¹IBTP-H (1.0 mol equiv) in toluene gave the disproportionation product [(C¹Fu¹IBTP)₂Zn] (1). Complex 2 further reacted with 4-dimethylaminopyridine (DMAP) or 1-methylimidazole (Melm) in stoichiometric proportion, producing the penta-coordinated monomeric zinc complex (3,

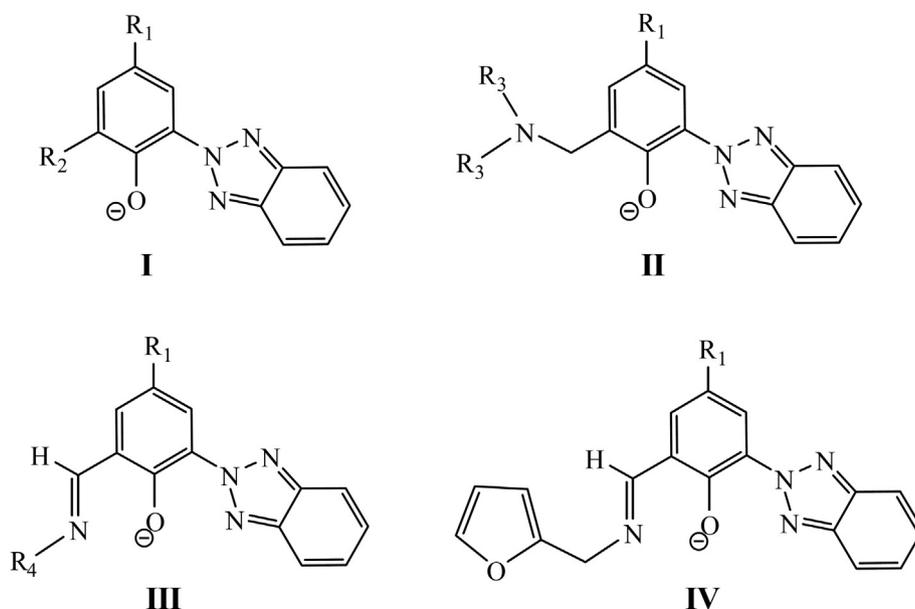


Chart 1. Several types of benzotriazole phenoxide (BTP) derivatives.

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