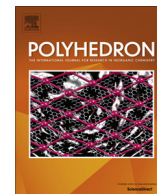




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Synthesis, characterization, and cycloaddition reaction studies of zinc(II) acetate complexes containing 2,6-bis(pyrazol-1-yl)pyridine and 2,6-bis(3,5-dimethylpyrazol-1-yl)pyridine ligands

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ABSTRACT

The complexes [Py(Pz)₂]Zn(OC(=O)Me)₂ (**1**) and [Py(Me₂Pz)₂]Zn(OC(=O)Me)₂ (**2**), where ligands Py(Pz)₂ and Py(Me₂Pz)₂ are tridentate 2,6-bis(pyrazol-1-yl)pyridine and 2,6-bis(3,5-dimethylpyrazol-1-yl)pyridine, respectively, have been synthesized and characterized. The single crystal X-ray diffraction analysis confirmed compound **2** to be monomeric with six-coordinate zinc center. In addition to tridentate ligand Py(Me₂Pz)₂, both κ¹-acetate and κ²-acetate ligands are ligated to zinc metal atom in **2**. The synthesized complexes **1** and **2** were used as effective catalysts for the cycloaddition between CO₂ and epoxides in the presence of various kinds of cocatalysts such as *n*-Bu₄PBr, *n*-Bu₄NI, *n*-Bu₄NBr, *n*-Bu₄NCl, PPNCl, and DMAP under the condition of 75 °C, 10 bar CO₂ pressure, 0.1 mol% catalyst loading, and 24 h. The reaction temperature, CO₂ pressure, and catalyst loading ratio applied in this study are somewhat milder condition than those for other reported zinc-based catalysts. In addition, **1**/*n*-Bu₄PBr system showed the best catalytic activity for the cycloaddition of CO₂ to propylene oxide, which showed the highest reactivity among seven other kinds of epoxides.

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1. Introduction

The chemical transformation of carbon dioxide into valuable chemicals is currently one of significant themes in both academic and industrial fields [1]. Since aliphatic cyclic carbonates, which have broad applications for aprotic solvents [2], electrolytes for secondary batteries [3], and intermediates for polycarbonates [4], were commercialized in 1950s [5], a wide range of catalytic systems including transition metal complexes [6,7], quaternary ammonium salt [8,9], ionic liquids [10–12], and so on have been tested to make cyclic carbonates from carbon dioxide and epoxides. Despite the fact that some excellent initiators have been found among these systems for aliphatic cyclic carbonates, the search for new catalysts with eco-friendly and low toxic properties is still remain of interest. In the aspect of solving environmental

and poisonous problem, one of possible candidates would be zinc complexes bearing chelating ligands.

There are many kinds of reported zinc compounds as catalysts for aliphatic cyclic carbonates. Examples include Zn(II) complexes chelated by monodentate pyridinium alkoxy ligand [13,14], bidentate imine-benzotriazole phenolate [15], bidentate 2,2'-bipyridine derivatives [16], bidentate acetylacetonato [17], bidentate pyridine *N*-oxide [18], bidentate carboxylate [19], tridentate bis(aryliminomethyl)pyrrole derivatives [20], tridentate pyridino-imino-phenolato derivatives [21], tetradentate salen derivatives [22,23], tetradentate salphen derivatives [24–30], and tetradentate porphyrin derivatives [31]. Most reports of zinc catalysts for cyclic carbonates [13–31] have focused on compounds chelated by bidentate [15–19] or tetradentate ligands [22–31]; much less attention has been directed towards complexes containing tridentate ligands [20,21].

Tridentate 2,6-bis(pyrazol-1-yl)pyridine (PyPz₂) ligand [32] and its derivatives have been extensively studied as ligands in coordination chemistry for 25 years [33,34]. A variety of their metal-based inorganic systems, including those with Cr [35], Fe [36–40], Co [39–41], Ni [41,42], Cu [43,44], Ag [45], Re [46],

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Ru [47–50], Pd [50], Pt [51], Eu [52], and Zn [53–56] have been developed. They have some applications in the field of polymerization catalysts [35,36,39], spin-crossover material [40], cross-coupling catalysts [42], dye-sensitized solar cells [49], and luminescent materials [51,52]. Interestingly, chromium- and vanadium-based catalysts containing 2,6-bis(3,5-dimethylpyrazol-1-ylmethyl)pyridine, similar to **PyPz₂**, have good catalytic activity for ethylene polymerization [57,58]. Unlike other metal complexes, zinc-based complexes with **PyPz₂** ligand are not widely studied. Even though the molecular structure of zinc(II) chloride complex containing **PyPz₂** ligand was determined [53], to our best knowledge, any zinc compound with 2,6-bis(3,5-dimethylpyrazol-1-yl)pyridine (**Py(Me₂Pz)₂**) ligand has never been reported in the literature. Good ethylene polymerization behavior for chromium and vanadium-based catalysts containing its related ligand such as 2,6-bis(3,5-dimethylpyrazol-1-ylmethyl)pyridine prompted us to search for new catalysts.

This work reports the synthesis and their catalysis of the cycloaddition reaction between CO₂ and epoxides using new zinc acetate complexes with **PyPz₂** and **Py(Me₂Pz)₂**. In addition, the solid state structure of zinc(II) acetate complex chelated by **Py(Me₂Pz)₂** was confirmed by single crystal X-ray diffraction.

2. Experimental

2.1. General Procedure

All manipulations were carried out under an atmosphere of dinitrogen by using standard Schlenk-type glassware on a dual manifold Schlenk line in a glove box [59]. Dinitrogen was deoxygenated using activated Cu catalyst and dried with drierite [60]. All chemicals including 2,6-dibromopyridine, 3,5-dimethylpyrazole, pyrazole, zinc acetate dihydrate and epoxides were purchased from Aldrich and used as supplied unless otherwise indicated. Carbon dioxide (99.999%) was used as received without further purification. CD₃OD and CDCl₃ were dried over 4 Å activated molecular sieves and used after vacuum transfer to a Schlenk tube equipped with a J. Young valve [60]. CD₃OD and CDCl₃ were dried over 4 Å activated molecular sieves and used after vacuum transfer to a Schlenk tube equipped with a J. Young valve [60].

2.2. Measurements

¹H and ¹³C NMR spectra were recorded at ambient temperature on a 400 MHz NMR spectrometer using standard parameters. All chemical shifts are reported in δ units with reference to the peaks of residual CDCl₃ (δ 7.24, ¹H NMR; δ 77.0, ¹³C NMR) or CD₃OD (δ 3.30, ¹H NMR; δ 49.0, ¹³C NMR) [61]. Elemental analyses was performed with EA 1110-FISONS analyzer.

2.3. Synthesis

Compounds **PyPz₂** and **Py(Me₂Pz)₂** were prepared according to literature method reported previously [32]; however, they were achieved in a slightly modified way and with different results including yields and spectroscopic data.

2.3.1. Synthesis of 2,6-bis(pyrazol-1-yl)pyridine (**PyPz₂**)

To a stirred solution of pyrazole (2.72 g, 40.0 mmol) in 20.0 mL of dimethoxyethane (DME) were added sliced pieces of potassium (1.56 g, 40.0 mmol) at room temperature. After refluxing for 3 h, 2,6-dibromopyridine (4.74 g, 20.0 mmol) in 20 mL of DME was slowly added to reaction vessel by cannula at 70 °C. The mixture was then heated to 110 °C and stirred for 4 days. The reaction mixture was allowed to cool to room temperature and then 50 mL of

water was added to the reaction vessel. Organic portion was separated and the aqueous layer was extracted with diethyl ether (3 × 20 mL). The combined organic portions were dried with MgSO₄, filtered, and concentrated. After column chromatography, desired product **PyPz₂** was obtained as a colorless powder (42.0%, 1.83 g).

¹H NMR (CD₃OD, 400.13 MHz): δ 8.73 (dd, *J* = 2 Hz and 0.4 Hz, 2H), 8.04 (t, *J* = 6.4 Hz, 1H), 7.80 (d, *J* = 6.4 Hz, 2H), 7.77 (d, *J* = 0.8 Hz, 2H), 6.56 (dd, *J* = 2.4 Hz and 1.6 Hz, 2H).

¹³C NMR (CD₃OD, 100.61 MHz): δ 151.4, 143.7, 143.1, 128.8, 110.3, 109.2.

2.3.2. Synthesis of 2,6-bis(3,5-dimethylpyrazol-1-yl)pyridine (**Py(Me₂Pz)₂**)

In a manner analogous to that used in the procedure for **PyPz₂**, the desired product **Py(Me₂Pz)₂** as a colorless powder was prepared from 3,5-dimethylpyrazole (1.92 g, 20.0 mmol), potassium (0.78 g, 20.0 mmol), and 2,6-dibromopyridine (2.37 g, 10.0 mmol) in a yield of 55.7 % (1.49 g).

¹H NMR (CD₃OD, 400.13 MHz): δ 8.03 (t, *J* = 8.0 Hz, 1H), 7.64 (d, *J* = 8.0 Hz, 2H), 6.08 (s, 2H), 2.53 (s, 6H), 2.25 (s, 6H).

¹³C NMR (CDCl₃, 100.61 MHz): δ 152.5, 151.7, 142.8, 142.3, 115.5, 110.0, 14.01, 13.37.

2.3.3. Synthesis of (PyPz₂)Zn(OC(=O)Me)₂ (**1**)

A mixture of 0.211 g (1.00 mmol) of **PyPz₂** and 0.219 g (1.00 mmol) of zinc acetate dihydrate was suspended in 30 mL of methanol at room temperature and heated to 80 °C. After 24 h stirring, all volatiles were removed under vacuo and the obtained colorless solid was washed with hexane. The desired product **1** was obtained as a colorless powder in a yield of 69.8 % (0.275 g).

¹H NMR (CD₃OD, 400.13 MHz): δ 8.77 (d, *J* = 2.4 Hz, 2H), 8.24 (t, *J* = 6.4 Hz, 1H), 7.97 (s, 2H), 7.91 (d, *J* = 6.4 Hz, 2H), 6.70 (s, 2H), 1.94 (s, 6H).

¹³C NMR (CD₃OD, 100.61 MHz): δ 180.8, 148.7, 145.7, 143.9, 129.7, 111.0, 110.0, 22.69.

Elemental Analysis Calc. for C₁₅H₁₅N₅O₄Zn: C, 45.65; H, 3.83; N, 17.74. Found: C, 45.53; H, 3.98; N, 17.70.

2.3.4. Synthesis of (Py(Me₂Pz)₂)Zn(OC(=O)Me)₂ (**2**)

In a manner analogous to that used in the procedure for **1**, the desired product **2** as a colorless solid was prepared from **Py(Me₂Pz)₂** (0.267 g, 1.00 mmol) and zinc acetate dihydrate (0.219 g, 1.00 mmol) in a yield of 67.9 % (0.306 g).

¹H NMR (CD₃OD, 400.13 MHz): δ 8.28 (t, *J* = 8 Hz, 1H), 7.73 (d, *J* = 7.2 Hz, 2H), 6.34 (s, 2H), 2.71 (s, 6H), 2.35 (s, 6H), 1.88 (s, 6H).

¹³C NMR (CD₃OD, 100.61 MHz): δ 180.5, 153.3, 147.6, 146.5, 144.1, 113.5, 110.4, 22.89, 14.74, 12.99.

Elemental Analysis Calc. for C₁₉H₂₃N₅O₄Zn: C, 50.62; H, 5.14; N, 15.54. Found: C, 50.88; H, 5.04; N, 15.38.

2.3.5. X-ray structure determination of **2**

Crystallographic assessment of **2** was performed at ambient temperature using a Bruker APEXII CCD area detector diffractometer with graphite-monochromated Mo Kα (λ = 0.71073 Å) radiation. A single crystal of suitable size and quality was selected and mounted on a glass capillary using Paratone[®] oil and centered in the X-ray beam using a video camera. Multi-scan reflection data were collected with a frame width of 0.5° in *w* and *θ* and 5 s exposures per frame. Cell parameters were determined and refined by SMART [62], while data reduction was performed using SAINT software [63]. Data were corrected for Lorentz and polarization effects. Empirical absorption correction was applied using SADABS [64]. The structures of the compounds were solved by direct methods and refined by the full matrix least-squares method, using the SHELXTL program package and applying anisotropic thermal parameters

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