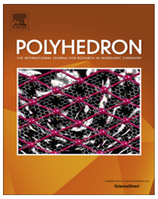
Polyhedron xxx (2016) xxx–xxx

Contents lists available at ScienceDirect

Polyhedron

journal homepage: www.elsevier.com/locate/poly



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

Min Seok Shin [a,1], Beom Jin Oh [a,1], Ji Yeon Ryu [b], Myung Hwan Park [c], Min Kim [a], Junseong Lee [b,*], Youngjo Kim [a,*]

[a] *Department of Chemistry and BK21+ Program Research Team, Chungbuk National University, Cheongju, Chungbuk 28644, Republic of Korea*
[b] *Department of Chemistry, Chonnam National University, Gwangju 61186, Republic of Korea*
[c] *Department of Chemistry Education, Chungbuk National University, Cheongju, Chungbuk 28644, Republic of Korea*

ARTICLE INFO

Article history:
Received 9 July 2016
Accepted 4 October 2016
Available online xxxx

Keywords:
Zinc
Tridentate ligand
Cycloaddition
CO_2
Epoxide

ABSTRACT

The complexes $[Py(Pz)_2]Zn(OC(=O)Me)_2$ (**1**) and $[Py(Me_2Pz)_2]Zn(OC(=O)Me)_2$ (**2**), where ligands $Py(Pz)_2$ and $Py(Me_2Pz)_2$ 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 $Py(Me_2Pz)_2$, both κ^1-acetate and κ^2-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 CO_2 and epoxides in the presence of various kinds of cocatalysts such as n-Bu_4PBr, n-Bu_4NI, n-Bu_4NBr, n-Bu_4NCl, PPNCl, and DMAP under the condition of 75 °C, 10 bar CO_2 pressure, 0.1 mol% catalyst loading, and 24 h. The reaction temperature, CO_2 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-Bu_4PBr system showed the best catalytic activity for the cycloaddition of CO_2 to propylene oxide, which showed the highest reactivity among seven other kinds of epoxides.

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 (**$PyPz_2$**) 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],

---

* Corresponding authors. Fax: +82 43 267 2279.
E-mail addresses: leespy@chonnam.ac.kr (J. Lee), ykim@chungbuk.ac.kr (Y. Kim).

[1] These authors contributed equally to this work.

http://dx.doi.org/10.1016/j.poly.2016.10.005
0277-5387/© 2016 Elsevier Ltd. All rights reserved.

Please cite this article in press as: M.S. Shin et al., Polyhedron (2016), http://dx.doi.org/10.1016/j.poly.2016.10.005

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 **$PyPz_2$**, have good catalytic activity for ethylene polymerization [57,58]. Unlike other metal complexes, zinc-based complexes with **$PyPz_2$** ligand are not widely studied. Even though the molecular structure of zinc(II) chloride complex containing **$PyPz_2$** ligand was determined [53], to our best knowledge, any zinc compound with 2,6-bis(3,5-dimethylpyrazol-1-yl) pyridine (**$Py(Me_2Pz)_2$**) 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 CO_2 and epoxides using new zinc acetate complexes with **$PyPz_2$** and **$Py(Me_2Pz)_2$**. In addition, the solid state structure of zinc(II) acetate complex chelated by **$Py(Me_2Pz)_2$** 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. CD_3OD and $CDCl_3$ were dried over 4 Å activated molecular sieves and used after vacuum transfer to a Schlenk tube equipped with a J. Young valve [60]. CD_3OD and $CDCl_3$ 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

^{1}H and ^{13}C 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 $CDCl_3$ (δ 7.24, ^{1}H NMR; δ 77.0, ^{13}CNMR) or CD_3OD (δ 3.30, ^{1}H NMR; δ 49.0, ^{13}C NMR) [61]. Elemental analyses was performed with EA 1110-FISONS analyzer.

2.3. Synthesis

Compounds **$PyPz_2$** and **$Py(Me_2Pz)_2$** 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 (**$PyPz_2$**)

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 $MgSO_4$, filtered, and concentrated. After column chromatography, desired product **$PyPz_2$** was obtained as a colorless powder (42.0%, 1.83 g).

^{1}H NMR (CD_3OD, 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).

^{13}C NMR (CD_3OD, 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 (**$Py(Me_2Pz)_2$**)

In a manner analogous to that used in the procedure for **$PyPz_2$**, the desired product **$Py(Me_2Pz)_2$** 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).

^{1}H NMR (CD_3OD, 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).

^{13}C NMR ($CDCl_3$, 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 $(PyPz_2)Zn(OC(=O)Me)_2$ (**1**)

A mixture of 0.211 g (1.00 mmol) of **$PyPz_2$** 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).

^{1}H NMR (CD_3OD, 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).

^{13}C NMR (CD_3OD, 100.61 MHz): δ 180.8, 148.7, 145.7, 143.9, 129.7, 111.0, 110.0, 22.69.

Elemental Analysis Calc. for $C_{15}H_{15}N_5O_4Zn$: C, 45.65; H, 3.83; N, 17.74. Found: C, 45.53; H, 3.98; N, 17.70.

2.3.4. Synthesis of $(Py(Me_2Pz)_2)Zn(OC(=O)Me)_2$ (**2**)

In a manner analogous to that used in the procedure for **1**, the desired product **2** as a colorless solid was prepared from **$Py(Me_2Pz)_2$** (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).

^{1}H NMR (CD_3OD, 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).

^{13}C NMR (CD_3OD, 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 $C_{19}H_{23}N_5O_4Zn$: 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

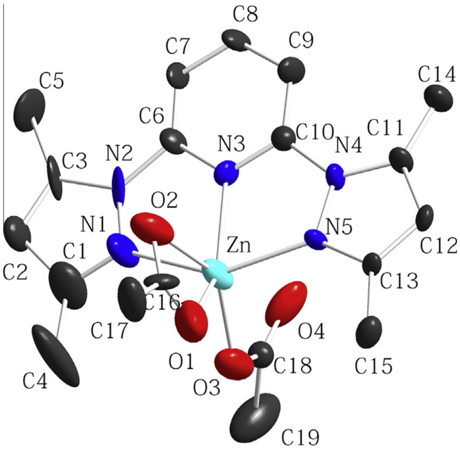


Fig. 1. X-ray molecular structure of compound **2** with 50% thermal ellipsoids. H atoms are omitted for clarity.

Table 1
Crystallographic data and parameters for compound **2**.

	2
Empirical formula	'C19 H23 N5 O4.50 Zn'
Formula weight	458.79
Crystal system	monoclinic
Space group	$P2_1/c$
Unit cell dimensions	
a (Å)	10.5679(3)
b (Å)	12.7067(3)
c (Å)	15.5972(4)
α (°)	90
β (°)	94.3689(13)
γ (°)	90
V (Å^3)	2088.35(9)
Z	4
D_{calc} (g/cm^3)	1.459
μ (mm^{-1})	1.214
$F(000)$	952
Index ranges	$-14 \leqslant h \leqslant 14$, $-15 \leqslant k \leqslant 15$, $-18 \leqslant l \leqslant 18$
θ range (deg)	1.933–25.402
Reflections collected	27434
Independent reflections	3840
Number of observed reflections ($I > 2\sigma(I)$)	3026
Number of parameters refined	546
GOF($I > 2\sigma(I)$)	1.048
R_1 (all data)	0.0682
$R_1(I > 2\sigma(I))$[a]	0.0532
wR_2 (all data)	0.1190
$wR_2(I > 2\sigma(I))$[a]	0.1107
Largest diff. peak and hole	0.464/−0.370

[a] $R_1 = \Sigma||Fo| - |F_c||/\Sigma\ |F_o|$ and $wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$.

for all non-hydrogen atoms [65]. Due to the disorder of acetate parts, several restraints (SADI for Zn–O1 and Zna–O1a, C18–O3 and C18–O4; Zn–O3 and Zna–O3a; ISOR for C2, C16, C5, O4A, C10, C18) were applied in the structure refinement process. The molecular structure of **2** (Fig. 1) was drawn using the program DIAMOND [66]. Details of the crystallographic parameters and selective bond length and angles are listed in Tables 1 and 2, respectively.

2.4. Representative procedures for the cycloaddition between epoxide and CO$_2$

The cycloaddition reaction of CO$_2$ to epoxide was carried out by charging a stirring bar, epoxide (10 mmol), catalyst (10 μmol), and cocatalyst (10 μmol), into a stainless steel pressure reactor (10 mL inner volume). Then, CO$_2$ was charged in the reactor and the pressure was adjusted to desired pressure at appropriate temperature. The reactor was maintained for the desired time. After then, the pressure reactor was cooled to ambient temperature, and the excess CO$_2$ was vented. A small sample of mixture was taken for ^{1}H NMR analysis.

3. Results and discussion

The aim of this work is the synthesis, characterization, and the comparison of cycloaddition reaction behaviors of novel zinc complexes with N,N,N-type tridentate ligands such as **PyPz$_2$** and **Py(Me$_2$Pz)$_2$**. As shown in Scheme 1, the preparation of **PyPz$_2$** and **Py(Me$_2$Pz)$_2$** was achieved by the reaction of potassium and corresponding pyrazole in dimethoxyethane, followed by the addition of 2,6-dibromopyridine. Suitable workup gave **PyPz$_2$** and **Py(Me$_2$Pz)$_2$** as colorless powder in 42.0 % and 55.7%, respectively. Zinc acetate complexes **1** and **2** were obtained from reactions of Zn(OAc)$_2$·(OH$_2$)$_2$ with **PyPz$_2$** and **Py(Me$_2$Pz)$_2$** in methanol, respectively. The colorless crystalline solids **1** and **2** are freely soluble in methanol and methylene chloride and insoluble in hexane and toluene.

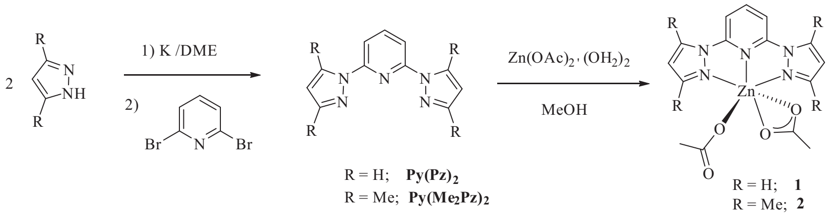
All compounds were fully characterized by ^{1}H and ^{13}C NMR spectroscopy. As given in Table 3, aromatic signals of tridentate ligands bound to zinc metal in the ^{1}H and ^{13}C NMR spectra for **1** and **2** are shifted downfield compared to the signals for corresponding free ligands, indicating that **PyPz$_2$** and **Py(Me$_2$Pz)$_2$** as π-donor ligands were strongly bound and chelated to zinc metal. In addition, methyl protons of two acetate ligands in both **1** and **2** showed a single peak at about 1.9 ppm. This observation means two acetate ligands in solution structure may have the same chemical environments in NMR time scale. Thus, solid state structure and solution structure for **2** may be different because two acetates showed different bind modes to zinc metal as shown in Fig. 1. The NMR signals were sharp and variable-temperature NMR spectrum did not change.

Recrystallization from methanol at −20 °C gave **2** as a colorless crystalline solid suitable for X-ray diffraction analysis, which assessed its solid-state structure (Fig. 1). Tables 1 and 2 list detailed crystallographic data and selected interatomic distances and angles, respectively. The structure was confirmed as the monomeric complex, and crystallized in the $P2_1/c$ space group. The ligand **Py(Me$_2$Pz)$_2$** acts in a tridentate manner through its three *N*-donors. The maximum value of the dihedral angle between the planes of the aromatic rings is about 9°, which suggests the high planarity of **Py(Me$_2$Pz)$_2$** in complex **2**. The Zn–N bond lengths of

Table 2
Selected interatomic distances (Å) and angles (°) of compound **2**.

Distances			
Zn–O1	2.105(14)	O1–C16	1.118(24)
Zn–O2	2.488(15)	O2–C16	1.142(27)
Zn–O3	2.067(10)	O3–C18	1.324(13)
Zn–N1	2.182(20)	O4–C18	1.178(13)
Zn–N3	2.152(16)	C16–C17	1.430(15)
Zn–N5	2.119(13)	C18–C19	1.551(15)
N1–N2	1.330(26)	N3–C10	1.331(18)
N4–N5	1.379(18)	N3–C6	1.355(25)
Angles			
O1–Zn–O2	50.12(56)	O2–Zn–N5	99.04(52)
O1–Zn–O3	94.95(56)	O3–Zn–N1	94.67(57)
O2–Zn–O3	140.41(46)	O3–Zn–N3	126.12(46)
O1–Zn–N1	107.56(60)	O3–Zn–N5	104.78(43)
O1–Zn–N3	138.92(54)	N1–Zn–N3	71.93(67)
O1–Zn–N5	98.24(50)	N1–Zn–N5	146.12(58)
O2–Zn–N1	81.92(65)	N3–Zn–N5	74.19(47)
O2–Zn–N3	90.47(55)		

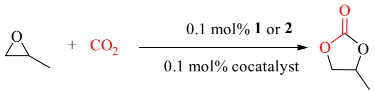
Please cite this article in press as: M.S. Shin et al., Polyhedron (2016), http://dx.doi.org/10.1016/j.poly.2016.10.005



Scheme 1. Synthetic routes to **1** and **2**.

Table 3

Cocatalyst screening for the cycloaddition of CO_2 to epoxides using complexes **1** and **2**.[a]



Entry	Cat.	Cocatalyst	TON[b]	Selectivity(%)[c]
1	**1**	*n*-Bu_4PBr	783	>99
2		*n*-Bu_4NI	430	>99
3		*n*-Bu_4NBr	617	>99
4		*n*-Bu_4NCl	578	>99
5		PPNCl	411	>99
6		DMAP	225	>99
7	**2**	*n*-Bu_4PBr	774	>99
8		*n*-Bu_4NI	578	>99
9		*n*-Bu_4NBr	646	>99
10		*n*-Bu_4NCl	744	>99
11		PPNCl	578	>99
12		DMAP	147	>99
13	None	*n*-Bu_4PBr	40	–
14		*n*-Bu_4NI	90	–
15		*n*-Bu_4NBr	50	–
16		*n*-Bu_4NCl	30	–
17		PPNCl	50	–
18		DMAP	0	–

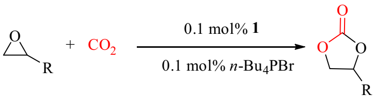
[a] Cycloaddition conditions: [propylene oxide] = 10 mmol, [Zn] = 0.01 mmol, [cocatalyst] = 0.01 mmol, [propylene oxide]/[Zn] = 1000/1, CO_2 = 10 bar, Temperature = 75 °C, time = 24 h.

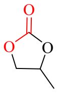
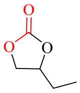
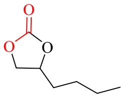
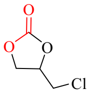
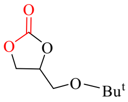
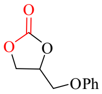
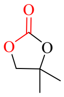
[b] Turnover number (TON) = (mol of propylene oxide consumed)/(mol of zinc).

[c] Calculated by ^1H NMR spectral integration.

Table 4

The scope of epoxides on the cycloaddition reaction of epoxide and CO_2 using catalyst **1**.[a]



Entry	Product	TON[b]	Selectivity (%)[c]
1		783	>99
2		482	>99
3		381	>99
4		586	>99
5		367	>99
6		484	>99
7		103	>99

[a] Cycloaddition conditions; [epoxide] = 10 mmol, [**1**] = 0.01 mmol, [*n*-Bu_4PBr] = 0.01 mmol, [epoxide]/[**1**] = 1000/1, CO_2 = 10 bar, Temperature = 75 °C.

[b] Turnover number (TON) = (mol of propylene oxide consumed)/(mol of catalyst).

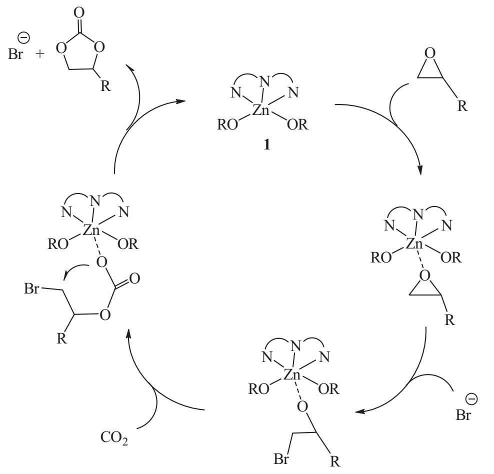
[c] Calculated by ^1H NMR spectral integration.

2.18–2.12 Å is within the normal range of previously reported Zn–N bond lengths [53–56]. Interestingly, two acetate anions chelated to zinc metal have different binding mode. Since bond lengths of Zn–O1, Zn–O2, Zn–O3, and Zn–O4 are 2.105(14) Å, 2.488(15) Å, 2.067(10) Å, and 3.004(9) Å, respectively, one acetate anion has κ^2-type binding mode and the other has κ^1-mode. Furthermore, O–C bonds in acetate ion have relatively three short and double bond of O1–C16 (1.118(24) Å), O2–C16 (1.142(27) Å), and O4–C18 (1.178(13) Å) and one long and single bond of O3–C18 (1.324(13) Å). Thus, the solid state structure of **2** could be defined as [κ^3-2,6-bis(3,5-dimethylpyrazol-1-yl)pyridine](κ^2-acetato)(κ^1-acetato)zinc(II). The coordination geometry of **2** around zinc metal is close to pseudo-octahedral. The N1-Zn-N5 provided most wide angle (146.1(5)°) and could be considered as trans position of octahedral structure.

The cycloaddition of CO_2 to propylene oxide was performed without solvent using the zinc compounds **1** and **2** as catalysts in the presence of cocatalyst. The cycloaddition results are summarized in Table 3. We carried out the reaction at 75 °C and 10 bar CO_2 pressure under the condition of a fixed 0.1 mol% catalyst loading. Propylene oxide was easily converted into the cyclic carbonate with high selectivity (99%) without any polymerized products. Interestingly, our reaction conditions applied for cycloaddition of CO_2 to propylene oxide are relatively milder than those for reported zinc catalysts [13–21,24,27,30,31]. Harsh conditions such as more elevated temperature [13–16,18,21,24], higher CO_2 pressure [13–18,21,24,27,30], and larger amount of catalyst loading [13–21,27,30,21] than our systems were applied in the literature. However, longer reaction time of 24 h for our system was needed.

To check the cocatalyst effect on the catalytic activity, we used six different kinds of cocatalysts, such as *n*-Bu_4PBr, *n*-Bu_4NI, *n*-Bu_4NBr, *n*-Bu_4NCl, bis(triphenylphosphoranylidene)ammonium chloride (PPNCl), and 4-dimethylaminopyridine (DMAP). Cocatalyst *n*-Bu_4PBr for catalysts **1** and **2** is superior compared with the five others (Table 3, entries 1–12). In addition, catalyst **1** showed the best catalytic activity in the presence of *n*-Bu_4PBr (entry 1). Compounds **1** and **2** showed marginal difference in catalytic activity (entries 1–12). Both **1** and **2** with non-salt-type cocatalyst DMAP

Please cite this article in press as: M.S. Shin et al., Polyhedron (2016), http://dx.doi.org/10.1016/j.poly.2016.10.005



Scheme 2. Plausible mechanism for the cycloaddition of CO_2 to epoxides catalyzed by **1**/*n*-Bu_4PBr.

showed very low activities (entries 6 and 12). Interestingly, six cocatalysts without **1** and **2** showed low conversion in the TON range of 0–90 (entries 13–18). Thus the coupling of catalyst and cocatalyst showed the synergistic activity for this cycloaddition reaction.

With the optimized condition in hands, we next moved to investigate the scope of substrates (Table 4) using **1** as a catalyst and *n*-Bu_4PBr as a cocatalyst. Substrates include various kinds of epoxides such as propylene oxide (Table 4, entry 1), 1,2-epoxybutane (entry 2), 1,2-epoxyhexane (entry 3), epichlorohydrin (entry 4), *tert*-butyl glycidyl ether (entry 5), 1,2-epoxy-3-phenoxypropane (entry 6), and 1,2-epoxy-2-methylpropane (entry 7). Epoxides with simple alkanes (R = Me, Et, and *n*-Bu) showed high dependence on chain length (entries 1–3), whereas reported zinc systems displayed the similar activities for those epoxides [16,18,21,24]. While propylene oxide gave an excellent conversion (entry 1), a quick loss of reactivity was observed from ethyl to butyl side chains (entries 2 and 3). Interestingly, when heteroatom was introduced at 3-position, high reactivity was restored [16,18,21]. In addition to epichlorohydrin (entry 4), epoxides with $–CH_2OMe$ and $–CH_2OBu^t$ substituents gave good TONs (entries 5 and 6). However, substrate with multi-substituents such as 1,2-epoxy-2-methylpropane (entry 7) exhibited lower conversion, this being ascribed to the steric effect. Consequently, both steric and electronic effects of substituents within the epoxides play a significant role in the cycloaddition between CO_2 and epoxides.

A plausible mechanism for our best catalytic system, *i.e.* **1**/*n*-Bu_4PBr, catalyzed coupling of CO_2 into epoxides was proposed and shown in Scheme 2. The catalytic cycle starts with the coordination of epoxide to the Lewis acidic Zn center in complex **1**, followed by the ring opening by nucleophilic attack of the bromide anion to form the zinc intermediate containing bromoalkoxide moiety. Then, the newly formed nucleophile such as bromoalkoxide attacks CO_2 to make the zinc carbonate species, which could undertake an intramolecular ring-closing reaction to form the desire product, cyclic carbonate and regenerate the catalyst.

In summary, zinc compounds containing tridentate 2,6-bis(pyrazol-1-yl)pyridine (**$PyPz_2$**) and 2,6-bis(3,5-dimethylpyrazol-1-yl)pyridine (**$Py(Me_2Pz)_2$**) were prepared. The solid state structure of $(Py(Me_2Pz)_2Zn(OAc)_2$ was determined by single-crystal X-ray analysis. Two zinc compounds in the presence of cocatalysts showed comparable catalytic activities for the cycloaddition of CO_2 to epoxides under the mild condition of 75 °C, 10 bar CO_2 pressure, and 0.1 mol% catalyst loading.

Acknowledgments

Y. K. thanks the National Research Foundation of Korea (NRF), the Korean Ministry of Education (MOE) through the Creative Human Resource Training Project for Regional Innovation (grant number 2014H1C1A1066874) and Basic Science Research Program (grant number 2015R1D1A1A01061043) for financial support. J. L. acknowledges financial supports by the BRL Program (2015R1A4A1041036) through the National Research Foundation of Korea (NRF) funded by the Ministry of Science, ICT & Future Planning.

Appendix A. Supplementary data

CCDC 1490123 contains the supplementary crystallographic data for **2**. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk. Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.poly.2016.10.005.

References

[1] E. Lichtfouse, J. Schwarzbauer, D. Robert, CO2 Sequestration: Biofuels and Depollution, Springer, Switzerland, 2015.
[2] J. Bayardon, J. Holz, B. Schäffner, V. Andrushko, S. Verekin, A. Preetz, A. Börner, Angew. Chem., Int. Ed. 46 (2007) 5971.
[3] M. Arakawa, S. Tobishima, T. Hirai, J. Yamaki, J. Electrochem. Soc. 133 (1986) 1527.
[4] T. Takata, Y. Furusho, K. Murakawa, T. Endo, H. Matsuoka, T. Hirasa, J. Matsuo, M. Sisido, J. Am. Chem. Soc. 120 (1998) 4530.
[5] W.J. Peppel, Ind. Eng. Chem. 50 (1958) 767.
[6] A. Decortes, A.M. Castilla, A.W. Kleij, Angew. Chem., Int. Ed. 49 (2010) 9822.
[7] X.-B. Lu, D.J. Darensbourg, Chem. Soc. Rev. 41 (2012) 1462.
[8] A.R. Hajipour, Y. Heidari, G. Kozehgary, RSC Adv. 5 (2015) 61179.
[9] J.-Q. Wang, K. Dong, W.-G. Cheng, J. Sun, S.-J. Zhang, Catal. Sci. Technol. 2 (2012) 1480.
[10] Q. He, J.W. O'Brian, K.A. Kitselman, L.E. Tompkins, G.C.T. Curtis, F.M. Kerton, Catal. Sci. Technol. 4 (2014) 1513.
[11] Y. Zhang, S. Yin, S. Luo, C.T. Au, Ind. Eng. Chem. Res. 51 (2012) 3951.
[12] J. Zhang, J. Sun, X. Zhang, Y. Zhang, S. Zhang, Greenhouse Gas Sci. Technol. 1 (2011) 142.
[13] H.S. Kim, J.J. Kim, B.G. Lee, O.S. Jung, H.G. Jang, S.O. Kang, Angew. Chem., Int. Ed. 39 (2000) 4096.
[14] H.S. Kim, J.J. Kim, S.D. Lee, M.S. Lah, D. Moon, H.G. Jang, Chem. Eur. J. 9 (2003) 678.
[15] T.-Y. Chen, C.-Y. Li, C.-Y. Tsai, C.-H. Li, C.-H. Chang, B.-T. Ko, C.-Y. Chang, C.-H. Lin, H.-Y. Huang, J. Organomet. Chem. 754 (2014) 16.
[16] R. Luo, X. Zhou, W. Zhang, Z. Liang, J. Jiang, H. Ji, Green. Chem. 15 (2014) 4179.
[17] S. Kumar, S.L. Jain, B. Sain, Catal. Lett. 142 (2012) 615.
[18] R. Ma, L.-N. He, Y.-B. Zhou, Green Chem. 18 (2016) 226.
[19] Y. Yang, Y. Hayashi, Y. Fujii, T. Nagano, Y. Kita, T. Ohshima, J. Okuda, K. Mashima, Catal. Sci. Technol. 2 (2012) 509.
[20] H.V. Babu, K. Muralidharan, Dalton Trans. 42 (2013) 1238.
[21] L. Cuesta-Aluja, A. Campos-Carrasco, J. Castilla, M. Reguero, A.M. Masdeu-Bultó, A. Aghmiz, J. CO2 Util. 14 (2016) 10.
[22] C.-Y. Yu, H.-J. Chang, B.-T. Ko, Catal. Sci. Technol. 6 (2016) 1779.
[23] S. Bhunia, R.A. Molla, V. Kumari, S.K.M. Islam, A. Bhaumik, Chem. Commun. 51 (2015) 1573.
[24] S. He, F. Wang, W.-L. Tong, S.-M. Yiu, M.C.W. Chan, Chem. Commun. 52 (2016) 1017.
[25] C. Martin, C.J. Whiteoak, E. Martin, M.M. Belmonte, E.C. Escudero-Adán, A.W. Kleij, Catal. Sci. Technol. 4 (2014) 1615.
[26] M.V. Escárcega-Bobadilla, M.M. Belmonte, E. Martin, E.C. Escudero-Adán, A.W. Kleij, Chem. Eur. J. 19 (2013) 2641.
[27] A. Decortes, M. Martínez Belmonte, J. Benet-Buchholza, A.W. Kleij, Chem. Commun. 46 (2010) 4580.
[28] A. Decortes, A.W. Kleij, ChemCatChem 3 (2011) 831.
[29] M. Taherimehr, A. Decortes, S.M. Al-Amsyar, W. Lueangchaichaweng, C.J. Whiteoak, E.C. Escudero-Adán, A.W. Kleij, P.P. Pescarmona, Catal. Sci. Technol. 2 (2012) 2231.
[30] Z. Wang, Z. Bu, T. Cao, T. Ren, L. Yang, W. Li, Polyhedron 32 (2012) 86.
[31] Z. Dai, Q. Sun, X. Liu, C. Bian, Q. Wu, S. Pan, L. Wang, X. Meng, F. Deng, F.-S. Xiao, J. Catal. 338 (2016) 202.
[32] D.L. Jameson, K.A. Goldsby, J. Org. Chem. 55 (1990) 4992.
[33] M.A. Halcrow, New J. Chem. 38 (2014) 1868.
[34] M.A. Halcrow, Coord. Chem. Rev. 249 (2005) 2880.

Please cite this article in press as: M.S. Shin et al., Polyhedron (2016), http://dx.doi.org/10.1016/j.poly.2016.10.005

[35] D. Gong, X. Jia, B. Wang, X. Zhang, K.-W. Huang, J. Organomet. Chem. 766 (2014) 79.
[36] D. Gong, X. Jia, B. Wang, X. Zhang, L. Jiang, J. Organomet. Chem. 702 (2012) 10.
[37] T.D. Roberts, M.A. Little, L.J.K. Cook, S.A. Barrett, F. Tuna, M.A. Halcrow, Polyhedron 64 (2013) 4.
[38] J. Elhaïk, C.A. Kilner, M.A. Halcrow, Dalton Trans. (2006) 823.
[39] A.R. Karam, E.L. Catarí, F. López-Linares, G. Agrifoglio, C.L. Albano, A. Díaz-Barrios, T.E. Lehmann, S.V. Pekerar, L.A. Albornoz, R. Atencio, T. González, H.B. Ortega, P. Joskowics, Appl. Catal. A Gen. 280 (2005) 165.
[40] L.J.K. Cook, F.L. Thorp-Greenwood, T.P. Comyn, O. Cespedes, G. Chastanet, M.A. Halcrow, Inorg. Chem. 54 (2015) 6319.
[41] J.M. Holland, C.A. Kilner, M. Thornton-Pett, M.A. Halcrow, Polyhedron 20 (2001) 2829.
[42] K.M. Arendt, A.G. Doyle, Angew. Chem., Int. Ed. 54 (2015) 9876.
[43] S. Chakrabarty, P. Sarkhel, R.K. Poddar, J. Coord. Chem. 61 (2008) 3260.
[44] V.D. Dolzhenko, N.M. Kurnosov, S.I. Troyanov, Z. Anorg, Allg. Chem. 640 (2014) 347.
[45] O. Atakol, H. Fuess, R. Kurtaran, A. Akay, C. Arici, Ü. Ergun, K.C. Emregül, J. Therm. Anal. Cal. 90 (2007) 517.
[46] B. Machura, R. Penczek, R. Kruszynski, Polyhedron 26 (2007) 2470.
[47] C.A. Bessel, R.F. See, D.L. Jameson, M.R. Churchill, K.J. Takeuchi, J. Chem. Soc. Dalton Trans. (1993) 1563.
[48] N.J. Beach, G.J. Spivak, Inorg. Chim. Acta 343 (2003) 244.
[49] A.I. Philippopoulos, A. Terzis, C.P. Raptopoulou, V.J. Catalano, P. Falaras, Eur. J. Inorg. Chem. (2007) 5633.
[50] S. Chakrabarty, P. Sarkhel, R.K. Poddar, J. Coord. Chem. 63 (2010) 1563.
[51] S.A. Willison, H. Jude, R.M. Antonelli, J.M. Rennekamp, N.A. Eckert, J.A.K. Bauer, W.B. Connick, Inorg. Chem. 43 (2004) 2548.
[52] J.M. Stanley, X. Zhu, X. Yang, B.J. Holliday, Inorg. Chem. 49 (2010) 2035.
[53] Z.N. Yang, T.T. Sun, Acta Cryst. E64 (2008) m1374.
[54] M.A. Halcrow, C.A. Kilner, M. Thornton-Pett, Acta Cryst. C56 (2000) 1425.
[55] N.K. Solanki, M.A. Leech, E.J.L. McInnes, F.E. Mabbs, J.A.K. Howard, C.A. Kilner, J. M. Rawson, M.A. Halcrow, J. Chem. Soc. Dalton Trans. (2002) 1295.
[56] C. Hopa, R. Kurtaran, A. Azizoğlu, M. Alkan, N.B. Arslan, C. Kazak, Z. Anorg, Allg. Chem. 637 (2011) 1238.
[57] J. Hurtado, D.M-L. Carey, A. Munoz-Castro, R. Arratia-Perez, R. Quijada, G. Wu, R. Rojas, M. Valderrama, J. Organomet. Chem. 694 (2009) 2636.
[58] H.S. Abbo, S.F. Mapolie, J. Darkwa, S.J.J. Titinchi, J. Organomet. Chem. 692 (2007) 5327.
[59] D.F. Shriver, M.A. Drezdzon, The Manipulation of Air-Sensitive Compounds, 2nd ed., Wiley, New York, 1986.
[60] W.L.F. Armarego, C.L.L. Chai, Purification of Laboratory Chemicals, sixth ed., Elsevier, New York, 2009.
[61] G.R. Fulmer, A.J.M. Miller, N.H. Sherden, H.E. Gottlieb, A. Nudelman, B.M. Stoltz, J.E. Bercaw, K.I. Goldberg, Organometallics 29 (2010) 2176.
[62] SMART, Version 5.0, Data Collection Software, Bruker AXS Inc., Madison, WI, 1998.
[63] SAINT, Version 5.0, Data Integration Software, Bruker AXS Inc., Madison, WI, 1998.
[64] G.M. Sheldrick, SADABS, University of Gottingen, Gottingen, Germany, 1998.
[65] G.M. Sheldrick, SHELXL-2014, University of Gottingen, Gottingen, Germany, 2014.
[66] K. Brandenburg, DIAMOND Crystal Impact GbR, Bonn, Germany, 1999.

Please cite this article in press as: M.S. Shin et al., Polyhedron (2016), http://dx.doi.org/10.1016/j.poly.2016.10.005