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(Pyrazolylethyl-amine)zinc(II) carboxylate complexes as catalysts for the copolymerization of CO_2 and cyclohexene oxide

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ABSTRACT

Pyrazolyl compounds 2-(3,5-di-*tert*-butyl-1H-pyrazol-1-yl)ethyl-amine) (**L1**), 2-(3,5-diphenyl-1H-pyrazol-1-yl)ethyl-amine (**L2**), and 2-(3-phenyl-5-(trifluoromethyl)-1H-pyrazol-1-yl)ethyl-amine (**L3**) were reacted with a mixture of zinc(II) acetate and 3,5-dinitrobenzoic acid to form the bidentate complexes [(2-(3,5-di-*tert*-butyl-1H-pyrazol-1-yl)-ethyl-amine)-Zn($C_6H_5COO(NO_2)_2$] (**1**), [(2-(3,5-diphenyl-1H-pyrazol-1-yl)ethyl-amine)Zn($C_6H_5COO(NO_2)_2$] (**2**), and [(2-(5-phenyl-3-(trifluoro-methyl)-1H-pyrazol-1-yl)ethyl-amine)Zn($C_6H_5COO(NO_2)_2$] (**3**) respectively. All three zinc complexes were tested as catalysts for the copolymerization of CO_2 and cyclohexene oxide (CHO) and found active to form poly(cyclohexene carbonate) (PCHC) and cyclohexene carbonate (CCHC) at CO_2 pressures as low as 1.5 MPa and under solvent-free conditions in the absence of a co-catalyst. Increase in CO_2 pressure resulted in activity and showed selectivity up to 99% selectivity for the formation of the copolymer PCHC. Optimum temperature for the polymerization was 100 °C and even at this temperature selectivity towards formation of PCHC was found to be 99%. The copolymers obtained have moderate molecular weights (3860–11,500 g/mol) and polydispersity indices varying from 2.73 to 4.93.

1. Introduction

Carbon dioxide (CO_2) is an industrial waste product and also the main component of the greenhouse gases [1]. These greenhouse gases, particularly CO_2 in the atmosphere, are the cause of global warming which has become the most serious environmental concern worldwide recently [2]. Due to the fact that CO_2 is an abundant, inexpensive, and a nontoxic bio-renewable resource, it has become an attractive industrial raw material [3]. Studies to convert CO_2 into more useful products in order to reduce its accumulation in the atmosphere have increased over the years [4]. The most promising of this is utilizing CO_2 as a source of carbon in metal-catalyzed copolymerization of CO_2 and epoxide for the synthesis of bio-degradable polycarbonates [5,6]. After the first report of the alternating copolymerization of CO_2 and epoxide by Inoue and co-workers [7] using heterogeneous zinc catalyst, several other catalysts have been investigated for this reaction [8].

Homogenous zinc complexes have subsequently been widely explored as catalysts due to their rich structural chemistry, importance in organic synthesis and in polymerization chemistry [9]. These zinc catalysts are anchored on wide range of ligands, mainly N- and O-donors, with the aim of fine-tuning the properties of the catalysts and the polymer produced. However, pyrazole and its derivatives as *N*-donor ligands have been explored less in CO_2 and epoxide copolymerization reactions, although this class of late transition metal *N*-donor compounds have been excellent catalysts for polymerization reactions as exemplified by some selected examples [10]. This is because of the relatively weak σ-donor ability of pyrazole-based ligands compared to pyridine-based and imine-based ligands. Thus pyrazolyl ligands are able to form stable metal complexes that are highly electrophilic that makes them excellent catalysts for reactions where catalytic process involves coordination of a substrate. The electrophilicity of the metal centre allows for the catalyst to rapidly coordinate to substrates before the substrates are transformed into products. As a result of these properties, pyrazole-based catalysts are beginning to be used in CO_2-epoxide co-polymerization studies. For instance Darensbourg and co-workers have used soluble pyrazolyl-borate Cd(II) complexes for CO_2 and propylene oxide (PO) or Cyclohexene oxide (CHO) copolymerization [11]. Although these pyrazolyl cadmium complexes serve as excellent models for the initiation step in copolymerization of epoxides and CO_2, they do not high catalytic activities. A recent study by Darkwa and co-workers [10b] with (bis-pyrazole)zinc(II) benzoate complexes has shown that the introduction of carboxylate ligands in the pyrazole metal

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complex provide excellent initiation for the copolymerization of CO_2/CHO. We have extended the pyrazole ligands to pyrazolylethylamine compounds that to synthesize zinc carboxylate complexes for the copolymerization of epoxide and CO_2. The effect of the electrophilicity of the metal centre on the copolymerization reaction has allowed us to make catalysts that have good activities and excellent selectivity and report our results in this paper.

2. Experimental

2.1. Materials and methods

Syntheses of all complexes were carried out under nitrogen atmosphere. All solvents were of analytical grade and were dried and distilled prior to use. Dichloromethane and hexane were purchased from Sigma-Aldrich and stored under inert conditions in a solvent drying system. All reagents used in the synthesis of the complexes were purchased from Sigma-Aldrich and used as received. The ligands 2-(3,5-di-*tert*-butyl-1H-pyrazol-1-yl)ethanamine) (**L1**), 2-(3,5-diphenyl-1H-pyrazol-1-yl)ethanamine (**L2**), 2-(3-phenyl-5-(trifluoromethyl)-1H-pyrazol-1-yl)ethanamine (**L3**) were synthesized according to the literature which involves a reaction between 2-bromoethylamine hydrobromide and the corresponding pyrazole [12].

Infrared and NMR (^{1}H and ^{13}C{^{1}H}) spectra were recorded on a Bruker FR-IR Tensor27 spectrometer fitted with an ATP-IR probe and on a Bruker 400 and 500 MHz NMR instrument, respectively. The chemical shifts are reported in δ (ppm) and referenced to the residual proton carbon signals (7.24 ppm and 77.0 ppm) of the NMR solvent $CDCl_3$. Elemental analyses were performed on a Vario elementar III microcube CHNS analyzer. FT-IR spectra were recorded at on a diamond ATR Perkin-Elmer Spectrum BX FTIR. ESI-mass spectra were recorded on a Waters API Qualtro Micro Spectrophotometer at the University of Stellenbosch. Crystal structures were determined on a Bruker APEXII diffractometer with Mo Kα (λ = 0.71073 Å) radiation sources. The initial cell matrix was obtained from three series of scans at different starting angles. The reflections were successfully indexed by an automated indexing routine built in the APEXII program.

2.2. Synthesis of [(2-(3,5-di-tert-butyl-1H-pyrazol-1-yl)ethanamine) $Zn(C_6H_3COO(NO_2)_2]$ – 1

To a MeOH solution of $Zn(OAc)_2$ (0.04 g, 0.24 mmol) was added dinitrobenzoic acid (0.100 g, 0.47 mmol) and stirred for 3 h after which MeOH solution of **L1** (0.11 g, 0.47 mmol) was added and further stirred overnight. The solvent was evaporated and the crude product recrystallized with hexane and dichloromethane to afford yellow solid. Yield: (0.11 g) 33%. ^{1}H NMR ($CDCl_3$, 400 Hz): δ 1.40 (s, 18H, $(CH_3)_3$); 3.55 (s, 2H, CH_2-NH_2); 4.66 (s, 2H, CH_2-N(Pz)); 6.08 (s, 1H, CH(Pz)); 9.08 (s, 2H, CH-Bz); 9.16 (s, 4H CH-Bz). ^{13}C{^{1}H} NMR ($CDCl_3$, 500 Hz): δ 29.9; 30.4; 31.9; 41.7; 49.0; 100.8; 120.5; 129.6; 139.7; 148.1; 153.1; 161.9; 168.2; 179.0. ESI-MS (*m*/*z*) (%): 139.212 (100%) $[M\text{-}ZnC_6H_3COO(NO_2)_2]^+$); 414.046 (63%) $[M\text{-}C_6H_3COO(NO_2)]^+$. IR (ATR, cm^{-1}): 1629 ν(C=O). Anal. Calcd for $C_{21}H_{19}N_7O_{12}Zn$: C 40.24; H 3.06; N 15.64%. Found: C 40.65; H 3.71; N 15.88%.

Complex **2 and 3** were synthesized in a similar manner as complex **1**, further details of which are provided below.

2.3. Synthesis of [2-(3,5-diphenyl-1H-pyrazol-1-yl)ethanamine Zn $(C_6H_3COO(NO_2)_2]$ – 2

To a solution of $[Zn(OAc)_2]$ (0.06 g, 0.34 mmol) and 3,5-dinitrobenzoic acid (0.15 g, 0.68 mmol) acid in MeOH (20 mL), **L2** (0.15 g, 0.68 mmol) was added and gave a yellow-orange precipitate. The precipitate was purified to give a white precipitate. Yield: (0.25 g) 49%. ^{1}H NMR ($CDCl_3$, 400 Hz): δ 3.37 (2H-CH_2-NH_2); 4.41 (2H, CH_2-N); 6.56 (1H, Pz); 7.54 (8H, Ph); 7.76 (2H, Ph); 8.94 (2H, OBz $(NO_2)_2$); 9.06 (1H, OBz $(NO_2)_2$).^{13}C{^{1}H} NMR ($CDCl_3$, 500 Hz): δ 28.4; 58.1; 105.1; 121.4; 128.1; 129.7; 131.2; 132.9; 144.6; 149.5; 153.3; 174.8. ESI-MS (*m*/*z*) (%): 264.14 (71%) $[M\text{-}ZnC_6H_3COO(NO_2)_2]^+$; 538.076 (100%) $[M\text{-}C_6H_3COO(NO_2)]^+$. IR (ATR, cm^{-1}): 1634 ν(C=O). Anal. Calcd for $C_{31}H_{23}N_7O_{12}Zn$: C 49.58; 3.09; N 13.06%. Found: C 50.01; H 2.99; N 13.65%.

2.4. Synthesis of [2-(5-phenyl-3-(trifluoromethyl)-1H-pyrazol-1-yl) ethan-amine $Zn(\text{-}(NO_2)_2]$ – 3

The reaction of $[Zn(OAc)_2]$ (0.13 g, 0.70 mmol), 3,5-dinitrobenzoic acid (0.30 g, 1.40 mmol) and **L3** (0.25 g, 0.70 mmol) in MeOH (15 mL) afforded complex **3** as a white powder which was characterized as follows. Yield: (0.35 g) 49%. ^{1}H NMR ($CDCl_3$, 400 Hz): δ, δ' 3.52 (2H, CH_2-NH_2); 3.63 (2H, CH_2-NH_2); 4.49 (2H, CH_2-N) 4.60 (2H, CH_2-N); 4.90 (4H, NH_2); 6.56 (1H, Pz); 6.85 (1H, Pz); 7.56 (10*H*, Ph); 8.97 (8H, OBz $(NO_2)_2$). ^{13}C{^{1}H}NMR ($CDCl_3$, 500 Hz): δ 25.1; 49.9; 100.4; 121.4; 127.9; 129.8; 130.5; 133.1; 149.8; 153.7; 177.9. ESI-MS (*m*/*z*) (%): 256.10 (100%) $[M-ZnC_6H_3COO(NO_2)_2]^+$; 530.99 (45%) $[M-C_6H_3COO(NO_2)]^+$. IR (ATR, cm^{-1}): 1626 ν(C=O). Anal. Calcd for $C_{26}H_{18}F_3N_7O_{12}Zn$: C 42.04; 2.44; N 13.20%. Found: C 42.66; H 2.26; N 11.88%.

2.5. Molecular structure determination by single crystal X-ray analysis

A typical single-crystal X-ray diffraction data was collected on a Bruker APEXII diffractometer with Mo Kα (λ = 0.71073 Å) radiation and diffractometer to crystal distance of 5.00 cm. The following is a typical experiment conducted in the case of structure **1** and **3**. The initial cell matrix was obtained from three series of scans at different starting angles. Each series consisted of 12 frames collected at intervals of 0.5° in a 6° range about with an exposure time of 10 s per frame. The reflections were successfully indexed by an automated indexing routine built in the APEXII program suite. The data were collected using the full sphere data collection routine to survey the reciprocal space to the extent of a full sphere to a resolution of 0.75 Å. Data were harvested by collecting 2982 frames at intervals of 0.5° scans in ω and φ with exposure times of 10 s per frame [13]. A successful solution by the direct methods of SHELXS97 provided all non-hydrogen atoms from the *E*-map. All non-hydrogen atoms were refined with anisotropic displacement coefficients. All hydrogen atoms were included in the structure factor calculation at idealized positions and were allowed to ride on the neighbouring atoms with relative isotropic displacement coefficients [13].

2.6. General reaction procedure for the copolymerization of epoxide and CO_2

All the complexes were used for the coupling of CHO and CO_2. CHO was purchased from TSI chemicals and vacuum distilled over calcium hydride twice before use. The catalysis was carried out in a high pressure Parr autoclave reactor in neat CHO. Generally, to a clean autoclave (dried at 120 °C overnight) containing the appropriate amount of the catalyst, was added CHO under inert conditions. These catalysts were completely soluble in the epoxide which meant that the reaction was homogenous. The reaction was initiated by pressurizing the autoclave with CO_2 and left to stir at the required temperature for the appropriate time. The autoclave was allowed to cool to room temperature then vented to remove the CO_2. Some of the reactions performed were observed to have an occurrence of viscosity as a result of polymerization

having occurred. The mixture was dissolved in methylene chloride and transferred to a flask. A measured amount of phenanthrene (internal standard) was added and a small aliquot was removed for ^{1}H NMR analysis at the end of each reaction. The remaining mixture was quenched with few drops of a 1 M HCl solution and precipitated in a large amount of methanol to obtain the copolymer. The precipitate was re-dissolved in methylene chloride followed by removal of solvent, which afforded the copolymer as a brittle white solid.

3. Results and discussions

3.1. Synthesis of pyrazolylethyl-amine zinc(II) carboxylate complexes

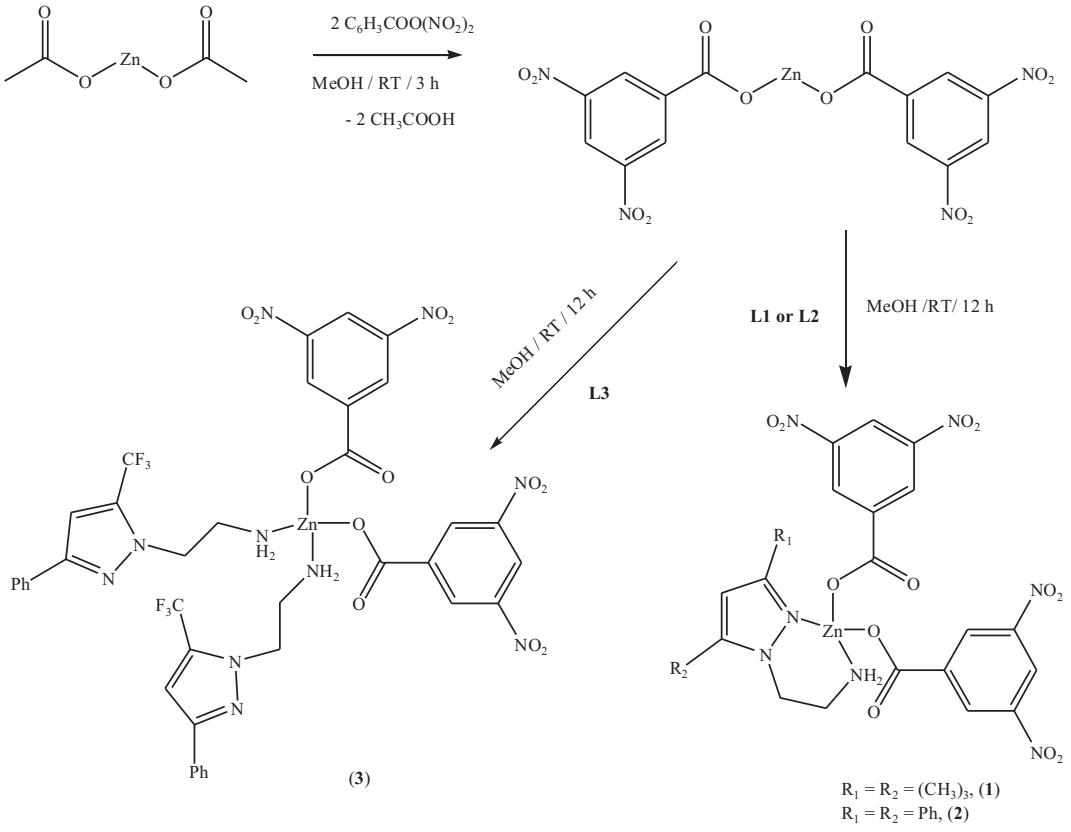
Complexes **1**–**3** were prepared by a modified method reported by Baruah *et al.* [14] which involves a room temperature reaction of a MeOH (15 mL) solution of 3,5-nitrobenzoic acid with Zn $(OAc)_2$ in a 2:1 mol ratio for 3 h, followed by addition of the appropriate ligand (**L1** or **L2** or **L3**) dissolved in MeOH (5 mL) (Scheme 1). The reactions involved the elimination of two acetic acid molecules obtained after the addition of the 3,5-nitrobenzoic acid to Zn $(OAc)_2$. All the complexes, except **2**, are soluble in chlorinated organic solvents and MeOH. All the complexes are pale yellow in colour and thermally stable up 120 °C as confirmed by ^{1}H NMR spectroscopy after heating all complexes in solution up this temperature. It was necessary to heat these complexes to 120 °C as this is the temperature where most epoxide and CO_2 co-polymerization reactions are performed.

Characterization of the complexes by NMR spectroscopy showed significant chemical shifts of the proton peaks of the ligands and compared their corresponding complexes. Complexes with the same alkyl group on the pyrazole, for example complex **1**, (Fig. S1) did not show isomerization as expected. However, Complex **3** exhibit structural isomer due to tautomerization arising from the pyrazolyl nitrogen as shown in Scheme S1. The tautomerizaion is evident in both the ^{1}H NMR (Fig. S2) and ^{19}F{^{1}H} NMR spectra (Fig. S3). In the ^{1}H NMR spectrum, there are two peaks for each proton in the ligand are four peaks in the region between 3.52 ppm and 4.60 ppm. Each peak integrates for two protons, assignable to protons of the CH_2 linker of the ligand and have 1:1 integration indicating they are structural isomers. The ^{19}F{^{1}H} NMR spectrum further confirms the presence of isomerization as two different CF_3 peaks at −59.72 ppm and −62.24 ppm. One important observation in the bonding of **L3** to the zinc in complex **3**, which could not be deduced from the ^{1}H HMR spectrum, is that **L3** is bonded to the Zn as a monodentate ligand and through the primary amine nitrogen. This bonding mode was only confirmed by the molecular structure determined single crystal X-ray diffraction (*vide infra*, Fig. 2). This bonding mode is different to complex **1** (Fig. 1) bonding mode of **3** and can be attributed to the electron withdrawing effect of CF_3 that weakens the donor ability of the pyrazolyl nitrogen atoms that could have made **L3** a bidentate ligand.

The IR spectra of the complexes revealed the presence of the carbonyl (C=O) stretching vibration at 1629 cm^{-1} (**1**) (Fig. S4), 1634 cm^{-1} (**2**) and 1626 cm^{-1} (**3**).

3.2. Molecular structures 1 and 3

Complexes **1** and **3** were crystallized by slow evaporation of methanol at −4 °C to give yellow single crystals suitable for structural analysis. The X-ray diffraction data were collected at 296 K with Mo Kα radiation (k = 0.71073 Å) using on a Bruker APEX-II CCD diffractometer and the structures were solved by direct



Scheme 1. Preparation of (pyrazolyl)zinc(II) 3,5-nitrobenzoate complexes using **L1**-**L3**.

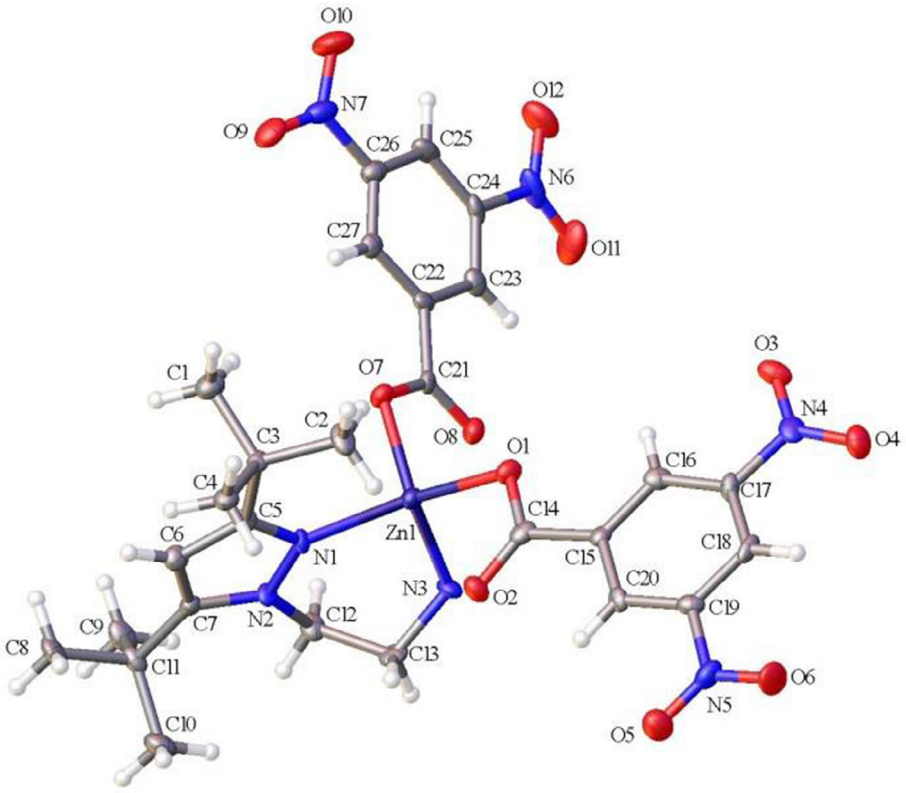


Fig. 1. A molecular structure drawing of **1** with 50% probability ellipsoids. Selected bond lenght [Å] and angles [°]: N1-N2, 1.381(6); Zn1-N1, 2.062(5); Zn1-N3, 2.034(4); N3-C13, 1.493(8); Zn1-O1, 1.998(4); Zn1-O7, 2.007(4); N1-Zn1-N3, 98.07(19); O1-Zn1-O7, 102.88(16); C13-C12-N2, 114.1(5); Zn1-O7-C21, 109.0(3); Zn1-O1-C14, 104.9(4).

methods and refined by least squares techniques using OLEX2: a complete structure solution, refinement and analysis program [13].

Complex **1** crystallized in a triclinic crystal system (Table S1) and is represented in Fig. 1 and shows a distorted trigonal pyramidal geometry with bond angles between 98.07° and 109.0° about the Zn center. The bond length for N(1)-Zn(1), (2.062(5) Å), was found to be longer than N(3)-Zn(1) (2.034(3) Å). However, they are both in the range of Zn-N bond lengths [15]. Bond lengths O (7)-Zn(1), 2.007(4) Å and O(1)-Zn(1) 1.998(4) Å are also in the acceptable range for Zn-O bond length reported in the Cambridge Structural Database (CSD) [16].

Ligand **L3** contains two potential nitrogen donor atoms and was expected to bind to the zinc in complex 3 as a bidentate ligand. However, the crystal structure of complex **3** indicates that **L3** binds as a monodentate ligands and thus have two **L3** per a zinc atom through the amino group in the ligand (Fig. 2). The geometry around the zinc atom is a distorted tetrahedron, with Zn-N bond lengths that are slightly shorter than similar bond lengths for **1**. The bond angles vary from 103.91° for O(7)-Zn(1)-N(4) to 119.15° for N(3)-Zn(1)-N(4). These bond angles confirm the distorted tetrahedral geometry adopted by the complex about the Zn centre.

3.3. Copolymerization of CO_2 and epoxide using complex 1–3

3.3.1. Screening of complex 1–3

Catalysts **1**–**3** were screened for their abilities in catalyzing the copolymerization of CHO and CO_2. All three complexes were found active as catalysts for the copolymerization of CHO/CO_2. As the monomer/catalyst ([M]/[C]) ratio is increased, the selectivity toward poly(cyclohexene carbonate) (PCHC) and activity of **1** and **3** decreases. The optimum activity and selectivity towards the formation of PCHC for these catalysts were found to be [M]:[C] = 250:1 (Table 1: Entries 1–3 and 7–9). However, catalyst **1** was found to be more active and selective compared to **3** (Table 1). A different observation was made for catalyst **2**, with optimum activity and selectivity toward formation of PCHC observed at [M]:[C] ratio of 500:1 (Table 1: Entries 4–6). Further experiments were performed using 250:1 for **1** while 500:1 was used for **2**.

Generally [17], it is expected that incorporation of electron-withdrawing groups should result in higher activity/selectivity of the catalysts. This is attributed to increase electrophilicity of the Zn-centre thus weakening the Zn-carboxylate bond and facilitates insertion into the Zn-O bond. This trend was observed for catalysts **1** and **2** but for catalyst **3** the introduction of additional electron-withdrawing groups (CF_3) drastically decreased the activity and selectivity of the catalyst. This is likely due to the high Lewis acidity of the Zn centre which results in a very strong, irreversible Zn-epoxide bond. A similar observation has been made by Coates and co-workers, in which the introduction of both CN and CF_3 group to their catalysts completely deactivates the catalyst, yielding neither the polymer nor the cyclic carbonate expected in the epoxide-CO_2 ring opening reaction [18].

3.3.2. Effects of pressure, temperature and time variation on catalysis

The effect of pressure on selectivity can be better understood by looking at the pressure of the CO_2 added. Increase in pressure can

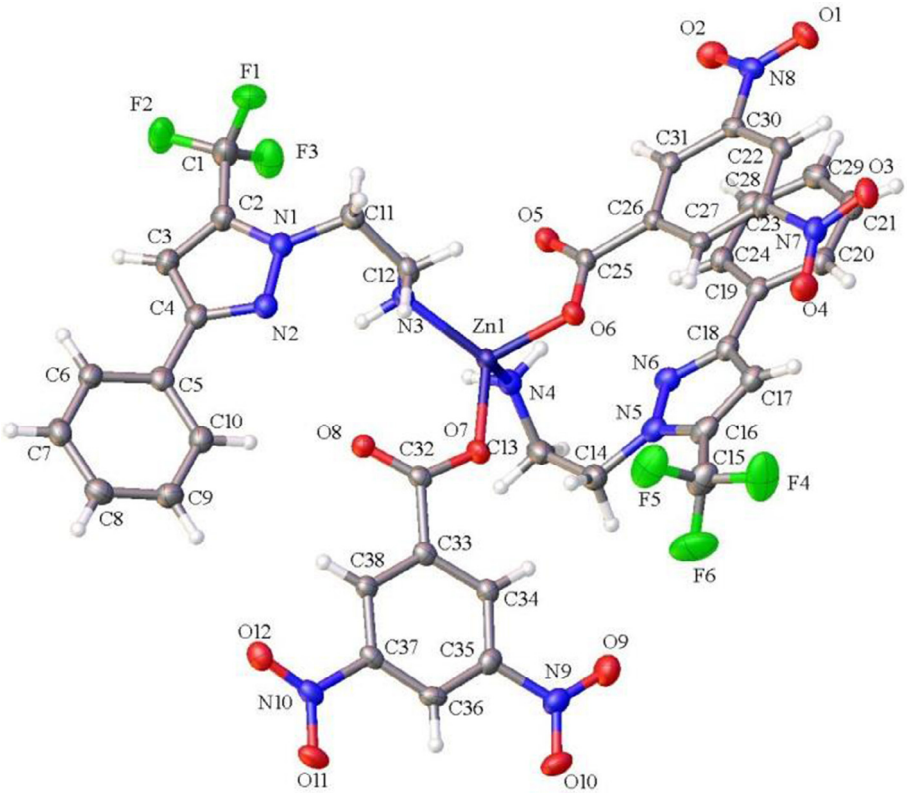


Fig. 2. A molecular structure drawing of **3** with 50% probability ellipsoids. Selected bond lenght [Å] and angles [°]: N1-N2, 1.349(3); Zn1-N3, 2.026(19); Zn1-N4, 2.056(2); Zn1-O6, 1.976(15); Zn1-O7, 1.940(15); N4-Zn1-N3, 119.15(8); O6-Zn1-O7, 108.43(7); O6-Zn1-N3, 108.25(7); N4-Zn1-O7, 103.91(7); O6-Zn1-N4, 104.42(7); N3-Zn1-O7, 112.05(7).

Table 1
Effect of concentration on selectivity and catalytic activity.

Entry	Catalyst	M/C ratio	[a]Selectivity (%)		TON	TON	[b]TOF	[a]Carbonate linkages	[a]Ether linkages
			PCHC	CCHC	(PCHC)	(CCHC)			
1	**1**	1000:01	34.7	65.3	3.1	5.8	0.1	9.1	90.9
2	**1**	500:01	42.9	57.1	4.9	3.6	0.2	58.5	41.5
3	**1**	250:01	87.2	12.8	125.1	18.4	5.2	94.7	5.3
4	**2**	1000:01	42.0	58.0	12.4	17.3	0.5	11.0	89.9
5	**2**	500:01	92.8	8.1	195.4	17.3	8.1	90.9	9.1
6	**2**	250:01	89.7	10.3	136.8	15.7	5.7	30.2	69.8
7	**3**	1000:01	76.0	24.0	57.4	10.1	2.4	60.6	39.4
8	**3**	500:01	71.0	28.2	25.8	1.0	1.1	87.2	12.8
9	**3**	250:01	79.3	20.7	84.1	22.0	3.5	72.0	27.9

Reaction conditions: CO_2 pressure = 3 MPa, temperature = 120 °C, time = 24 h. [a]Determined by ^{1}H NMR spectroscopy of the product obtained (Phenanthrene was used as internal standard to compare the selectivity between PCHC and CCHC at 4.00 ppm and 4.60 ppm). [c]Moles of CHO consumed per mole of catalyst per hour from ^{1}H NMR spectroscopy.

decrease catalyst-to-monomer distance in reactor which facilitates copolymerization (Table 2). This increase in pressure is also beneficial in suppressing cyclic carbonate formation while increasing the selectivity of polymer formation. Fig. 3 illustrates clearly how increase in pressure increases the formation PCHC while decreasing the formation of CCHC. Table 2 also shows the effect of pressure which was investigated on the copolymerization of CO2/CHO using complexes **1** and **2**. The catalysis was carried out at constant temperature of 120 °C and constant [M]/[C] of 500:1 and 250:1 for **1** and **2**, respectively. The pressure was varied from 1.5 to 4.5 MPa and the variation of pressure was found to increase the selectivity. Catalyst **1** revealed a drastic increase in the selectivity from 3.5 to 4.5 MPa while **2** showed no significant increase in the selectivity.

Time variation was studied to investigate its effect on the formation of polycarbonates. It was observed that as the reaction time increased from 4 to 8 h, selectivity for PCHC increased between 77.51% and 98.01% (Table 3). It is clear that the rate at which the polycarbonate is formed is higher than the rate at which cyclic carbonate is formed; hence polycarbonate formation is favoured; similar to an earlier by us that the rate of formation of PCHC and CCHC were 0.4510 and 0.1445 respectively [10b]. Our current data is also comparable to the kinetic data reported by Darensbourg and coworkers for the copolymerization of CO_2 and CHO [19].

The time variation reaction was monitored by ^{1}H NMR spectroscopy from 4 to 30 h. From the ^{1}H NMR studies, it was found that after a few hours of the copolymerization, there is CHO ring-opening taking place. This is observed by a broad peak at 3.5 ppm and assigned to the ether linkages (Fig. S5) and also by the minute methine peak at 4.6 ppm for the polycarbonate formation. It is proposed that in the early hours of the reaction, there is

Table 2
Effect of pressure on selectivity, catalytic activity and molecular weight.

Entry	Catalyst	Pressure	[a]Selectivity (%)		TON	TON	[b]TOF	[a]Carbonate linkages	[a]Ether linkages	[c]Mn (g/mol)	[d]M_w/M_n
			PCHC	CCHC	(PCHC)	(CCHC)					
1	**1**	1.5	89.7	10.3	237.04	25.7	11.38	95.9	4.1	10 700	3.29
2	**1**	2.5	90.8	9.2	127.24	12.89	5.30	97.9	2.1	6 340	3.17
3	**1**	3.5	92.7	7.3	109.32	8.57	4.56	96.4	3.6	6 160	2.73
4	**1**	4.5	98.6	1.4	162.66	2.27	6.78	99.0	1.0	6 270	3.05
5	**2**	1.5	89.8	10.2	96.16	11.58	4.00	89.0	11.0	3 860	3.30
6	**2**	2.5	94.0	6.0	255.33	16.31	10.63	89.9	10.1	8 860	3.60
7	**2**	3.5	96.2	3.8	174.79	6.91	7.28	88.1	11.9	10 500	3.82
8	**2**	4.5	97.4	2.6	438.46	0.0047	18.27	97.0	3.0	11 500	4.93

Reaction conditions: temperature = 120 °C, time = 24 h. [M]/[C] ratio of 250:1 for **1** and 500:1 for **2**. [a]Determined by ^{1}H NMR spectroscopy of the product obtained (Phenanthrene was used as internal standard to compare the selectivity between PCHC and CCHC at 4.00 ppm and 4.60 ppm). [b]Moles of CHO consumed per mole of catalyst per hour from ^{1}H NMR spectroscopy. [c]Obtained from GPC.

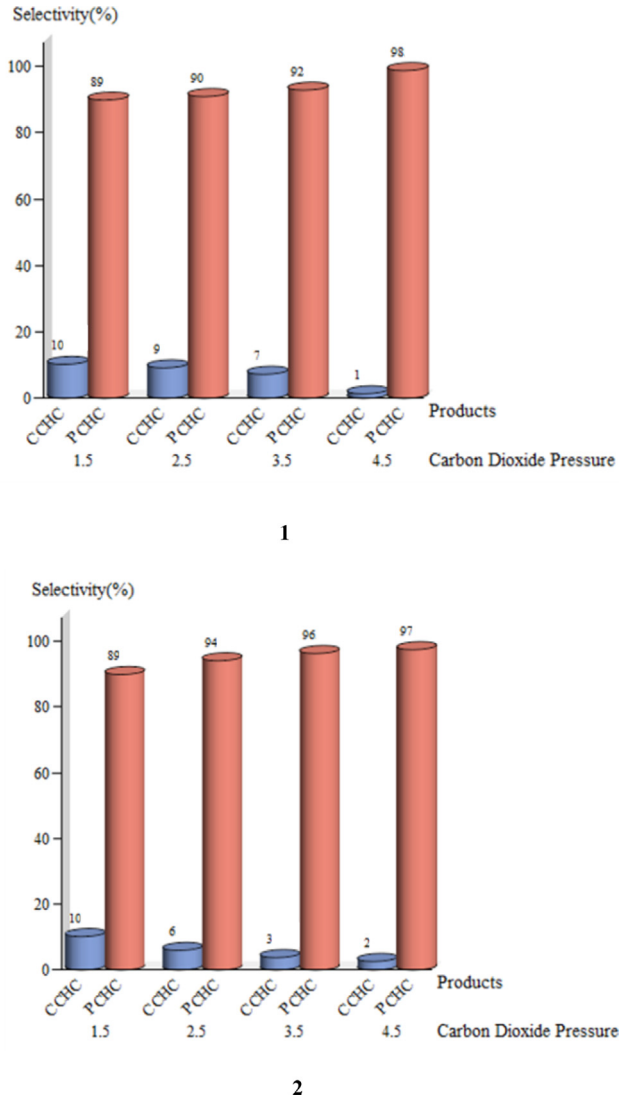


Fig. 3. Bar chart showing the dependence of percentage selectivity of both PCHC and CCHC on CO_2 pressure using catalyst **1** and **2**.

CHO ring-opening and as time is increased there is CO_2 insertion which may either undergo ring closure *via* the back-biting mechanism to form CCHC or produce polymer chains of PCHC. The formation of carbonate species is confirmed by the clear appearance of carbonate linkages peak at 4.0 ppm for cyclic carbonate and 4.6 ppm for polycarbonate formation. This mechanism in the initiation step in the copolymerization process follows the mechanistic model documented by Jacobsen for the ring opening of the epoxide [20]. Similar conclusions are reported by Coates and co-workers using *in-situ* infrared monitored copolymerization reaction with carbonyl stretching at approximately 1750 cm^{-1} [21].

It is proposed that the rate at which the polycarbonate is formed is higher than the rate at which cyclic carbonate is formed hence polycarbonate is favoured. Fig. S6 shows the carbonate and ether linkages of the product with time. It is observed that as time increases, PCHC carbonate content increases while the ether linkages decrease. This data was comparable to the kinetic data by Darensbourg for the copolymerization of CO2/CHO [19].

The effect of temperature on the selectivity of the catalysts in the copolymerization reactions was studied when the following reaction conditions were kept constant while temperature was varied: time (8 h), CO_2 pressure (4.5 MPa) and [M]:[C] ratio of 500:1 using **2**. At lower temperatures (80 °C), the selectivity was quite low for the formation of polycarbonates (Table 4). The optimum temperature was 100 °C, with selectivity of PCHC formation up to 99.9% (Table 4: Entry 2). When Beyond this optimum temperature (i.e. from120 to 160 °C) PCHC selectivity decreased. Conversely, CCHC, which is believed to occur *via* back-biting mechanism, increased in selectivity. This could be the result of depolymerization of the polycarbonate which occurs at high temperatures, forming a thermodynamically stable cyclic carbonate. Literature reports indicates that the activation energies for the formation of PCHC and CCHC to be 46.9 kJ and 133.0 kJ, respectively [22]. This confirms the propensity to form cyclic carbonate over polycarbonate at high temperatures.

Comparing the activities of the catalysts reported here to other similar catalysts containing nitrogen donor atoms and zinc show that the stronger the sigma donor ability of the nitrogen atom the higher the activity of the resulting catalyst [23].

3.3.3. Characterization of ring opening products

The molecular weight of the copolymers obtained using **1** and **2** was determined by gel permeation chromatography (GPC) (Table 2). The observed M_n values range from 3 860–11 500 g/mol. The low molecular weight is the result of chain transfer reactions during the polymerization.

The copolymer from catalyst **2** was found to have a higher M_n as pressure increased. Conversely, for catalyst **1**, as pressure increased M_n of the polymer decreased from 10 700 to 6 270 g/mol. Generally polymer polydispersity index (PDI or M_w/M_n) was found to range from 3.05 to 4.93. Taherimehr *et al.* have reported that minimizing the presence of a compound that can cause chain transfer (such as water and ethanol) is essential in order to prepare poly(cyclohexene carbonate) with high average molecular weight [24]. This

Table 3
Effect of time on selectivity and catalytic activity.

Entry	Time(h)	Selectivity (%)[a]		TON		TOF[b] (h^{-1})	Carbonate linkages[a]	Ether linkages[a]
		PCHC	CCHC	PCHC	CCHC			
1	4	77.5	22.5	3.0	0.9	0.8	8.8	91.2
2	8	95.8	4.2	109.3	4.8	13.7	86.7	13.3
3	12	91.6	8.4	114.6	10.6	9.6	92.1	7.9
4	24	97.4	2.6	438.5	0.0047	18.3	97.0	3.0
5	26	97.0	3.0	203.5	6.2	7.8	94.2	5.8
6	30	98.0	2.0	276.2	5.6	9.2	92.1	7.9

Reaction conditions: CO_2 pressure = 4.5 MPa, temperature = 120 °C, [M]/[C] ratio of 500:1, using catalyst **2**. [a]Determined by ^{1}H NMR spectrum of the product in percentages. [b]Moles of CHO consumed per mole of catalyst per hour from ^{1}H NMR spectroscopy.

Table 4
Effect of temperature on selectivity and catalytic activity.

Entry	Temperature (°C)	[a]Selectivity (%)		[a]TON		TOF[b] (h^{-1})	[a]Carbonate linkages	[a]Ether linkages
		PCHC	CCHC	(PCHC)	(CCHC)			
1	80	77.1	22.9	5.8	1.7	0.7	41.8	58.2
2	100	99.9	0.1	128.2	1.2	16.0	91.1	8.9
3	120	95.8	4.2	109.3	4.8	13.7	86.7	13.3
4	140	91.5	8.5	62.0	0.1	7.8	93.3	6.7
5	160	60.7	39.3	34.6	22.6	4.3	77.6	22.4

Reaction conditions: CO_2 pressure = 4.5 MPa, time = 8 h. [M]/[C] ratio of 500:1. [a]Determined by ^{1}H NMR spectroscopy of the product in percentages. [b]Moles of CHO consumed per mole of catalyst per hour from ^{1}H NMR spectroscopy.

low molecular weight observed in our study can be attributed to the presence of small amounts of adventitious water which can act as chain-transfer agents by reacting with the growing polymer chain to yield a hydroxyl-terminated polycarbonate thus preventing chain growth. Furthermore, it is evident that the molecular weight can be controlled by the CO_2 pressure. At high CO2 pressures (4.5 MPa) using **2**, the molecular weight increases to 11,500 g/mol. This demonstrates that high CO_2 pressure favours the contact between the catalyst and CO_2 which results in a more efficient insertion of CO_2 in the growing polymer chain, generating a long chain with high content of carbonate linkages.

The copolymers were characterized by ^{1}H NMR and ^{13}C{^{1}H} NMR spectroscopy, GPC, MALDI-TOF MS, TGA and DSC. ^{1}H NMR spectroscopy studies revealed that $n \gg > \gg m$ (where n and m) are the carbonate and ether linked repeating units respectively) (Fig. S7) while ^{13}C{^{1}H} NMR spectroscopy showed that the copolymers have both isotactic and syndiotactic stereo-sequences (Fig. S8 and S9). MALDI-TOF MS (Fig. S10) studies revealed that the benzoate group of the Zn(II) complexes is the initiation group for the copolymerization reaction of CO_2/CHO. Due to mixed tacticity of these copolymers, crystallization and melting temperatures were not observed in the DSC thermogram while T_g were found to be between 98 °C and 116 °C (Fig. S11). TGA measurements showed that any trace of impurities can affect the thermal stability of the copolymer. The maximum observed T_d is 309 °C (Fig. S12). Solvent evaporation occurred at 100 °C likely water from least dried copolymer. The copolymer began to decompose rapidly around 256 °C. Some of the copolymers also revealed a decomposition of the metal residue around 400 °C (Fig. S13).

4. Conclusions

All three zinc complexes in this study are active for the formation of PCHC with high carbonate content. The catalytic activities, in terms of TOFs, of these catalysts are moderate compared to the Zn(II) catalysts reported in literature. In general, complexes with substituted ^{t}Bu and Ph were very active compared to CF_3-Ph substituted complex. The presence of an electron-withdrawing group (NO_2) on the benzoate group enhances the activity and selectivity towards PCHC as it renders the metal centre highly electrophilic, thus allowing for easy insertion of CHO and CO_2 during the polymerization reaction. It is important that the optimum temperature for the copolymerization reaction be kept to100 °C, because increasing the temperature beyond 100 °C will result in depolymerization.

CRediT authorship contribution statement

Anelisa Matiwane: Data curation, Formal analysis, Investigation. **Collins Obuah:** Conceptuation, Project administration, Supervision, Writing - original draft, Writing - review & editing, Validation. **James Darkwa:** Suervision, Funding acquisition, Writing - review and editing, Validation.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

This material is available free of charge. Crystallographic data has been deposited with the Cambridge Crystallographic Data Centre with CCDC 2013142 (1), and 2013143 (3). Copies of this information may be obtained free of charge from the Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44-1223-336063; e-mail: deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk. Supplementary data to this article can be found online at https://doi.org/10.1016/j.poly.2020.114767.

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