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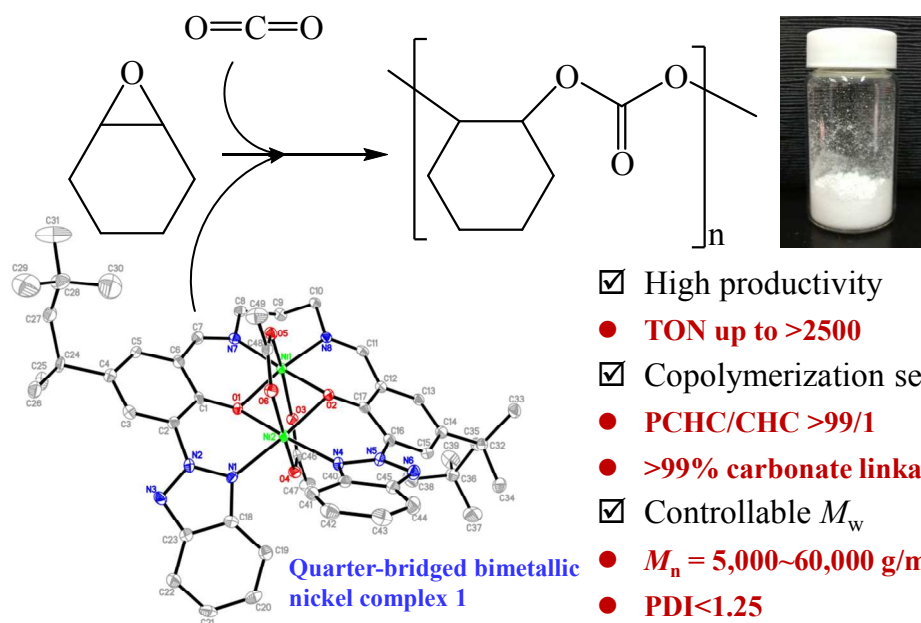
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Table of Contents**Bimetallic nickel and cobalt complexes as high-performance catalysts for copolymerization of carbon dioxide with cyclohexene oxide**Chi-Huan Li,^{a,b} Hui-Ju Chuang,^a Chen-Yu Li,^b Bao-Tsan Ko,^{a*} and Chia-Her Lin^b^aDepartment of Chemistry, National Chung Hsing University, Taichung 402, Taiwan^bDepartment of Chemistry, Chung Yuan Christian University, Chung-Li 320, Taiwan

Text: Bimetallic nickel acetate **1** is a high-performance catalyst for CO₂/CHO copolymerization in a controlled fashion.

Colour graphic:**Nickel-catalysed CHO/CO₂ copolymerization**

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ARTICLE TYPE

Bimetallic nickel and cobalt complexes as high-performance catalysts for copolymerization of carbon dioxide with cyclohexene oxide

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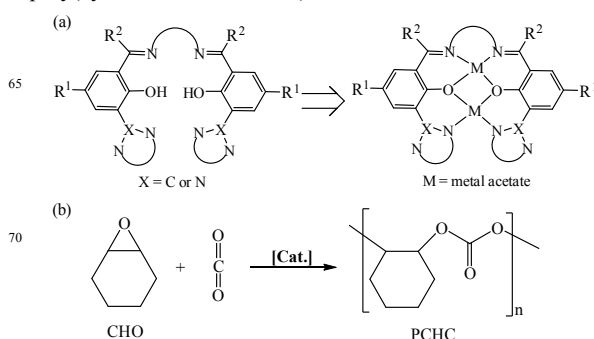
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New bimetallic nickel, cobalt and zinc complexes bearing a bis(benzotriazole iminophenolate) ligand and ancillary acetate groups were developed for CO₂/epoxide copolymerization. Ni and Co complexes are active catalysts towards copolymerization of cyclohexene oxide (CHO) and CO₂ without co-catalysts. Particularly, well-defined di-Ni **1** was found to effectively copolymerize CHO with CO₂, giving copolymers with high molecular weight and highly carbonate linkages. This is the first example of a dinuclear nickel acetate complex that is efficient for CO₂/CHO copolymerization as well as the formation of highly alternative poly(cyclohexene carbonate) in a controllable manner.

Considerable attention has been attracted to metal-catalysed epoxide/carbon dioxide (CO₂) coupling because it provides a promising and safe method for synthesis of important fine chemicals such as cyclic carbonates and aliphatic polycarbonates. This process also gives the advantages of CO₂ removal and reuse. Consequently, various homogeneous catalysts with cobalt, chromium, iron, magnesium, titanium and zinc metal centre, supported by diverse ancillary ligands such as porphyrin, phenoxide, β-diimine, salen, anilido-aldimine, macrocyclic, and many others have been demonstrated to achieve efficient activities with good turnover frequencies (TOFs).¹ Of these investigations, Williams and co-workers reported a series of impressive bimetallic Co(II/III),² Fe(III),³ Zn(II)⁴, Zn(II)-Mg(II)⁵ and Mg(II)⁶ acetate catalysts coordinated by macrocyclic ligands for copolymerization of cyclohexene oxide (CHO) and CO₂; the latter di-nuclear magnesium complexes were very active catalysts at pressure only 1 atm and displayed excellent selectivity with >99% carbonate repeated units.⁶ Considering practical applications, nickel(II)-based catalysts seem to be a potential alternative in virtue of their air-insensitive nature and abundant availability. However, to the best of our knowledge, no nickel acetate complex was developed to evaluate the catalytic activity of CO₂/epoxides copolymerization to date.

Inspired by the good catalytic performance for CO₂/epoxides copolymerization catalysed by salen-type metal complexes,⁷ we

were motivated to develop bimetallic catalytic systems containing a nitrogen heterocycles-modified salen ligand. We envisaged that introducing nitrogen heterocycles into the *ortho*-position of phenoxy groups might lead to effectively chelate and thus form stable bimetallic complexes (Scheme 1(a)); benzotriazole phenolate derivatives are expected to be suitable ligand candidates for such metal complex synthesis.⁸ To this end, a multidentate bis(benzotriazole iminophenol) ligand precursor was prepared to complex divalent metal (Ni, Co, Zn) acetate salts and to explore the potential utilization of such bimetallic acetate complexes in CO₂/CHO copolymerization (Scheme 1(b)). Herein we report for the first time the use of a well-characterized nickel complex as a high-performance catalyst for the formation of poly(cyclohexene carbonate).



Scheme 1 (a) Design strategy for bimetallic complexes; (b) Copolymerization of CO₂ and CHO.

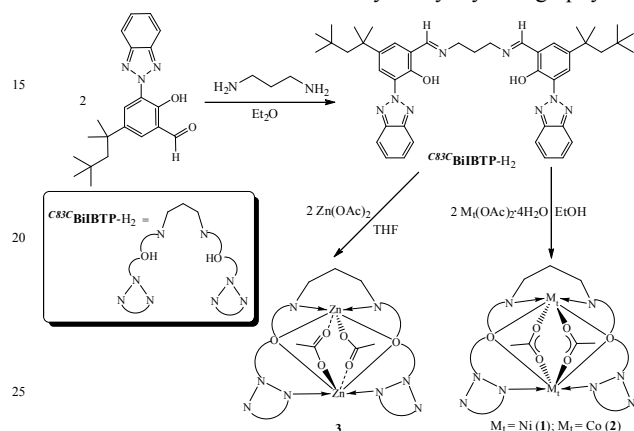
The multidentate bis(benzotriazole iminophenol) pro-ligand, ¹³C-BiIBTP-H₂, was prepared in 70% yield on condensation of 3-(2*H*-benzotriazol-2-yl)-2-hydroxy-5-(2,4,4-trimethylpentan-2-yl)-benzaldehyde with 1,3-diaminopropane (0.5 mol equiv.) in diethyl ether.⁹ Crystal structure of ¹³C-BiIBTP-H₂ (Fig. S1, ESI†) displays that two intramolecular hydrogen bonds for the O-H⋯N interaction exist between the phenol and aldimine groups. Metal complexes containing the mono-¹³C-BiIBTP ligand and two acetate (-OAc) groups were facilely synthesized *via* one-step procedure of divalent metal acetate salts with the ¹³C-BiIBTP-H₂ derivative as shown in Scheme 2. The reactions of ¹³C-BiIBTP-H₂ with 2.0 molar equivalents of M₁(OAc)₂·4H₂O (M₁ = Ni or Co) in refluxing ethanol solution furnished acetato-bridged bimetallic nickel and cobalt complexes (**1**): [(¹³C-BiIBTP)Ni₂(OAc)₂]; **2**: [(¹³C-BiIBTP)Co₂(OAc)₂]. Similarly, the zinc acetate analogue [(¹³C-BiIBTP)Zn₂(OAc)₂] (**3**) resulted from treatment of Zn(OAc)₂ as the metal precursor in anhydrous THF at 30 °C with

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ligand to metal salt ratio of 1:2. The ^1H NMR spectrum of bimetallic Zn complex **3** exhibited one set of OAc signal at 1.65 ppm, suggesting that complex **3** forms a C_2 -symmetry structure in solution. All complexes are isolated as air-stable crystalline solids and are soluble in common organic solvents (CH_2Cl_2 , CHCl_3 , THF, CHO) but insoluble in hexane and pentane. These complexes are also structurally characterized by MS, IR and NMR spectroscopy as well as microanalyses. IR spectroscopic studies exhibited two strong vibration bands of acetate groups at 1567 and 1395 cm^{-1} for **1** and 1558 and 1397 cm^{-1} for **2**, which are typical for bridged acetate groups.¹⁰ Their single-crystal structures were further confirmed by X-ray crystallography.



Scheme 2 Synthetic routes for (a) ligand $C^{83}C\text{BiIBTP-H}_2$ and (b) complexes (**1**–**3**).

An ORTEP drawing of the molecular structure of compound **1** is shown in Fig. 1. Complex **1** reveals a dinuclear conformation that contains two distinct environments of six-coordinated Ni centres; the Ni(1) atom is chelated by two N atoms from propyl-bridged aldimine groups, whereas two discrete benzotriazole N atoms bond to the Ni(2) centre. The geometry around the Ni(1) or Ni(2) atom is a distorted octahedral coordination sphere, evidenced from the angles $\text{O}(2)\text{-Ni}(1)\text{-N}(7)$ ($171.61(8)^\circ$) and $\text{O}(2)\text{-Ni}(2)\text{-N}(1)$ ($173.53(8)^\circ$) constructed by the axial bonds (Table S2, ESI ‡). The principal structural feature in **1** reveals the $C^{83}C\text{BiIBTP}$ moiety behaves a hexa-dentate ligand to coordinate two metal centres, forming a Ni_2O_2 core bridging through the phenoxy oxygen atoms and five Ni-involving six-membered rings with N,O- or N,N-chelating. The average bond distances of Ni-O(phenoxy) ($2.0312(18)\text{ \AA}$), Ni-O(OAc) ($2.091(2)\text{ \AA}$) and Ni-N(aldimine) ($2.041(2)\text{ \AA}$) are all within the normal ranges reported in the literature for the six-coordinated nickel(II) acetate complexes containing the salen-type derivatives.¹¹ For comparison, the average bond length between the Ni atom and N(benzotriazole) is $2.082(2)\text{ \AA}$, which is slightly longer than that ($2.041(2)\text{ \AA}$) of Ni-N(imine), indicating the weaker coordinate covalent bonding between the nickel atom and benzotriazole nitrogen atom. The molecular structure of Co complex **2** (Fig. S2, ESI ‡) is isostructural with nickel analogue **1**, except the cobalt(II) ion replaces the metal centre. As expected, the average six-coordinated Co-containing bond distances (Table S2, ESI ‡) are longer than those found around cobalt(III) centres incorporated by salen-type Schiff-base ligands and bridging acetate groups.¹² It is worth noting that two ancillary acetate groups in complexes **1** and **2** assume bridging bidentate bonding modes to coordinate

metal centre(s), which is consistent with the observations of IR spectroscopic studies. As illustrated in Fig. S3 (ESI ‡), the solid structure of **3** also exhibits a homologous bimetallic acetate complex with the Zn(II) ion as the metal element. However, both zinc atoms are penta-coordinated by the N_2O_2 framework of a $C^{83}C\text{BiIBTP}^{2-}$ ligand and one ancillary acetate group, adopting a distorted square pyramidal geometry ($\tau = 0.21$ for Zn(1) and $\tau = 0.39$ for Zn(2)).¹³ Interestingly, two acetate groups in crystal structure **3** are bonded to Zn atoms in a terminal acetate coordination mode that is different from those observed for bimetallic acetate **1** and **2** in the solid state. This difference might suggest the formation of the five-coordinated environment in **1** or **2** by the dissociation of a bridging metal-OAc bond and open a coordination sphere as an active site to activate monomers during CO_2 /epoxide coupling.

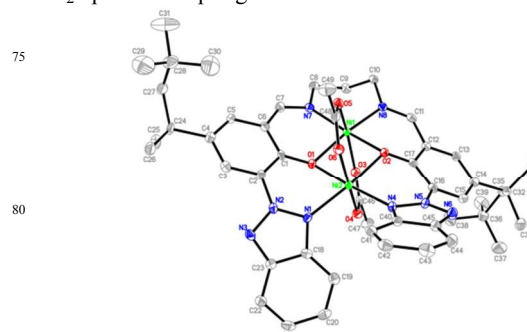


Fig. 1 ORTEP drawing of complex **1** with probability ellipsoids drawn at level 60%.

We performed the bimetallic acetate complexes **1**–**3** as catalysts to investigate the copolymerization of cyclohexene oxide (CHO) and carbon dioxide (CO_2), and representative results are listed in Table 1. Bi-nickel acetate **1** was first utilized to examine the effect of catalyst concentrations at $80\text{ }^\circ\text{C}$ and 300 psi initial CO_2 pressure for 72 h. Experimental results displayed that Ni complex **1** was able to produce poly(cyclohexene carbonate) (PCHC) over a wide range of concentrations and even only a 0.0625% catalyst loading (Table 1, entry 3) could give rise to a moderate catalytic activity with turnover frequency (TOF) of 8.9 h^{-1} as well as highly copolymer selectivity ($\text{PCHC}/\text{CHC} > 99/1$). The catalytic performance of **1** was susceptible to the copolymerization temperature. As increasing the temperature to $120\text{ }^\circ\text{C}$, CHO/ CO_2 copolymerization catalysed by **1** reached 84% CHO conversion within 24 h with the retaining good copolymerization selectivity (Fig. S4, ESI ‡) as depicted by entry 5 of Table 1. Adjustment of the initial pressure of CO_2 pressure also affected the catalytic efficiency: lower (170 psi) or higher (500 psi) CO_2 pressure was demonstrated to result in a lower CHO conversion or an obvious decrease in molecular weight (M_n) of PCHC (Table 1, entries 6–7). The trend of effect of CO_2 pressure in our catalytic system agrees with the previous observations in the literature.¹⁴ Under the optimal conditions ($[\text{CHO}]_0/[\text{I}]_0 = 1600/1$, $p\text{CO}_2^0 = 300\text{ psi}$, $120\text{ }^\circ\text{C}$), bi-metallic Ni complex **1** displayed high productivity (CHO conversion = 90%, TON = 1440) as well as an improved TOF (40 h^{-1}) for 36 h. All copolymerization selectivities and molecular weights control of the PCHCs by di-Ni catalyst **1** are excellent. The produced copolymers with a highly alternating microstructure up to >99% carbonate-linkage content was observed based on ^1H NMR spectrum (Fig. S5, ESI ‡). However,

¹³C NMR spectrum displayed that all PCHCs obtained by **1** are almost atactic (Fig. S6, ESI†). In comparisons, the catalytic performance of bimetallic acetate catalysts has the order **1** ~ **2** > **3** under the same catalytic conditions, and their activities seem to be dependent on the nature of metal centres (entries 5 & 9-10 in Table 1). Despite the similar activity of bimetallic complexes **1** and **2**, a slightly decreased copolymer selectivity (PCHC/CHC = 94/6) with di-Co **2** as the catalyst was found (Fig. S7, ESI†), implying a backbiting reaction of the growing polymeric chains occurred during copolymerization. The “controlled” character of **1** was further demonstrated by kinetic experiments involving the variation of M_n and polydispersity index (PDI) with various reaction periods (Table S3, entries S1-S3). It was found that a linear relationship (Fig. S8 in the SI) between M_n (GPC) and time as well as the remaining narrow PDIs (<1.25), suggesting the controllable copolymerization by di-nickel acetate catalyst **1**. All the produced polycarbonates possess a bimodal molecular weight distribution (Fig. S9, ESI†), which is similar to those reported by the previous literatures.¹⁵ To demonstrate further the capability of producing PCHC with a larger M_n in a controlled fashion, we pursued CHO/CO₂ copolymerization in a lower catalyst loading (0.03125%) of Ni complex **1** under the optimal conditions. High molecular weight PCHC (M_n = 57,100 g/mol) with a narrow PDI (<1.20) as well as highly carbonate linkages was obtained on copolymerizing CHO and CO₂ with [CHO]₀/[**1**]₀ = 3200/1 for 72h (Table 1, entry 11). The superior catalytic performances of dinuclear complexes **1** and **2** might suggested a cooperative ring-opening copolymerization *via* a bimetallic mechanism.^{1n,16} Although the best catalytic activity of CHO/CO₂ copolymerization by **1** is attributed to moderate (TOF: 80 h⁻¹), the results presented here are the first example of the generation of high molecular weight PCHC (M_n > 50,000 g/mol) with highly carbonate linkages (>99%) using a bimetallic nickel(II) acetate complex.

Table 1 Copolymerization of CHO and CO₂ catalysed by using bimetallic complexes **1**–**3**

Entry	Catalyst (mol%)	Time /h	% CHO Conv. ^a	% CHC ^a	% Copolymer (% carbonate)	TON ^b	TOF /h ⁻¹ ^c	M_n (PDI) ^d
1 ^e	1 (0.25)	72	94	<1(trans)	>99(>99)	376	5.2	10400(1.19)
2 ^e	1 (0.125)	72	60	<1(trans)	>99(>99)	480	6.7	13000(1.20)
3 ^e	1 (0.0625)	72	40	<1(trans)	>99(>99)	640	8.9	12700(1.20)
4 ^f	1 (0.0625)	72	92	<1(trans)	>99(>99)	1472	20.4	30500(1.22)
5	1 (0.0625)	24	84	<1(trans)	>99(>99)	1344	56	24900(1.21)
6 ^g	1 (0.0625)	24	74	<1(trans)	>99(>99)	1184	49.3	22400(1.19)
7 ^h	1 (0.0625)	24	72	<1(trans)	>99(>99)	1152	48	9800(1.16)
8	1 (0.0625)	36	90	<1(trans)	>99(>99)	1440	40	34500(1.24)
9	2 (0.0625)	24	80	6(trans)	94(>99)	1279	53.3	31900(1.27)
10	3 (0.0625)	24	11	66(trans)	34(>99)	175	7.3	-
11 ⁱ	1 (0.03125)	72	87	<1(trans)	>99(>99)	2784	38.7	57100(1.19)

Copolymerization conditions: CHO 5.0 mL, $p\text{CO}_2^0$ = 300 psi, T = 120°C. ^a Determined by comparison of the integrals of signals arising from the methylene protons in the ¹H NMR spectra, including PCHC carbonate (δ : 4.65 ppm), PCHC ether (δ : 3.45 ppm), and CHC (δ : 3.9 (trans) or 4.63 ppm (cis)). ^bTON= number of moles of CHO consumed per mole of catalyst. ^c TOF=TON per hour. ^d Determined by GPC, in THF. ^e T = 80°C. ^f T = 100°C. ^g $p\text{CO}_2^0$ = 170 psi. ^h $p\text{CO}_2^0$ = 500 psi. ⁱ 10.0 mL CHO, 0.016 mmol catalyst.

In conclusion, novel bimetallic bis(benzotriazole iminophenolate) catalysts with Ni(II), Co(II) and Zn(II) metal centres towards CO₂/CHO copolymerization are reported. Dinuclear nickel and cobalt complexes displayed high

productivity (TON > 1200) under the optimal conditions (120 °C, $p\text{CO}_2^0$ = 300 psi) and afforded poly(cyclohexene carbonate) (PCHC) with a highly alternating microstructure up to >99% carbonate linkages. In Particular, di-Ni acetate **1** was able to effectively copolymerize CHO with CO₂ in a controlled character, yielding PCHC with high molecular weight (M_n > 50,000 g/mol) and narrow PDI (<1.25). This di-nickel acetate complex is the first example of a high-performance catalyst for CO₂/CHO copolymerization in a controlled fashion.

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