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

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Experimental

General conditions

Solvents and reagents were dried by refluxing for at least 24 h over sodium/benzophenone (hexane, toluene, tetrahydrofuran (THF)), or over phosphorus pentoxide (CH₂Cl₂). Deuterated solvents were dried over 4 Å molecular sieves. 1,3-Diaminopropane, hexamethylenetetramine, 2-(2H-benzotriazol-2-yl)-4-(2,4,4-trimethylpentan-2-yl)phenol (CBTP-H), nickel(II) acetate tetrahydrate, cobalt(II) acetate tetrahydrate, zinc(II) acetate and carbon dioxide (CO₂, 99.95%) were purchased and used without further purification. Cyclohexene oxide (CHO) was purified by distillation over calcium hydride (CaH₂) prior to use. 3-(2H-benzotriazol-2-yl)-2-hydroxy-5- (2,4,4-trimethylpentan-2-yl)benzaldehyde (C8AldBTP-H) was synthesized according to the previous literature procedures.^{S1} ¹H NMR and ¹³C NMR spectra were recorded on Bruker Aveance (300 and 400 MHz) spectrometer with chemical shifts given in parts per million from the peak of internal TMS. Microanalyses were performed using a Heraeus CHN-O-RAPID instrument. Gel permeation chromatography (GPC) measurements were performed on a Jasco PU-2080 plus system equipped with a RI-2031 detector using THF (HPLC grade) as an eluent. The chromatographic column was Phenomenex Phenogel 5 μ 103 Å and the calibration curve used to calculate M_n (GPC) was produced from polystyrene standards. The calibration curve was constructed by ten polystyrene standards, in which their molecular weights range from

1580 to 288000. The GPC results were calculated using the Scientific Information Service Corporation (SISC) chromatography data solution 3.1 edition. Mass analyses were performed using positive electron spray ionization (ESI+ or APCI+) technique on a Thermo Finnigan TSQ Quantum mass spectrometer for all these complexes upon dissolving in DMSO solvent.

Synthesis of C83CBiIBTP-H₂ ligand

A mixture of 3-(2*H*-benzotriazol-2-yl)-2-hydroxy-5-(2,4,4-trimethylpentan-2-yl)benzaldehyde (3.51 g, 10.0 mmol) and 1,3-diaminopropane (0.37 g, 5.0 mmol) in ether (35 mL) was stirred for 24 h. Volatile materials were removed under vacuum to yield yellow residues. The residue was recrystallized by the mixture of CH₂Cl₂ and hexane, and the yellow solids were obtained after filtration. Yield: 2.59 g (70%). Anal. calc. for C₄₅H₅₆N₈O₂: N, 15.12; C, 72.94; H, 7.62%. Found: N, 15.24; C, 72.40; H, 7.82%. ¹H NMR (CDCl₃, ppm) : δ 8.48 (s, 2H, *CH*=NCH₂), 8.00 (d, 4H, Ar-*H*), 7.86 (s, 2H, Ar-*H*), 7.43 (t, 4H, Ar-*H*), 7.39 (s, 2H, Ar-*H*), 3.74 (t, 4H, N-CH₂), 2.10 (m, 2H, NCH₂-CH₂), 1.74 (s, 4H, -C(CH₃)₂CH₂C(CH₃)₃), 1.39 (s, 12H, -C(CH₃)₂CH₂C(CH₃)₃), 0.76 (s, 18H, -C(CH₃)₂CH₂C(CH₃)₃). ¹³C NMR (CDCl₃, ppm): δ 165.5 (CH=NCH₂), 153.9, 144.8, 140.3, 130.2, 128.8, 127.8, 126.8, 119.3, 118.4 (Ar-*C*), 56.7 (CH=NCH₂), 55.8, 38.1, 32.4, 31.9, 31.5, 31.3.

Synthesis of complex [(^{C83C}BiIBTP)Ni₂(OAc)₂] (1)

To a mixture of ^{*C83C*}**BiIBTP-H**₂ (0.74 g, 1.0 mmol) and Ni(OAc)₂·4H₂O (0.5 g, 2.0 mmol) was dissolved in EtOH (20 mL). The solution was heated under reflux for 24 h, during which the formation of a green precipitate was observed. The resulting precipitate was collected by filtration and purified with hexane to give green solids. Yield: 0.63 g (65%). Anal. calc. for $C_{49}H_{60}N_8O_6Ni_2$: N, 11.50; C, 60.40; H, 6.21%; Found: N, 11.13; C, 59.90; H, 6.44%. APCIMS (m/z): 913.5 [100%, (M-OAc)⁺]; calculated for [$C_{49}H_{60}N_8O_6Ni_2$]: 972.3 (m/z: 100%). Characteristic IR absorptions (cm⁻¹, neat): 1636 ($\nu_{C=N}$), 1567 ($\nu_{asymmetric acetate}$), 1395 ($\nu_{symmetric}$).

acetate).

Synthesis of complex [(^{C83C}BiIBTP)Co₂(OAc)₂] (2)

To a mixture of ^{*C83C*}**BiIBTP-H**₂ (0.74 g, 1.0 mmol) and Co(OAc)₂·4H₂O (0.5 g, 2.0 mmol) was dissolved in ethanol (20 mL). The solution was heated under reflux for 24 h, and the dark brown precipitate occurred during the reaction. The resulting precipitate was collected by filtration and purified with hexane solution to give brown solids. Yield: 0.60 g (62%). Anal. calc. for C₄₉H₆₀N₈O₆Co₂: N, 11.49; C, 60.37; H, 6.20%; Found: N, 11.90; C, 60.62; H, 6.58%. APCIMS (m/z): 915.4 [100%, (M-OAc)⁺]; calculated for [C₄₉H₆₀N₈O₆Co₂]: 974.3 (m/z: 100%). Characteristic IR absorptions (cm⁻¹, neat): 1630 ($v_{C=N}$), 1558 ($v_{asymmetric acetate}$), 1397 ($v_{symmetric acetate}$).

Synthesis of complex [(C83CBiIBTP)Zn₂(OAc)₂] (3)

To a mixture of *C83C*BilBTP-H₂ (0.74 g, 1.0 mmol) and Zn(OAc)₂ (0.37 g, 2.0 mmol) was dissolved in anhydrous THF (50 mL), and the solution was stirred at 30 °C for 24 h. Volatile materials were removed under vacuum to yield yellow residues. The residue was washed with hexane, and the yellow powder was obtained after filtration. Yield: 0.77 g (78%). ¹H NMR (CDCl₃, ppm) : δ 8.53 (s, 2H, N-*H*), 8.27 (s, 2H, Ar-*H*), 7.31 (d, 4H, Ar-*H*), 7.27 (s, 2H, Ar-*H*), 7.05 (t, 4H, Ar-H), 4.18 (t, 4H, N-CH₂), 2.19 (m, 2H, NCH₂-CH₂), 1.80 (s, 4H, CH₂), 1.65 (s, 6H,CH₃COO), 1.43 (s, 12H, C(CH₃)₂), 0.82 (s, 18H, C(CH₃)₃). ¹³C NMR (CDCl₃, ppm) : δ 178.5 (O=*C*), 168.9 (N=*C*), 156.8, 142.4, 137.9, 135.2, 129.1, 127.6, 126.6, 122.1, 117.5, (Ar-*C*), 63.6 (CH=NCH₂), 56.5, 37.9, 32.4, 32.0, 31.6, 30.2, 22.5. Anal. calc. for C₄₉H₆₀N₈O₆Zn₂: N, 11.34; C, 59.58; H, 6.12%; Found: N, 11.44; C, 59.90; H, 6.15%. APCIMS (m/z): 929.4 [100%, (M-OAc)⁺]; calculated for [C₄₉H₆₀N₈O₆Zn₂]: 988.3 (m/z: 100%). Characteristic IR absorptions (cm⁻¹, neat): 1634 (*v*_{C=N}), 1646 (*v*_{asymmetric acetate}), 1402 (*v*_{symmetric acetate}).

Copolymerization of CHO and CO₂ catalysed by nickel complex 1

A representative procedure for the copolymerization of cyclohexene oxide with CO₂ (Table 1, entry 8) was exemplified. Ni catalyst **1** (30.5 mg, 0.0313 mmol) was dissolved in 5.0 mL of neat cyclohexene oxide under a dry nitrogen atmosphere. To a mixing solution was added to the 100-mL autoclave with magnetic stirrer under CO₂ atmosphere. CO₂ was then charged into the reactor until the pressure of 300 psi was reached, and the stirrer was started. The reaction was performed at 120 °C for 36 h. Then the reactor was placed into ice water and excess CO₂ was released. The CHO conversion (90%) was analyzed by ¹H NMR spectroscopic studies. Spectral characteristics of cyclohexene carbonate: PCHC carbonate (δ : 4.65 ppm), PCHC ether (δ : 3.4-3.5 ppm), and CHC (δ : 3.9 (*trans*) or 4.63 ppm (*cis*)). The mixture was diluted by CH₂Cl₂(50 mL), followed by the addition of 1 N HCl solution (0.5 mL) to quench this reaction, and the final mixture was passed through a short column of neutral alumina to remove the metal salt. After precipitation by adding polymer solution in CH₂Cl₂ into methanol (150 mL) twice, the white polymer was collected by filtration and dried under vacuum overnight.

X-ray crystallographic studies

Suitable crystals of ligand ^{C83C}BiIBTP-H₂ and complexes 1-3 were mounted onto glass fiber using perfluoropolyether oil and cooled rapidly in a stream of cold nitrogen gas to collect diffraction data at 100K using Bruker APEX2 diffractometer. Intensity data were collected in 1350 frames with increasing *w* (width of 0.5° per frame). The absorption correction was based on the symmetry-equivalent reflections using SADABS program.^{S2} The space group determination was based on a check of the Laue symmetry and systematic absence, and was confirmed by the structure solution. The structures were solved with direct methods using a SHELXTL package.^{S2} All non-H atoms were located from successive Fourier maps, and hydrogen atoms were treated as a riding model on their parent C atoms. Anisotropic thermal parameters were used for all non-H atoms, and fixed isotropic parameters were used for Hatoms. Drawing of the molecules was done using Oak Ridge Thermal Ellipdoid Plots (ORTEP).^{S3} Crystallographic data of ligand C83C BiIBTP-H₂ and complexes 1-3 are summarized in Table S1. The selected bond length (Å) and bond angles (°) for complexes 1-3 were listed in Table S2.

Reference:

S1 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. 2014, 754, 16–25.

S2 G. M. Sheldrick, Acta Cryst. 2008, A64, 112–122.

S3 Burnett, M. N. & Johnson, C.K.(1996) ORTEPIII, Report ORNL-6895. Oak Ridge National Laboratory, Oak Ridge, Tennessee, U.S.



Fig. S1 ORTEP drawing of ligand *C83C***BiIBTP-**H₂ with probability ellipsoids drawn at level 50%.



Fig. S2 ORTEP drawing of Cobalt complex 2 with probability ellipsoids drawn at level 50%. Hydrogen atoms are omitted for clarity. Selected bond lengths/Å and angles/deg: Co(1)-O(1) 2.051(3), Co(1)-O(2) 2.048(3), Co(1)-O(3) 2.208(3), Co(1)-O(5) 2.195(3), Co(1)-N(7) 2.090(4), Co(1)-N(8) 2.085(4), Co(2)-O(1) 2.095(3), Co(2)-O(2) 2.091(3), Co(2)-O(4) 2.054(3), Co(2)-O(6) 2.039(3), Co(2)-N(1) 2.139(4), Co(2)-N(4) 2.111(4), O(1)-Co(1)-O(2) 93.95(12), O(2)-Co(1)-N(8) 87.37(14), O(1)-Co(1)-N(8) 168.75(15), O(2)-Co(1)-N(7) 168.26(15), O(1)-Co(1)-N(7) 87.61(14), N(7)-Co(1)-N(8) 93.37(16), O(2)-Co(1)-O(5) 81.51(12), O(1)-Co(1)-O(5) 83.82(12), O(5)-Co(1)-N(8) 107.42(14), O(5)-Co(1)-N(7) 87.10(14), O(2)-Co(1)-O(3) 82.00(12), O(1)-Co(1)-O(3) 80.30(12), O(3)-Co(1)-N(8) 88.84(14), O(3)-Co(1)-N(7) 109.72(14), O(3)-Co(1)-O(5) 156.18(12), O(4)-Co(2)-O(6) 171.54(13), O(2)-Co(2)-O(6) 87.68(13), O(2)-Co(2)-O(4) 87.31(13), O(1)-Co(2)-O(6) 87.12(13), O(1)-Co(2)-O(4) 86.20(12), O(1)-Co(2)-O(2) 91.43(12), O(6)-Co(2)-N(4) 92.91(14), O(4)-Co(2)-N(4) 92.96(14), O(2)-Co(2)-N(4) 80.26(14), O(1)-Co(2)-N(4) 171.67(14), O(6)-Co(2)-N(1) 90.88(14), O(4)-Co(2)-N(1) 93.40(14), O(2)-Co(2)-N(1) 173.95(13), O(1)-Co(2)-N(1) 82.63(13), N(1)-Co(2)-N(4) 105.70(15).



Fig. S3 ORTEP drawing of complex **3** with probability ellipsoids drawn at level 50%. Hydrogen atoms are omitted for clarity. Selected bond lengths/Å and angles/deg: Zn(1)-O(1) 2.0194(14), Zn(1)-O(2) 2.1855(15), Zn(1)-O(3) 1.9702(15), Zn(1)-N(7) 2.0714(18), Zn(1)-N(8) 2.0455(18), Zn(2)-O(1) 2.0365(14), Zn(2)-O(2) 2.0140(15), Zn(2)-O(5) 1.9617(18), Zn(2)-N(1) 2.1520(17), Zn(2)-N(4) 2.0878(18), O(1)-Zn(1)-O(2) 74.31(6), O(1)-Zn(1)-O(3) 98.96(6), O(2)-Zn(1)-O(3) 105.14(6), O(3)-Zn(1)-N(8) 103.15(7), O(1)-Zn(1)-N(8) 152.28(7), O(3)-Zn(1)-N(7) 113.51(7), O(1)-Zn(1)-N(7) 88.29(6), N(7)-Zn(1)-N(8) 97.89(7), O(2)-Zn(1)-N(8) 83.86(6), O(2)-Zn(1)-N(7) 139.63(7), O(1)-Zn(2)-O(2) 77.78(6), O(1)-Zn(2)-O(5) 102.74(7), O(2)-Zn(2)-O(5) 134.52(7), O(5)-Zn(2)-N(4) 99.25(8), O(2)-Zn(2)-N(4) 86.11(6), O(1)-Zn(2)-N(1) 82.34(6), N(1)-Zn(2)-N(4) 97.59(7).



Fig. S4 ¹H NMR spectrum of the crude sample from the reaction mixture of CO₂/CHO copolymerization by di-Ni complex **1** with 84% conversion in CDCl₃ (Table 1, entry 5), PCHC carbonate (δ : 4.65 ppm), PCHC ether (δ : 3.45 ppm) and CHC (δ : 3.9 (*trans*)). No obvious signals at 3.9 ppm confirms <1% trans-CHC.



Fig. S5 ¹H NMR spectrum of the purified copolymer produced by using di-nickel acetate complex 1 (Table 1, entry 8) in CDCl₃. Peak A (δ = 4.65 ppm) is assigned to the methine protons in PCHC, and no significant signals at 3.4-3.5 ppm confirms >99% carbonate linkages in PCHC. Peaks B (4.42 and 3.58 ppm) are assigned to the methine protons on the end group (OC*H*C4H₈C*H*OH).



Fig. S6 The carbonyl region of ¹³C NMR spectra of the resultant copolymer (Table 1, entry 8) in CDCl₃.



Fig. S7 ¹H NMR spectrum of the crude sample from the reaction mixture of CO_2/CHO copolymerization by Co complex 2 with 80% conversion in $CDCl_3$ (Table 1, entry 9). The signal at 3.9 ppm corresponds to the 6% of CHC.



Fig. S8 Plot of M_n (\blacktriangle) and PDI (\blacksquare) (determined from GPC analysis) vs time for the copolymerization of cyclohexene oxide and CO₂ using di-nickel acetate complex **1** as the catalyst at 120 °C and 300 psi CO₂.



Fig. S9 GPC traces for the produced PCHC with a bimodal molecular weight distribution catalysed by 1 (Table 1, entry 8).

	<i>свзс</i> віІВТР-Н ₂	$1 \cdot CH_2Cl_2$	2	3·CH ₂ Cl ₂
formula	C45H56N8O2	$C_{50}H_{62}Cl_2N_8Ni_2O_6$	$C_{49}H_{60}N_8O_6Co_2$	$C_{50}H_{62}Cl_2N_8O_6Zn_2$
Formula weight	740.98	1059.40	974.92	1072.72
Temp (K)	153(2) K	100(2) K	100(2) K	100(2) K
Crystal system	Monoclinic	Triclinic	Triclinic	Triclinic
Space group	C 2/c	<i>P</i> -1	<i>P</i> -1	<i>P</i> -1
a (Å)	30.8673(7)	12.0189(3)	11.7828(3)	13.4923(2)
b (Å)	14.8514(3)	14.7702(4)	14.8129(4)	13.5958(2)
c (Å)	10.3727(2)	14.7768(4)	17.4408(5)	15.0327(2)
α (deg)	90	107.972(2)	94.041(2)	108.1070(10)
β (deg)	94.543(2)	96.642(2)	107.638(2)	104.8200(10)
$\gamma(\text{deg})$	90	95.331(2)	95.432(2)	90.8680(10)
$V(Å^3)$	4740.14(17)	2455.39(11)	2872.13(13)	2520.35(6)
Ζ	8	2	2	2
$D_{\text{calc}}(\text{Mg/m}^3)$	1.156	1.433	1.273	1.414
μ (Mo Kα)(mm ⁻¹)	0.566	0.934	0.634	1.114
<i>F</i> (000)	1760	1112	1148	1120
Reflections collected	21755	45158	51512	44579
No. of parameters	291	622	671	643
Indep. reflns (R_{int})	4475 (0.0333)	12170 (0.0713)	14270 (0.1502)	12470 (0.0318)
$R1[I > 2\sigma(I)]$	0.0575	0.0469	0.0796	0.0380
$wR2 [I > 2\sigma(I)]$	0.1533	0.0979	0.1716	0.0956
Goodness-of-fit on F^2	1.039	1.011	1.002	1.026

Table S1 Crystallographic data of $^{\it C83C}BiIBTP-H_2$ and complexes 1-3

	1 (M = Ni)	2 (M = Co)	3 (M = Zn)	
M(1)-O(1)	2.0328(17)	2.051(3)	2.0194(14)	
M(1)-O(2)	2.0340(18)	2.048(3)	2.1855(15)	
M(1)-O(3)	2.1291(19)	2.208(3)	1.9702(15)	
M(1)-O(5)	2.1584(19)	2.195(3)	-	
M(1)-N(7)	2.046(2)	2.090(4)	2.0714(18)	
M(1)-N(8)	2.035(2)	2.085(4)	2.0455(18)	
M(2)-O(1)	2.0233(18)	2.095(3)	2.0365(14)	
M(2)-O(2)	2.0347(17)	2.091(3)	2.0140(15)	
M(2)-O(4)	2.036(2)	2.054(3)	-	
M(2)-O(5)	-	-	1.9617(18)	
M(2)-O(6)	2.0393(19)	2.039(3)	-	
M(2)-N(1)	2.077(2)	2.139(4)	2.1520(17)	
M(2)-N(4)	2.086(2)	2.111(4)	2.0878(18)	
O(1)-M(1)-O(2)	91.37(7)	93.95(12)	74.31(6)	
O(3)-M(1)-O(5)	158.04(7)	156.18(12)	-	
N(7)-M(1)-N(8)	94.68(9)	93.37(16)	97.89(7)	
O(1)-M(1)-N(8)	171.00(8)	168.75(15)	152.28(7)	
O(2)-M(1)-N(7)	171.61(8)	168.26(15)	139.63(7)	
O(1)-M(2)-O(2)	91.62(7)	91.43(12)	77.78(6)	
O(2)-M(2)-O(5)	-	-	134.52(7)	
O(4)-M(2)-O(6)	170.99(7)	171.54(13)	-	
N(1)-M(2)-N(4)	102.77(8)	105.70(15)	97.59(7)	
O(1)-M(2)-N(4)	175.25(8)	171.67(14)	157.98(7)	
O(2)-M(2)-N(1)	173.53(8)	173.95(13)	131.25(7)	

Table S2 Selected bond lengths (\AA) and angles (deg) for complexes 1, 2 and 3.

Entry	Catalyst	Time	% CHO	% CHC ^a	% Copolymer	TON ^b	TOF	M _n
	(mol%)	/h	Conv. ^a		(% carbonate)		/ h -1 <i>c</i>	$(\mathbf{PDI})^d$
S1	1(0.0625)	4	20	<1(trans)	>99(>99)	320	80	5400(1.13)
S2	1 (0.0625)	8	37	<1(trans)	>99(>99)	592	74	9100(1.18)
S 3	1(0.0625)	12	51	<1(trans)	>99(>99)	816	68	17300(1.16)

Table S3 Copolymerization of CHO and CO₂ catalysed by using bimetallic Ni complex 1

Copolymerization conditions: CHO 5.0 mL, $pCO_2^0 = 300$ 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*)).^{3 *b*} TON= number of moles of CHO consumed per mole of catalyst. ^{*c*} TOF=TON per hour. ^{*d*} Determined by GPC, in THF.