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Synthesis of mixed-ligand cobalt complexes and their applications in high *cis*-1,4-selective butadiene polymerization

Wen Liu^a, Weijing Pan^a, Peng Wang^a, Wei Li^a, Jingshan Mu^a, Gengsheng Weng^a, Xiaoyu Jia^{b,c}, Dirong Gong^{a*}, Kuo-Wei Huang^d

^a Department of Polymer Science and Engineering, Faculty of Materials Science and Chemical Engineering, Ningbo University, Ningbo 315211, P. R. China

^b Key Laboratory of Urban Environment and Health, Institute of Urban Environment, Chinese Academy of Sciences, No.1799, Jimei Road, Xiamen, Fujian 361021, P. R. China.

^c Ningbo Urban Environment Observation and Research Station-NUEORS, Chinese Academy of Sciences, Ningbo, Zhejiang 315830, P. R. China.

^d King Abdullah University of Science and Technology, Division of Physical Sciences and Engineering and KAUST Catalysis Center, Thuwal 23955-6900, Saudi Arabia.

Corresponding to: Gongdirong@nbu.edu.cn

Abstract

Incomplete oxidation of (N-di-tert-butylphosphino)-6-(2-methyl-2'*H*-benzoimidazole)-2-aminepyridine dichlorocobalt (PN³CoCl₂) in DMF results in a unique co-crystal **I** formed with three parts including DMF, unit **A** and unit **B** complex with Co1 and Co2, respectively, (PN³ ligand in unit **A**: (N-di-tert-butylphosphino)-6-(2'-methyl-2'*H*-benzoimidazole)-2-aminepyridine, and O=PN³ ligand in unit **B**: (N-di-tert-butylphosphinooxide)-6-(2'-methyl-2'*H*-benzoimidazole)-2-aminepyridine) with 1:1:1 molar ratio. Co1 and Co2 complexes both display a five-coordinated distorted-square-pyramidal geometry around the metal center. The Co1 center is coordinated with PN³ ligand via two N atoms from pyridine, benzoimidazole moiety as well as one P atom, and the Co2 center is coordinated with the oxidized ligand O=PN³ via two N atoms from pyridine, benzoimidazole moiety as well as one O atom from DMF molecule, while the oxidized phosphine moiety (O=P) being excluded from the coordination sphere. Activated with AlEt₂Cl, the co-crystallized complexes **I** are able to actively convert butadiene to polybutadiene, affording *cis*-1,4 polybutadiene with *cis*-1,4 unit up to 95.5-97.8% and number average molecular weight of *cal.* 10⁵g/mol. The high *cis*-1,4 selectivity and monomodal GPC curve of resultant polymer imply that the identical active species generated from two distinctive cobalt centers.

Keywords: co-crystal structure, cobalt catalyst, PN³ ligand, butadiene polymerization

1. Introduction

One of our main interests lies in the field of homogeneous catalysis of butadiene to *cis*-1,4-polybutadiene, as it has been one of the most regarded materials suitable for many practical applications such as tire, tube and shoes. The development of catalysts plays an important role for efficient control in chain architectures such as stereochemistry, functionality and chain length in polybutadiene synthesis [1-6]. Recently, tri-dentate pincer ligands have emerged as attractive auxiliary ligands in iron and cobalt based catalysts promoted for olefin and diene polymerizations [7,8]. We have currently been exploring well-defined cobalt catalysts for (co-) controllable (co-) polymerization for conjugated dienes to afford desirable product. The extensive and diverse coordination chemistry of the cobalt complexes have provided diversified catalytic properties as the product microstructures, such as *cis*-1,4, *trans*-1,4, 1,2 enchainment and their combinations crucially depends on catalyst formulation, controlling of the product's properties by catalyst design and chosen has thus been feasible. Publications to date have described various ligands supported metal complexes, in particular, asymmetry PN^2 and PN^3 type ligands, which developed by us and Milstein, respectively, [9-13] have attracted much attention as the dissociation of labile metal-phosphine bond (metal-P bond is weak with respect to metal-N bond) tends to generation of open site available for small molecule coordination and activation, while the intact two metal-N bonds could effectively chelate, stabilize the metal center, as well as induce regio- and stereoselectivity. Relevant ligands in this context are specified in scheme 1. Besides the well known PN^2 ligand **A** which forms a labile five-membered-ring chelate with ruthenium, iron and iridium, e.g. $\{2\text{-diethylamine-6-(N,N-di-tert-butylphosphine)methylpyridine}, [14]\}$, there are also established ligands recently explored in our lab which give rise to various frameworks and the corresponding coordination chemistry e.g. **B** $\{2\text{-diethylamine-6-(N,N-di-tert-butylphosphine)aminepyridine}, [9]\}$, **C** $\{2\text{-pyrazol-6-(N,N-di-}$

tertbutylphosphine)aminepyridine, [10]], **D** {6-(*N,N*-di-tert-butylphosphine)amine-2-(3',3'-dimethyloxaline)pyridine, [11]], **E**{6-(*N,N*-di-tert-butylphosphine)amine-2,2-bipyridine, [12]], **F** {2-*O*-di-tert-butylphosphine)-6-aryliminepyridine, [15]}. However, due to the air sensitivity of phosphine (III) moiety of PN^3 ligand in presence of oxidant, transformation to its oxide $\text{P}=\text{O}(\text{V})$ analogues is usually resulted, as such, a twist six-membered-rings chelate could be produced and the formed metal-O bond is typical weaker than the corresponding metal-P, which ultimately could lead to a more open active center for monomer activation and insertion in process of polymerization. For investigating structural variation before and after oxidation and their effect on the catalytic behavior, we design, synthesize (*N*-di-tert-butylphosphino)-6-(2'-methyl-2'-*H*-benzoimidazole)-2-aminepyridine ligand, complex it with anhydrous CoCl_2 , and oxidize the corresponding cobalt complex in DMF in presence of H_2O_2 , interestingly, recrystallization of product results in a cocrystal comprised of CoCl_2PN^3 , the oxidized $\text{CoCl}_2\text{O}=\text{PN}^3$ (with a coordinated DMF) and a free DMF molecule. The resultant complexes have been examined for selective polymerization of butadiene, and comparison of the catalytic performance with respect to the activity and selectivity to that of the intact complex has been also discussed.

(Scheme 1)

2. Experimental

2.1. General procedure

All manipulation of air or moisture sensitive compounds was carried out under nitrogen or argon atmosphere. Ammonia, phenylenediamine, 6-bromopyridine-2-carboxylic acid, diethyl aluminum chloride, methyl iodide, polyphosphoric acid (PPA), *n*-butyllithium and di-tert-butylphosphinechloride were commercially available and used as received. All solvents were purified by the standard procedures. Polymerization grade 1,3-butadiene was purified by passing columns packed with KOH and molecular sieves prior to use.

NMR analysis of ligands and polymers were recorded on a Bruke spectrometer in CDCl_3 . IR spectra were processed on BRUKE Vertex-70 FIR spectrophotometer. Elemental analyses were recorded on an elemental Vario EL spectrometer. The number average molecular weights (M_n) and polydispersity index (PDI) of polymer were determined at 30 °C by VISCOTEK GPC1000 with TDA305 (Triple Detector Array) as detector and calibration was made against standard polystyrene.

X-ray analysis data were collected on a Bruker SMART APEX diffractometer with a CCD area detector, using graphite monochromated Mo K radiation ($\lambda = 0.71073 \text{ \AA}$). Crystal class and unit cell parameters were determined by the SMART program package. Reflection data file was yielded from raw frame data by SAINT and SADABS and the structures were solved based on SHELXTL program. Refinement was processed on F^2 anisotropically for all non-hydrogen atoms by the full-matrix least-squares method.

CCDC reference numbers is 1061305 deposited for complexes **I**. Crystal data and structure refinements were tabulated in table 1.

(Table 1)

2.1. Synthesis and characterization

2-(2-methyl-2'-*H*-benzimidazole)-6-(*N,N*-di-*tert*-butylphosphine)aminepyridine ligand (PN^3) was synthesized according to our reported method (scheme 2) [10,16].

6-Bromo-2-(2'-methyl-2'-*H*-benzoimidazole)pyridine **L-1**

The 6-bromopyridine-2-carboxylic acid (2.01 g) and phenylenediamine (1.08 g) were homogenized in PPA (20 mL) at sintered ceramic vessel, and reaction was triggered by microwave for 5 mins. The crude product was put into water, neutralized with aqueous sodium carbonate (20.0 wt-%) and extracted by dichloromethane. The collected solid was dissolved in ketone (50 mL) in presence of excess KOH and then methyl iodide (2.6 g) was added for *N*-methylation overnight. The final product was recrystallized in ethanol (2.60 g, 90% in yield).

^1H NMR (400 MHz, CDCl_3 , ppm): 8.38 (m, 1H), 7.81 (s, 1H), 7.70 (t, 1H, $J = 8 \text{ Hz}$), 7.53 (d, 1H, $J = 8 \text{ Hz}$), 7.44-7.37 (d, 1H), 7.36-7.32 (m, 2H), 4.28 (s, 3H).

6-Amino-2-(2'-methyl-2'-*H*-benzoimidazole)pyridine **L-2**:

To a mixture of 6-bromo-2-(2'-methyl-2'*H*-benzoimidazole)pyridine (2.60 g, 10 mmol) and Cu₂O (0.1 mmol, 16 mg) in glycol (20 mL) in autoclave, excess NH₃ (*cal.* 10 equiv.) was fed at -30 °C. The reaction was processed under 10 atm of NH₃ at 110 °C for 24 h. After cooling to room temperature, water was added and the aqueous phase was extracted with DCM (10 mL). The combined organic layers were washed with brine (20 mL) and dried over MgSO₄. The crude product was purified by column chromatography on silica gel (hexanes: ethyl acetate = 15:1 as eluent) to afford a white solid (2.16 g, 90 % in yield). ¹H NMR (400 MHz, CDCl₃, ppm): 8.45 (s, 1H), 7.70 (s, 1H), 7.55 (m, 1H), 7.28 (m, 1H), 6.41-6.36 (m, 2H), 4.51 (br, 2H), 3.74 (s, 3H). ¹³C NMR (100 MHz, CDCl₃, ppm): 157.49, 150.71, 148.52, 142.23, 138.59, 137.05, 123.16, 122.59, 119.90, 118.16, 115.45, 109.81, 108.98, 32.63.

6-(*N*-di-tert-butylphosphino)-2-(2'-methyl-2'*H*-benzoimidazole)-aminepyridine **L**:

To a suspension of 6-amino-2-(2'-methyl-2'*H*-benzoimidazole)pyridine (1.12, 5.0 mmol) in toluene (50 mL) was sequentially added NEt₃ (1.47 mL, 10 mmol) and ^tBu₂PCl (1.17 mL, 6.0 mmol) at 0 °C. Upon further cooling to -78 °C, *n*-BuLi (7.0 mmol, 4.48 mL of a 1.6 M solution in hexane) was slowly added. The solution was allowed to reach room temperature and then stirred overnight at 80 °C. After quenching with of water (0.5 mL), the solvent was removed under vacuum. The resultant yellow solid was purified by column chromatography on silica gel (hexanes: ethyl acetate = 10:1 as eluent) to afford a white solid (1.23 mg, 66.7 % yield). ³¹P NMR (162 MHz, CDCl₃, ppm): 59.77 (s). ¹H NMR (400 MHz, CDCl₃, ppm): 8.46 (m, 2H), 7.68 (m, 2H), 7.53 (m, 2H), 7.03 (m, 1H), 6.40 (br, 1H), 3.60 (s, 3H), 1.10 (s, 9H), 1.08 (s, 9H). ¹³C NMR (100 MHz, CDCl₃, ppm): 160.02, 149.86, 141.27, 139.93, 126.86, 106.85, 105.90, 101.35, 33.64, 27.75.

(Scheme 2)

Equal equivalent of cobalt dichloride (0.0127 g, 0.1 mmol) was added to a solution of ligand C₂₁H₂₉N₄P (0.0368 g, 0.1 mmol) in anhydrous THF (5 mL) at room temperature under argon atmosphere. The suspension was allowed to stir overnight under room temperature, diethyl ether was added and a green precipitate was obtained, which was washed with hexane and dried in vacuum overnight. The chemical components of

complex was verified by IR and elemental analysis for C, H, N, unfortunately, access to solution and solid structure information is unsuccessfully due to the paramagnetic properties and poor quality of crystal. The obtained complex A was dissolved in dry and air free DMF in presence of 0.6 equivalent of H_2O_2 in a sealed vessel, stirred overnight and then crystallized from DMF by slow diffusion of hexane at room temperature under argon atmosphere, finally, 0.0258 g of green crystals suitable for X-ray diffraction analysis were obtained (45% in total yield).

Complex A: IR (KBr, cm^{-1}): 1624, 1628 ($\nu_{\text{C}=\text{N}}$). Anal. Calc. for $\text{C}_{21}\text{H}_{29}\text{Cl}_2\text{CoN}_4\text{P}$ (%): C, 50.62; H, 5.87; N, 11.24. Found: C, 50.93; H, 6.00; N, 11.04.

Complexes I: IR (KBr, cm^{-1}): 1620, 1628 ($\nu_{\text{C}=\text{N}}$), 1248 ($\nu_{\text{P}=\text{O}}$). Anal. Calc. for $\text{C}_{48}\text{H}_{72}\text{Cl}_4\text{Co}_2\text{N}_{10}\text{O}_3\text{P}_2$ (%): C, 49.75; H, 6.26; N, 12.09. Found: C, 50.13; H, 6.13; N, 12.34.

2.2. Polymerization

Polymerization was performed in 100 mL glass bottle capped with rubber (typical example as run 3): A toluene (20 mL) solution of butadiene (0.54 g, 0.01 mmol) was introduced to the glass bottle preloaded with complexes I (2.90 mg, 2.5 μmol), then AlEt_2Cl (2.0 mmol) was injected for initiating polymerization. After 4 h, the reaction was terminated by acidified methanol (0.5% HCl, 1 mL) containing 1.0% 2,6-di-tert-butyl-4-methylphenol, and the polymer precipitate was collected by filtration, washed with methanol (10 mL) and dried in vacuum at 50°C to a constant weight (0.53g, 99% in yield).

3. Results and discussion

3.1. Synthesis and characterization of ligand and complexes

The PN^3 ligand was prepared via reaction of 6-bromopyridine-2-carboxylic acid and phenylene diamine in presence of PPA in microwave conditions, followed by the N-methylation of NH in benzoimidazole moiety and N-substitution with di-tert-butylphosphine chloride in NH_2 . The obtained ligand was well characterized by NMR (see in the supporting information), and the results are well in consistent with expected formula. The corresponding cobalt complex was synthesized by the conventional

refluxing condition in THF, and the mixed ligand supported complexes were obtained by recrystallization in DMF after deliberately oxidation.

3.2. Crystal structure description

The X-ray study of **I** co-crystallized as green crystals in the centrosymmetric space group P-1 with one molecule of independent DMF in each unit. The crystal structure reveals that one ligand in each unit is oxidized, and the other is intact, therefore, three crystallographically independent molecules (PN^3CoCl_2 in unit **A**, $\text{O}=\text{PN}^3\text{CoCl}_2$ in unit **B** and DMF) in the asymmetric unit are observed. In the crystal structure of unit **A** in the title complexes (Figure 1, left), the cobalt atom lies in a typical five-coordinated distorted-trigonal-bipyramidal geometry formed by coordination of the P atoms with two tert-butyl-group, two N atoms donors from pyridine ligand and unsaturated benzoimidazole moiety as well as two chloride anions. The bond distance of Co1-N(1) is found to be shorter than that of Co1-P1 (table 2). The pyridine nitrogen atom (N(1)) and two chlorides (Cl(3) and Cl(4)) compose an equatorial plane, with the sum of three equatorial angles ($110.34(10)^\circ$, $106.64(7)^\circ$ and $142.97(12)^\circ$) being 359.95° , indicative of the central metal located exactly on the plane, and the Co1-N1 and Co-P1 occupying the apical position with forming a subtended angle N1-Co1-P1 of $151.15(8)^\circ$. The Cl3-Co1-Cl4 is $110.34(10)^\circ$ and N1-Co1-P1 is $151.15(8)^\circ$, which both are very close to values of the five coordinated cobalt dichloride complexes. These values regarding to the bond lengths and angles in the coordination environments (table 2) are in the same ranges as for reported CoCl_2NNN complexes [16-17].

(Figure 1)

The oxidized complex (unit **B**) tends to co-crystallize with DMF under the conditions employed to satisfy the six coordination, in which the three in-plane donors also come from the N,O,N,-tridentate and the axial position is positioned with the P atom from ligand and O atom from the DMF molecule, which indicates DMF has stronger coordination capability (Figure 1, right) compared to the oxygen of phosphine oxide. The

N(5) turns to be axial and trans to O(2A) atom, although in similar symmetry, the bond distance of Co2-O2 is shorter than that of Co2-P2 (table 2), at the same time, Co(2)-N(5) is shorter than Co(1)-N(1) (table 3). We notice that exist of O atom from DMF precluding the coordination of O from ligand, thus a tridentate conformation from pincer ligand set is not formed.

(Figure 2)

(Table 2)

(Table 3)

3.3. Butadiene polymerization

The polymerization results in this manuscript discussed are included of the effects of cocatalyst, monomer concentration and polymerization temperature. The polymerization parameters and polymerization results were collected in table 4, and those of CoCl₂/AlEt₂Cl were also added for comparison (run 11). We begin our study with AlEt₂Cl as cocatalyst, as it has been demonstrated as a powerful activator in cobalt catalyzed conjugated butadiene and isoprene polymerization at ambient temperature in toluene [17-19]. The polymer yield increases with increasing of AlEt₂Cl used and reaches a plateau about 99.1 % at [Al]/[Co] = 400, however, further increasing of AlEt₂Cl amount ([Al]/[Co] = 800) does not observe beneficial effect on the polymer yield (run 1-4). Of note is that the *cis*-1,4 selectivity maintains at a high level ranging from 95.9 % to 97.3 % (figure 3 and 4 for ¹H NMR and ¹³C NMR, respectively) with negligible *trans*-1,4 unit, depending on the AlEt₂Cl amount, generally, the more AlEt₂Cl used, the higher selectivity observed in the examined AlEt₂Cl amount range. The *cis*-1,4 specified regioselectivity in combination with monomodal GPC curve of polymer and narrow PDI (2.1-2.6, representative GPC profile is shown in fig. S7 in supporting information) indicates a single active site is generated, and such result could be explained that in presence of AlEt₂Cl, the metal-phosphine bond in Co1 center presumably disassociate to provide bi-dentate metal center similar to that of Co2 center (DMF in Co2 should be

removed by AlEt_2Cl), which could result in 13e cobalt σ -allylic species $[\text{Co}-(\eta^1\text{-CH}_2\text{-CH=CHR})]^+$ available for butadiene coordination (figure 5 **a**). Alternatively, Co-P (Co-O) and one Co-N could be removed for generation of mono-dentate 13e cobalt π -allylic species $[\text{Co}-(\eta^3\text{-CH}_2\text{-CH=CHR})]^+$, which could be commonly accepted (figure 5 **b**). Based on this deduction, the two cobalt active centers derived from Co1 and Co2 have a unified chemical environment and this can be verified the fact that various bi-dentate even mono-dentate cobalt dichlorides all have demonstrated as high active catalysts [20-21], though the possibility that the active center derived from one metal center could not be precluded. One should admit that the structure of the active species in cobalt catalyzed butadiene is to date largely unknown and the mechanistic considerations remain most probably the most tricking aspect of this chemistry. The improved polymerization performances demonstrate that the ligand affect the metal center thus increasing the stability of active species as well as inducing high selectivity compared those of pure CoCl_2PN^3 (run 10, table 4). Overall, the mixed complexes **I** catalyst exhibits superior catalytic activity (per cobalt) to its pure analogue CoCl_2PN^3 , and the open space around the metal center after oxidation responsible for increased polymer productivity. The polymerization temperature has affected the catalytic selectivity and activity. The optimal performances are achieved at 25°C, the polymer yield was decreased both at 0°C and 50°C, interestingly, the selectivity is found to increase in the reversed trend of temperature with 97.7% of *cis*-1,4 selectivity observed at 0°C (run 5), which can be justified by the diene mechanism proposed by the L. Friebe: the kinetically controlled product *cis*-1,4 enchain polymer originated from *anti*-allylic polymer terminal bond to metal center favored at lower polymerization temperature [22-24]. The effect of monomer concentration on catalysis is also investigated (run 7-8), and the productivity improves with higher monomer concentration, and the selectivity is also benefited slightly due to the fact that the faster monomer insertion rate could lead to kinetically favored *anti* π -allylic intermediate for higher *cis*-1,4 selectivity [22, 24]. The cocatalyst screening result shows that MAO is inferior to more Lewis acid AlEt_2Cl in terms of polymer yield and selectivity, and other cocatalyst such as AlEt_3 and Al^iBu_3 activated

catalyst do not form detectable polymer. Overall, the current catalyst show comparable or superior performance to the most tri-dentate CoCl_2N_3 and bi-dentate ligand CoCl_2N_2 supported systems [20-21], in particular, the activity is slightly improved by introducing a labile phosphine coordinative atom.

(Table 4)

(Figure 3)

(Figure 4)

(Figure 5)

Conclusion

We have prepared N-di-tert-butylphosphino-6-(2'-methyl-2'-H-benzoimidazole)-2-aminepyridine ligand supported CoCl_2PN^3 complex. Reaction with H_2O_2 in DMF provides an incomplete cocrystal **I** comprised of intact CoCl_2PN^3 , oxidized $\text{CoCl}_2\text{O}=\text{PN}^3$ and free DMF. In combination with AlEt_2Cl , the complexes are found to be high active in butadiene polymerization, producing polybutadiene with high *cis*-1,4 enchainment. The *cis*-1,4 specified selectivity and monomodal of molecular weight distribution imply that a unified active specie is formed.

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Scheme 1 PN^3 ligand studied in the literatures

Scheme 2 The synthetic route for PN^3 ligand and the corresponding cobalt complex

Figure 1 The chemical structure of co-crystal **1**

Figure 2 ORTEP drawing of unit **A** (left) and **B** (right) of co-crystallized complex with thermal ellipsoids at 30% probability level. Carbon atoms are non-labeled and hydrogen atoms have been omitted for clarity.

Figure 3 The ^1H NMR of polybutadiene obtained at 0°C (run 5)

Figure 4 The ^{13}C NMR of polybutadiene obtained at 0°C (run 5)

Figure 5 The proposed profile of active species

This study

Scheme 1

Scheme 2

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Table 1 Crystal data and structure refinements of co-crystal complexes

Formula	$C_{48}H_{72}Cl_4Co_2N_{10}O_3P_2$
Molecular weight	1158.76
Crystal system	Triclinic
Space group	<i>P1</i>
a (Å)	13.7080(7)
b (Å)	13.7434(13)
c (Å)	14.8577(13)
α (deg)	96.383(7)
β (deg)	89.943(6)
γ (deg)	98.580(6)
V (Å ³)	2750.3(4)
Z	2
D _{calcd} (Mg/m ³)	1.399 Mg m ⁻³
Absorpcoeff (mm ⁻¹)	0.905
F(000)	1212
Crystal size(mm)	0.21×0.21×0.15
θ Range (deg)	2.99 to 25.00
No. of reflns collected	38789
No. of indepreflns	9400
	(R _{int} = 0.046)
No. of data/restraint /params	9400/49/650
GOF on F ²	1.004
R ₁ (I>2sigma(I))	0.0462
wR ₂	0.1082

Table 2

Selected bond distance (Å) and bond angle (°) of unit A

Co1-Cl3	2.3054(9)	N1-Co1N3	76.49(10)°	Cl3-Co1-P1	100.31(3)°
Co1-Cl4	2.307(3)	N1-Co1Cl3	98.16(7)°	Cl4-Co1-P1	97.79(8)°
Co1-N1	2.108(3)	N3-Co1Cl3	106.64(7)°	N1-Co1-P1	151.15(8)°
Co1-N3	2.132(3)	Cl3-Co1-Cl4	110.34(10)°	N3-Co1-P1	77.09(7)°
Co1-P1	2.5014(9)	N1-Co1-Cl4	96.32(11)°	N3-Co1-Cl4	142.97(12)°

Table 3Selected bond distance (Å) and bond angle (°) of unit **B**

Co2-Cl1	2.3227(9)	N5-Co2-N7	77.07(10)°	O2-Co2-Cl2	93.28(7)°
Co2-Cl2	2.2886(9)	N7-Co2-Cl2	91.27(7)°	O2-Co2-Cl1	92.07(7)°
Co2-N7	2.208(3)	N5-Co2-Cl2	111.78(7)°	O2-Co2-N7	172.28(10)°
Co2-N5	2.038(3)	Cl2-Co2-Cl1	125.09(4)°	N5-Co2-O2	95.45(10)°
Co2-O2	2.111(2)	N7-Co2-Cl1	90.40(7)°	N5-Co2-Cl1	121.99(8)°

Table 4Polymerization of butadiene performance by using cobalt complexes **I**

Run	[Bd]/ [Co]	T_p (°C)	Cocatalyst	[Al]/ [Co]	Yield (%)	Microstructure (%)			M_n ($\times 10^4$)	PDI
						<i>Cis</i> -1,4	<i>Trans</i> -1,4 ^e	1,2		
1	2000	25	AlEt ₂ Cl	100	76.1	95.9	2.3	2.1	12.9	2.1
2	2000	25	AlEt ₂ Cl	200	83.2	96.4		3.6	10.9	2.1
3	2000	25	AlEt ₂ Cl	400	99.1	96.6		3.4	9.5	2.1
4	2000	25	AlEt ₂ Cl	800	96.7	97.3		2.7	9.3	2.3
5	2000	0	AlEt ₂ Cl	400	68.1	97.7		2.3	13.9	2.6
6	2000	50	AlEt ₂ Cl	400	63.1	96.2		3.8	9.9	2.9
7 ^a	4000	25	AlEt ₂ Cl	400	88.9	97.6		2.4	16.8	2.7
8 ^b	8000	25	AlEt ₂ Cl	400	76.9	97.9		2.1	22.7	2.8
9	2000	25	MAO	400	61.2	90.1	1.7	8.2	7.2	3.9
10 ^c	2000	25	AlEt ₂ Cl	400	69.5	96.8	0.5	2.7	10.9	1.9
11 ^d	2000	25	AlEt ₂ Cl	400	60.5	95.3	0.9	3.8	16.9	2.9

Polymerization conditions: complexes **I**, 2.5 μ mol; butadiene, 0.54 g, ^a1.08g, ^b2.16g, ^cCoCl₂PNN, 5.0 μ mol, ^dCoCl₂ was used as catalyst, ^eNegligible *trans*-1,4 unit is detected; polymerization time: 4h.

Graphic Abstract (pictogram)

Synthesis of mixed-ligand cobalt complexes and their applications in
high *cis*-1,4-selective butadiene polymerization

**Wen Liu^a, Weijing Pan^a, Peng Wang^a, Wei Li^a, Jingshan Mu^a, Gengsheng Weng^a,
Xiaoyu Jia^{b,c}, Dirong Gong^{a*}, Kuo-Wei Huang^d**

^a Department of Polymer Science and Engineering, Faculty of Materials Science and Chemical Engineering, Ningbo University, Ningbo 315211, P. R. China

^b Key Laboratory of Urban Environment and Health, Institute of Urban Environment, Chinese Academy of Sciences, No.1799, Jimei Road, Xiamen, Fujian 361021, P. R. China.

^c Ningbo Urban Environment Observation and Research Station-NUEORS, Chinese Academy of Sciences, Ningbo, Zhejiang 315830, P. R. China.

^d King Abdullah University of Science and Technology, Division of Physical Sciences and Engineering and KAUST Catalysis Center, Thuwal 23955-6900, Saudi Arabia.

Corresponding to: Gongdirong@nbu.edu.cn

The mixed-ligands coordinated cobalt complexes

Graphic Abstract (synopsis)

Synthesis of mixed-ligand cobalt complexes and their applications in high *cis*-1,4-selective butadiene polymerization

Wen Liu^a, Weijing Pan^a, Peng Wang^a, Wei Li^a, Jingshan Mu^a, Gengsheng Weng^a, Xiaoyu Jia^{b,c}, Dirong Gong^{a*}, Kuo-Wei Huang^d

^a Department of Polymer Science and Engineering, Faculty of Materials Science and Chemical Engineering, Ningbo University, Ningbo 315211, P. R. China

^b Key Laboratory of Urban Environment and Health, Institute of Urban Environment, Chinese Academy of Sciences, No.1799, Jimei Road, Xiamen, Fujian 361021, P. R. China.

^c Ningbo Urban Environment Observation and Research Station-NUEORS, Chinese Academy of Sciences, Ningbo, Zhejiang 315830, P. R. China.

^d King Abdullah University of Science and Technology, Division of Physical Sciences and Engineering and KAUST Catalysis Center, Thuwal 23955-6900, Saudi Arabia.

Corresponding to: Gongdirong@nbu.edu.cn

1. Mixed-ligands ligated cobalt complexes were prepared.
2. The complexes are high active in butadiene polymerization.
3. The obtained polymer has *cis*-1,4 unit up to 95.5-97.8%.

Synthesis of mixed-ligand cobalt complexes and their applications in high *cis*-1,4-selective butadiene polymerization

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^a Department of Polymer Science and Engineering, Faculty of Materials Science and Chemical Engineering, Ningbo University, Ningbo 315211, P. R. China

^b Key Laboratory of Urban Environment and Health, Institute of Urban Environment, Chinese Academy of Sciences, No.1799, Jimei Road, Xiamen, Fujian 361021, P. R. China.

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1. The novel PN^3 and the CoCl_2PN^3 are synthesized and characterized.
2. The CoCl_2PN^3 is half-oxidized to $\text{CoCl}_2\text{O}=\text{PN}^3$ in presence of H_2O_2 .
3. X-ray finds CoCl_2PN^3 and $\text{CoCl}_2\text{O}=\text{PN}^3$ are co-crystallized in one unit.
4. The complexes are active in *cis*-1,4 selective butadiene polymerization.