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Highly *cis*-1,4 Selective Polymerization of 1,3-Butadiene with Co(II) Complexes Bearing N-aryl-Phenanthrene-o-iminoquinones

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## Highly *cis*-1,4 Selective Polymerization of 1,3-Butadiene with Co(II) Complexes Bearing N-aryl-Phenanthrene-o-iminoquinones Bo Gao,<sup>a</sup> Dongni Li,<sup>\*a, b</sup> and Qian Duan<sup>\*a, c</sup>

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### articleinfo

### abstract

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#### 1. Introduction

Polybutadiene is one of the polydiene and is the most commonly used synthetic rubber. [1-3] The microstructure of the polymer plays an important role in determining performance. The polymerization process of conjugated dienes has been known for a long time, but a real breakthrough has been achieved by stereospecific polymerization of conjugated dienes and transition metal-based coordination catalysts. [4] A homogeneous Ziegler-Natta catalyst system consisting of various transition metal complexes, such as Ti,[5, 6] V,[7, 8] Fe,[9, 10] Co,[11-15] Ni,[16] Cr[17-20], and the co-activators aluminum alkyls or the aluminum alkyl chloride have been extensively investigated. Cobalt complexes have attracted attention due to their unique properties as diene polymerization catalysts. Ricci found that the CoCl<sub>2</sub> (PR<sub>3</sub>)<sub>2</sub>-MAO(R=alkyl) system obtained polymers of different structures from butadiene (cis-1, 4; cis-1, 4/1, 2 mixed; predominantly 1, 2) depending on the type of phosphine ligand, this meant that the ligand had a large influence on the chemical selectivity of the polymerization.[21] He has also reported on the synthesis of CoCl<sub>2</sub>(PiPrPh<sub>2</sub>)<sub>2</sub> and its behavior in the polymerization of butadiene, [22] when used in association with MAO[23], it was found to be extremely active and stereospecific, giving a highly syndiotactic 1, 2-polybutadiene. Other papers concerning the polymerization of 1,3-butadiene with catalysts based on cobalt complexes with nitrogen ligands have also been reported, [24-25] but an in-depth investigation on the influence of the ligand nature on chemo- and stereoselectivity has not been carried out. Schiff base ligands were important ligands and were widely used in stabilizing metal complexes. [17, 18, 26-38] To date, only a few metal complexes with phenanthrene-oarylene (PI) ligands have been demonstrated.[17,27,31]

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Several chlorine-bridging dinuclear Co(II) complexes bearing the Schiff base ligands N-aryl-phenanthrene-o-iminoquinones (Ar-

PICoCl<sub>2</sub>) were synthesized and characterized by elemental analyses, infrared analyses and X-ray crystallography. The X-ray

crystallography analysis of Co(II) complex 2 revealed that the geometry around the cobalt centers is twisted quadrilateral configuration. Upon activation with MAO, these complexes showed good activities (82.5%-98.3%) for 1,3-butadiene

polymerization affording predominantly cis-1,4 polybutadiene (up to 96.2%). GPC showed that the polybutadiene have relatively

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Scheme 1. Synthesis route of Co complexes.

In our previous studies, we reported a monoanionic Cr(III) complex produced by reduction of PIQ ligands with CrCl<sub>2</sub>. It exhibits moderate activity in the polymerization of diene *cis*-1,4 units.[17] In other our recent studies, we demonstrated that the reaction of PIQ ligands with magnesium produces a free radical anion- or amide-phenol-type magnesium complex depending on the ratio of reactants. [27, 31] To the best of our knowledge, cobalt complexes containing this ligand have not been explored. In the chemical process of extending PIQ ligands, we report the synthesis and characterization of cobalt(II) complexes based on N-aryl-phenanthrene-o-imidazolium ligands. When activated by MAO, these complexes showed good activity in the polymerization of butadiene to give *cis* 1,4-polybutadiene.

#### 2.Experimental

#### 2.1. General Considerations

All manipulations involving air and moisture-sensitive compounds were carried out under an atmosphere of dried and purified nitrogen using standard Schlenk and vacuum-line techniques. Toluene and hexane were dried over sodium metal and distilled under nitrogen. Elemental analyses were performed on a Varian EL microanalyzer; infrared spectra were recorded as KBr disks with a Nicolet Avatar 360. NMR spectra were performed on Bruker AV 300MHz apparatu at room temperature in CDCl<sub>3</sub> solution for ligands and polymers. The molecular weight and molecular weight distribution of the polymers were measured by TOSOH HLC 8220 GPC at 40 °C using THF as eluent against polystyrene standards. The UV-Vis spectra of the samples were recorded over different irradiation time intervals by using a Thermo Scientific Evolution 220 spectrophotometer. Aniline, 2,6-dimethylaniline, 2,6-

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diethylaniline and 2,6-diisopropylaniline were bought from Aldrich Chemical Co. and used without further purification. The ligands N-phenylphenanthrene-o-iminoquinones  $(N-C_6H_5-PI),$ N-dimethylphenylphenanthrene-o-iminoquinones (N-2,6-Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub>-PI), N-diethylphenylphenanthrene-o-iminoquinones (N-2,6-Et<sub>2</sub>C<sub>6</sub>H<sub>3</sub>-PI), N-diisopropylphenylphenanthrene-o-iminoquinones (N-2,6-<sup>i</sup>Pr<sub>2</sub>C<sub>6</sub>H<sub>3</sub>-PI), and were synthesized according to the literatures.[17, 18, 27, 31]

## 2.2 Synthesis of Co(II) complexes (Ar-PI)CoCl(µ-Cl)<sub>2</sub>ClCo(Ar-PI) 1-4

General process: ligand L1-L4 (1.0 mmol) and anhydrous CoCl<sub>2</sub> (0.130 g, 1.0 mmol) were dissolved in 30 mL of dry THF under nitrogen atmosphere. The mixture was stirred at 60 °C for 2 h, concentrated to 5 mL, and added to 20 mL of hexane. The suspension solution was filtered over a sifting funnel, and the filter cake was washed twice with 3 mL of dry diethyl ether and dried in vacuo to give a dark brown powder, yield: 76-87 % .

2.2.1 Co(II) complex 1 yield: 0.314 g, 76%. Anal. Calcd for C40H26Cl4Co2N2O2: C, 58.14; H, 3.17; N, 3.39; Found: C, 58.16; H, 3.19; N, 3.42 . IR (KBr) v (cm<sup>-1</sup>) 3488w, 3181w, 3082w, 1686m, 1660w, 1630m, 1591m, 1555m, 1449m, 1390w, 1363w, 1300w, 1248w, 1231w, 1161w, 1125w, 1020w, 944w, 894w, 773s, 713w, 677w, 617w, 535w, 492w, 436w.

2.2.2 Co(II) complex 2 yield: 0.271 g, 87 %. The crystals of Co(II) complex 2 were cultured in a mixed solvent of hexane and THF, black. Anal. Calcd for C44H34Cl4Co2N2O2 : C, 59.89; H, 3.88; N, 3.17 ; Found: C, 59.90; H, 3.89; N, 3.18; IR (KBr) v (cm<sup>-1</sup>) 3381w, 3070w, 2976w, 2921w, 1677w, 1651m, 1594s, 1549s, 1487w, 1452s, 1386m, 1345s, 1310w, 1300w, 1262w, 1243w, 1172w, 1125w, 1094w, 1039w, 955w, 878w, 796w, 786s, 772s, 722w, 671w, 603w, 565w, 433w.

2.2.3 Co(II) complex 3 yield: 0.366 g, 78%. Anal. Calcd for C48H42Cl4Co2N2O2: C, 61.43; H, 4.51; N, 2.98; Found: C, 61.39; H, 4.53; N, 2.97; IR (KBr) v (cm<sup>-1</sup>) 3452m, 3067m, 2854w, 2800w, 1675w, 1645s, 1589s,

C(1)- N(1)

C(1)- C(14)

C(14)- O(1)

C(15)- N(1)

N(1)-C(1)-C(2)

O(1)- Co(1) Cl(3)

N(1)-Co(1)-O(1)

Cl(3)-Co(1)-Cl(2)#1

C(14)-O(1)-Co(1)

Co(1)#1-Cl(2)-Co(1)-Cl(2)#1

1448s, 1483w, 1383m, 1318s, 1303m, 1290w, 1259w, 1246w, 1187w, 1135w, 1067w, 1018w, 968m, 760s, 718m, 659w, 582w, 563m, 519m, 504m.

2.2.4 Co(II) complex 4 yield: 0.294 g, 80%. Anal. Calcd for C52H50Cl4Co2N2O2 : C, 62.79; H, 5.07; N, 2.82; Found: C, 62.70; H, 5.03; N, 2.89; IR (KBr) v (cm<sup>-</sup> <sup>1</sup>) 3498w, 3167w, 2977s, 2930w, 2858w, 2359w, 1651s, 1599s, 1525m, 1499s, 1454m, 1344m, 1298m, 1260w, 1171w, 1096w, 879w, 784W, 764s, 726m, 671w, 605w, 565w, 512w, 493w.

#### 2.3 X-ray crystal structural determination of 2

The crystal was mounted on the glass fibers using oil droplets. Data obtained in the  $\omega$ -2 $\theta$  scan mode were collected on a Bruker SMART 1000 CCD diffractometer with graphite-monochromatic Mo-K<sub>a</sub> radiation ( $\lambda = 0.71073$ Å). A direct method is used to parse the structure, and a further refinement of the full matrix least squares method on  $F_2$  is obtained using the SHELXTL package [39]. All non-hydrogen atoms are anisotropically refined. The hydrogen atoms are introduced into the calculation position using the displacement factor of the host carbon atom.

#### 2.4 General procedure for butadiene polymerization

In the glove box, toluene (5 mL), butadiene (8 mmol), and MAO (8 mmol) were added into a 12 mL ampule. Complex 1 (10 µmol, 20 µmol based on Co) was then added to initiate the polymerization. After 60 min, methanol was added to the system to quench the polymerization. The mixture was poured into a large quantity of methanol containing 2,6ditert-butyl-4-methylphenol (1.0 wt%) as a stabilizer to precipitate the white solids, which were filtered and dried under vacuum at 35 °C for 24 h.

#### 3. Result and discussion

#### 3.1 Synthesis of the complexes

Reaction of the preformed complexes of ligands (Ar-PI)CoCl(µ-Cl)2ClCo(Ar-PI) 1-4 (Ar =  $2,6-Me_2C_6H_3$ ,  $2,6-Et_2C_6H_3$ ,  $2,6-Pr_2C_6H_3$ ) with CoCl<sub>2</sub> in THF, after evaporation of the solvent and recrystallization of the residue in toluene/hexane mixed solution, afforded 1-4 as black solid in good yield (Scheme 1). These cobalt complexes were characterized by elemental analysis and infrared characterization. Crystal of 2 suitable for X-ray structure determination was grown from in a mixed solution of THF and hexane. The

molecular structure is shown in Fig. 1, the selected bond distances and angles are listed in Table 1, and the crystallographic data are summarized in Table S1 in supporting information. From the Fig. 1, we can see that it is a Cl-bridged dinuclear complex, in which the surrounding environment of two Co atoms can be described as a distorted square pyramidal configuration with ligands of monoimine and Cl atoms. The amount of distortion in a five coordinate metal complex can be quantified using the geometric calculation,  $\tau = (\beta - \alpha)/60.[40-42]$ As shown in Fig. 2,  $\alpha$  (c-e) and  $\beta$  (b-d) are the two largest angles at the metal, where a lies along the z axis and is not associated with either of the two largest interligand angles. By convention  $\beta$  is the most obtuse angle. The  $\tau$  value ranges from 0 (perfectly square pyramidal) to 1 (perfectly trigonal bipyramidal). In this case, the  $\tau$  value is 0.353, suggesting that the geometry of the cobalt centre in 2 is square pyramid. In complex 2, the Co atoms and the phenanthrene ring are almost in the same plane (N(1)-Co(1)-O(1)-C(14) has an angle of -18.01(16) ° in the ligand. The ring phase is vertical. The bond length of Co-Cl bridge is (2.3266(7)-2.3911(6) Å), while the Co-Cl termial bond length is 2.2498(5)-2.2500(8) Å, which is slightly shorter than the bond length of Co-Cl bridge. This is close to the Co-Cl bond length in the complexes, [Py(Bm-R)2]CoCl2 reported by Appukuttan [43] [Co(1)-Cl(2): 2.283(4) Å, Co(1)-Cl(1): 2.324(3) Å], trident Co complexes reported by Gong [44] [Co(1)-Cl(1): 2.2680(6) Å, Co(1)-Cl(2): 2.2613 (6) Å], Co<sub>2</sub>(PymPz)<sub>2</sub>Cl<sub>4</sub> ,reported by Jana [45] [Co(1) - Cl(1): 2.2825(5) Å], [(bpma)Co(µ - Cl)Cl]<sub>2</sub> reported by Park [46] [Co(1) - Cl(1): 2.2886(2) Å], hemilabile ligand supported cobalt(II) complex reported by Chen [47] [Co(1)-Cl(1): 2.2656(9) Å], diisopropylphenyl(pyridyl)imine derived chloro-bridged dimeric Co(II) complex reported by Murugavel [48] [Co(1)-Cl(1): 2.399(1) Å] and  $\mu$  -Cl dicobalt complexes reported by Gao [49] [Co–Cl(2): 2.2761(6) Å]. The angle of N-Co-O is  $75.49(7)^{\circ}$ . Unlike the BIP Cr complex [17], the intermediate complex has a C-C bond length of (1.513(3) Å), a C-N bond length of (1.290(3) Å), and a C-O bond length of (1.228(3). Å). By carefully analyzing these bond length data, it is not difficult to find that the PI ligands in the Co complex 2 does not have the same free radical anion state as the IP ligand in the Cr complex[17],

> but a simple coordination function, and Co is Co (II).

Table 1. Selected bond length [Å] and bond angle[°] of complex 2



Fig. 1 Structure of complex 2 (Thermal ellipsoids are drawn at the 30% probability level). Hydrogen atoms and uncoordinated solvent are omitted for clarity.



#### Fig. 2 $\tau = (\beta - \alpha)/60$ .

To further verified that cobalt in complex 2 was Co(II), X-ray photo electron spectroscopy (XPS) was used to test on it. The XPS pattern of Co 2p in complex 2 showed two peaks at 787 and 804 eV (see Fig. S1), corresponding to the Co 2p<sub>3/2</sub> and 2p<sub>1/2</sub> peaks of Co(II) species, respectively, which suggested the cobalt atoms in **2** were indeed in the Co(II) state. [50-52]

The typical absorption spectra for L4 and 4 were recorded in THF. The spectra are shown in Fig. S2. The absorption spectrum of L4 exhibited three bands at 263, 301 and 370 nm which are assignable to  $\Pi$ - $\Pi$ \* transitions of the benzene rings, the C=N and the C=O linkage, respectively. Corresponding transitions undergo a blue shift to 252, 291 and 337 nm for complex 4 as a result of complex formation.

2.3266(7) Cl(2)- Co(1) 1.513(3) 2.2500(8) Cl(3)- Co(1) 1.228(3) 2.0694(19) Co(1)- N(1) 1.444(3) 2.1472(16)Co(1)- O(1) 130.5(2) N(1)-C(1)-C(14) 111.6(2) 85.24(5) O(1)-C(14)-C(1)118.1(2)75.49(7) N(1)-Co(1)-Cl(2)#1 121.82(6) 100.67(3) Cl(2)-Co(1)-Cl(2)#1 89.04(2)

C(26)-O(2)-C(23)

N(1)-Co(1)-O(1)-C(14)

105.5(2)

-18.01(16)

1.290(3

112.55(15)

0

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#### 3.2 Butadiene polymerization

All complexes were used to catalyze the polymerization of butadiene. Aggregate data is listed in Table 2. These catalysts did not exhibit butadiene polymerization activity when AlR<sub>3</sub> was used as a cocatalyst. However, when these complexes were activated by MAO, they exhibited moderate to high activity (82.5%-98.3%) at room temperature and the resulting unit was a cis-1,4 structure-based polybutadiene with relatively narrow PDI ( $M_w/M_n = 1.20$ -2.21, representative GPC profile of polybutadiene was listed in Fig. S4). The catalytic activity decreased as the volume of the ligand substituent increased, and the molecular weight of the polymer increased significantly as the volume of the ligand increased. The reason for the analysis may be that when MAO was used as a cocatalyst, a complex having a small steric hindrance had a high activation efficiency, and thus the activity was relatively high, and the molecular weight of the polymer was low. We can see that in entries 1-4, the selectivity of the catalyst increased mildly as the volume of the ligand's substituent increased. When the catalyst was selected to be complex 4/MAO, the selectivity was the highest, which was 96.2% (see Fig. S3, Table 2, entry 4). The volume of the ligand had little effect on selectivity (92.1%-96.2%). These results obtained by the Co(II) complexes are close to the previous work which was reported by Appukuttan.[39] The initial concentration of the cobalt catalyst is reduced by half and a longer reaction time is required (Table 2, entry 5). Kinetic study using 4/MAO polymerization system revealed that the yield could reach up to 98.3% within 60 min (Table 2, entry 5). The cis-1,4content of the polymers decreased from 96.2% to 82.3%, and the trans -1,4and 1,2- levels increased from 2.5% and 1.3% to 12.0% and 5.7%, respectively, when the temperature rose from 25 to 50 °C. This trend may be attributed to *anti-syn* isomerization promoted at high temperatures through  $\pi$ - $\sigma$  rearrangement. [8] In principle, the polybutadiene-based chain can be in the form of  $\pi$ -allylic the metal center coordination, which includes inversion and formation; the former isomer produces cis-1,4- and 1,2-units, and the latter isomers produce trans -1,4- and 1,2-parts (Fig. S5). At lower temperatures, the path 1 is dynamically advantageous due to the combination of  $\pi$ -back-bonding, and the 1,3-butadiene monomer tends to form a *cis*-1,4structure. With the increase of temperature, the anti-syn isomerization through  $\pi$ - $\sigma$ - rearrangement is gradually promoted, because the syn isomers are more stable in thermodynamics, so the content of trans -1,4- and 1,2units increases.

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Table 2. Polymerization of butadiene	under v	arious o	onditi	ons <sup>a</sup>								69 (4), (2016) 656.
a Unless otherwise specified, the	entry	Cat.	Т	Al/Co	time	Conv.	$M_{\rm n}^{\rm b}$	PDI	microstructurec (%) <sup>c</sup>			[30] Z. Wen, D. Li, J. Qi, X. Chen, Y. Jiang, L
cat (20 umol based on Co) butadiene 8			°C		min	%	(×10 <sup>-4</sup> )		cis-1,4	trans-1, 4	1, 2	Chen, B. Gao, Y. Cui, Q. Duan, Colloid Polym
mmol, Monomer/Co = $400$ ,	1	1	25	400	60	93.8	1.70	2.21	92.1	5.9	2.0	Sci. 293 (12), (2015)3449.
MAO/Monomer = 1. b Determined by gel permeation chromatography (GPC) with	2	2	25	400	60	90.3	2.24	1.51	94.9	3.3	1.8	[31] Y. Liu, Z. Chen, L. Liu, Y. Peng, X.
respect to a polystyrene standard. $c$	3	3	25	400	60	87.2	4.09	1.35	95.3	3.2	1.5	Dalton Trans., 0 (48), (2009) 10813.
Determined by <sup>13</sup> C NMR spectrum and IR.	4	4	25	400	60	82.5	7.63	1.20	96.2	2.5	1.3	[32] B. Gao, R. Duan, X. Pang, X. Li, Z.
d cat. (10 µmol based on Co).	5	<b>⊿</b> <sup>d</sup>	25	400	360	88.9	9.02	1.32	95.8	2.9	13	Qu, Z. Tang, X. Zhuang, and X. S. Chen,
4.Conclusion	6	4	50	400	60	08.3	0.77	1.32	82.3	12.0	57	Organometallics, 32 (19), (2013) 5435.
	0	4	50	400	00	90.5	9.11	1.29	62.5	12.0	5.7	[33] B. Gao, D. Li, X. Li, R. L. Duan, X.

In this work, a series of Co(II)

phenanthrenequinone complexes based on different substituted monoimine ligands were synthesized. All the complexes were characterized by elemental analysis and infrared characterization, and a complex was characterized by single crystal structure and XPS. Under the action of MAO, these complexes catalyzed the polymerization of butadiene to exhibit different catalytic activities, and obtained predominantly cis-1,4-polybutadiene.

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### Appendix A. Supplementary data

CCDC 1893440 contains the supplementary crystallographic data for 2. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge Catal. Sci. Technol. 5 (9), (2015) 4644.

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### **Graphical Abstract**

A series of cobalt(II) complexes bearing N-aryl-Phenanthrene-o-iminoquinones have been prepared and characterized. The catalyst system  $(Ar-PI)CoCl(\mu-Cl)_2ClCo(Ar-PI)/MAO$  shows good catalytic activity and cis- 1,4 selectivity (up polymerization.