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# Isoprene Polymerization with Pyrazolylimine Cobalt (II) Complexes: Manipulation 3,4-Selectivities by Ligand Design and Triphenyl Phosphine

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**Abstract:** A series of pyrazolyimine  $CoCl_2$  complexes were synthesized and well-characterized. The single crystal structures and coordination geometries of these complexes were confirmed by X-ray diffractions, which revealed dimeric and monomeric structures respectively, and thereby distorted trigonal bipyramid and distorted tetrahedral geometries. In combination with diethylaluminum chloride (DEAC) and methylaluminoxane (MAO) as cocatalysts, the present cobalt complexes displayed high activity toward isoprene polymerization, affording *cis*-1,4/3,4- polyisoprenes. Polymerization paprameters posed significant influence on the polymerization behaviors. Additionally, incorporation of the external donor triphenylphosphine led to the selectivity of the system switch from *cis*-1,4- to 3,4- manner, providing an effective method to adjust the 3,4-moieties in large scope

#### Introduction

The microstructure of a macromolecule is an important chain parameter that governs its mechanical properties and thereof its application categories. Design and synthesis of polymers with well-defined microstructures from catalyst level has been a longstanding central theme in the research area of coordination polymerization. Highly *cis*-1,4-stereoregular polyisoprene (PI) has been widely used as bulk tire raw materials due to its excellent elastomeric property since the beginning of the automobile industry,<sup>[1]</sup> however, the contradictory relationships of rolling resistance, wet skid resistance and wear resistance reflected from these tires makes them not good enough to cope with complicated application environments, and developing novel polyisoprenes based tire materials to balance this contradictory relationship is highly desirable. Incorporation of 3,4-units into the cis-1,4-PI main chain is an effective chemical strategy to decrease the rolling resistance and meanwhile

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Supporting information for this article is given via a link at the end of the document. CCDC number for **2d**, **3a**, **3d** and **3e** are 1866572-1866575.

keeping the high wet skid resistance and high elasticity,<sup>[2]</sup> hence developing cis-1,4/3,4- PIs with varied composition and sequence distributions are ideally targeted. Unfortunately, in strikingly contrast to the myriad of cis-1,4 polymerization systems, [3] 3,4-selective precatalysts are relatively scarce, and only a handful of middle/late transition metal, rare earth metal precatalysts are available, such as Cr/Fe/Co complexes chelated by bidentate, tridentate pyridine or phosphine containing ligands,<sup>[4]</sup> lanthanide complexes supported by Cp,<sup>[5]</sup> N^P^N,<sup>[6]</sup> N^N,<sup>[7]</sup> and *N*-heterocyclic carbene<sup>[8]</sup> ligands. Compared to the lanthanide counterparts which are highly air-/moisture- sensitive and thus need delicate handling, late transition metal complexes display unique advantages, such as highly stable, high functional tolerance, cheap and earth abundant, etc., and therefore attract extensive investigations in the past few years.<sup>[9]</sup> Porri et al. reported diethylbis(2,2'bipyridine)Fe/MAO system for highly 3,4- regio-polymerization to afford crystallizable 3,4-PI;<sup>[4b]</sup> Ricci et al. reported the preparation of cis-1,4-alt-3,4- Pls from CoCl<sub>2</sub>(PRPh<sub>2</sub>)<sub>2</sub>/MAO system;[10] a similar breakthrough was recently achieved by Gong et al., in which aminophophine fused bipyridine Co(II) complexes were reported as effective catalytic precursor for precise synthesis of cis-1,4-alt-3,4- PIs.[11] Besides the above chelating ligands, imine-based ligands were also another important type of skeletons to support late transition metal for selective polymerization of 1,3-dienes because of the ease manipulation and regulation of imine moiety.<sup>[12]</sup> However, different from the high catalytic activity and high cis-1,4selectivity displayed in 1,3-butadiene polymerization, the iminebased late transition metal complexes demonstrated some challenges in mediating isoprene polymerization, such as lower catalytic activities, formation of insoluble gels,<sup>[13]</sup> etc., therefore, up to date, the examples of imine-based late transition metal in catalyzing isoprene polymerization are very limited,[13-14] and exploring new catalyzing systems with high activity and meanwhile the ability to afford *cis*-1,4-/3,4- PI is an obviously challenging and promising project.

We have been engaged in exploring highly efficient catalytic precursors for stereoselective polymerization of 1,3-dienes using imine-based late transition metal complexes.<sup>[15]</sup> Our previous research has demonstrated some effective methods to improve the catalytic performance of catalyst system,<sup>[16]</sup> such as enhancing the eletrophilicity of the cationic metal centre, increasing the coordination sphere, *etc.*, we also found that addition of external donors was able to shift the selectivity from 1,4- to vinyl manner in diene polymerization.<sup>[17]</sup> Therefore, as an extension of our continuous research, in the present study, we disclose that a new family of pyrazolylimine Co(II) complexes exhibit high activity in catalyzing isoprene polymerization to afford *cis*-1,4-/3,4- PI products. Additionally, external phosphine

donors are able to act as an efficient agent in regulating the 3,4-moieties.



Scheme 1. Synthesis of complexes 3a - 3e.

#### **Results and Discussion**

# Synthesis and characterization of the ligands and corresponding cobalt(II) complexes

Ligands 2a-2e were prepared in high yields from reacting imidoylchloride and substituted pyrazole under refluxing conditions. The corresponding cobalt complexes were obtained by treating ligands 2a-2e with stoichiometric amounts of anhydrous CoCl<sub>2</sub> in dry THF, and subsequently being precipitated by Et<sub>2</sub>O (Scheme 1). The ligands and complexes were thoroughly characterized by NMR, FT-IR, and elemental analysis. In the FT-IR spectra, the absorption bands of the imine C=N moieties in ligands 2a-2e appear at 1650-1661 cm<sup>-1</sup>, which are obviously blue shifted in comparison with the corresponding absorption band of C=N in complexes **3a-3e** (1610 -1637 cm<sup>-1</sup>), indicating the formation of coordination bond between imine nitrogen atom and metal center. The structures of ligand 2d, complexes **3a**, **3d**, **3e** were further characterized by single X-ray crystallographic studies. The selected bond lengths and angles are summarized in Table S1-S4 (supporting information), and the molecular structures are depicted in Figures 1-3.



Figure 1. ORTEP view of ligand 2d, drawn at 35% of probability. Hydrogen atoms were omitted for clarity.

Single crystal of ligand **2d** was obtained by recrystallization from its hexane solution. As shown in Figure 1, it exhibits *E* 

conformation with typical imino C=N double bond distance of 1.273(2) Å. The aryl ring is approximately orthogonal to the pyrazol plane with a dihedral angle of  $87.26^{\circ}$ . The N(2)–C(7) bond is flexible and could be freely-rotating to meet the bidentate geometry in the presence of metal salts.



Figure 2. ORTEP view of complex 3a, drawn at 35% of probability. Hydrogen atoms and dichloromethane molecule were omitted for clarity.

Single crystal of **3a** was obtained by slow diffusion of diethyl ether into its  $CH_2Cl_2$  saturated solution, and the structure is shown in Figure 2. Complex **3a** was found to be a centrosymmetric dimer with slightly distorted trigonal bipyramid geometries at the each cobalt center, in which the equatorial plane contains Cl(1), Cl(2), and N(1), while N(3) and Cl(2A) occupied the axial positions. The two cobalt atoms are symmetrically bridged by the two chlorine atoms (Cl(1) and Cl(2A)), as evidenced by intramolecular distance of 3.600 Å, which were slightly shorter than the values observed in its Ni(II) analogues.<sup>[18]</sup> The iminophenyl ring is nearly perpendicular to the pyrazol ring, with a dihedral angle of 82.06°.



Figure 3. ORTEP view of complex 3d, drawn at 35% of probability. Hydrogen atoms and dichloromethane molecule were omitted for clarity.



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Figure 4. ORTEP view of complex 3e, drawn at 35% of probability. Hydrogen atoms were omitted for clarity.

Single crystals of **3d** and **3e** were obtained by slow diffusion of diethyl ether into its  $CH_2Cl_2$  solution, and as the structures shown in Figures 3 and 4, both of them display similar structures at the metal centres, the coordination geometries can be best described as distorted tetrahedral which were built up by two chlorine atoms and two nitrogen atoms. The planes formed by Cl(1)-Co(1)-Cl(2) and N(1)-Co(1)-N(3) are nearly perpendicular, and the angles of 76.52° and 79.11° respectively. The aryl rings are approximately perpendicular to the pyrazol planes and the dihedral angles are 85.40 and 85.69°.

#### **Isoprene polymerizations**

Complexes **3a-3e** activated by different aluminum compounds for isoprene polymerization were examined, and the results are summarized in Tables 1-3.

Table 1. Isoprene polymerization under different conditions using 3c. [a]									
			T (°C)		<i>M</i> ∩* 10⁻⁴		Microstructure		
Run	AI	Al/Co		Yield (%)		<i>M</i> w <sup>/</sup> <i>M</i> n [b]	<i>Ci</i> s- 1,4 (%) <sup>[c]</sup>	3,4 (%) <sup>[c]</sup>	
1	DEAC	50	30	97.7	14.5	2.6	65.1	34.9	
2	EASC	50	30	100	13.8	3.2	72.7	27.3	
3	MAO	100	30	10.5	9.3	2.7	82.6	17.4	
4	TIBA	50	30	trace	nd	nd	nd	nd	
5	TEA	50	30	trace	nd	nd	nd	nd	
6	DEAC	20	30	93.7	17.9	2.8	65.2	34.8	
7	DEAC	100	30	96.5	14.8	2.2	68.9	31.1	
8	DEAC	200	30	86.2	15.2	2.0	69.3	30.7	
9	DEAC	50	0	25.9	7.3	1.4	67.7	32.3	
10	DEAC	50	50	100	15.0	3.3	62.0	38.0	
11	DEAC	50	70	100	14.5	3.6	60.3	39.7	

[a] Polymerization conditions: precatalyst 7.35 µmol, isoprene 14.7 mmol, toluene 20 mL, 3h. [b] Obtained by GPC, THF was used as eluent and polystyrene was used as internal standard. [c] The microstructure was determined by NMR and FT-IR.

The polymerization parameters were firstly investigated in order to obtain the optimized conditions, and complex **3c** was selected as a representative precatalyst. As the results shown in Table 1, the typre of cocatalyst displayed significant influence on the isoprene polymerizations. Aluminum chloride copounds were efficient cocatalysts in promoting the polymerization process, affording polyisorenes in high yields, nearly quantitative conversions were obtained in the circumstance of diethylaluminum chloride (DEAC) and ethylaluminum sesquichloride (EASC), which showed much difference to our previously investigated imine based cobalt complexes that bearly displayed no activitity in isoprene polymerization. By contrast, methylaluminoxane (MAO), triethyl aluminum (TEA), and triisobutylaluminum (TIBA)-based systems gave polymers in quite low yields. The systems based on chloroaluminum cocatalysts afforded cis-1,4/3,4- polyisoprenes. It was satifying to find that no crosslinking gels were fromed during the polymerization process, which indicats the homogeneous singlesite active center across polymerization process. The effect of cocatalyst loadings were also inverstigated in our subsequent studies, and obvious decreasing polymer yields were observed when increasing the amount of cocatalysts, probably due to the overreducation of the active center.

The influence of polymerization temperature on the catalytic performance was further investigated with 3c/DEAC system. Significant increment of activity was observed when increasing the temperature from 0 °C to 70 °C, and almost quantatiive conversion were obtained at temperature above 30 °C. Besides, it was suprisingly found that this system exhibited high thermostability, no decay of the polymerizaiton yields was observed at high temperatures. This is different from most of the previously reported late transition metal complexes, which suffers from decay of active species at elevated temperatures. On the other hand, increasing the temperature resulted in continuous broadening of the molecular weight distribution, indicating the occurrence of rapid chain transfer at high temperatures. Meanwhile, the 3,4- content increased from 32.3% to 39.7% along with the cis-1,4- content decreased from 67.7% to 60.3% when elevating the tempearture (Figure 5), which was attributable to the facilitation of anti-syn isomerization through  $\pi$ - $\sigma$  rearrangement at elevated temperatures. As the active species proposed in Scheme 2, the terminal  $\pi$ -allylic unit of the polybutadienyl chain could be coordianted to the cobalt center in the anti- or syn- conformation, the anti- conformation is generated from  $cis-\eta^4$  coordinated isoprene which gives rise to cis-1,4 and 3,4- polymerization, while the syn- conformation is derived from *trans*- $\eta^4$  or  $\eta^2$  coordianted monomer, giving corresponding trans-1,4- and 3,4- enchainment. At a lower tempeature, the anti- isomer is more kinetically favored due to the presence of  $\pi$ -back-bonding, which subsequently produce cis-1,4/3,4- polymers. The predominance of cis-1,4- vs. 3,4- unit is probably ascribed to the lower insertion energy at C1 of the polybutadienyl end. With increasing the temperature, anti-syn isomerization is gradually facilitated owing to the reason that the syn- isomer is more thermodynamically stable, thus leading to an increment of 3,4- contents (path 4).



**Scheme 2**. The proposed enchainment manner for cobalt active species.



Figure 5. The influence of temperature on the microstructure of the resultant polyisoprenes.

In order to understand the influence of ligand structure on the catalytic performances, cobalt complexes bearing different ligand skeletons were employed for isoprene polymerization. Complexes **3a**, **3c**, and **3d** with Me/H, iPr/H, and iPr/Me on the pyrazoyl ring displayed very high activities, affording polyisoprenes in 88.8%, 97.7%, and 96.4% yields, respectively. 3,5-Dimethyl substituted complex **3b** displayed relatively low activity (64.3%), probably due to the increased steric hindrance on the 3,5-position of the pyrazoyl ring, which gave a small spanned angle for monomer coordination (Figure 6). Similarly, the more steric congested 3,5-diphenyl substituted complex **3e** displayed the lowest activity, giving only 20.6% yield under identical conditions. It is worthy to note that the ligand

1,4/3,4- products with 3,4-contents ranging from 33.8% to 39.2%.

Table 2. Isoprene polymerization by different catalysts. [a]									
Run	Cat.	Yield	Mn*	<i>M</i> <sub>w</sub> ∕ <i>M</i> n	Microstructure [c]				
		(%)	10-4	[b]	Cis-1,4 (%)	3,4(%)			
12	3a	88.8	13.8	2.2	65.4	34.6			
13	3b	64.3	8.3	2.3	63.8	36.2			
14	3c	97.7	14.5	2.6	65.1	34.9			
15	3d	96.4	14.4	2.6	60.8	39.2			
16	3e	20.6	6.9	2.2	66.2	33.8			

[a] Polymerization conditions: precatalyst 7.35 μmol, DEAC/Co = 50, isoprene 14.7 mmol, toluene 20 mL, 3h. [b] Obtained by GPC, THF was used as eluent and polystyrene was used as internal standard. [c]The microstructure was determined by NMR and FT-IR.



Figure 6. Proposed monomeric cobalt active species for isoprene polymerization. (P stands for polybutadienyl chain).

It is known that addition of external pyridine or phosphine containing electron donors to cobalt mediated diene polymerization systems were able to shift the stereoselectivty from 1,4- to 1,2- (3,4-) manner. Therefore, in order to regulate the 3,4- contents of the resulting polyisoprene products in a larger scope, triphenylphosphine (PPh<sub>3</sub>) as an external donor was introduced into the present systems. As seen from Table 3, with 3c as precatalyst, the amount of PPh<sub>3</sub> showed little influence on the selectivity of the 3c/DEAC system. By contrast, the MAO-based system, increasing PPh<sub>3</sub> from 0 to 4.0 equvalents led to the increase in the 3,4- content from 17.4% to 67.8%, and the polymer yield increased simultaniously. In the <sup>1</sup>H NMR spectra (Figure 7), the 3,4-content of the polymer obtained in the presence of PPh<sub>3</sub> is much higher than that with PPh<sub>3</sub>-free system. The increment of 3,4- units also resulted in the glass transition temperature of the resulting polyisoprene,  $T_g$  increased from -41.49 °C to -15.45 °C when the 3,4-content increased form 17.4% to 67.8%. No melting point was detected for this high 3,4polyisoprene, indicating that the polymer is amorphous (Figure 8).

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Figure 7. <sup>1</sup>H NMR spectra obtained in the presence/absence of PPh<sub>3</sub> for 3c/MAO system (runs 21 to 27).

Run	AI	A1/Q-	5/0	\/:-1-1 (0/ )	11 * 10-1	44 /44 [b]	Microstr	T <sub>q</sub> (°C)	
		AI/Co	P/C0	rieid (%)	<i>M</i> n <sup>*</sup> 10 <sup>+</sup>	IVI <sub>w</sub> IVI <sub>n</sub> [5]	Cis-1,4 (%) <sup>[c]</sup>	3,4- (%) <sup>[c]</sup>	[d]
17	DEAC	50	-	97.7	14.5	2.6	65.1	34.9	-36.43
18	DEAC	50	1.0	98.2	17.9	4.7	64.5	35.5	-35.37
19	DEAC	50	4.0	56.6	10.9	2.0	55.7	44.3	-32.85
20	DEAC	100	4.0	98.5	25.1	2.3	61.3	38.7	-34.70
21	MAO	100	-	10.5	9.3	2.7	82.6	17.4	-41.49
22	MAO	100	0.1	23.1	12.5	2.8	62.4	37.6	-35.60
23	MAO	100	0.2	34.3	13.2	2.4	46.5	53.5	-27.29
24	MAO	100	0.5	52.6	16.1	2.0	39.3	60.7	-21.83
25	MAO	100	1.0	61.8	13.5	1.9	37.9	62.1	-17.80
26	MAO	100	2.0	88.4	14.8	1.9	35.6	64.4	n.d.
27	MAO	100	4.0	92.5	16.4	2.0	32.2	67.8	-15.45

Table 3. Isoprene polymerization by complex 3c in the presence of external phosphine donors. [a]

[a] Polymerization conditions: precatalyst 7.35 µmol, isoprene 14.7 mmol, toluene 20 mL, 3h. [b] Obtained by GPC, THF was used as eluent and polystyrene was used as internal standard. [c] The microstructure was determined by NMR and FT-IR. [d] n.d. is for not determined.

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Figure 8. The increasing of glass transition temperature caused by the increased 3,4- units.

Since 3,4-polyisoprene and 1,2-polybutadiene are promising candidates for production of high performance tire, isoprene/1,3butadiene copolymerization was carried out by using 3c/EASC system, and the detailed results are shown in Table 4. The copolymerizations proceed smoothly to give the copolymers in high yields, regardless of the comonomer feed ratio. The GPC curves of the resulting copolymers are monodisperse, indicating the sucessful formation of copolymer rather than blends of homopolymers. With increasing the feed ratio of [IP]/[BD], a monotonous increase of the IP cotent in the copolymer was observed. Moreover, the copolymer composition practically coincided with the comonomer composition, suggesting that both the monomers have similar reactivity ratios in the copolymerization (Figure 9). The 1,2-content of the 1,3butadiene in the copolymer increased from 2.2% to 32.5% with increasing isoprene loading level, and increasing polymerization temperature also resulted the increase in 1,2-content, while the comonomer feed ratio and reaction temperature hardly influnced the structure of isoprene unit, the 3,4-content stayed around 10%. Similar to the case of isoprene homopolymerization, the addition of PPh<sub>3</sub> led to the increases of 3,4-content of the isoprene unit and 1,2-content of 1,3-butadiene unit in the copolymer as well as the polymer yield.

#### Conclusions

Five pyrazolyimine cobalt dichloride complexes were prepared and well-charactetrized herein. These complexes activated by aluminum chlordie compounds and methylaluminoxane exhibited high activities in isoprene polymerization, affording *cis*-1,4 rich polyisoprene. The selectivities of the complexes could be regulated by incoporation of external donor; the addition of PPh<sub>3</sub> into the MAO-system resulted in the production of polyisoprene with 3,4-content up to 67.8%. The 3,4-content of the resulting were dependent on polymerization parameters, including cocatalyst loading, temperatures, *etc.* In the presence of DEAC, **3c** copolymerized isoprenene and 1,3-butadiene to give the copolymer with 1,4-rich structure in high yields. Moreover, the **3c**/MAO/PPh<sub>3</sub> system produced 1,3butadiene/isoprene copolymer with 1,2-content of 78.1% and 3,4-content of 57.6% for butadiene and isoprene units, respectively. Since 1,2-polybutadiene and 3,4-polyisoprene have great potential for production of high performance tire with good wet-skid and rolling resistence, the newly sythesized 3,4-polyisoprene as well as the copolymer with both 1,2 and 3,4-contents may exhibit interesting properties for tire manufacture materials.

#### **Experimental section**

#### **General considerations**

All manipulations of air and/or moisture sensitive compounds were carried out under a dry and oxygen-free argon atmosphere by using Schlenk techniques or under a nitrogen atmosphere in a glovebox. The solvents were refluxed over CaH<sub>2</sub> orsodiumbenzophenone and distilled prior to use. Isoprene monomer was obtained from Lanzhou Petrochemical Company and purified by distillation from CaH<sub>2</sub> and stored at low temperature. Other chemicals were commercially available and used without further purification.

<sup>1</sup>H NMR(400 MHz) and <sup>13</sup>C NMR (100 MHz) were recorded on a VarianUnity spectrometer in CDCl<sub>3</sub> at ambient temperature using tetramethylsilane as an internal standard. FTIR spectra were recorded using a BRUKER Vertex-70 FTIR spectrometer. Elemental analysis was performedusing an elemental Vario EL spectrophotometer. The proportion of microstructures of the polyisoprene products was determined by FTIR spectra, <sup>1</sup>H NMR and <sup>13</sup>C NMR. Melting points of the ligands were determined on a TECH X-4 micro-melting point apparatus. The number-average molecularweights  $(M_n)$  and molecular weight distributions  $(M_w/M_n)$  of polymers were measured at 30 °C by gel permeationchromatography (GPC) equipped with a Waters 515 HPLC pump, four columns (HMW 7 THF, HMW 6E THF x 2, HMW 2THF), and a Waters 2414 refractive index detector. Tetrahydrofuran was used as the eluent at a flow rate of 1.0 mL min<sup>-1</sup> against polystyrene as the calibration.

#### Preparation and characterization of ligands and complexes

All the pyrazolylimine ligand the corresponding chelated cobalt(II) complexes were prepared in the same manner, a typical example of synthesis of ligand **2a** and complex **3a** is described as follows:

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				Microstructure <sup>[c]</sup>							
I Run f (	IP in feed (mol%)	T (°C)	Yield (%)	IP (mol%)	<i>M</i> n	M <sub>w</sub> /M <sub>n</sub>	BD		IP		<i>T</i> g (°C) <sup>[e]</sup>
				(110170)	X IU II		1,4(%)	1,2(%)	1,4(%)	3,4(%)	
28	0	30	94.5	0	6.4	2.8	97.8	2.2	- A-		n.d.
29	10	30	97.1	9.2	3.6	2.9	86.0	14.0	90.7	9.3	-91.18
30	20	30	96.0	17.1	5.5	3.0	79.9	20.1	89.4	10.6	-85.99
31	30	30	95.4	25.9	4.0	3.5	76.8	23.2	90.1	9.9	-80.47
32	50	30	92.3	44.6	4.3	3.2.	67.5	32.5	85.1	14.9	-68.57
33	10	0	90.7	8.3	3.0	2.6	90.5	9.5	89.7	10.3	n.d.
34	10	50	98.9	9.4	21.3	2.5	81.3	18.7	88.2	11.8	n.d.
35 <sup>[d]</sup>	50	30	82.3	44.3	15.2	2.8	67.2	32.8	85.6	14.4	n.d.
36 <sup>[d]</sup>	50	30	92.3	40.5	9.2	2.9	21.9	78.1	42.4	57.6	-21.28

[a] Polymerization conditions: precatalyst 9  $\mu$ mol, monomer (BD+IP) 18 mmol, toluene 20 mL, DEAC/Co = 50, 3h. [b] Obtained by GPC, THF was used as eluent and polystyrene was used as internal standard. [c] The microstructure was determined by NMR and FT-IR. [d] MAO was used as cocatalyst, MAO/Co = 50, PPh<sub>3</sub>/Co = 1.0 for run 36. [e] n.d. is for not determined.



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For synthesis of ligand 1a, to a solution of 2,6-dimethylaniline (3.2 g, 26.4 mmol) in THF (50 mL) and triethylamine (4.2 mL, 30 mmol) were added dropwise benzoyl chloride (24 mmol). The reaction mixture was stirred overnight at ambient temperature. After the filtration of (C<sub>2</sub>H<sub>5</sub>)<sub>3</sub>N·HCl and evaporated of THF under reduced pressure, the residue solid was washed with water several times and dried under vacuum at 40 °C. Finally, the white solid amide product was obtained and used directly in the next procedure. The thionyl chloride (1 mL, 13.3 mmol) was added to the amide (2 g, 8.9 mmol), then, the reaction mixture was heated to reflux 3 h. The remaining unreacted thionyl chloride was removed by distillation under reduced pressure to afford 1a, which was directly used for the next step. Toluene (50 mL), triethylamine (1.5 mL, 10.8 mmol) and pyrazole (0.61 g, 8.9 mmol) were added to the reaction mixture, then the mixture was heated to reflux for 6 h. The (C<sub>2</sub>H<sub>5</sub>)<sub>3</sub>N·HCl was removed through filtration, toluene was distilled under reduced pressure, and the residue was recrystallized from hexane, the ligand 2a as light yellow crystal in 21.6% yield (0.53 g) was obtained. M.p. 98-99 °C. <sup>1</sup>H NMR(400 MHz, DMSO, δ, ppm): δ: 8.68 (s,1H, Pz-H); 7.74 (s,1H, Pz-H); 7.36~6.78 (m, 10H, Ar-H), 1.99 (s,6H, Ar-CH<sub>3</sub>). <sup>13</sup>C NMR (100 MHz, DMSO, δ, ppm):152.3, 142.4, 131.1, 129.5, 129.2, 127.7, 126.2, 123.1, 18.1. FT-IR (KBr; cm<sup>-1</sup>): 3066, 3014, 2970, 1660, 1588, 1558, 1493, 1444, 1416, 1386, 1346, 1238, 1193, 1181, 916, 903, 868, 783, 764, 693. Anal. calc. for C<sub>18</sub>H<sub>17</sub>N<sub>3</sub>: C, 78.52; H, 6.22; N, 15.26. Found: C, 78.34; H, 6.26; N, 15.4. MS (APCI, m/z): calcd. 275.1422; found 298.1320 (M+Na)<sup>+</sup>.

For synthesis of complex **3a**, a solution of **2a** (0.2 g, 0.73 mmol) in 3 mL THF was added dropwise to a suspension of anhydrous CoCl<sub>2</sub> (0.094 g, 0.73 mmol) in 3 mL THF, the reaction solution was stirred for 4 h, a blue suspension was obtained. The resultant reaction solution was concentrated and diethyl ether was added to precipitate the complex. The resultant precipitate was filtered, subsequently washed with diethyl ether and dried in vacuum at 40 °C overnight, finally, a blue powder **3a** was obtained in 82.3% yield. Single crystals for X-ray analysis grew from *n*-hexane and dichloromethane mixed solution. FTIR (KBr; cm<sup>-1</sup>): 2974, 1616, 1560, 1531, 1489, 1445, 1396, 1358, 1317, 1206, 1164, 1097, 1058, 1001, 944, 913, 881, 784, 756, 703. Anal. calc. for C<sub>18</sub>H<sub>17</sub>N<sub>3</sub>Cl<sub>2</sub>Co: C, 53.36; H, 4.23; N, 10.37. Found: C, 53.21; H, 4.16; N, 10.26.

For synthesis of ligand **2b**, a procedure similar to **2a** was adopted. Yield, 0.41 g (55.2 %). M.p. 72-73 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>,  $\delta$ , ppm): 7.29~7.12 (m, 5H, Ar-H); 6.91~6.82 (m, 3H, Ar-H); 6.05 (s,1H,Pz-H); 2.62 (s, 3H, Pz-CH<sub>3</sub>); 2.22 (s, 3H, Pz-CH<sub>3</sub>); 2.06 (s, 6H, Ar-CH<sub>3</sub>). <sup>13</sup>C NMR (100 MHz, DMSO,  $\delta$ , ppm):153.28, 148.54, 145.24, 142.48, 131.18, 129.60, 128.28, 127.36, 125.58, 122.66, 109.4, 18.07, 14.18, 13.10. FTIR (KBr; cm<sup>-1</sup>): 3099, 2965, 2920, 1661, 1593, 1567, 1492, 1466, 1379, 1355, 1260, 1162, 1128, 1091, 1025, 982, 915, 841, 792, 776, 769, 752, 698. Anal. calc. for C<sub>20</sub>H<sub>21</sub>N<sub>3</sub>: C, 79.17; H, 6.98; N, 13.85. Found: C, 79.12; H, 7.21; N, 13.67. MS (APCI, m/z): calcd. 303.1735; found 326.1616 (M+Na) \*.

For synthesis of ligand **2c**, a procedure similar to **2a** was adopted. Yield, 25.2%. M.p. 103-104 °C. <sup>1</sup>H NMR (400 MHz,DMSO,  $\delta$ , ppm): 8.61 (s,1H,Pz-H); 7.76 (s,1H,Pz-H); 7.64~6.98 (m, 8H,Ar-H); 6.63 (s,1H,Pz-H); 2.84 (s, 2H,*i*Pr-H); 1.06~0.89 (d, 12H,*i*Pr-CH<sub>3</sub>). <sup>13</sup>C NMR (100 MHz, CDCl3,  $\delta$ , ppm):142.33, 136.18, 131.38, 130.06, 129.40, 127.57, 123.98, 122.85, 108.60, 27.89, 23.75, 21.66. FTIR (KBr; cm<sup>-1</sup>): 3063, 2959, 2867, 1660, 1558, 1523, 1492, 1458, 1384, , 1257, 1241, 1184, 1162, 1040, 936, 913,864, 842,797, 773, 757, 694.Anal. calc. for C<sub>22</sub>H<sub>25</sub>N<sub>3</sub>: C, 79.72; H, 7.6; N, 12.68. Found: C, 79.68; H, 7.61; N, 12.68. MS (APCI, m/z): calcd. 331.2048; found 354.1928 (M+Na) \*.

For synthesis of ligand **2d**, a procedure similar to **2a** was adopted. Yield, 60.1%. M.p. 94-95 °C. <sup>1</sup>H NMR (400 MHz,DMSO, $\delta$ , ppm): 7.28~6.99 (m, 8H, Ar-H); 6.18 (s,1H,Pz-H); 3.24 (s,3H,Pz-CH<sub>3</sub>); 2.89 (m,2H,/Pr-H); 2.09 (s, 3H,Pz-CH<sub>3</sub>); 1.07~0.89 (d,12H,/Pr-CH<sub>3</sub>). <sup>13</sup>C NMR (100 MHz, DMSO,  $\delta$ , ppm):152.40, 145.93, 142.26, 135.64, 129.57, 128.93, 127.36, 123.56, 122.61, 109.16, 27.63, 23.87, 21.40, 13.11. FTIR (KBr; cm<sup>-1</sup>): 3058, 3034, 2961, 2867, 1653, 1598, 1567, 1490, 1444, 1406, 1379, 1321, 1273,1184, 1108,1078,1021, 966, 913, 834, 775, 752, 696.Anal. calc. for C<sub>24</sub>H<sub>29</sub>N<sub>3</sub>: C, 80.18; H, 8.13; N, 11.69. Found: C, 80.01; H, 8.18; N, 11.81. MS (APCI, m/z): calcd. 359.2361; found 382.2240 (M+Na)<sup>+</sup>.

For synthesis of ligand **2e**, a procedure similar to **2a** was adopted. M.p. 147-148 °C. <sup>1</sup>H NMR (400 MHz,DMSO, $\delta$ , ppm): 7.8~6.94 (m, 18H, Ar-H); 2.73 (m, 2H ,/Pr-H); 1.23~0.73 (m, 12H,/Pr-CH<sub>3</sub>). <sup>13</sup>C NMR (100 MHz, DMSO,  $\delta$ , ppm):151.01, 146.14, 135.68, 128.76, 128.43, 127.44, 125.59, 125.06, 124.03, 122.88, 28.13, 23.24, 21.96. FTIR (KBr; cm<sup>-1</sup>): 3067, 2971,1650, 1597, 1556, 1483, 1460, 1400, 1350, 1306, 1281, 1207, 1173, 1113, 1043, 999, 941, 917, 843, 804,755, 727,699. Anal. calc. for C<sub>34</sub>H<sub>33</sub>N<sub>3</sub>: C, 84.43; H, 6.88; N, 8.69. Found: C, 84.39; H, 7.01; N, 8.58. MS (APCI, m/z): calcd. 483.2674; found 506.2572 (M+Na)<sup>+</sup>.

For synthesis of complex **3b**, a procedure similiar to **3a** was adopted using **2b** and CoCl<sub>2</sub>, which gave **3b** as a bluish violet powder in 77.9% yield. FTIR (KBr; cm<sup>-1</sup>): 3109, 2956, 2924, 1611, 1589, 1567, 1494, 1459, 1385, 1258, 1212, 1173, 1159, 1114, 986, 918, 838, 797, 780, 744, 704.Anal. calc. for  $C_{20}H_{21}N_3Cl_2Co$ : C, 55.45; H, 4.89; N, 9.7. Found: C, 55.29; H, 4.82; N, 9.58.

For synthesis of complex **3c**, a procedure similiar to **3a** was adopted using **2c** and CoCl<sub>2</sub>, which gave **3c** as a green powder in 71.2% yield. FTIR (KBr; cm<sup>-1</sup>): 2966, 2929, 2867, 1617, 1559, 1528, 1508, 1492, 1459, 1420, 1387, 1356, 1325, 1202, 1160, 1098, 1079, 1058, 995, 942, 913, 902, 779, 759, 696.Anal. calc. for  $C_{22}H_{25}N_3Cl_2Co$ : C, 57.28; H, 5.46; N, 9.11. Found: C, 57.23; H, 5.39; N, 9.01.

For synthesis of complex **3d**, a procedure similiar to **2a** was adopted using **2d** and  $CoCl_2$ , which gave **3d** as a bluish violet powder in 80.1% yield. FTIR (KBr; cm<sup>-1</sup>): 2982, 2964, 2928,

For synthesis of complex **3e**, a procedure similiar to **2a** was adopted using **2e** and CoCl<sub>2</sub>, which gave **4e** as a green powder in 65.8% yield. FTIR (KBr; cm<sup>-1</sup>): 2961, 2865, 1636, 1604, 1596, 1576, 1552, 1509, 1488, 1463, 1434, 1411, 1385, 1345, 1327, 1307, 1241, 1206, 1176, 1098, 1071, 1028, 1011, 965, 957, 933, 833, 783, 760, 691.Anal. calc. for  $C_{34}H_{33}N_3Cl_2Co$ : C, 66.56; H, 5.42; N, 6.85. Found: C, 66.33; H, 5.28; N, 6.69.

#### The general procedure for isoprene polymerization

A typical procedure for the polymerization is as follows: a toluene (20 mL) solution of isoprene (14.7 mmol) was added to a moisture free ampule bottle preloadedwith complex **3c** (4.3 mg, 0.009 mmol), then DEAC (0.46 mmol) was injected to initiate the polymerizationat 20 °C. After 3 h, methanol was added to the system toquench the polymerization. The mixture was poured into alarge quantity of methanol containing 2,6-di-*tert*-butyl-4-methylphenol (1.0 wt%) as a stabilizer. Filtered and driedunder vacuum at 40 °C, polyisoprene was resulted at a constant weight.

#### X-ray crystallographic studies

Crystals for X-ray analyses were obtained as described in the Experimental section. Data collections were performed at lowor room temperature on a Bruker SMART APEX diffractometer with a CCD area detector using graphite monochromated MoK radiation ( $\lambda = 0.71073$  Å). The determination of crystal class and unit cell parameters was carried out using the SMART program package. The raw frame data were processed using SAINT and SADABS to yield the reflection data file. The structures were solved using the SHELXTL program. Refinement was performed on F2 anisotropically for all non-hydrogenatoms by the fullmatrix least-squares method. The hydrogenatoms were placed at the calculated positions and were included in the structure calculation without further refinement of the parameters. Details of X-ray structure determinations and refinements are provided in Table S1 in the ESI. CCDC number for 2d, 3a, 3d and 3e are 1866572-1866575.

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# **FULL PAPER**

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### Co = Co/EASC ols-1,4/3,4- binary High activities and tunable 3,4-moieties

Pyrazolyimine cobalt dichloride complexes displayed high activities in isoprene polymerization, affording polymer prodcuct with cis-1,4-/3,4- structures, which is of high importance from practical industrial applications.

\*one or two words that highlight the emphasis of the paper or the field of the study

#### Polymerization catalysts\*

Liang Fang,<sup>#</sup> Wenpeng Zhao,<sup>#</sup> Chao Han, Heng Liu,\* Yanming Hu,\* Xuequan Zhang\*

#### Page No. - Page No.

**Isoprene Polymerization with** Pyrazolylimine Cobalt (II) Complexes: Manipulation 3,4-Selectivities by Ligand Design and Triphenyl Phosphine

