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# Synthesis of cationic cobalt(II) complexes and their efficiency as catalysts for the polymerization of 1,3-butadiene

Li Liu [a,b], Xu Zhang [a,b], Heng Liu [b], Xuequan Zhang [b], Guangping Sun [a,*], Hexin Zhang [b,*]

[a] Materials Science and Engineering, Jilin University, Changchun 130022, PR China
[b] Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Changchun 130022, PR China

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ABSTRACT [1]

A series of novel cationic cobalt(II) compounds accompanied by various counter ions ($[BF_4]^-$, $[PF_6]^-$, $[SbF_6]^-$) and N-bearing ligands (1,10-phenanthroline, bipyridine, benzimidazole, and imidazole) were synthesized. Neutral compounds, $CoCl_2$-nLigands, were prepared as reference compounds. All the compounds were characterized using IR spectral analysis and elemental analysis and some of the compounds were further characterized by single-crystal X-ray diffraction analysis. The synthesized compounds were evaluated as precursors for butadiene polymerization in conjunction with ethylaluminum sesquichloride as a cocatalyst, and the polymerization mechanism was proposed to involve anionic coordination polymerization. The active centers of the catalysts were cationic in nature, and the catalytic activities were affected by the electronegativity of the counter ion.

## 1. Introduction

Regio- and/or stereo-selective polybutadiene have been extensively and diversely applied throughout the rubber industry since the discovery of Ziegler–Natta-type catalyst systems [1–9]. Hence, investigation of butadiene polymerization, structures of catalyst precursors and catalyst-polymer correlations has served as a fascinating and challenging subject over the past decades and has promoted studies of catalyst design and catalysis mechanisms. Recently, late transition metal catalysts have initiated a completely new catalytic domain and have attracted a significant amount of interest due to their simple synthesis, stability and negligible environmental impact [10–21]. However, some late transition metal catalysts suffer from low activity, comparatively low *cis*-1,4 selectivity, and uncertain catalytic mechanism. Therefore, efficient catalysts that can produce polybutadiene with a high *cis*-1,4 content are highly desirable.

Metallocenes are known to show much higher catalytic activity toward olefin polymerization as compared to the Zielger–Natta catalyst [22–24]. A plausible explanation for this difference is the formation of a cationic active metal center in the metallocene catalyst activated with methylaluminoxane or borates [25–29], which increases the coordination and insertion rates of the olefin monomer during the polymerization process. In our previous research [30], a titanium-based Ziegler–Natta catalyst with a cationic active metal center was prepared via modification of the commercial Ziegler–Natta catalyst, and the catalytic activity was found to drastically increased after the modification.

Herein, we report for the first time, highly active cationic cobalt(II) catalysts. The effects of the catalyst structure (e.g., counter ions, ligands) and reaction conditions on the polymerization were studied. Furthermore, a plausible catalysis mechanism was put forward to explain the differences between the traditional and cationic cobalt(II) catalysts.

## 2. Experimental

### 2.1. Materials and methods

Cobalt carbonate ($CoCO_3$), tetrafluoroboric acid ($HBF_4$), hexafluorophosphoric acid (HPF6), and fluoroantimonic acid ($HSbF_6$) were purchased from Alfa Aesar, China. 1,10-phenanthroline (Phen), bipyridine (Bipy), benzimidazole (BZI), and imidazole (Im) were supplied by J&K, China. Ethylaluminum sesquichloride (EASC) was purchased from Akzo Nobel, USA. Polymerization-grade butadiene was supplied by Jinzhou Petrochemical Corporation and purified by passing through four columns packed with molecular sieves and solid potassium hydroxide. Toluene was distilled by heating to reflux in the presence of sodium and benzophenone. Other chemicals were used as received. Infrared (IR) spectra were

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* Corresponding authors. Tel.: +86 431 85262889; fax: +86 431 85262274 (H.X. Zhang).

*E-mail addresses:* sungp@jlu.edu.cn (G. Sun), polyhx@ciac.ac.cn (H. Zhang).

[1] Phen, 1,10-phenanthroline; Bipy, bipyridine; BZI, benzimidazole; Im, imidazole; EASC, ethylaluminum sesquichloride; GPC, gel permeation chromatography.

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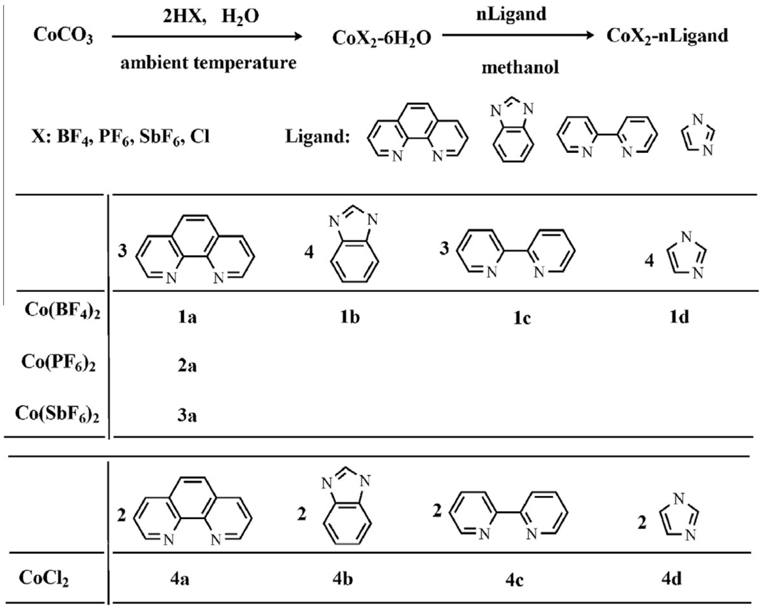
obtained on a Bruker Vertex-70 FT-IR spectrophotometer. The weight-average molecular weights ($M_w$) and polydispersity ($M_w/M_n$) of the resulting polymers were measured at 30 °C by gel permeation chromatography (GPC), using a chromatographic system equipped with a Waters 515 HPLC pump, four columns, and a Waters 2414 refractive index detector. THF was used as the eluent at a flow rate of 1.0 mL/min. Crystals for X-ray diffraction were obtained as described in the Results and discussion section. Data collection for compound **1b** was perfromed at 22 °C, and data for the other compounds were collected at −88.5 °C on a Bruker SMART APEX diffractometer with a CCD area detector. Determination of the crystal class and unit cell parameters was carried out using the SMART program package. The raw frame data were processed by SAINT and SADABS to yield the reflection data file. The structures were determined using the SHELXTL program. Refinement was performed on $F^2$ anisotropically for all non-hydrogen atoms by the full-matrix least-squares method.

### 2.2. Syntheses and characterization of compounds

A general synthetic route to cobalt(II) compounds is shown in Scheme 1. The typical synthetic procedure for **1a** is as follows: Cobalt(II) tetrafluoroborate hexahydrate (0.5 g, 1.47 mmol), prepared by mixing excess $CoCO_3$ with $HBF_4$ in $H_2O$ at ambient temperature, was mixed with Phen (0.79 g, 4.39 mmol) in methanol (20 mL) to afford a yellow transparent solution. Compound **1a** was obtained



**Scheme 1.** Syntheses of cobalt(II) compounds.

**Table 1**
Crystal data and structure refinements of compounds **1a**, **1b**, and **4a**.

| | **4a** | **1a** | **1b** |
|---|---|---|---|
| Formula | $C_{27}H_{23}C_{l2}CoN_4$ | $C_{38}H_{29.5}B_2CoF_8N_6$ | $C_{31}H_{31}B_2CoF_8N_8$ |
| Molecular weight | 533.32 | 810.73 | 1496.38 |
| Wavelength (Å) | 0.71073 | 0.71073 | 0.71073 |
| Crystal system | triclinic | triclinic | triclinic |
| Space group | $P\bar{1}$ | $P\bar{1}$ | $P\bar{1}$ |
| Color of crystal | yellow | purple | yellow |
| $a$ (Å) | 10.7724 | 11.1961 | 10.3908 |
| $b$ (Å) | 10.8378 | 12.9138 | 10.6832 |
| $c$ (Å) | 10.9523 | 14.3453 | 19.3985 |
| $\alpha$ (°) | 85.6420 | 81.2415 | 87.055 |
| $\beta$ (°) | 84.4350 | 75.9587 | 75.488 |
| $\gamma$ (°) | 78.6430 | 68.5142 | 71.841 |
| $V$ (Å$^3$) | 1245.60 | 1867.7 | 1980.01 |
| $Z$ | 2 | 2 | 2 |
| $D_{calc.}$ (mg/m$^3$) | 1.442 | 1.442 | 1.255 |
| Absorption coefficient (mm$^{-1}$) | 0.926 | 0.538 | 0.502 |
| $F(000)$ | 548.0 | 825.0 | 764.0 |
| Crystal size (mm) | 0.28 × 0.2 × 0.12 | 0.29 × 0.16 × 0.10 | 0.24 × 0.18 × 0.10 |
| $\theta$ (°) | 1.87–26.04 | 1.47–25.35 | 1.08–26.19 |
| No. of reflections collected | 6826 | 9766 | 11218 |
| No. of independent reflections | 4806 | 6739 | 7833 |
| No. of data/restraints/params | 4806/0/308 | 6739/12/534 | 7833/0/452 |
| Goodness-of-fit (GOF) on $F^2$ | 1.054 | 1.007 | 1.087 |
| $R_1(1 > 2\sigma(1))$ | 0.0460 | 0.0666 | 0.0690 |
| $wR_2$ | 0.1217 | 0.2030 | 0.1612 |