Influences of Alkyl and Aryl Substituents on Iminopyridine Fe(II)- and Co(II)-Catalyzed Isoprene Polymerization

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Abstract: A series of alkyl- and aryl-substituted iminopyridine Fe(II) complexes 1a–7a and Co(II) complexes 2b, 3b, 5b, and 6b were synthesized. The activator effect, influence of temperature, and, particularly, the alkyl and aryl substituents’ effect on catalytic activity, polymer molecular weight, and regio-/stereoselectivity were investigated when these complexes were applied in isoprene polymerization. All of the Fe(II) complexes afforded polyisoprene with high molecular weight and moderate cis-1,4 selectivity. In contrast, the Co(II) complexes produced polymers with low molecular weight and relatively high cis-1,4 selectivity. In the iminopyridine Fe(II) system, the alkyl and aryl substituents’ effect exhibits significant variation on the isoprene polymerization. In the iminopyridine Co(II) system, there is little influence observed on isoprene polymerization by alkyl and aryl substituents.

Keywords: iminopyridine; Iron(II); Cobalt(II); isoprene polymerization; selectivity

1. Introduction

The polymerization of isoprene can afford polymers with various regio- and/or stereoregularities such as isotactic or syndiotactic polyisoprene via 1,2 or 3,4 addition, and cis- or trans-1,4 polyisoprene via 1,4 addition. The structures of polyisoprene strongly influence the properties of the resulting material. For example, the properties of cis-1,4 polyisoprene is very similar to those of natural rubber [1], while the properties of trans-1,4 polyisoprene is very close to those of gutta-percha [2]. The development of highly efficient and highly regio- and stereoselective catalysts plays a key role in the field of metal-catalyzed polymerization of conjugate dienes [3]. Titanium and rare-earth metal catalysts can afford cis-1,4 and trans-1,4 polybutadienes and polyisoprenes with up to 98% selectivity [4–15]. In addition, some late transition-metal catalytic systems were successfully applied in olefins [16–34], butadiene [4,35–45], and isoprene [36,37,46–50] polymerization. Late transition-metal catalysts have lower Lewis acid characteristics and may possess high tolerance towards functional groups and polar additives. Special attention was paid to low-cost and earth-abundant iron- and cobalt-based catalysts with well-defined molecular structures that could be easily prepared.

Recently, Dai et al. [41] showed that an aryl-substituted iminopyridine Co(II) catalyst exhibited high catalytic activity and cis-1,4-selectivity for 1,3-butadiene polymerization. Raynaud et al. [51] reported that the combination of the iminopyridine Fe(II) complexes, alkylaluminum, and dealkylating...
reagent [Ph3C][B(C6F5)4] can polymerize isoprene with high stereoselectivity. The octyl-substituted imines favor trans-1,4 insertion, whereas supermesityl-substituted imines favor cis-1,4 insertion. The authors suggested that higher electron density at the iron center may increase the trans-1,4 selectivity. However, this accidental discovery and studies of only these two catalysts make it difficult draw any rational conclusions.

Inspired by these works, we became very interested in the influence of iminopyridine ligand substituents on the selectivity of isoprene polymerization. In this work, various alkyl- and aryl-substituted iminopyridine Fe(II) and Co(II) complexes were synthesized and employed in isoprene polymerization when activated using an alkylaluminum (methylaluminoxane (MAO) or AlEtCl2) (Scheme 1). The effects of the imine moiety on the catalytic activity, molecular weight, and, particularly, the regio- and stereoselectivity were investigated.

![Scheme 1](image)

**Scheme 1.** Alkyl- and aryl-substituted iminopyridine Fe(II) and Co(II) complexes for isoprene polymerization.

### 2. Experimental Section

#### 2.1. General Information

All manipulations of air-and-moisture sensitive materials were performed under a dry nitrogen atmosphere by using standard Schlenk techniques. Nitrogen was purified by passing through a MnO oxygen-removal column and an activated 4 Å molecular sieve column. 1H and 13C NMR spectra were recorded using CDCl3 as solvent on a Bruker Ascend™ 500 spectrometer (Bruker, Karlsruhe, Germany) at room temperature unless otherwise stated. The chemical shifts of the 1H and 13C NMR spectra (Bruker, Karlsruhe, Germany) were referenced to tetramethylsilane (TMS). Coupling constants are in units of hertz. Fourier-transform infrared (FTIR) spectrometry was performed on a Thermo Scientific Nicolet iS5 (Thermo Fisher Scientific Corporation, Waltham, MA, USA) using the conventional KBr wafer technique. Elemental analysis was performed by the Analytical Center of the University of Science and Technology of China (Hefei, China). Mass spectra were recorded on a P-SIMS-Gly of Bruker Daltonics Inc. (EI, Bruker Daltonics Inc., Billerica, MA, USA). X-ray Diffraction data were collected at 298(2) K on a Bruker Smart CCD area detector (Bruker, Karlsruhe, Germany) with graphite-monochromated MoKα radiation (λ = 0.71073 Å). Molecular weights and molecular weight distributions were determined by gel permeation chromatography (GPC, Waters, Milford, MA, USA) employing a series of two linear Styragel columns (HR2 and HR4) at an oven temperature of 45 °C. A Waters 1515 pump and Waters 2414 differential refractive index detector (30 °C) were used. The eluent was tetrahydrofuran (THF) at a flow rate of 1.0 mL·min⁻¹. A series of low-polydispersity polystyrene standards was used for calibration. Hexane (Tianjin Fuyu Fine Chemical Limited Company, Tianjin, China), toluene (Laiyang Fine Chemical Factory, Laiyang, China) and THF (tetrahydrofuran, Tianjin Fuyu Fine Chemical Limited Company, Tianjin, China) were refluxed over sodium benzophenone ketyl until the solution turned blue and then distilled before use. CH2Cl2 (Tianjin Fuyu Fine Chemical Limited Company, Tianjin, China) was refluxed over phosphorus pentoxide for 8 h and distilled under a nitrogen atmosphere. Isoprene (Aladdin Industrial Corporation, Shanghai, China) was dried over CaH2 prior to use in polymerization. Ligands L2 and L5–L7 were prepared according to reported procedure [51–53]. Complexes 2a, 5a, 6a, and 6b were synthesized according the reported method [41,51,54]. All other reagents were purchased from commercial sources and used without purification.
2.2. General Procedure for the Synthesis of Ligands L1, L3, and L4

A solution of the corresponding amine (30 mmol) in methanol (30 mL) was added to pyridine-2-carbaldehyde (30 mmol) and a drop of formic acid was subsequently added. The mixture was stirred at room temperature overnight.

Cyclohexyl(pyridin-2-yl-methylene)amine (L1): the reaction mixture was concentrated under reduced pressure. The residue was purified by distillation under vacuum to give the colorless oil. Yield: 5.37 g (95.1%). 1H NMR (500 MHz, CDCl3) δ 8.63 (d, J = 3.9 Hz, 1H), 8.40 (s, 1H, CH=N), 7.99 (d, J = 7.8 Hz, 1H), 7.70 (dd, J = 10.6, 4.1 Hz, 1H), 7.43–7.13 (m, 1H), 3.53–3.19 (m, 1H, N–CH), 2.05–1.52 (m, 7H), 1.53–1.04 (m, 3H). 13C NMR (126 MHz, CDCl3) δ 157.97 (CH=N), 153.79, 147.76, 134.52, 122.80, 119.47, 67.83, 32.84, 24.30, 23.13. Anal. calcd. for C12H10N2: C, 76.13; H, 8.37; N, 11.72. Found: C, 76.32; H, 5.63; N, 7.98.

Adamantyl(pyridin-2-yl-methylene)amine (L3): the reaction mixture was concentrated under reduced pressure. The residue was purified by distillation under vacuum to give the light-yellow oil which quickly changed to solid at room temperature. Yield: 6.76 g (93.7%). 1H NMR (500 MHz, CDCl3) δ 8.63 (d, J = 3.6 Hz, 1H), 8.36 (s, 1H, CH=N), 8.01 (t, J = 16.1 Hz, 1H), 7.73 (t, J = 7.3 Hz, 1H), 7.35–7.27 (m, 1H), 2.23–2.13 (m, 3H, CH(CH2)3), 1.83 (s, 6H, CH(CH2)3), 1.79–1.65 (m, 6H, CH(CH2)3). 13C NMR (126 MHz, CDCl3) δ 156.08 (CH=N), 155.58, 149.17, 136.38, 124.24, 120.82, 58.02, 42.89, 36.44, 29.44. Anal. calcd. for C16H20N2: C, 79.96; H, 8.39; N, 11.66; found: C, 79.81; H, 8.37; N, 11.72.

Triphenyl(pyridin-2-yl-methylene)amine (L4): the white solid precipitated from the solution and was separated by filtration. The white solid was washed with methanol (3 × 5 mL). Yield: 8.18 g (78.3%). 1H NMR (500 MHz, CDCl3) δ 8.61 (d, J = 3.9 Hz, 1H), 8.38 (d, J = 7.9 Hz, 1H, CH=N), 7.99 (s, 1H), 7.81 (t, J = 7.5 Hz, 1H), 7.34 (m, 16H, ). 13C NMR (126 MHz, CDCl3) δ 160.95 (CH=N), 155.27, 149.28, 145.25, 136.61, 129.76, 127.85, 126.93, 124.84, 121.32. Anal. calcd. for C25H20N2: C, 86.17; H, 5.79; N, 8.04; found: C, 86.32; H, 5.63; N, 7.98.

2.3. General Procedure for the Synthesis of Iron Complexes

All complexes were prepared in a similar manner by the reaction of anhydrous FeCl2 with the corresponding ligands in tetrahydrofuran (THF). A typical synthetic procedure used for complexes 1a, 3a, 4a, and 7a is as follows. Ligand (1.0 mmol) and FeCl2 (1.0 mmol) were stirred at room temperature overnight. The precipitate was collected by filtration, washed with methanol (3 × 5 mL) and dried under vacuum to obtain orange, purple, or burgundy solid.

(Cyclohexyl Iminopyridine)FeCl2 (1a) (purple solid, 0.30 g, 95%): MALDI-TOF-MS (m/z): calcd. for C12H16ClFeN2: 279.0351, found: 279.0351 [M – Cl]+. Anal. calcd. for C12H16ClFeN2: C, 45.75; H, 5.12; N, 8.89; found: C, 46.20; H, 4.99; N, 9.12. IR/cm−1: 1563, ν(C=N).

(Adamantyl Iminopyridine)FeCl2 (3a) (orange solid, 0.35 g, 95%): MALDI-TOF-MS (m/z): calcd. for C16H20ClFeN2: 330.0664, found: 330.0664 [M – Cl]+. Anal. calcd. for C16H20ClFeN2: C, 52.35; H, 5.49; N, 7.63; found: C, 52.55; H, 5.33; N, 7.29. IR/cm−1: 1588, ν(C=N).

(Triphenyl Iminopyridine)FeCl2 (4a) (light-orange solid, 0.46 g, 96%): MALDI-TOF-MS (m/z): calcd. for C25H20ClFeN2: 439.0664, found: 439.0664 [M – Cl]+. Anal. calcd. for C25H20ClFeN2: C, 63.19; H, 4.24; N, 5.90; found: C, 62.88; H, 4.18; N, 5.67. IR/cm−1: 1588, ν(C=N).

(dibenzhydryl Iminopyridine)FeCl2 (7a) (burgundy solid, 0.61 g, 93%): MALDI-TOF-MS (m/z): calcd. for C39H22ClFeN2: 619.1603, found: 619.0200 [M – Cl]+. Anal. calcd. for C39H22ClFeN2: C, 71.47; H, 4.92; N, 4.27; found: C, 71.99; H, 4.87; N, 4.17. IR/cm−1: 1593, ν(C=N).

2.4. General Procedure for the Synthesis of Cobalt Complexes

All complexes were prepared in a similar manner by the reaction of anhydrous CoCl2 with the corresponding ligands in tetrahydrofuran (THF). A typical synthetic procedure used for complexes
2b, 3b, and 5b is as follows. Ligand (1.0 mmol) and CoCl$_2$ (1.0 mmol) were stirred in 10 mL of THF overnight at room temperature. The precipitate was collected by filtration, washed with hexane (10 mL × 2) and dried under vacuum to obtain a blue or green solid.

$^{(\text{octyl iminopyridine})\text{CoCl}_2}$ (2b) (blue solid, 0.30 g, 87%): MALDI-TOF-MS ($m/z$): calcd. for C$_{14}$H$_{22}$ClCoN$_2$: 312.0804, found: 311.9917 [M−Cl]$^+$. Anal. calcd. for C$_{14}$H$_{22}$ClCoN$_2$: C, 48.30; H, 6.37; N, 8.05; found: C, 49.41; H, 6.45; N, 7.91. IR/cm$^{-1}$: 1597, \(\nu(C=N)\).

$^{(\text{adamantyl iminopyridine})\text{CoCl}_2}$ (3b) (blue solid, 0.33 g, 90%): MALDI-TOF-MS ($m/z$): calcd. for C$_{16}$H$_{20}$ClCoN$_2$: 334.0647, found: 333.9984 [M−Cl]$^+$. Anal. calcd. for C$_{16}$H$_{20}$ClCoN$_2$: C, 51.91; H, 5.45; N, 7.57; found: C, 52.03; H, 5.23; N, 7.88. IR/cm$^{-1}$: 1595, \(\nu(C=N)\).

$^{(\text{supermesityl iminopyridine})\text{CoCl}_2}$ (5b) (green solid, 0.49 g, 91%): MALDI-TOF-MS ($m/z$): calcd. for C$_{30}$H$_{22}$ClCoN$_2$: 504.0804, found: 503.9194 [M−Cl]$^+$. Anal. calcd. for C$_{30}$H$_{22}$ClCoN$_2$: C, 66.68; H, 4.10; N, 5.18; found: C, 66.11; H, 3.96; N, 5.31. IR/cm$^{-1}$: 1597, \(\nu(C=N)\).

### 2.5. General Procedure for Isoprene Polymerization

The polymerization of isoprene in toluene was carried out in a 50 mL Schlenk reactor. In a typical experiment, the reactor was heated, dried in a vacuum, and recharged with nitrogen more than three times before the required amount of an aluminum coactivator, toluene (7 mL), and isoprene (2 mL) were added into the reactor. Then, 8.0 \(\mu\)mol of iron or cobalt complex in 1 mL CH$_2$Cl$_2$ was injected to initiate the polymerization at the desired temperature. After 2 h, the polymerization was quenched with a diluted HCl solution of methanol (methanol/HCl = 50/1). The polymer was collected by filtration and washed with ethanol several times and dried at room temperature for 24 h under vacuum.

### 2.6. Calculation of Microstructure Contents of Polyisoprenes

According to the calculated area of the characteristic signals at 4.66–4.72 and 5.12 ppm, the molar content of 3,4 units and 1,4 units based on $^1$H NMR spectra can be calculated by Equations (1) and (2) where $I$ (5.12 ppm) and $I$ (4.66–4.72 ppm) represent signal areas at 5.12 and 4.66–4.72 ppm.

\[
\%1,4\text{-units} = \frac{I(5.12 \text{ ppm})}{I(5.12 \text{ ppm}) + \frac{I(4.66-4.72 \text{ ppm})}{2}}
\]  

\[
\%3,4\text{-units} = \frac{\frac{I(4.66-4.72 \text{ ppm})}{2}}{I(5.12 \text{ ppm}) + \frac{I(4.66-4.72 \text{ ppm})}{2}}
\]

According to the calculated area of the characteristic signals at 16.2 and 23.8 ppm, the molar content of cis-1,4 units and trans-1,4 units based on $^{13}$C NMR spectra can be calculated by Equations (3) and (4), where $I$ (23.8 ppm) and $I$ (16.2 ppm) represent signal areas at 23.8 and 16.2 ppm.

\[
\%\text{cis-1,4-units} = \frac{I(23.8 \text{ ppm})}{I(23.8 \text{ ppm}) + I(16.2 \text{ ppm})}
\]  

\[
\%\text{trans-1,4-units} = \frac{I(16.2 \text{ ppm})}{I(23.8 \text{ ppm}) + I(16.2 \text{ ppm})}
\]

The microstructures of the polyisoprenes based on the FTIR spectra can be calculated according to the equations in the literature [50].

\[
A_{1375} = 24[\text{cis-1,4-units}]L + 32.6[\text{3,4-units}]L
\]  

\[
A_{890} = 101[\text{3,4-units}]L
\]
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\[
\text{[\%cis-1, 4-units]} = 100 \times \frac{[\text{cis-1, 4-units}]}{[\text{cis-1, 4-units}] + [\text{3, 4-units}]}
\]

\[
\text{[\%3, 4-units]} = 100 \times \frac{[\text{3, 4-units}]}{[\text{cis-1, 4-units}] + [\text{3, 4-units}]}
\]

where \(A_{1375}\) and \(A_{890}\) are the absorption intensity at 1375 and 890 cm\(^{-1}\), expressed by the peak height, [cis-1,4-units] represents the molar content of cis-1,4-units, [3,4-units] represents the molar content of 3,4-units, and \(L\) indicates the thickness of the sample.

3. Results and Discussion

3.1. Synthesis and Characterization of the Iron and Cobalt Complexes

The synthetic route for the iminopyridine complexes is shown in Scheme 2. The ligands were prepared at high yields by acid-catalyzed condensation between corresponding anilines and 2-pyridinecarboxaldehyde in methanol and identified by NMR (See Supplementary Materials, Figures S1–S6) and elemental analysis. The corresponding Fe(II) and Co(II) complexes (1a–7a, 2b, 3b, 5b, 6b) were prepared from the reaction of the ligands with 1 equiv of anhydrous FeCl\(_2\) or CoCl\(_2\) in CH\(_2\)Cl\(_2\) and THF, respectively. These complexes were characterized by mass spectroscopy (See Supplementary Materials, Figures S7–S13) and elemental analysis.

![Scheme 2. Synthesis of the ligands and the Fe(II) and Co(II) complexes.](image)

The structures of the complexes 1a–7a should be those drawn in Scheme 2. This is supported by the elemental analysis, mass spectroscopy, and literature results on similar Fe(II) complexes [51]. Multiple attempts to grow single crystals of complexes 1a–7a failed. However, during this process, single crystals of complex 7a′ were obtained and analyzed by X-ray diffraction (Figure 1, See Supplementary Materials, Tables S2 and S3). Complex 7a′ probably arises from the oxidation of 7a during the recrystallization process. This unusual complex 7a′ is interesting, and can prove the connectivity of the iminopyridine ligand to the metal center. The X-ray crystal structure analysis of 7a′ shows a distorted trigonal bipyramidal coordination geometry around the Fe(II) center. The steric environment of the ligand and the blocking of the axial position of the metal center from the dibenzhydryl moiety can be clearly observed from this molecular structure. Single crystals of pure complex 2b could be obtained and the X-ray structure is shown in Figure 2. In a solid state, the cobalt center adopts a distorted tetrahedral coordination geometry with N1–Co–N2 angle of 81.61° and Cl1–Co–Cl2 angle of 112.06° (See Supplementary Materials, Tables S2 and S4). Complex 2b shows shorter Co–N bond distance (2.040 and 2.046 Å) than aryl-substituted Co(II) complexes reported in literature [41] (2.044–2.181 Å), which may be attributed to the strong electron-donating effect of the octyl substituents.
3.2. Isoprene Polymerization Studies

3.2.1. Polymerization of Isoprene with Iron Catalysts

The isoprene polymerization was evaluated using various common alkylaluminum reagents as cocatalysts. Triisobutylaluminum (TIBA) or AlEt2Cl cocatalysts were not effective at all. Both AlEtCl2 and MAO were able to activate the aryl-substituted complexes 5a–7a for isoprene polymerization (Table 1, entries 1 and 2). However, the 2a/MAO system can generate high molecular polyisoprenes. Therefore, MAO was chosen as the activator in the iminopyridine Fe(II) system (See Supplementary Materials, Table S1).

Table 1. Isoprene polymerization results with Fe(II) catalyst.

| Entry | Complex | T (°C) | Yield (%) | Activity c | Mw d (×10^4) | PDI d | Microstructure (%) e | cis-1,4 trans-1,4 cis/trans 3,4 |
|-------|---------|--------|-----------|------------|--------------|-------|----------------------|-----------------------------|
| 1 b   | 2a      | 25     | 83.4      | 7.1        | 0.18         | 4.70  | -                    | -                           |
| 2     | 2a      | 25     | 83.1      | 7.1        | 6.1          | 1.57  | -                    | -                           |
| 3     | 2a      | -25    | 66.3      | 5.6        | 7.9          | 2.45  | -                    | -                           |
| 4     | 1a      | 25     | 64.1      | 5.4        | 6.0          | 2.11  | -                    | -                           |
| 5     | 3a      | 25     | 58.2      | 4.9        | 7.0          | 1.82  | -                    | -                           |
| 6     | 4a      | 25     | 61.3      | 5.2        | 6.1          | 2.08  | -                    | -                           |
| 7     | 5a      | -25    | 81.0      | 6.9        | 15.4         | 2.13  | 63.9                 | 30 96:4 33.1                |
| 8     | 5a      | 25     | 98.1      | 8.3        | 10.3         | 2.05  | 62.7                 | 28 96:4 34.5                |
| 9     | 6a      | 25     | 83.2      | 7.1        | 18.0         | 1.75  | 69.9                 | 4.5 94:6 25.6               |
| 10    | 7a      | 25     | 85.7      | 7.3        | 18.2         | 1.61  | 71.4                 | 4.8 94.6 23.8               |

a Polymerization conditions: 8.0 µmol of Fe(II) complex; MAO/Fe = 500; 7 mL toluene and 1 mL CH2Cl2; isoprene = 2 mL; time = 2 h; b activator = AlEtCl2, Al/Fe = 150; c 10^4 g of polyisoprene (mol of Fe)^−1 h^−1; d determined by gel permeation chromatography (GPC); e determined by 1H NMR and 13C NMR.

Figure 1. Molecular structure of complex 7a’. (Thermal ellipsoids are shown at the 50% probability level.) Hydrogen atoms have been omitted for clarity.

Figure 2. Molecular structure of complex 2b. (Thermal ellipsoids are shown at the 50% probability level.) Hydrogen atoms have been omitted for clarity.
The alkyl and aryl moiety significantly influenced the catalytic performances of the complexes. The alkyl-substituted complexes 5a–7a produced polymers at higher yields (83.2%–98.1%) than the alkyl-substituted complexes 1a–4a (58.2%–83.1%). The aryl moiety is electronically more withdrawing than the alkyl moiety, which can reduce the electron density on the metal center, leading to better monomer coordination and faster chain propagation. This is supported by the fact that complex 5a bears the strongest electron-withdrawing substituent and displays the highest yield. In addition, the molecular weight of polyisoprenes obtained by aryl-substituted complexes 5a–7a is higher than alkyl-substituted complexes 1a–4a (10.3 × 10^4–18.2 × 10^4 vs. 6.0 × 10^4–7.9 × 10^4). Probably, the steric environment of the aryl moiety retards chain transfer reaction more effectively than the alkyl moiety (See Supplementary Materials, Figures S14–S20). This is supported by the fact that complex 7a bears a sterically bulky dibenzhydryl-derived ligand framework and generates polyisoprene with the highest molecular weight (18.2 × 10^4). The temperature influence on the catalytic performance was also investigated. Polymerization of isoprene at −25 °C showed lower yields (2a: 66.3% vs. 83.1%, 5a: 81.0% vs. 98.1%) and afforded the polymer with higher molecular weight (2a: 7.9 × 10^4 vs. 6.1 × 10^4; 5a: 15.4 × 10^4 vs. 10.3 × 10^4) than those at 25 °C.

The microstructures of the resulting polyisoprenes were analyzed via 1H NMR and 13C NMR (See Supplementary Materials, Figures S23–S26) [51]. The representative 1H NMR spectra of the polyisoprenes obtained by the Fe(II) catalysts are shown in Figure 3. The 1,2-unit was not observed. The polyisoprene obtained by aryl-substituted complex 5a contains 34.5% 3,4-units (Table 1, entry 10), which was much higher than that of the aryl-substituted complex 3a (15.0%, entry 5). Similar trends were observed for other alkyl-substituted complexes (14.0%–15.0%) and aryl-substituted complexes (greater than 23.8%). Interestingly, the R group in the alkyl-substituted complexes only slightly influenced 3,4-selectivity from 14.0% to 15.0%. However, the selectivity of 3,4-units was increased from 23.8% to 34.5% when the steric hindrance of the aryl-substituted complexes was decreased. The high 3,4 units of polyisoprene can increase the toughness of the synthetic rubber and show outstanding wet skid resistance and low heat build-up when applied as car tires [55], thus representing a big advantage of this catalyst system. Additionally, the alkyl-substituted complexes 1a–4a produced polymers with higher cis-1,4 content (77.1%–78.2%) than the aryl-substituted complexes 5a–7a (62.7%–71.4%). At the same time, the alkyl-substituted complexes produced polyisoprene with 7.6%–8.9% trans-1,4 content, which was ca. twice as much as that by aryl-substituted complexes (2.8%–4.8%). However, polymers generated from the aryl-substituted complexes had the higher cis-1,4/trans-1,4 ratio (e.g., 5a: 96:4, entry 8) than the alkyl-substituted complexes (e.g., 3a: 90:10, entry 5). These results indicated that the electron-donating alkyl-substituted complexes tend to polymerize isoprene with trans-1,4-selectivity when 1,4-addition occurred. It was also observed that the steric hindrance of both kinds of complexes almost have minimum influence on cis-1,4/trans-1,4 stereoselectivity with 1a–4a (ca. 90:10) and 5a–7a (ca. 95:5).

Previously, Raynaud et al. used alkylaluminum/[Ph3C][B(C6F5)4] cocatalysts to activate the Fe(II) complexes, and the 1,4-trans,1,4-cis selectivity was affected by the alkyl/aryl substituents and the alkylaluminum agents (TIBA and AlEt3) [51]. In our system, the alkylaluminum/[Ph3C][B(C6F5)4] cocatalysts led to highly unrepeatable results, which may originate from the high sensitivity of these Fe(II) complexes. As a result, MAO was chosen as the cocatalyst. These Fe(II) complexes showed high activities and high polymer molecular weight when activated using MAO as cocatalyst. Furthermore, in our Fe(II)/MAO system, the aryl-substituted iminopyridine iron complexes also favor 3,4-insertion and give rise to higher amounts of 3,4-units than the alkyl-substituted iminopyridine iron complexes, which is similar to the Fe(II)/alkylaluminum/[Ph3C][B(C6F5)4] system. However, there are some notable differences between these two systems. In our Fe(II)/MAO system, the ratio between 1,4-cis/trans units was not affected by the aryl or alkyl substituents. Although this difference is not fully understood, it is clear that the cocatalysts may play an important role in determining the stereoselectivity.
3.2.2. Polymerization of Isoprene with Co(II) Catalysts

The polymerization results using Co(II) complexes 2b, 3b, 5b, and 6b are summarized in Table 2. Four cocatalysts (TIBA, AlEtCl₂, AlEtCl₂, and MAO) were used in attempts to generate the active catalysts. Only cocatalyst AlEtCl₂ was able to activate Co(II) complex 2b for isoprene polymerization. Although the yields (greater than 76.9%) of polyisoprene generated from Co(II) complexes are similar with those of Fe(II) complexes, there are some apparent differences between the Co(II) and the Fe(II) systems. In sharp contrast to the Fe(II) complexes, the polymers produced by Co(II) complexes were white powder with molecular weights below 2000 and broad molecular distribution of above 4.76 (See Supplementary Materials, Figures S21 and S22). Moreover, complexes 5b and 6b containing electron-withdrawing aryl substituents afforded polymers with higher molecular weights (5b: 1700, 6b: 1800) at higher yields (5b: 97.3%, 6b: 94.9%) than those by complexes 2b and 3b containing electron-donating alkyl substituents (2b: 1400 and 78.2%, 3b: 1500 and 76.9%). This is similar with the trend observed in the Fe(II) systems.

Table 2. Isoprene polymerization results with Co(II) catalyst a.

| Entry | Complex | Yield (%) | Activity b | Mₙ c (×₁₀⁻³) | PDI c | Microstructure d (%) |
|-------|---------|-----------|------------|---------------|-------|----------------------|
| 1     | 2b      | 78.2      | 6.6        | 1.4           | 7.97  | 91.1 8.9            |
| 2     | 3b      | 76.9      | 6.5        | 1.5           | 4.76  | 90.8 9.2            |
| 3     | 5b      | 97.3      | 8.3        | 1.7           | 8.05  | 88.1 11.9           |
| 4     | 6b      | 94.9      | 8.1        | 1.8           | 9.38  | 89.7 10.3           |

a Polymerization conditions: 8.0 µmol of Co(II) complex; activator = AlEtCl₂, Al/Co = 150; 7 mL toluene and 1 mL CH₂Cl₂; isoprene = 2 mL; time = 2 h; b 10⁻⁴ g of polyisoprene (mol of Co)⁻¹·h⁻¹; c determined by GPC; d determined by Fourier-transform infrared (FTIR) spectroscopy.

The ¹H NMR and ¹³C NMR spectra of polyisoprene obtained by Co(II) complexes have the broad peaks and low resolution because of the low molecular weight of the polymers (See Supplementary Materials, Figures S27–S30). It was difficult to assign the peaks of these polymers in the ¹H NMR and ¹³C NMR spectra, so FTIR measurements were carried out to determine and analyze the microstructures of the polyisoprenes (See Supplementary Materials, Figures S31–S34). The absorption bands at 1375 and 890 cm⁻¹ correspond to the cis-1,4 and the 3,4-units [50]. The typical bands of trans-1,4 units are at 845, 1152, 1325, and 1385 cm⁻¹ and the band of 1,2-units is at 911 cm⁻¹ [50]. As shown in Figure 4, no bands were observed for the trans-1,4 unit or 1,2-unit in the spectrum. Based on the
equations shown in the experimental section, the polymer generated with the Co(II)/AlEtCl₂ system is composed of predominantly cis-1,4 units (ca. 90%) along with a small amount of 3,4-units (ca. 10%). Interestingly, the Co(II) system produced polymers with higher cis-1,4 content (ca. 90%) than the Fe(II) system (65%–85%). The stereoregularity of the polyisoprenes was only slightly influenced by the ligand environment.

![FTIR spectra of polyisoprenes obtained by Co(II) catalysts (entry 6).](image)

**Figure 4.** FTIR spectra of polyisoprenes obtained by Co(II) catalysts (entry 6).

### 4. Conclusions

In conclusion, a series of iminopyridine Fe(II) and Co(II) complexes bearing various alkyl and aryl substituents was prepared. The aim is to systematically investigate the influence of alkyl and aryl substituents on the isoprene polymerization. Activated by MAO, the Fe(II) complexes exhibited moderate cis-1,4 selectivity, generating high molecular weight polyisoprenes. The Fe(II) catalyzed polymerization of isoprene was relatively sensitive to alkyl and aryl substituents. High 3,4-units (up to 34.5%) and high molecular weight (10.3 × 10⁴–18.2 × 10⁴) polyisoprenes can be obtained using aryl-substituted Fe(II) complexes. Meanwhile, the Co(II)/AlEt₂Cl system exhibited relatively high cis-1,4-selectivity, affording low molecular weight polyisoprenes. The alkyl and aryl substituents in Co(II) complexes did not significantly influence the selectivity and molecular weight of the resulting polymers.

**Supplementary Materials:** The following are available online at www.mdpi.com/2073-4360/8/11/389/s1. Optimization of MAO/Fe Ratio with 3a (Table S1), NMR spectra of the ligands L₁, L₃ and L₄ (Figures S1–S6), MALDI-TOF-MS of complexes (Figures S7–S13), crystal data of complex 7a’ (CCDC number: 1503575) and 2b’ (CCDC number: 1503576) (Tables S2–S4), GPC curves of polyisoprene samples (Figures S14–S22), NMR spectra of the representative polyisoprenes (Figures S23–S30) and FTIR spectra of representative polyisoprenes (Figures S31–S34).

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**Conflicts of Interest:** The authors declare no conflict of interest.

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