

Article

Synthesis, Characterization, and Catalytic Behaviors in Isoprene Polymerization of Pyridine–Oxazoline-Ligated Cobalt Complexes

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Abstract: A family of pyridine–oxazoline-ligated cobalt complexes L_2CoCl_2 **3a–h** were synthesized and characterized. Determined via single-crystal X-ray diffraction, complexes **3a** and **3d**, ligated by two ligands, displayed a distorted tetrahedral coordination of a cobalt center. The X-ray structure indicated the pyridine–oxazoline ligands acted as unusual mono-dentate ligands by coordinating only to $N_{oxazoline}$. Upon activation with $AlEt_2Cl$ (diethylaluminum chloride), these cobalt complexes all exhibited high catalytic activity (up to $2.5 \times 10^6 \text{ g} \cdot \text{mol}_{Co}^{-1} \cdot \text{h}^{-1}$), affording *cis*-1,4-*co*-3,4-polyisoprene with molecular weights of 4.4–176 kg mol^{-1} and a narrow $\bar{M}$ of 1.79–3.42, suggesting a single-site nature of the active sites. The structure of cobalt catalysts and reaction parameters, especially co-catalysts and the reaction temperature, all have significant influence on the polymerization activity but not on the microstructure of polyisoprene.

Keywords: pyridine–oxazoline ligand; cobalt catalyst; isoprene polymerization; isoprene



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1. Introduction

Due to the high demand for high-performance synthetic rubbers and the limited supply of natural rubbers, the importance of developing high-quality elastomers through conjugated diene polymerization has become increasingly prominent [1–3]. Isoprene is an attractive and versatile monomer, which could be stereospecifically incorporated in *trans*-1,4-, *cis*-1,4-, 1,2-, and 3,4- incorporation fashions in the polymerization process, the quantity and nature of which play a crucial role in its mechanical properties and application orientations [4,5]. Given its outstanding elastic properties, highly *cis*-1,4-polyisoprene exhibits marvelous flexibility and a low crystallinity, rendering it useful as an alternative to natural rubber [6], while 3,4-polyisoprene imparts enhanced wet skid resistance. In this context, the incorporation of 3,4-units into *cis*-1,4 enchainment, producing *cis*-1,4-*alt*-3,4-polyisoprene materials, is highly desirable to the rubber industry.

Isoprene coordination–insertion polymerization catalyzed by a transition metal has witnessed great success in both industry practices and academia, since the introduction of the Ziegler–Natta catalyst. Thus, a great deal of novel high-activity and selective catalysts based on a wide range of late and early transition metals have been disclosed. The catalytic systems commonly used for isoprene polymerization are lithium, titanium, and lanthanide metal-based catalysts, which can effectively control the microstructure of isoprene polymers [7–12]. In particular, compared with lanthanide and early transition metals, cobalt complexes, as late transition metal catalysts [13–15], are extremely attractive, due to their low cost, ease of preparation, high moisture, and air stability, and have demonstrated high activity and versatile selectivity for conjugated diene polymerization,

which therefore has attracted much attention for the large-scale polymer synthesis of conjugated dienes [16–19]. Therefore, more and more well-defined-structure cobalt complexes containing nitrogen ligands are being investigated in conjugated diene polymerization (Figure 1) [20–30]. In 2016, Chen's group reported iminopyridine-ligated iron/cobalt complexes with different substituents in catalyzed isoprene polymerization to obtain polymers with different microstructures and molecular weights upon activation with methylaluminoxane (MAO) or ethylaluminum dichloride (AlEt_2Cl) [31]. In 2018, Gong's group demonstrated that *cis*-1,4-*alt*-3,4 polyisoprene can be achieved with aminophosphine(ory)-fused bipyridine-based cobalt complexes in combination with MMAO [3]. Subsequently, Wang and coworkers investigated the effect of fluorine substituents on isoprene polymerization catalyzed by iminopyridine-supported cobalt catalysts activated by AlEt_2Cl or MAO/ $[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]$ [32–34]. The binary system exhibited high catalytic activity and *cis*-1,4 selectivity, and also obtained high-molecular-weight polyisoprene. However, the opposite trend was observed, i.e., the cobalt complexes displayed high *cis*-1,4 selectivity but gave a low-molecular-weight polymer, when replacing the binary system with a ternary system. Following these pioneering works of research, lots of cobalt complexes were developed to systemically investigate the effects of ligand skeletons on isoprene polymerization. In 2019, Zhang's group showed that the cobalt complexes bearing pyrazolyl-imine displayed high activity in isoprene polymerization and afforded *cis*-1,4/3,4 polyisoprene under the activation of ethylaluminum sesquichloride (EASC) [35]. Very recently, Sun and coworkers reported that using rigid iminopyridine-ligated cobalt complexes for catalyzed isoprene polymerization can obtain a polymer with a high molecular weight and high *cis*-1,4 selectivity in the presence of AlEt_2Cl [36].

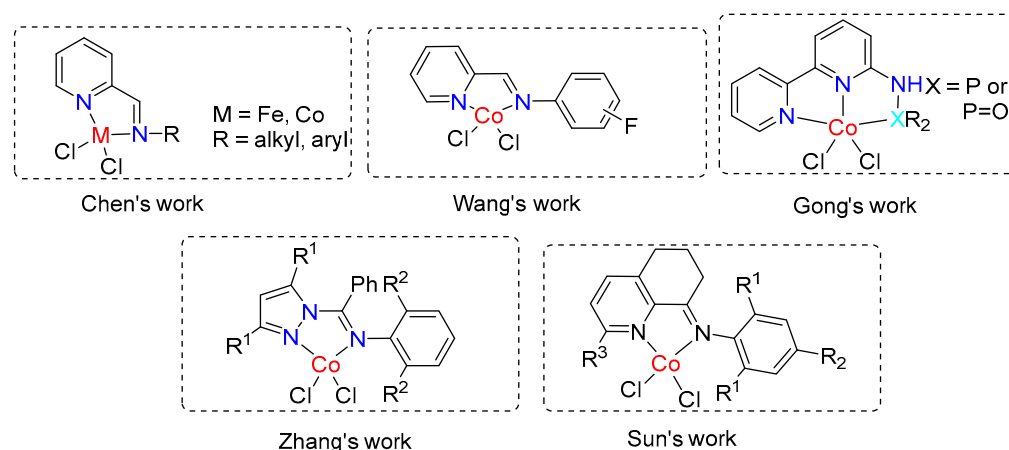
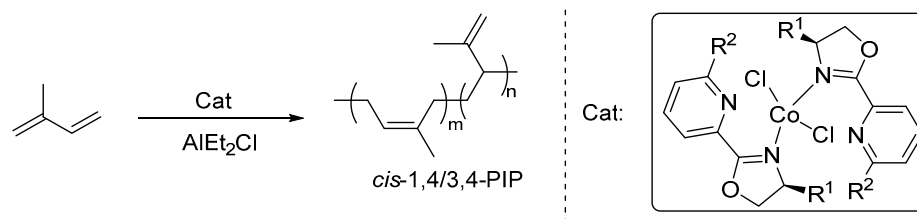


Figure 1. Cobalt complexes for isoprene polymerization.

To the best of our knowledge, ligands coordinated to a metal have a very significant effect on the catalytic activity and microstructure of polymers. To further investigate the effect of the ligand structure, we designed and synthesized a series of cobalt complexes with special structures to prepare high-performance polyisoprene rubber. It is well known that chiral pyridine–oxazoline ligands are a relatively common and important class of ligands that have been widely used in asymmetric catalytic reactions [37–39]. However, reports of metal catalysts based on this ligand for olefin polymerization are relatively rare [40,41]. Following our continued research interests in this field [42,43], cobalt complexes supported by pyridine–oxazoline ligands with different chiral groups were synthesized to investigate their effect on the polymerization of isoprene (Scheme 1). Furthermore, the effects of the reaction parameters and ligand properties were studied in detail.



Scheme 1. Pyridine–oxazoline-ligated cobalt complexes in catalyzed isoprene polymerization.

2. Experimental Section

2.1. General Conditions

All procedures and manipulations were carried out in an argon atmosphere by using a standard Schlenk line or a glovebox filling with argon unless otherwise mentioned. All solvents and monomers were heated to reflux temperature and distilled over sodium/benzophenone (toluene, tetrahydrofuran, and ether) or calcium hydride (CH_2Cl_2 and isoprene) in the argon atmosphere, then stored in the bottle with activated molecular sieves. Other reagents can be used directly without further purification.

^1H , $^{13}\text{C}\{^1\text{H}\}$, and $^{19}\text{F}\{^1\text{H}\}$ NMR spectrometry was performed on a Bruker 600 MHz instrument (Switzerland) with CDCl_3 as the solvent and TMS as an internal standard at ambient temperature. Chemical shift multiplicities are represented as follows: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, dd = doublet of doublets, td = triplet of doublets. The elemental analyses were recorded on a Flash Smart analyzer. HRMS for ligands was determined on a Waters Xevo G2-XS Q-ToF Micro LC/MS System ESI spectrometer operating in electrospray ionization mass spectrometry (ESI-MS) mode, and for cobalt complexes, on the Orbitrap Exploris 480 operating in matrix-assisted laser desorption/ionization time of flight mass spectrometry (MALDI-TOF-MS) mode. FT-IR spectra were collected with the PerkinElmer C100444. Optical rotations were recorded on a PerkinElmer 341 polarimeter. The X-ray diffraction analysis was conducted on a diffractometer with graphite-monochromated Mo and Cu $\text{K}\alpha$ radiation. M_n and $\bar{M}_w$ were determined via gel permeation chromatography (GPC) using a PL-220 equipped with two Agilent PLgel Olexis columns at 35°C using THF as a solvent, with polystyrene as the standard and a flow rate of 1.0 mL/min.

2.2. General Procedure for the Synthesis of Ligands

Synthesis of 6-Aryl-2-Picolinaldehyde 1: The synthesis process was carried out according to the reported literature and the data obtained were consistent with those already reported [44]. Using commercial 6-bromo-2-picolinaldehyde (10 mmol, 1.0 eq) as the starting material, a coupling reaction with arylboronic acid (11 mmol, 1.1 eq) catalyzed by $\text{Pd}(\text{PPh}_3)_4$ (0.1 mmol, 1%) was carried out in toluene at reflux temperature. After 10 h, CH_2Cl_2 extracted the mixture and the obtained organic layer was dried over Na_2SO_4 and concentrated. The organic residue was purified with column chromatography on silica gel with petroleum ether/dichloromethane (1/1) as the eluent to obtain 6-aryl-2-picolinaldehyde 1.

6-phenylpicolinaldehyde (1a): White solid (1.69 g, 92%). ^1H NMR (600 MHz, CDCl_3): δ 10.17 (s, 1H, CHO), 8.11–8.06 (m, 2H, ArH), 7.98–7.87 (m, 3H, ArH), 7.54–7.44 (m, 3H, ArH) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, CDCl_3): δ 193.9, 157.9, 152.6, 138.1, 137.8, 129.7, 128.9, 127.0, 124.4, 119.8 ppm.

6-(naphthalen-1-yl)picolinaldehyde (1b): Yellow solid (1.75 g, 75%). ^1H NMR (600 MHz, CDCl_3): δ 10.18 (s, 1H, CHO), 8.07–7.91 (m, 5H, ArH), 7.79 (dd, $J = 7.4, 1.4$ Hz, 1H, ArH), 7.64 (dd, $J = 7.0, 1.3$ Hz, 1H, ArH), 7.61–7.55 (m, 1H, ArH), 7.55–7.46 (m, 2H, ArH) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, CDCl_3): δ 193.8, 160.0, 152.7, 137.5, 137.3, 134.0, 131.0, 129.6, 129.3, 128.6, 127.8, 126.8, 126.2, 125.4, 125.2, 119.9 ppm.

6-(4-(trifluoromethyl)phenyl)picolinaldehyde (1c): White solid (2.24 g, 89%). ^1H NMR (600 MHz, CDCl_3): δ 10.17 (s, 1H, CHO), 8.22 (d, $J = 8.2$ Hz, 2H, ArH), 8.03–7.93 (m,

3H, ArH), 7.78 (d, $J = 7.9$ Hz, 2H, ArH) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, CDCl_3): δ 193.7, 156.5, 153.1, 141.5, 138.3, 131.6 (q, $^2J_{\text{C-F}} = 32.7$ Hz), 127.5, 126.0 (q, $^3J_{\text{C-F}} = 3.6$ Hz), 124.8, 124.2 (q, $^1J_{\text{C-F}} = 272.4$ Hz), 120.7 ppm. $^{19}\text{F}\{^1\text{H}\}$ NMR (565 MHz, CDCl_3): δ −62.68 ppm.

6-(4-methoxyphenyl)picolinaldehyde (1d): White solid (1.94 g, 91%). ^1H NMR (600 MHz, CDCl_3): δ 10.15 (s, 1H, CHO), 8.06 (d, $J = 8.8$ Hz, 2H, ArH), 7.92–7.87 (m, 2H, ArH), 7.84 (dd, $J = 5.7, 3.0$ Hz, 1H, ArH), 7.04 (d, $J = 8.9$ Hz, 2H, ArH), 3.89 (s, 3H, OCH_3) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, CDCl_3): δ 194.2, 161.2, 157.7, 152.8, 137.8, 130.9, 128.5, 123.8, 119.2, 114.5, 55.5 ppm.

General Procedure for the Synthesis of 2-Aryl-6-(oxazoliny)pyridines 2: According to the known literature, the procedures for the ligands **2** are as follows [45]: Chiral amino alcohol (11.0 mmol, 1.1 eq) was added to the tert-butanol solution of 6-Aryl-2-Picolinaldehyde (10 mmol, 1.0 eq) in an argon atmosphere and kept stirring at room temperature for 2 h. Then, K_2CO_3 (30 mmol, 3.0 eq) and I_2 (20 mmol, 2.0 eq) were added subsequently to the above reaction system and stirred at 70 °C. After 16 h, saturated aqueous $\text{Na}_2\text{S}_2\text{O}_3$ was added to quench the mixture until the color of the iodine disappeared. Then, CH_2Cl_2 extracted the mixture and the obtained organic layer was washed with brine, dried over Na_2SO_4 , and concentrated. The organic residue was purified via column chromatography on silica gel with petroleum ether/ethyl acetate (10/1) as the eluent to obtain the ligands **2**. The analytical data of the compound are given as follows.

(S)-4-benzyl-2-(6-phenylpyridin-2-yl)-4,5-dihydrooxazole (2a): White solid (1.92 g, 61%). ^1H NMR (600 MHz, CDCl_3): δ 8.07–8.00 (m, 3H, ArH), 7.87–7.80 (m, 2H, ArH), 7.49–7.40 (m, 3H, ArH), 7.32 (t, $J = 7.6$ Hz, 2H, ArH), 7.29–7.21 (m, 3H, ArH), 4.72–4.64 (m, 1H, OxH), 4.47 (dd, $J = 9.5, 8.5$ Hz, 1H, OxH), 4.27 (dd, $J = 8.5, 7.6$ Hz, 1H, OxH), 3.33 (dd, $J = 13.8, 5.1$ Hz, 1H, CH_2Ph), 2.78 (dd, $J = 13.8, 9.2$ Hz, 1H, CH_2Ph) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, CDCl_3): δ 163.6, 157.7, 146.9, 138.8, 138.0, 137.4, 129.4, 128.9, 128.7, 127.3, 126.7, 122.6, 122.5, 72.6, 68.3, 41.9 ppm.

2-(6-phenylpyridin-2-yl)-4,5-dihydrooxazole (2a’): White solid (1.54 g, 69%). ^1H NMR (600 MHz, CDCl_3): δ 8.07–8.03 (m, 2H, ArH), 7.97 (dd, $J = 6.1, 2.6$ Hz, 1H, ArH), 7.86–7.80 (m, 2H, ArH), 7.49–7.38 (m, 3H, ArH), 4.54 (t, $J = 9.7$ Hz, 2H, OxH), 4.15 (t, $J = 9.7$ Hz, 2H, OxH) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, CDCl_3): δ 164.2, 157.6, 146.8, 138.7, 137.4, 129.3, 128.8, 127.2, 122.33, 122.28, 68.3, 55.2 ppm. FT-IR (cm^{-1}): 1636, 1565, 1449, 1367, 1267, 1244, 1110, 1062, 946, 823, 769, 739, 708, 691. HRMS (ESI-TOF) m/z : $[\text{M} + \text{Na}]^+$ calcd for $\text{C}_{14}\text{H}_{20}\text{N}_2\text{O}^+\text{Na}^+$: 247.0842, found: 247.0839.

(S)-4-benzyl-2-(6-(naphthalen-1-yl)pyridin-2-yl)-4,5-dihydrooxazole (2b): Yellow solid (1.97 g, 54%). $[\alpha]_D^{25} = -20.30$ (c 0.109, CH_2Cl_2). ^1H NMR (600 MHz, CDCl_3): δ 8.16 (dd, $J = 7.8, 1.1$ Hz, 1H, ArH), 8.01 (d, $J = 8.4$ Hz, 1H, ArH), 7.94–7.88 (m, 2H, ArH), 7.68 (dd, $J = 7.8, 1.1$ Hz, 1H, ArH), 7.64 (dd, $J = 7.0, 1.3$ Hz, 1H, ArH), 7.54 (dd, $J = 8.2, 7.0$ Hz, 1H, ArH), 7.51–7.44 (m, 2H, ArH), 7.32 (t, $J = 7.5$ Hz, 2H, ArH), 7.30–7.22 (m, 2H, ArH), 4.72–4.63 (m, 1H, OxH), 4.45 (t, $J = 9.0$ Hz, 1H, OxH), 4.5 (dd, $J = 8.6, 7.6$ Hz, 1H, OxH), 3.32 (dd, $J = 13.8, 5.1$ Hz, 1H, CH_2Ph), 2.79 (dd, $J = 13.8, 9.1$ Hz, 1H, CH_2Ph) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, CDCl_3): δ 163.5, 159.3, 147.0, 138.0, 137.9, 136.9, 133.9, 131.4, 129.3, 129.1, 128.7, 128.4, 127.9, 127.1, 126.63, 126.59, 125.9, 125.5, 125.3, 122.5, 72.6, 68.2, 41.8 ppm. FT-IR (cm^{-1}): 1639, 1567, 1453, 1250, 1109, 992, 961, 800, 776, 741, 700, 622. HRMS (ESI-TOF) m/z : $[\text{M} + \text{H}]^+$ calcd for $\text{C}_{25}\text{H}_{21}\text{N}_2\text{O}^+$: 365.1648, found: 365.1653.

(S)-4-benzyl-2-(6-(4-(trifluoromethyl)phenyl)pyridin-2-yl)-4,5-dihydrooxazole (2c): White solid (2.37 g, 62%). $[\alpha]_D^{25} = -46.26$ (c 0.235, CH_2Cl_2). ^1H NMR (600 MHz, CDCl_3): δ 8.16 (d, $J = 8.1$ Hz, 2H, ArH), 8.08 (dd, $J = 7.5, 1.2$ Hz, 1H, ArH), 7.92–7.84 (m, 2H, ArH), 7.73 (d, $J = 8.2$ Hz, 2H, ArH), 7.32 (t, $J = 7.5$ Hz, 2H, ArH), 7.29–7.22 (m, 3H, ArH), 4.73–4.65 (m, 1H, OxH), 4.48 (dd, $J = 9.5, 8.5$ Hz, 1H, OxH), 4.28 (dd, $J = 8.5, 7.6$ Hz, 1H, OxH), 3.32 (dd, $J = 13.8, 5.1$ Hz, 1H, CH_2Ph), 2.79 (dd, $J = 13.8, 9.1$ Hz, 1H, CH_2Ph) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, CDCl_3): δ 163.3, 156.2, 147.3, 142.1, 137.9, 137.7, 131.3 (q, $^2J_{\text{C-F}} = 32.5$ Hz), 129.4, 128.8, 127.7, 126.8, 125.8 (q, $^3J_{\text{C-F}} = 3.8$ Hz), 124.3 (q, $^1J_{\text{C-F}} = 272.3$ Hz), 123.4, 122.8, 77.4, 77.2, 77.0, 72.7, 68.3, 41.8 ppm. $^{19}\text{F}\{^1\text{H}\}$ NMR (565 MHz, CDCl_3): δ −62.60 ppm. FT-IR (cm^{-1}):

1641, 1564, 1458, 1368, 1327, 1162, 1105, 1070, 1051, 1014, 960, 862, 813, 753, 736, 703, 583. HRMS (ESI-TOF) m/z : $[M + H]^+$ calcd for $C_{22}H_{18}F_3N_2O^+$: 383.1366, found: 383.1375.

(S)-4-benzyl-2-(6-(4-methoxyphenyl)pyridin-2-yl)-4,5-dihydrooxazole (2d): White solid (2.24 g, 65%). $[\alpha]_D^{25} = -32.50$ (c 0.169, CH_2Cl_2). ^1H NMR (600 MHz, $CDCl_3$): δ 8.04–7.99 (m, 2H, ArH), 7.96 (dd, $J = 7.4, 1.3$ Hz, 1H, ArH), 7.84–7.75 (m, 2H, ArH), 7.32 (t, $J = 7.6$ Hz, 2H, ArH), 7.29–7.20 (m, 3H, ArH), 7.02–6.96 (m, 2H, ArH), 4.71–4.63 (m, 1H, OxH), 4.46 (dd, $J = 9.4, 8.5$ Hz, 1H, OxH), 4.27 (dd, $J = 8.5, 7.5$ Hz, 1H, OxH), 3.86 (s, 3H, OCH_3), 3.33 (dd, $J = 13.8, 5.0$ Hz, 1H, CH_2Ph), 2.77 (dd, $J = 13.8, 9.2$ Hz, 1H, CH_2Ph) ppm. $^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$): δ 163.7, 160.9, 157.4, 146.8, 138.1, 137.3, 131.5, 129.4, 128.8, 128.7, 126.7, 121.9, 121.8, 114.3, 72.6, 68.3, 55.5, 41.9 ppm. FT-IR (cm^{-1}): 1644, 1606, 1563, 1512, 1450, 1368, 1296, 1243, 1114, 1025, 962, 809, 737, 705, 695, 656, 579. HRMS (ESI-TOF) m/z : $[M + H]^+$ calcd for $C_{22}H_{21}N_2O_2^+$: 345.1598, found: 345.1606.

(S)-4-phenyl-2-(6-phenylpyridin-2-yl)-4,5-dihydrooxazole (2e): White solid (1.77 g, 59%). ^1H NMR (600 MHz, $CDCl_3$): δ 8.15–8.10 (m, 1H, ArH), 8.08–8.03 (m, 2H, ArH), 7.87–7.81 (m, 2H, ArH), 7.49–7.44 (m, 2H, ArH), 7.42 (t, $J = 7.3$ Hz, 1H, ArH), 7.39–7.33 (m, 4H, ArH), 7.32–7.26 (m, 1H, ArH), 5.47 (dd, $J = 10.3, 8.5$ Hz, 1H, OxH), 4.92 (dd, $J = 10.3, 8.5$ Hz, 1H, OxH), 4.41 (t, $J = 8.5$ Hz, 1H, OxH) ppm. $^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$): δ 164.4, 157.7, 146.8, 142.1, 138.8, 137.5, 129.4, 128.9, 127.8, 127.3, 127.0, 122.8, 122.7, 75.5, 70.5 ppm.

(S)-4-isopropyl-2-(6-phenylpyridin-2-yl)-4,5-dihydrooxazole (2f): White solid (1.73 g, 65%). ^1H NMR (600 MHz, $CDCl_3$): δ 8.07–8.01 (m, 3H, ArH), 7.85–7.79 (m, 2H, ArH), 7.49–7.44 (m, 2H, ArH), 7.44–7.39 (m, 1H, ArH), 4.54 (dd, $J = 9.7, 8.3$ Hz, 1H, OxH), 4.25 (t, $J = 8.3$ Hz, 1H, OxH), 4.21–4.14 (m, 1H, OxH), 1.96–1.87 (m, 1H, $CH(CH_3)_2$), 1.08 (d, $J = 6.8$ Hz, 3H, $CH(CH_3)_2$), 0.96 (d, $J = 6.8$ Hz, 3H, $CH(CH_3)_2$) ppm. $^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$): δ 162.9, 157.5, 146.2, 139.3, 137.2, 129.2, 128.7, 127.2, 122.5, 122.3, 72.9, 70.8, 32.9, 19.1, 18.2 ppm.

(S)-4-benzyl-2-(6-bromopyridin-2-yl)-4,5-dihydrooxazole (2g): White solid (1.93 g, 61%). ^1H NMR (600 MHz, $CDCl_3$): δ 8.03 (dd, $J = 7.4, 1.1$ Hz, 1H, ArH), 7.67–7.58 (m, 2H, ArH), 7.34–7.28 (m, 2H, ArH), 7.26–7.21 (m, 3H, ArH), 4.69–4.61 (m, 1H, OxH), 4.45 (dd, $J = 9.5, 8.6$ Hz, 1H, OxH), 4.24 (dd, $J = 8.6, 7.7$ Hz, 1H, OxH), 3.28 (dd, $J = 13.8, 5.2$ Hz, 1H, CH_2Ph), 2.75 (dd, $J = 13.8, 9.0$ Hz, 1H, CH_2Ph) ppm. $^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$): δ 162.0, 147.7, 142.0, 138.8, 137.6, 130.4, 129.2, 128.6, 126.7, 122.9, 72.7, 68.2, 41.6 ppm.

(S)-4-benzyl-2-(pyridin-2-yl)-4,5-dihydrooxazole (2h): White solid (1.33 g, 56%). ^1H NMR (600 MHz, $CDCl_3$): δ 8.69 (d, $J = 4.8$ Hz, 1H, ArH), 8.04 (d, $J = 7.9$ Hz, 1H, ArH), 7.76 (td, $J = 7.7, 1.8$ Hz, 1H, ArH), 7.44–7.35 (m, 1H, ArH), 7.34–7.13 (m, 5H, ArH), 4.68–4.60 (m, 1H, OxH), 4.42 (dd, $J = 9.4, 8.6$ Hz, 1H, OxH), 4.21 (t, $J = 8.1$ Hz, 1H, OxH), 3.28 (dd, $J = 13.8, 5.1$ Hz, 1H, CH_2Ph), 2.74 (dd, $J = 13.8, 9.1$ Hz, 1H, CH_2Ph) ppm. $^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$): δ 162.8, 149.5, 146.5, 137.5, 136.4, 129.0, 128.3, 126.3, 125.3, 123.7, 72.2, 67.8, 41.4 ppm.

2.3. General Procedure for the Synthesis of Cobalt Complexes

All of the cobalt complexes were synthesized in a similar method. A classical synthesis process of the complex **3a** is described as follows: In a glovebox, the corresponding ligand **2a** (0.31 g, 1.0 mmol), anhydrous $CoCl_2$ (65 mg, 0.5 mmol), and freshly distilled THF (10 mL) were added subsequently to a 25 mL Schlenk bottle. The mixture was stirred for 24 h at ambient temperature. The product was obtained by removing the solvents, filtered, washed with dry diethyl ether three times, and then dried under vacuum at 40 °C for 24 h.

(S)-4-benzyl-2-(6-phenylpyridin-2-yl)-4,5-dihydrooxazole cobalt chloride (3a): Blue solid (315 mg, 83%). $[\alpha]_D^{30} = +69.62$ (c 0.26, CH_2Cl_2). FT-IR (cm^{-1}): 1652, 1601, 1579, 1445, 1425, 1375, 1249, 1173, 954, 822, 770, 748, 738, 723, 676, 624. Anal. Calcd for $C_{42}H_{36}Cl_2CoN_4O_2$: C, 66.50; H, 4.78; N, 7.39. Found: C, 66.53; H, 4.54; N, 7.12. HRMS (MALDI-TOF) m/z : $[M-Cl]^+$ calcd for $C_{42}H_{36}ClCoN_4O_2^+$: 722.1853, found: 722.1847.

2-(6-phenylpyridin-2-yl)-4,5-dihydrooxazole cobalt chloride (3a'): Blue solid. (223 mg, 77%). FT-IR (cm^{-1}): 1673, 1591, 1481, 1438, 1381, 1251, 1183, 927, 827, 768, 750, 719, 703.

Anal. Calcd for $C_{28}H_{24}Cl_2CoN_4O_2$: C, 58.15; H, 4.18; N, 9.69. Found C, 58.30; H, 4.02; N, 9.34. HRMS (MALDI-TOF) m/z : $[M-Cl]^+$ calcd for $C_{28}H_{24}ClCoN_4O_2^+$: 542.0914, found: 542.0911.

(S)-4-benzyl-2-(6-(naphthalen-1-yl)pyridin-2-yl)-4,5-dihydrooxazole cobalt chloride (3b). Blue solid (364 mg, 85%). $[\alpha]^{30}_D = -25.65$ (c 0.50, CH_2Cl_2). FT-IR (cm^{-1}): 1646, 1587, 1469, 1446, 1432, 1380, 1251, 1181, 938, 804, 779, 741, 706, 676, 627. Anal. Calcd for $C_{50}H_{40}Cl_2CoN_4O_2$: C, 69.93; H, 4.70; N, 6.52. Found: C, 70.18; H, 4.65; N, 6.40. HRMS (MALDI-TOF) m/z : $[M-Cl]^+$ calcd for $C_{50}H_{40}ClCoN_4O_2^+$: 822.2166, found: 822.2126.

(S)-4-benzyl-2-(6-(4-(trifluoromethyl)phenyl)pyridin-2-yl)-4,5-dihydrooxazole cobalt chloride (3c). Blue solid. (389 mg, 87%). $[\alpha]^{30}_D = +64.41$ (c 0.25, CH_2Cl_2). FT-IR (cm^{-1}): 1653, 1586, 1441, 1323, 1248, 1167, 1119, 1078, 1058, 1016, 953, 858, 815, 751, 710, 684. Anal. Calcd for $C_{44}H_{34}Cl_2CoF_6N_4O_2$: C, 59.07; H, 3.83; N, 6.26. Found: C, 59.05; H, 3.78; N, 6.15.

(S)-4-benzyl-2-(6-(4-methoxyphenyl)pyridin-2-yl)-4,5-dihydrooxazole cobalt chloride (3d). Blue solid (332 mg, 81%). $[\alpha]^{30}_D = +101.56$ (c 0.26, CH_2Cl_2). FT-IR (cm^{-1}): 1649, 1607, 1591, 1517, 1438, 1379, 1249, 1179, 1023, 934, 847, 815, 747, 707, 582. Anal. Calcd for $C_{44}H_{40}Cl_2CoN_4O_4$: C, 64.55; H, 4.93; N, 6.84. Found: C, 64.50; H, 4.86; N, 6.79.

(S)-4-phenyl-2-(6-phenylpyridin-2-yl)-4,5-dihydrooxazole cobalt chloride (3e). Blue solid (267 mg, 73%). $[\alpha]^{30}_D = +69.62$ (c 0.26, CH_2Cl_2). FT-IR (cm^{-1}): 1644, 1589, 1451, 1435, 1380, 1253, 1186, 929, 828, 764, 699. Anal. Calcd for $C_{40}H_{32}Cl_2CoN_4O_2$: C, 65.76; H, 4.42; N, 7.67. Found: C, 65.31; H, 4.49; N, 7.52. HRMS (MALDI-TOF) m/z : $[M-Cl]^+$ calcd for $C_{40}H_{32}ClCoN_4O_2^+$: 694.1540, found: 694.1525.

(S)-4-isopropyl-2-(6-phenylpyridin-2-yl)-4,5-dihydrooxazole cobalt chloride (3f). Blue solid (249 mg, 75%). $[\alpha]^{30}_D = +78.50$ (c 0.25, CH_2Cl_2). FT-IR (cm^{-1}): 1643, 1589, 1448, 1380, 1258, 1188, 1089, 1011, 928, 834, 768, 755, 734, 701. Anal. Calcd for $C_{34}H_{36}Cl_2CoN_4O_2$: C, 61.64; H, 5.48; N, 8.46. Found: C, 61.54; H, 5.42; N, 8.35. HRMS (MALDI-TOF) m/z : $[M-Cl]^+$ calcd for $C_{34}H_{36}ClCoN_4O_2^+$: 626.1853, found: 626.1852.

(S)-4-benzyl-2-(6-bromopyridin-2-yl)-4,5-dihydrooxazole cobalt chloride (3g). Blue solid (275 mg, 72%). $[\alpha]^{30}_D = +43.86$ (c 0.30, CH_2Cl_2). FT-IR (cm^{-1}): 1632, 1572, 1454, 1420, 1381, 1256, 1180, 1002, 948, 934, 864, 815, 756, 748, 702, 659. Anal. Calcd for $C_{30}H_{28}Br_2Cl_2CoN_4O_2$: C, 47.15; H, 3.43; N, 7.33. Found: C, 47.32; H, 3.36; N, 7.25. HRMS (MALDI-TOF) m/z : $[M-Cl]^+$ calcd for $C_{30}H_{26}Br_2ClCoN_4O_2^+$: 725.9438, found: 725.9429.

(S)-4-benzyl-2-(pyridin-2-yl)-4,5-dihydrooxazole cobalt chloride (3h). Blue solid (246 mg, 81%). $[\alpha]^{30}_D = +42.11$ (c 0.26, EtOH). FT-IR (cm^{-1}): 1652, 1594, 1493, 1401, 1300, 1260, 1148, 1050, 1017, 955, 935, 798, 762, 748, 723, 704, 674, 639. Anal. Calcd for $C_{30}H_{28}Cl_2CoN_4O_2$: C, 59.42; H, 4.65; N, 9.24. Found: C, 59.17; H, 4.71; N, 9.18. HRMS (MALDI-TOF) m/z : $[M-Cl]^+$ calcd for $C_{30}H_{28}ClCoN_4O_2^+$: 570.1227, found: 570.1213.

2.4. General Procedure for Isoprene Polymerization

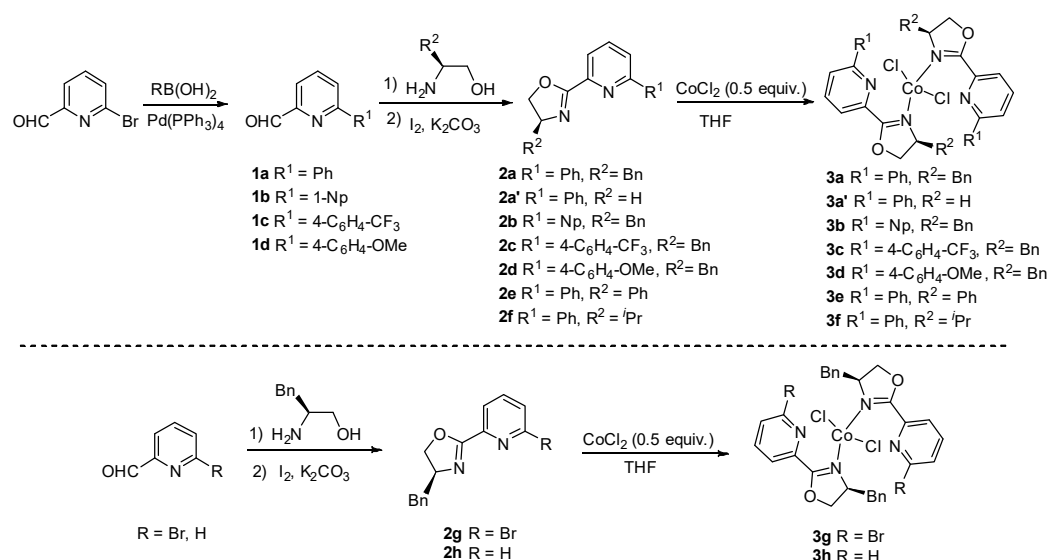
The general procedure for isoprene polymerization is as follows: In a glovebox, the cobalt complexes (5 μ mol) and toluene (5 mL) were added to an oven-dried 25 mL Schlenk bottle, stirred for 2 min, then $AlEt_2Cl$ was added and stirred for 2 min. Finally, isoprene (2 mL) was injected into the mixture with continuous stirring. After a certain period of time, acidic EtOH (5% HCl in EtOH) was added to quench the reaction. The resultant polymers were collected, washed with EtOH repeatedly, and dried in a vacuum oven at 50 $^{\circ}C$ to reach a constant weight. The conversion rate was obtained via the weight ratio of the resulting polyisoprene to the used isoprene.

3. Results and Discussion

3.1. Characterization of Pyridine–Oxazoline-Ligated Cobalt Catalysts

The synthetic route for pyridine–oxazoline-ligated cobalt complexes is shown in Scheme 2. These cobalt complexes were fully characterized through elemental analysis, FT-IR, and high-resolution mass spectrometry. By comparing the FT-IR of ligands **2a–h** (1636–1644 cm^{-1}) with the cobalt complexes **3a–h** (1586–1594 cm^{-1}), it is apparent that the oxazoline C=N absorption bands of the cobalt complexes are red-shifted (SI, Figure S59),

which can prove that there is an obvious coordination effect between the ligand and the cobalt center. The structure of the complexes **3a** and **3d** were further verified with single-crystal X-ray diffraction according to the slow diffusion of ether into a saturated dichloromethane solution containing the cobalt catalysts. Crystal data and structure refinement for complexes **3a** and **3d** are listed in Table S1. The structures of the complexes **3a** and **3d** are shown in Figure 2. The complexes **3a** and **3d** adopted similar structures, in which one cobalt atom was coordinated with two ligands. However, the N atom of pyridine does not coordinate with the cobalt center, which is inconsistent with previous reports [40,46] and the reason for this needs to be investigated further. As shown in Figure 2, the cobalt atom is coordinated with two N atoms of two oxazoline rings, respectively, and the complexes can be described as a distorted tetrahedron configuration. The Co1-N2 and Co1-N4 bond lengths of **3a** are 2.036(4) Å and 2.041(4) Å, whereas the Co1-N1 and Co1-N1' of **3d** are 2.025(3) Å and 2.024(3) Å, which indicated that the N atom in the oxazoline of **3d** had a stronger coordination ability to the cobalt center atom than that of the complex **3a**.



Scheme 2. The preparation of pyridine–oxazoline-ligated cobalt complexes.

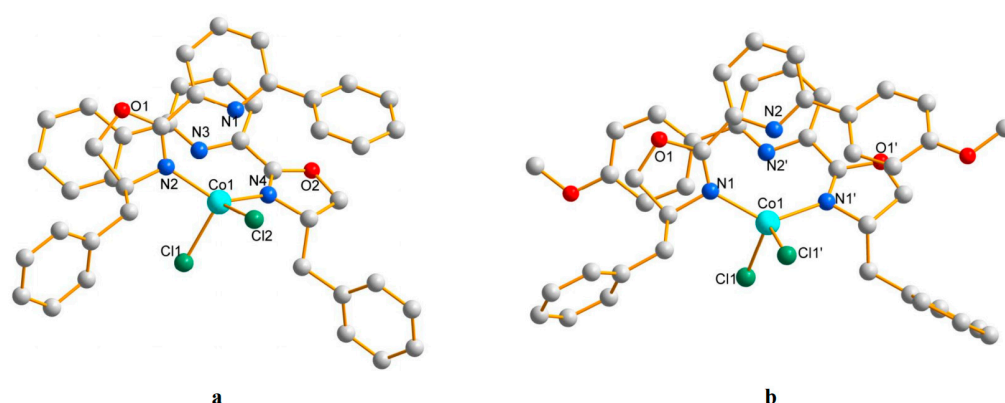


Figure 2. (a) Molecular structure of **3a** (CCDC number 2257610): selected bond lengths (Å) and angles (°): Co1–N2 2.036(4), Co1–N4 2.041(4), Co1–Cl1 2.2912(14), Co1–Cl2 2.2771(14), N2–Co1–Cl1 98.15(12), N2–Co1–Cl2 106.64(12), N2–Co1–N4 135.31(16), N4–Co1–Cl1 103.29(11), N4–Co1–Cl2 103.28(11). (b) Molecular structure of **3d** (CCDC number 2257612): selected bond lengths (Å) and angles (°): Co1–N1 2.025(3), Co1–N1' 2.024(3), Co1–Cl1 2.2710(9), Cl1'–Co1–Cl1 106.53(5), N1–Co1–Cl1 101.50(8), N1–Co1–Cl1' 106.60(8), N1'–Co1–N1 132.16(14). H atoms are omitted for clarity. Ellipsoids set at 50% probability.

3.2. Isoprene Polymerization Studies

Initially, we chose complex **3a** as the representative pre-catalyst to catalyze the polymerization of isoprene by using different kinds of co-catalysts, including MAO, AlEt₂Cl, trimethylaluminum (AlMe₃), triethylaluminum (AlEt₃) and triisobutylaluminum (Al^{*i*}Bu₃), and the resulting polymerization data are all exhibited in Table 1 (entries 1–5). It was apparent that the complex **3a** was activated for the isoprene polymerization only in the presence of AlEt₂Cl. Based on this, we further explored the effect of the amount of AlEt₂Cl as the co-catalyst on the isoprene polymerization (Table 1, entries 5–10). The amount of co-catalyst has a crucial effect on the activity of the catalyst and the molecular weight of the resulting polyisoprene. With the decrease in the amount of Al/Co, the catalytic activity was also decreased, while the molecular weight of the polyisoprene was increased first and then decreased (Figure 3). When the Al/Co ratio was 500, the isoprene monomer could achieve almost full conversion. With the Al/Co ratio decreasing from 500 to 50, we discovered that the catalytic activity of **3a** slightly decreased from $1.36 \times 10^5 \text{ g}\cdot\text{mol}^{-1}\cdot\text{h}^{-1}$ to $1.33 \times 10^5 \text{ g}\cdot\text{mol}^{-1}\cdot\text{h}^{-1}$, but the molecular weight increased from $1.33 \times 10^4 \text{ g}\cdot\text{mol}^{-1}$ to $1.76 \times 10^5 \text{ g}\cdot\text{mol}^{-1}$. However, the catalytic activity decreased sharply when Al/Co = 5, the monomer conversion was only 56% in two hours, and the molecular weight of the polymer was lower, at $3.56 \times 10^4 \text{ g}\cdot\text{mol}^{-1}$. These results may be ascribed to the fact that chain transfer to the aluminum occurs more readily in the presence of an excess of Al reagents. However, the percentage *cis*-1,4/3,4 remained almost the same, and the structure of polyisoprene basically remained, with *cis*-1,4/3,4 $\approx$ 2/1. The percentage of *cis*-1,4 and 3,4 units was calculated from the ¹H NMR (see Figure S29). The effect of monomer contents on polymerization was further investigated (Table 1, entries 11–12). The conversion of isoprene was slightly decreased (from 99% to 94%) when decreasing [IP]/[Co] from 4000 to 2000, while the conversion was sharply decreased to 59% when increasing [IP]/[Co] to 8000, since the formed active center was wrapped in superabundant monomers.

Table 1. Optimization of co-catalysts for isoprene polymerization catalyzed by **3a**. ^a

Entry	Co-Catalyst	Al/Co	Conv/%	Activity ^b	Microstructure ^c		<i>M_n</i> ^d	<i>Đ</i> ^d
					<i>cis</i> -1,4	3,4		
1	MAO	500	trace	-	-	-	-	-
2	AlMe ₃	500	-	-	-	-	-	-
3	AlEt ₃	500	-	-	-	-	-	-
4	Al ^{<i>i</i>} Bu ₃	500	-	-	-	-	-	-
5	AlEt ₂ Cl	500	99	1.36	67	33	1.33	2.81
6	AlEt ₂ Cl	200	99	1.36	65	35	5.74	2.45
7	AlEt ₂ Cl	80	99	1.36	64	36	12.5	2.05
8	AlEt ₂ Cl	50	97	1.33	67	33	17.6	2.35
9	AlEt ₂ Cl	20	84	1.15	62	38	12.2	2.03
10	AlEt ₂ Cl	5	56	0.76	65	35	3.56	2.56
11 ^e	AlEt ₂ Cl	80	94	0.64	63	37	10.5	2.82
12 ^f	AlEt ₂ Cl	80	59	1.61	63	37	11.5	1.95

^a General conditions: isoprene 2 mL, 4000 equiv.; Co(II) complex 5 μmol, 1 equiv.; toluene 5 mL; reaction temperature 25 °C; reaction time 2 h. ^b $10^5 \text{ g}\cdot\text{mol}^{-1}\cdot\text{h}^{-1}$. ^c Determined by ¹H/¹³C NMR in CDCl₃. ^d *M_n*: $10^4 \text{ g}\cdot\text{mol}^{-1}$, determined by GPC. ^e Isoprene 1 mL, 2000 equiv. ^f Isoprene 4 mL, 8000 equiv.

Subsequently, the effects of the reaction time and temperature on the polymerization of isoprene were also tested. With the reaction time decreasing from 120 min to 5 min, the conversion decreased from 99% to 76%, while the catalytic activity increased from $1.36 \times 10^5 \text{ g}\cdot\text{mol}^{-1}\cdot\text{h}^{-1}$ to $2.5 \times 10^6 \text{ g}\cdot\text{mol}^{-1}\cdot\text{h}^{-1}$ (Table 2, entries 1–5), which indicated that the active species of complex **3a** was formed rapidly and promoted the rate of isoprene polymerization. Obviously, the molecular weight was decreased with the shortening of the reaction time, but the *cis*-1,4 selectivity remained almost similar. The reaction temperature played a key role in polymerization, and when the temperature was elevated from 25 °C to 90 °C, it showed that the conversion of the isoprene monomers was decreased (Table 2

and Figure 4). For example, the catalytic activity at 70 °C was slightly decreased compared to the activity at room temperature ($1.19 \times 10^5 \text{ g}\cdot\text{mol}^{-1}\cdot\text{h}^{-1}$ vs. $1.36 \times 10^5 \text{ g}\cdot\text{mol}^{-1}\cdot\text{h}^{-1}$). However, the conversion decreased sharply to 16% when the temperature increased to 90 °C, because the formed active species were unstable at a higher temperature. It was notable that the molecular weight declined from $12.5 \times 10^4 \text{ g}\cdot\text{mol}^{-1}$ to $8.21 \times 10^4 \text{ g}\cdot\text{mol}^{-1}$, and $\bar{D}$ increased from 2.05 to 2.49 with the elevated temperature, which was probably related to the fast chain transfer reaction at the increased temperature.

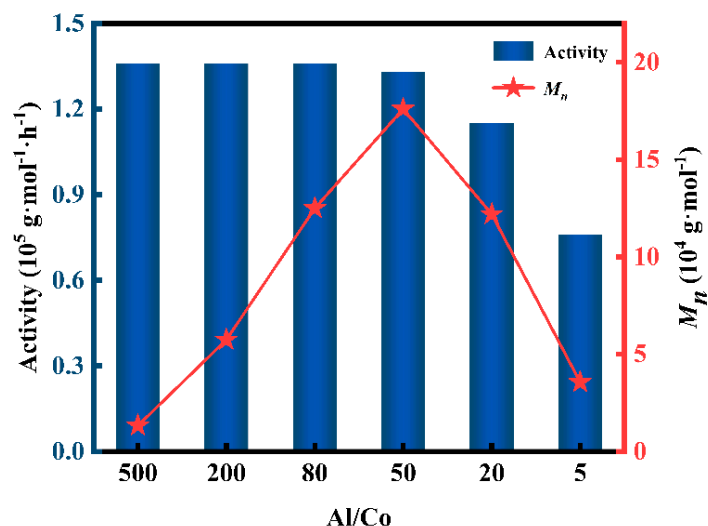


Figure 3. The effect of the Al/Co molar ratio on isoprene polymerization.

Table 2. Isoprene polymerization catalyzed by **3a** under various conditions. ^a

Entry	T/°C	t/min	Conv/%	Activity ^b	Microstructure ^c		M_n ^d	$\bar{D}$ ^d
					<i>cis</i> -1,4	3,4		
1	25	120	99	1.36	64	36	12.5	2.05
2	25	60	97	2.64	63	37	8.79	1.95
3	25	30	94	5.12	64	36	7.67	2.79
4	25	10	83	13.6	63	37	4.46	1.79
5	25	5	76	25.0	63	37	0.47	2.61
6	50	120	92	1.32	65	35	10.9	2.21
7	70	120	82	1.19	65	35	10.7	2.49
8	90	120	16	0.23	66	34	8.21	2.30

^a General conditions: isoprene 2 mL, 4000 equiv.; Co(II) complex 5 μmol , 1 equiv.; Al/Co = 80; toluene 5 mL.

^b $10^5 \text{ g}\cdot\text{mol}^{-1}\cdot\text{h}^{-1}$. ^c Determined by $^1\text{H}/^{13}\text{C}$ NMR in CDCl_3 . ^d M_n : $10^4 \text{ g}\cdot\text{mol}^{-1}$, determined by GPC.

To further explore the steric and electronic effects on catalytic performance, the complexes **3a–h** were tested in polymerization and the resultant data were concluded in Table 3. All complexes almost appeared to exhibit high catalytic activity ($1.31\text{--}1.36 \times 10^5 \text{ g}\cdot\text{mol}^{-1}\cdot\text{h}^{-1}$) in isoprene polymerization and obtained high-molecular-weight polyisoprene (up to $1.44 \times 10^5 \text{ g}\cdot\text{mol}^{-1}$, Figure S52), whereas the *cis*-1,4 selectivity almost remained unchanged (*cis*-1,4-unit contents: 62~67%). Among the complexes, complex **3a** displayed the higher catalytic activity ($1.36 \times 10^5 \text{ g}\cdot\text{mol}^{-1}\cdot\text{h}^{-1}$) with a higher molecular weight ($1.25 \times 10^5 \text{ g}\cdot\text{mol}^{-1}$, Figure S46) and the lowest $\bar{D}$ (2.05). Additionally, achiral complex **3a'** was also synthesized in order to make a comparison with chiral cobalt complex **3a** (Table 3, entry 2). The catalytic activity of **3a'** slightly decreased ($1.32 \times 10^5 \text{ g}\cdot\text{mol}^{-1}\cdot\text{h}^{-1}$ vs. $1.36 \times 10^5 \text{ g}\cdot\text{mol}^{-1}\cdot\text{h}^{-1}$) and the ratio *cis*-1,4/3,4 was almost the same. However, the molecular weight of the polymer was decreased ($12.5 \times 10^4 \text{ g}\cdot\text{mol}^{-1}$ vs. $3.15 \times 10^4 \text{ g}\cdot\text{mol}^{-1}$, Figure S46 vs. Figure S51) and the $\bar{D}$ became broader (2.05 vs. 2.64).

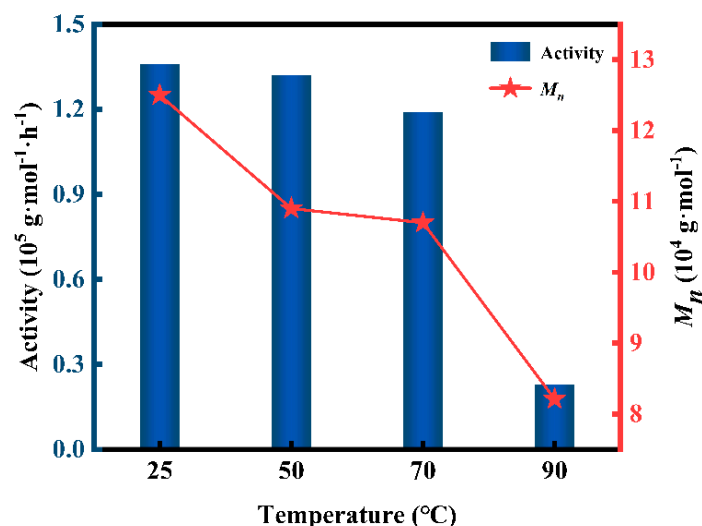


Figure 4. The effect of temperature on isoprene polymerization.

Table 3. Isoprene polymerization catalyzed by Co(II) complexes ^a.

Entry	Cat	Conv/%	Activity ^b	Microstructure ^c		M_n ^d	$\bar{D}$ ^d
				<i>cis</i> -1,4	3,4		
1	3a	99	1.36	64	36	12.5	2.05
2	3a'	97	1.32	64	36	3.15	2.64
3	3b	99	1.36	65	35	14.4	2.14
4	3c	99	1.36	65	35	1.92	2.75
5	3d	99	1.35	65	35	7.74	2.18
6	3e	98	1.32	65	35	4.66	2.65
7	3f	99	1.34	65	35	5.78	2.60
8	3g	96	1.31	62	38	1.70	3.42
9	3h	99	1.36	64	36	10.5	2.07

^a General conditions: isoprene 2 mL, 4000 equiv.; Co(II) complex 5 μmol , 1 equiv.; Al/Co = 80; toluene 5 mL; reaction temperature 25 °C; reaction time 2 h. ^b $10^5 \text{ g} \cdot \text{mol}^{-1} \cdot \text{h}^{-1}$. ^c Determined by $^1\text{H}/^{13}\text{C}$ NMR in CDCl_3 . ^d M_n : $10^4 \text{ g} \cdot \text{mol}^{-1}$, determined by GPC.

4. Conclusions

In conclusion, a family of well-defined pyridine–oxazoline cobalt complexes were synthesized and characterized, and single-crystal X-ray analysis displayed that the complexes **3a** and **3d** adopted a distorted tetrahedron configuration. In the presence of AlEt_2Cl as a co-catalyst, these cobalt complexes all exhibited high activity for isoprene polymerization. The resultant polymers had high molecular weights (up to $1.44 \times 10^5 \text{ g} \cdot \text{mol}^{-1}$) and moderate *cis*-1,4 selectivity. In particular, the complex **3a** still displayed a high activity even at a relatively high polymerization temperature of 70 °C, which revealed that the formed active species of **3a** exhibited better thermal stability.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/polym16050578/s1>.

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