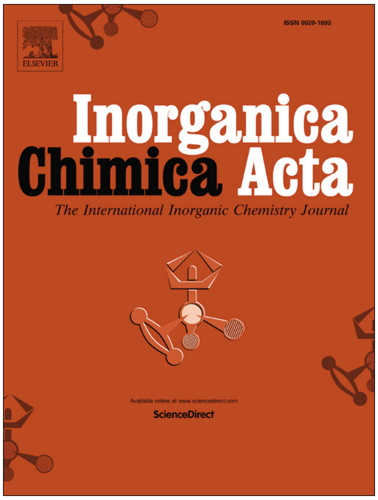

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Pyridine-oxazoline and Quinoline-oxazoline Ligated Cobalt Complexes: Synthesis, Characterization, and 1,3-Butadiene Polymerization Behaviors

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Abstract

A series of cobalt complexes supported by pyridine-oxazoline (Pyox) and quinoline-oxazoline (Quox) were synthesized. Determined by single crystal X-ray crystallography, complexes **6a** and **7c** adopted distorted octahedron and trigonal bipyramid geometries, respectively, while complex **6b** existed as an ion pair comprised of $[CoL_2]^{2+}$ and $[CoCl_4]^{2-}$, in which the cationic and anionic moieties displayed distorted octahedron and tetrahedral geometries, respectively. Upon activation with ethylaluminum sesquichloride (EASC), these cobalt complexes exhibited high catalytic activity and *cis*-1,4-selectivity towards 1,3-butadiene polymerization. The selectivity of the catalytic system could be switched from *cis*-1,4 to 1,2-fashion via the addition of PPh_3. The effects of ligand environment, polymerization temperature, and [Al]/[Co] ratio on the polymerization were investigated in detail.

Keywords: Pyridine; Oxazoline; Quinoline; Cobalt complex; 1,3-Butadiene polymerization

1. Introduction

The development of new catalysts for the chemo- and stereo-selective polymerization of conjugated dienes has attracted considerable attention in the past decades[1-5]. Numerous catalyst systems based on transition metals (Ti, Ni, Co, etc.) and rare earth metal have been developed so far[6-8]. Among them, cobalt-based catalyst systems are of particular interest because they can produce polybutadienes with versatile microstructures including *cis*-1,4, *trans*-1,4, and syndiotactic-1,2 isomers depending on the catalyst formulation[9-11]. Additionally, the catalytic activity and selectivity of catalysts mainly depend on the steric and electronic nature of the active site. In recent years, research interest has been focused on the design and synthesis of well-defined single-site catalysts in order to gain precise control of the catalysis behavior and polymer composition [12-15]. Since the discovery of bis(arylimino)pyridine ligated Co(II) and iron(II) complexes as effective catalysts for ethylene polymerization/oligomerization [16,17], a variety of transition metal complexes bearing α-diimine, pyridinediimine, and their derivatives have been synthesized and exploited as catalyst precursors for olefin polymerization [18-24]. Tremendous progress has also been made in the aspect of conjugated diene polymerization. For example, (salen)cobalt(II) [25] and bis(salicylaldiminate) cobalt(II) [26] were reported to be highly active for *cis*-1,4 polymerization of 1,3-butadiene. Cobalt dichloride complexes bearing various tridentate ligands such as 2,6-bis(imino)pyridine [6,27], 2,6-bis(pyrazol)pyridine [28], bis(N-arylcarboximidoylchloride)pyridine [29], 2-arylimino-6-(alcohol) pyridine/2-arylamino-6-(alcohol) pyridine [30], and 3-aryliminomethyl-2-hydroxybenzaldehyde [31] afforded *cis*-1,4 polybutadienes in high yields.

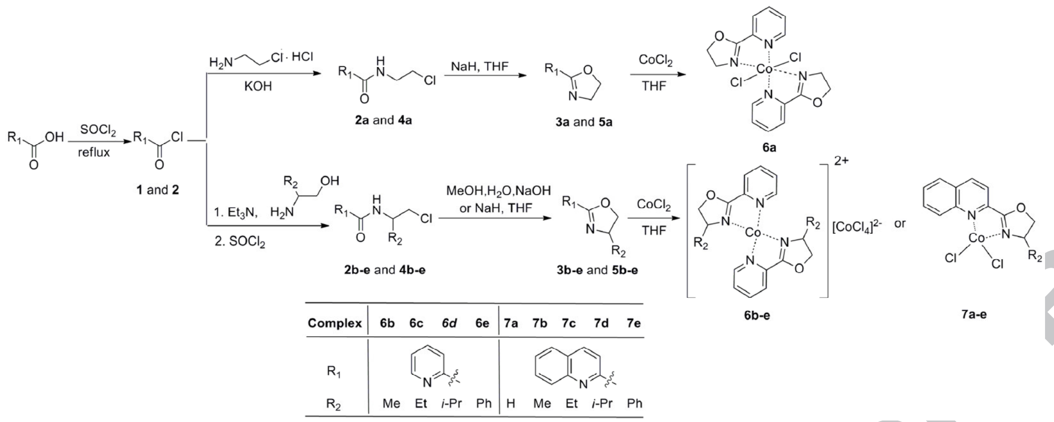
Pyridine bisoxazoline (Pybox) is an important class of ligands in scientific research owing to its facile preparation and easy modification of the parent framework [32,33]. Various Pybox/metal complexes have been synthesized and found applications in asymmetrical catalysis. However, its potential as coordination polymerization catalyst is quite limited. Iron(II) [34] and ruthenium(II) [35] complexes bearing 2,6-bis[4'-(S)-isopropyloxazolin-2'-yl]pyridine were reported as catalytic precursors for ethylene polymerization but exhibited low activities. To our knowledge, there is only one paper that reported the polymerization of 1,3-butadiene with 2,6-bis[4'-(S)-isopropyloxazolin-2'-yl]pyridine chromium trichloride/MMAO catalyst [36]. On the other hand, many studies have disclosed that the ligand environment of the complex affected catalytic behaviors significantly. In the present study, a series of pyridine-oxazoline and quinoline-oxazoline ligated Co(II) complexes were synthesized and characterized. Furthermore, the effects of the ligand and polymerization parameter on the activity and selectivity towards 1,3-butadiene polymerization was investigated in detail.

2. Experimental Part

2.1. General consideration

The molecular weights (M_n) and molecular weight distributions (MWD) of polymers were measured at 30 °C by gel permeation chromatography (GPC) equipped with a Waters 515 HPLC pump, four columns (HMW 7 THF, HMW 6E THF × 2, HMW 2 THF) and a Waters 2414 refractive index detector. THF was used as eluent at a flow rate of 1.0 mL/min. The molecular weight of polymer was determined using the polystyrene calibration. ^{1}H-NMR (400 MHz) and ^{13}C-NMR (100 MHz) were recorded on a Varian Unity spectrometer in $CDCl_3$ or DMSO-d_6 at room temperature. IR spectra were recorded on a BRUKER Vertex-70 FT-IR spectrophotometer. Elemental analysis was performed on an elemental Vario EL spectrometer. The proportion of 1,2, *cis*-1,4, and *trans*-1,4 units of polymer were determined by IR, ^{1}H-NMR, and ^{13}C-NMR spectra [37,38].

All the manipulations were performed under an atmosphere of dry argon by using standard Schlenk techniques or in a glove box. Toluene, tetrahydrofuran (THF), and diethyl ether were freshly obtained by distillation under nitrogen from sodium-benzophenone ketyl. $CHCl_3$ and triethylamine were refluxed over CaH_2 and distilled prior to use. N,N-dimethylformamide (DMF) was dried over CaH_2 and then distilled under reduced pressure before use. 1,3-Butadiene was supplied by Jinzhou Petrochemical Corporation and purified by passing through four columns packed with 4 Å molecule sieve and KOH prior to use. MAO (10 wt%) was purchased from Akzo Noble and used as received. Ethylaluminum sesquichloride (EASC) was purchased from Sigma-Aldrich Co. and diluted to 1.0 mol/L solution by toluene. Other chemicals were commercially available and used as received unless otherwise mentioned. The ligands were synthesized referring to the modified literature methods (**Scheme 1**) [32, 39-41].



Scheme 1. Synthesis of complexes **6a**-**e** and **7a**-**e**.

*2.2. Synthesis and characterization of ligands **3a**-**e** and **5a**-**e***

*2.2.1. Synthesis of 2-(oxazolin-2'-yl) pyridine, Pyox (**3a**).*

Pyridine-2-carboxylic acid (1.23 g, 10.0 mmol) was treated with $SOCl_2$ (15.0 mL) at reflux temperature under a nitrogen atmosphere. Excess $SOCl_2$ was then removed under reduced pressure to give the acid chloride as a white solid (100%). The chloroform solution of crude 2-pyridine carbonyl chloride was slowly added to an aqueous solution of chloroethylamine hydrochloride (2.55 g, 22.0 mmol) and KOH (1.69 g, 30.0 mmol) at 0 °C. After 1 h, the aqueous layer was discarded, the organic layer filtered and washed with water. After the solvent was removed under reduced pressure, the crude carboxamide was yielded as a light yellow solid. This solid was dissolved in THF and then added to a suspension of NaH (0.60 g, 60% in mineral oil) in THF at 0 °C. The reaction mixture was stirred at room temperature for 24 h, and then quenched with 10% HCl aq. The THF was removed under reduced pressure, and the residue was dissolved in dichloromethane. The resulting organic layer was dried over anhydrous $MgSO_4$. After evaporating the solvent, the product was obtained as a white powder in 60% yield (0.89 g). ^{1}H NMR ($CDCl_3$, ppm): 8.71 (d, *J* = 4.5 Hz, 1H), 8.05 (d, *J* = 7.9 Hz, 1H), 7.79 (td, *J* = 7.8, 1.4 Hz, 1H), 7.46 – 7.35 (m, 1H), 4.53 (t, *J* = 9.6 Hz, 2H), 4.14 (t, *J* = 9.7 Hz, 2H). ^{13}C NMR ($CDCl_3$, ppm): 163.93, 149.73, 146.95, 136.60, 125.49, 123.85, 68.23, 55.19. FT-IR (KBr; cm^{-1}): 1661, 1584, 1471, 1366, 1266, 1100, 940, 800, 748, 672. Anal. Calc. for $C_8H_8N_2O$ (148.16): C, 64.85; H, 5.44; N, 18.91. Found: C, 64.72; H, 5.59; N, 19.20.

*2.2.2. Synthesis of 2-[4'-(S)- methyloxazolin-2'-yl]pyridine, Me-Pyox (**3b**).*

Crude 2-pyridine carbonyl chloride was prepared by the same method as for **3a**. The obtained crude carbonyl chloride reacted with (S)-2-Amino-1-propanol with triethylamine as a deacid reagent, then excess $SOCl_2$ was added, and the solution was reflux for 2h. The resultant mixture was poured into ice water.

The organic layer was collected, washed with brine (20 mL × 3) and aqueous K_2CO_3 aq. (0.1 mol/L, 30 mL), and dried over anhydrous $MgSO_4$. After evaporating the solvent, the crude product was purified by silica gel column chromatography to give **2b** (1.59 g, ca. 8.0 mmol) as a light yellow solid. The solid (3.20 g) was treated with a THF suspension of NaH (0.60 g) at room temperature for 24 h. The THF was removed under reduced pressure, and the residue was dissolved in dichloromethane. The organic layer was dried over Na_2SO_4. After evaporation the solvent, the product was obtained as a colorless liquid (1.04g, 64% yield). ^{1}H NMR (CDCl$_3$, ppm): 8.71 (d, *J* = 4.4 Hz, 1H), 8.04 (d, *J* = 7.9 Hz, 1H), 7.77 (td, *J* = 7.8, 1.3 Hz, 1H), 7.44–7.33 (m, 1H), 4.69–4.57 (m, 1H), 4.53–4.38 (m, 1H), 4.05 (t, *J* = 8.1 Hz, 1H), 1.40 (d, *J* = 6.6 Hz, 3H). ^{13}C NMR (CDCl$_3$, ppm): 162.47, 149.61, 146.86, 136.42, 125.31, 123.70, 74.52, 62.22, 21.18. FT-IR (KBr; cm^{-1}): 1661, 1588, 1529, 1472, 1361, 1123, 1084, 1045, 960, 751, 622. Anal. Calc. for $C_9H_{10}N_2O$ (162.19): C, 66.65; H, 6.21; N, 17.27. Found: C, 66.86; H, 6.29; N, 17.34.

*2.2.3. Synthesis of 2-[4'-(S)- ethyloxazolin-2'-yl]pyridine, Et-Pyox (**3c**).*

This compound was prepared by the same method as for **3b**. Yield, 1.04 g (59%). ^{1}H NMR (CDCl$_3$, ppm): 8.71 (d, *J* = 4.3 Hz, 1H), 8.05 (d, *J* = 7.9 Hz, 1H), 7.84–7.71

(m, 1H), 7.45–7.35 (m, 1H), 4.58 (t, *J* = 8.9 Hz, 1H), 4.39–4.26 (m, 1H), 4.14 (t, *J* = 8.1 Hz, 1H), 1.83 (td, *J* = 13.7, 7.2 Hz, 1H), 1.72–1.58 (m, 1H), 1.03 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR ($CDCl_3$, ppm): 165.04, 149.95, 148.16, 137.44, 126.24, 122.38, 65.11, 53.70, 24.42, 10.64. FT-IR (KBr; cm^{-1}):1660, 1525, 1464, 1432, 1291, 1245, 1090, 997, 750, 616. Anal. Calc. for $C_{10}H_{12}N_2O$ (176.22): C, 68.16; H, 6.86; N, 15.90. Found: C, 67.95; H, 6.95; N, 15.73.

*2.2.4. Synthesis of 2-[4'-(S)-isopropyloxazolin-2'-yl]pyridine, i-Pr-Pyox (**3d**).*

This compound was prepared by the same method as for **3b**. Yield, 0.95 g (50%). ^{1}H NMR ($CDCl_3$, ppm): 8.71 (d, *J* = 4.3 Hz, 1H), 8.06 (d, *J* = 7.9 Hz, 1H), 7.77 (td, *J* = 7.8, 1.3 Hz, 1H), 7.45–7.33 (m, 1H), 4.51 (t, *J* = 8.4 Hz, 1H), 4.27–4.12 (m, 2H), 1.91 (dh, *J* = 13.2, 6.6 Hz, 1H), 1.06 (d, *J* = 6.7 Hz, 3H), 0.95 (d, *J* = 6.7 Hz, 3H). ^{13}C NMR ($CDCl_3$, ppm): 162.73, 149.87, 147.24, 136.64, 125.51, 124.07, 73.19, 70.91, 32.92, 19.14, 18.36. FT-IR (KBr; cm^{-1}): 1663, 1584, 1466, 1357, 1099, 1044, 963, 747, 674, 622. Anal. Calc. for $C_{11}H_{14}N_2O$ (190.24): C, 69.45; H, 7.42; N, 14.73. Found: C, 69.13; H, 7.28; N, 14.90.

*2.2.5. Synthesis of 2-[4'-(R)-phenyloxazolin-2'-yl]pyridine, Ph-Pyox (**3e**).*

This compound was prepared by the same method as for **3b**. Yield, 1.12 g (60%). ^{1}H NMR ($CDCl_3$, ppm): 8.75 (d, *J* = 4.1 Hz, 1H), 8.18 (d, *J* = 7.8 Hz, 1H), 7.82 (dd, *J* = 10.9, 4.4 Hz, 1H), 7.47–7.41 (m, 1H), 7.41–7.28 (m, 5H), 5.60–5.37 (m, 1H), 5.01–4.82 (m, 1H), 4.40 (t, *J* = 8.5 Hz, 1H). ^{13}C NMR ($CDCl_3$, ppm): 164.81, 149.79, 148.27, 139.27, 137.49, 128.94, 127.91, 127.00, 126.42, 122.51, 66.60, 56.24. FT-IR (KBr; cm^{-1}):1666, 1521, 1464, 1433, 1291, 1071, 1040, 748, 700, 614. Anal. Calc. for $C_{14}H_{12}N_2O$ (224.26): C, 74.98; H, 5.39; N, 12.49. Found: C, 74.83; H, 5.51; N, 12.37.

*2.2.6. Synthesis of 2-[oxazolin-2'-yl]quinoline, Quox (**5a**).*

This compound was prepared by the same method as for **3a**. Yield, 1.23 g (62%).^{1}H NMR ($CDCl_3$, ppm): 8.48–8.09 (m, 3H), 7.86 (d, *J* = 8.1 Hz, 1H), 7.76 (t, *J* = 7.3 Hz, 1H), 7.61 (t, *J* = 7.4 Hz, 1H), 4.61 (t, *J* = 9.6 Hz, 2H), 4.20 (t, *J* = 9.6 Hz, 2H). ^{13}C NMR ($CDCl_3$, ppm): 164.33, 147.79, 146.99, 136.82, 130.56, 130.15, 128.88, 128.03, 127.64, 120.81, 101.13, 68.58, 55.37. FT-IR (KBr; cm^{-1}): 1649, 1590, 1459, 1371, 1120, 1081, 839, 766, 624. Anal. Calc. for $C_{12}H_{10}N_2O$ (198.22): C, 72.71; H, 5.08; N, 14.13. Found: C, 72.64; H, 5.26; N, 14.17.

*2.2.7. Synthesis of 2-[4'-(S)- methyloxazolin-2'-yl]quinoline, Me-Quox (**5b**).*

This compound was prepared by the same method as for **3b**. Yield, 1.21 g (57%). ^{1}H NMR ($CDCl_3$, ppm): 8.35–8.10 (m, 3H), 7.86 (d, *J* = 8.1 Hz, 1H), 7.76 (t, *J* = 7.6 Hz, 1H), 7.61 (t, *J* = 7.5 Hz, 1H), 4.70 (t, *J* = 8.8 Hz, 1H), 4.59–4.45 (m, 1H), 4.15 (t, *J* = 8.0 Hz, 1H), 1.44 (d, *J* = 6.6 Hz, 3H). ^{13}C NMR ($CDCl_3$, ppm): 170.31, 164.94, 149.68, 146.48, 137.50, 130.14, 129.72, 129.31, 127.97, 127.76, 118.87, 66.83, 48.15, 17.24. FT-IR (KBr; cm^{-1}): 1658, 1530, 1498, 1426, 1052, 847, 775, 623. Anal. Calc. for $C_{13}H_{12}N_2O$ (212.25): C, 73.56; H, 5.70; N, 13.20. Found: C, 73.44; H, 5.92; N, 13.31.

*2.2.8. Synthesis of 2-[4'-(S)- ethyloxazolin-2'-yl]quinoline, Et-Quox (**5c**).*

This compound was prepared by the same method as for **3b**. Yield, 1.22 g (54%). ^{1}H NMR ($CDCl_3$, ppm): 8.46–8.18 (m, 3H), 8.11 (d, *J* = 8.5 Hz, 1H), 7.86 (d, *J* = 8.1 Hz, 1H), 7.75 (t, *J* = 7.6 Hz, 1H), 7.61 (t, *J* = 7.5 Hz, 1H), 4.17–4.04 (m, 1H), 3.87 (dd, *J* = 11.1, 3.5 Hz, 1H), 3.78 (dd, *J* = 11.1, 6.0 Hz, 1H), 1.88–1.66 (m, 2H), 1.06 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR ($CDCl_3$, ppm): 164.92, 149.54, 146.25, 137.26, 129.92, 129.53, 129.06, 127.75, 127.53, 118.70, 64.57, 53.53, 24.49, 10.57. FT-IR (KBr; cm^{-1}): 1662, 1530, 1501, 1426, 1168, 843, 773, 626. Anal. Calc. for $C_{14}H_{14}N_2O$ (226.27): C, 74.31; H, 6.24; N, 12.38. Found: C, 74.10; H, 6.65; N, 12.10.

*2.2.9. Synthesis of 2-[4'-(S)-isopropyloxazolin-2'-yl]quinoline, i-Pr-Quox (**5d**).*

This compound was prepared by the same method as for **3b**. Yield, 1.32 g (55%). ^{1}H NMR ($CDCl_3$, ppm): 8.34–8.20 (m, 3H), 7.86 (d, J = 8.1 Hz, 1H), 7.76 (t, J = 7.6 Hz, 1H), 7.61 (t, J = 7.5 Hz, 1H), 4.61 (t, J = 9.0 Hz, 1H), 4.32 (t, J = 8.3 Hz, 1H), 4.29 – 4.20 (m, 1H), 1.96 (dq, J = 13.3, 6.6 Hz, 1H), 1.09 (d, J = 6.7 Hz, 3H), 0.98 (d, J = 6.7 Hz, 3H). ^{13}C NMR ($CDCl_3$, ppm): 163.02, 147.77, 147.18, 136.79, 130.56, 130.14, 128.91, 128.02, 127.67, 121.06, 73.18, 71.18, 32.99, 19.22, 18.38. FT-IR (KBr; cm^{-1}): 1647, 1462, 1367, 1267, 1121, 1085, 968, 840, 762, 622. Anal. Calc. for $C_{15}H_{16}N_2O$ (240.30): C, 74.97; H, 6.71; N, 11.66. Found: C, 74.73; H, 6.74; N, 11.85.

*2.2.10. Synthesis of 2-[4'-(R)-phenyloxazolin-2'-yl]quinoline, Ph-Quox (**5e**).*

This compound was prepared by the same method as for **3b**. Yield, 1.34 g (49%). ^{1}H NMR ($CDCl_3$, ppm): 8.28 (m, 3H), 7.88 (d, J = 8.1 Hz, 1H), 7.78 (t, J = 7.5 Hz, 1H), 7.63 (t, J = 7.4 Hz, 1H), 7.44–7.28 (m, 5H), 5.60–5.47 (m, 1H), 5.05–4.93 (m, 1H), 4.48 (d, J = 17.1 Hz, 1H). ^{13}C NMR ($CDCl_3$, ppm): 164.29, 147.78, 146.87, 141.89, 136.92, 130.53, 130.25, 128.99, 128.19, 127.96, 127.71, 127.01, 121.17, 75.73, 70.61. FT-IR (KBr; cm^{-1}): 1645, 1560, 1451, 1365, 1126, 1088, 970, 838, 759, 697, 643. Anal. Calc. for $C_{18}H_{14}N_2O$ (274.32): C, 78.81; H, 5.14; N, 10.21. Found: C, 78.60; H, 5.25; N, 10.03.

*2.3. Synthesis and characterization of Cobalt complexes **6a-e** and **7a-e***

Complex **6a** was obtained by mixing $CoCl_2$ with 2.0 equivalents of ligand in THF and other complexes were prepared by mixing $CoCl_2$ with 1.0 equivalent of ligand in THF. The solution turned green immediately, and a green suspension was obtained after several minutes. The mixture was stirred at room temperature overnight. The precipitate was filtered, washed with dry diethyl ether, and then dried under vacuum at 40 °C for 24 h.

2.3.1. Synthesis of [Co (2,6-bis[oxazolin-2'-yl] pyridine) $_2]^{2+}[Cl_2]^{2-}$ *(**6a**).*

Yield, 0.15 g (69%). FT-IR (KBr; cm^{-1}):1647, 1590, 1398, 1276, 1146, 1014, 929, 671. Anal. Calc. for $C_{16}H_{16}Cl_2CoN_4O_2$(426.16): C, 45.09; H, 3.78; N, 13.15. Found: C, 45.25; H, 4.07; N, 13.04.

2.3.2. Synthesis of [Co(2-[4'-(S)- methyloxazolin-2'-yl]pyridine) $_2]^{2+}[CoCl_4]^{2-}$ *(**6b**).*

Yield, 0.25 g (65%). FT-IR (KBr; cm^{-1}):1653, 1593, 1400, 1256, 1161, 1014, 946, 753, 679. Anal. Calc. for $C_{18}H_{20}Cl_4Co_2N_4O_2$(584.06): C, 37.02; H, 3.45; N, 9.59. Found: C, 37.19; H, 3.75; N, 9.24.

2.3.3. Synthesis of [Co (2-[4'-(S)- ethyloxazolin-2'-yl]pyridine) $_2]^{2+}[CoCl_4]^{2-}$ *(**6c**).*

Yield, 0.21 g (71%). FT-IR (KBr; cm^{-1}): 1633, 1596, 1560, 1261, 1053, 1018, 877, 754. Anal. Calc. for $C_{20}H_{24}Cl_4Co_2N_4O_2$(612.11): C, 39.24; H, 3.95; N, 9.15. Found: C, 39.15; H, 4.16; N, 9.07.

2.3.4. Synthesis of [Co (2-[4'-(S)-isopropyloxazolin-2'-yl]pyridine) $_2]^{2+}[CoCl_4]^{2-}$ *(**6d**).*

Yield, 0.25 g (70%). FT-IR (KBr; cm^{-1}): 1648, 1593, 1403, 1257, 1159, 1016, 935, 805, 757, 674. Anal. Calc. for $C_{22}H_{28}Cl_4Co_2N_4O_2$(640.16): C, 41.28; H, 4.41; N, 8.75. Found: C, 41.23; H, 4.56; N, 8.55.

2.3.5. Synthesis of [Co (2-[4'-(R)-phenyloxazolin-2'-yl]pyridine) $_2]^{2+}[CoCl_4]^{2-}$ *(**6e**).*

Yield, 0.20 g (78%). FT-IR (KBr; cm^{-1}): 1631, 1595, 1558, 1474, 1171, 1022, 754, 702. Anal. Calc. for $C_{28}H_{24}Cl_4Co_2N_4O_2$(708.19): C, 47.49; H, 3.42; N, 7.91. Found: C, 47.17; H, 3.59; N, 7.65.

*2.3.6. Synthesis of 2-[oxazolin-2'-yl]quinoline Cobalt(II) chloride (**7a**).*

Yield, 0.18 g (77%). FT-IR (KBr; cm^{-1}): 1635, 1592, 1483, 1409, 1381, 1253, 1171, 1118, 838, 764, 629. Anal. Calc. for $C_{12}H_{10}Cl_2CoN_2O$ (328.06): C, 43.93; H, 3.07; N, 8.54. Found: C, 44.04; H, 3.28; N, 8.45.

*2.3.7. Synthesis of 2-[4'-(S)- methyloxazolin-2'-yl]quinoline Cobalt(II) chloride (**7b**).*

Yield, 0.30 g (75%). FT-IR (KBr; cm^{-1}): 1637, 1565, 1507, 1477, 1402, 1380, 1173, 958, 836, 766. Anal. Calc. for $C_{13}H_{12}Cl_2CoN_2O$ (342.09): C, 45.64; H, 3.54; N, 8.19. Found: C, 45.42; H, 3.27; N, 8.24.

*2.3.8. Synthesis of 2-[4'-(S)- ethyloxazolin-2'-yl]quinoline Cobalt(II) chloride (**7c**).*

Yield, 0.26 g (71%). FT-IR (KBr; cm^{-1}): 1639, 1616, 1564, 1512, 1481, 1406, 1379, 1174, 920, 837, 768. Anal. Calc. for $C_{14}H_{14}Cl_2CoN_2O$ (356.11): C, 47.22; H, 3.96; N, 7.87. Found: C, 47.08; H, 4.31; N, 7.96.

*2.3.9. Synthesis of 2-[4'-(S)-isopropyloxazolin-2'-yl]quinoline Cobalt(II) chloride (**7d**).*

Yield, 0.24 g (70%). FT-IR (KBr; cm^{-1}): 1635, 1617, 1591, 1476, 1405, 1384, 1220, 1175, 1121, 933, 839, 769. Anal. Calc. for $C_{15}H_{16}Cl_2CoN_2O$ (370.14): C, 48.67; H, 4.36; N, 7.57. Found: C, 48.70; H, 4.41; N, 7.35.

*2.3.10. Synthesis of 2-[4'-(R)-phenyloxazolin-2'-yl]quinoline Cobalt(II) chloride (**7e**).*

Yield, 0.18 g (82%). FT-IR (KBr; cm^{-1}): 1636, 1588, 1479, 1408, 1381, 1260, 1172, 929, 764. Anal. Calc. for $C_{18}H_{14}Cl_2CoN_2O$ (404.16): C, 53.49; H, 3.49; N, 6.93. Found: C, 53.40; H, 3.78; N, 6.75.

2.4. X-ray structure determinations

Crystals for X-ray analysis were obtained as described in the result and discussion section. Data collections were performed at -88.5 °C on a Bruker SMART APEX diffractometer with a CCD area detector, using graphite monochromated Mo K radiation (λ = 0.71073 Å). The determination of crystal class and unit cell parameters was carried out by the SMART program package. The raw frame data were processed using SAINT and SADABS to yield the reflection data file. The structures were solved by using SHELXTL program. Refinement was performed on F^2 anisotropically for all non-hydrogen atoms by the full-matrix least-squares method. The hydrogen atoms were placed at the calculated positions and were included in the structure calculation without further refinement of the parameters. CCDC 1013806 to 1013808.

2.5. Polymerization procedures

A typical procedure for the polymerization by **6b** is as follows: a toluene solution (10 mL) of 1,3-butadiene (1 g, 1.85×10^{-2} mol) was added to a oxygen- and moisture-free ampoule preloaded with complex **6b** (2.7 mg, 9.26×10^{-6} mol). Then, EASC (1.0×10^{-3} mol/mL, 0.185 mL) was injected to initiate the polymerization at 20 °C. After 15 min, acidified ethanol containing 2,6-di-tert-butyl-4-methylphenol (1.0 wt%) as a stabilizer was added to the system to quench the polymerization. The polymer was washed with ethanol repeatedly, and then dried under vacuum at 40 °C to constant weight. The polymer yield was determined by gravimetry.

3. Results and Discussion

3.1. Synthesis and characterization of complexes

Complexes **6a-e** and **7a-e** were synthesized by the reaction of $CoCl_2$ with the corresponding ligand at room temperature in good yields. The ligands and complexes were identified by FT-IR, NMR, and elemental analysis. In the IR spectra, the absorption bands of the arylimino C=N moieties of the complexes appeared at 1631−1653 cm^{-1}, which are obviously red-shifted compared to those of the corresponding ligands (1645−1666 cm^{-1}), indicating that the nitrogen atom of arylimino coordinates to the central metal. The structures of **6a**, **6b**, and **7c** were further analyzed by single crystal X-ray crystallography. Data collection and crystal and refinement parameters are listed in **Table S1**. The molecular structures of **6a**, **6b**, and **7c** are shown in **Fig. 1-3**.

Single crystals of **6a**, **6b**, and **7c** suitable for X-ray diffraction analysis were obtained by slow diffusion of Et_2O into their saturated solutions of DMF. Quite surprisingly, the three kinds of crystals displayed different geometries. Anchored by two ligands, complex **6a** can be best described as a distorted octahedron formed by the four coordinated nitrogen atoms of the two ligands and the two chlorine atoms. Due to the highly symmetric nature of complex **6a**, the cobalt atom is precisely on the plane defined by the four coordinated nitrogen atoms. The four imino C=N bonds in **6a** have typical double bond character with C=N bond lengths of 1.264(4) Å and 1.344(4) Å. **6b** crystallizes with two independent ion-pairs per asymmetric unit. Due to the fact that the bond distances and angles are similar in the two independent molecules (e.g Co(1)–N(1), 2.159(4); Co(3)–N(5), 2.154(5);Co(1)–N(2), 2.108(4); Co(3)–N(6), 2.105(4); Co(1)–N(3), 2.177(4); Co(3)–N(7), 2.158(5); Co(1)–N(4), 2.090(5); Co(3)–N(8), 2.104(5); N(1)–Co(1)–N(2), 77.63(16); N(5)–Co(3)–N(6), 77.23 (17); N(3)–Co(1)–N(4), 77.68 (18); N(7)–Co(3)–N(8), 77.9 (2)), reference can be made to the molecule identified by Co(1).

The analysis of X-ray crystallography revealed that **6b** is ion-paired complexed $[L_2Co]^{2+}[CoCl_4]^{2-}$ (**Fig. 2**). The cobalt center in the cationic moieties of $[Co(Me\text{-}Pyox)2]^{2+}[CoCl_4]^{2-}$ is six-coordinate and chelated by two ligands with Co-N (imino nitrogen and pyridine nitrogen) bonds ranging from 2.090(5) Å to 2.177(4) Å, a H_2O molecule, and a chloride atom, **6b** can be best described as a distorted octahedron. The oxygen atom (O1W) lies 0.014 Å out of one pyox plane (defined by N1, N2, O1) and the chloride atom (Cl1) lies 0.555 Å out of the other one (defined by N3, N4, O2). The incorporation of H_2O and chloride atom demonstrated the highly unsaturated nature of the cobalt core. The bond length of Co1-N1 (pyridine) (2.159(4) Å) is shorter than that of Co1-N2 (oxazoline) (2.108(4) Å), and Co1-N3 (pyridine) (2.177(4) Å) is shorter than Co1-N4 (oxazoline) (2.090(5) Å). The dihedral angles between the pyridine planes (defined by C5, N1, C3 and C10, N3, C14) and their corresponding oxazoline planes (defined by N2, C6, O1 and N4, C15, O2) is 2.66° and 2.88°, respectively, indicating the coplanar structure of this rigid ligand framework. The cobalt atom (Co1) slightly lies 0.138 Å out of one pyox plane (defined by N1, N2, O1W) and 0.0138 Å for the other one (defined by N3, N4, Cl1)..

The $[CoCl_4]^{2-}$ anion displays as a slightly distorted tetrahedral geometry with nearly uniform Co-Cl bond lengths of 2.2699–2.3080 Å and Cl-Co-Cl angles ranging from 106.61(6)° to 114.61(6)°. The two C=N bonds, N(1)=C(5) and N(2)=C(6), have a typical double bond character with bond length of 1.352 Å and 1.273 Å, respectively.

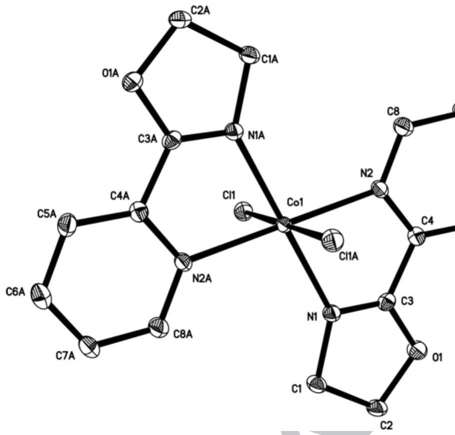


Fig. 1. ORTEP drawing of complex **6a** with thermal ellipsoids at the 30% probability level. Hydrogen atoms have been omitted for clarity (One H_2O molecule in the lattice is not included). Selected bond lengths (Å) and angles (deg): Co(1)−N(1), 2.123(2); Co(1)−N(2), 2.163(2); Co(1)−Cl(1), 2.4727(7); N(1)−C(3), 1.264(4); N(2)−C(4), 1.344(4); N(1)−Co(1)−N(2), 77.21(9); N(1)−Co(1)−Cl(1), 88.29(7) ; N(2)−Co(1)−Cl (1), 89.39(7).

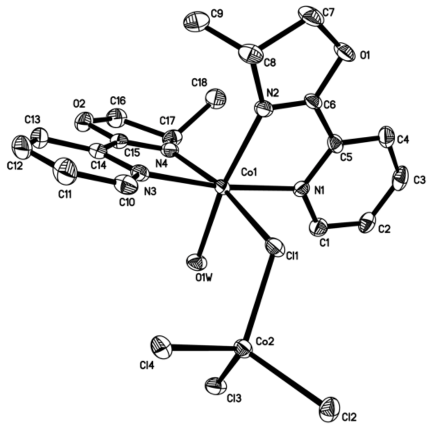


Fig. 2. ORTEP drawing of complex **6b·H$_2$O** with thermal ellipsoids at the 30% probability level. Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (deg): Co(1)−N(1), 2.159(4); Co(1)−N(2), 2.108(4); Co(1)−N(3), 2.177(4); Co(1)−N(4), 2.090(5); Co(1)−Cl(1), 2.5336(16); Co(2)−Cl(1), 2.3080(14); Co(2)−Cl(2), 2.2895(16); Co(2)−Cl(3), 2.2700(16); Co(2)−Cl(4), 2.2699(15); N(1)−Co(1)−N(2), 77.63(16); N(3)−Co(1)−N(4), 77.68 (18); Cl(1)−Co(2)−Cl(2), 108.68(6); Cl(1)−Co(2)−Cl(3), 108.98(6); Cl(1)−Co(2)−Cl(4), 106.99(6); Cl(2)−Co(2)−Cl(3), 106.61(6); Cl(2)−Co(2)−Cl(4), 110.84(6); Cl(3)−Co(2)−Cl(4), 114.61(6).

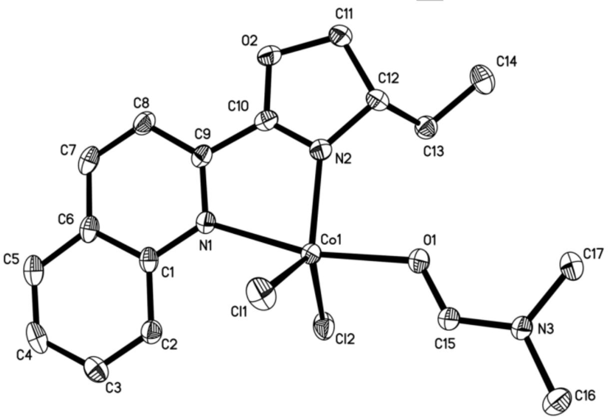


Fig. 3. ORTEP drawing of complex **7c·DMF** with thermal ellipsoids at the 30% probability level. Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (deg): Co(1)−N(1), 2.259(2); Co(1)−N(2), 2.055(2); N(1)−C(9), 1.328(3); N(2)−C(10), 1.271(3); Co(1)−Cl(1), 2.2815(8); Co(1)−Cl(2), 2.2836(7); Co(1)−O(1), 2.1134(15); N(1)−Co(1)−N(2), 76.71(8); Cl(1)−Co(2)−Cl(2), 120.03(3).

As depicted in **Fig. 3**, with coordination of one DMF molecule to the cobalt atom, **7c** adopted a penta-coordinate structure and the geometry around the metal centre can be best described as a distorted trigonal bipyramid in which the nitrogen atom of oxazoline and the two chloride atoms form the equatorial plane, the oxygen atom of DMF and the quinolyl nitrogen atom posit at the apical points. The deviations of the metal ion from the equatorial plane and the plane formed by the coordinated nitrogen atoms and oxygen atom are only 0.139 Å and 0.049 Å, respectively. The quinoline ring is approximately orthogonal to the equatorial plane, and the dihedral angle is 83.11°. The quinoline planes (defined by C1, N1, C9) and the oxazoline planes (defined by N2, C10, O2) are nearly coplanar with a dihedral angle of 4.63°.

3.2. 1,3-Butadiene polymerization

3.2.1. Effect of the ligand on 1,3-butadiene polymerization

The complexes activated by EASC for the polymerization of 1,3-butadiene were examined, and the results are summarized in **Table 1**. For **6a-e** (Entry 1-5), when the bulkiness of the substituent at 4-position of oxazoline ring increased, namely from hydrogen (**6a**), methyl (**6b**), ethyl (**6c**), and isopropyl (**6d**) to phenyl (**6e**), a decrease in catalytic activity was observed (from 91.2% to 36.1%). These results indicate that the spacial steric of the lignad significantly affects the activity of the catalytic precursor. All the complexes gave *cis*-1,4-rich polybutadienes (86.8%~97.2%), and the *cis*-1,4 content increased with the increasing bulkiness of the attached substituent on the oxazoline ring. On the other hand, the complex with bulkier substituent produced polymer having higher M_n and narrower MWD. Similar tendency was observed in the case of quinoline-oxazoline-based **7a**-**e**. Probably due to the more open nature revealed by the single crystal structure analysis, complex **6a** exhibited higher activity than **6b**. Complex **7c** afforded polybutadienes with the highest molecular weight, which might be ascribed to the steric and highly rigid skeleton of quinoline. In contrast, $CoCl_2$-based system under the identical conditions or EASC alone could not initiate 1,3-butadiene polymerization. Since **6b** and **7b** exhibited high activity and high *cis*-1,4 selectivity, they were selected for further experiments.

Table 1. Polymerization of 1,3-butadiene with **6a-e** and **7a-e** activated by EASC.[a]

					Microstructure[b] (%)		
Entry	Cat.	Yield (%)	$M_n \times 10^{-4}$[c]	M_w/M_n[c]	*Cis*-1,4	*Trans*-1,4	1,2
1	**6a**	91.2	4.3	4.3	86.8	8.5	4.7
2	**6b**	83.1	7.0	4.0	92.2	4.8	3.0
3	**6c**	79.2	8.7	4.0	95.4	2.8	1.8
4	**6d**	58.3	14.7	3.1	97.0	1.6	1.5
5	**6e**	36.1	21.4	2.3	97.2	1.5	1.3
6	**7a**	95.2	6.7	3.6	92.3	2.3	5.3
7	**7b**	87.5	11.5	3.3	95.1	3.1	1.8
8	**7c**	86.5	11.6	3.0	95.5	2.7	1.7
9	**7d**	72.2	16.0	2.8	97.2	1.4	1.4
10	**7e**	35.5	21.0	2.2	98.0	1.0	1.0
11	$CoCl_2$	trace	–	–	–	–	–
12	–	–	–	–	–	–	–

[a] Polymerization in toluene at 20 °C for 15 min, precatalyst: 9.26 μmol, [BD]/[Co] = 2000, [Al]/[Co] = 20.

[b] Determined by ^1H NMR and FT-IR.

[c] Determined by GPC against polystyrene standards.

3.2.2. Effects of [Al]/[Co] ratio and polymerization temperature on 1,3-butadiene polymerization

The effects of [Al]/[Co] ratio and polymerization temperature on catalytic behaviors were investigated (**Table 2** and **Table 3**). For **6b**, upon activation with EASC, as increasing [Al]/[Co] ratio from 20 to 150, the polymer yield increased slightly, while the *cis*-1,4 content, the M_n, and MWD of the resultant polymers remained almost the same. Similar results were observed in previously reported Co-based catalyst systems, in which [Al]/[Co] ratio did not have large influence on the M_n and MWD of the polymers [41,42]. On the other hand, polymerization temperature significantly affected the catalytic behaviors of the complex. The polymer yield sharply increased from 2.7% at 0 °C to 81.1% at 20 °C, and then almost practically leveled off to 80% at 40 °C and above, indicating high thermal stability of the active species. Meanwhile, the M_n decreased from 11.5×10^4 to 2.6×10^4, and the MWD increased from 1.7 to 6.6. This result is attributable to the facilitated chain transfer reaction at the elevated temperature. When the polymerization temperature increased from 0 °C to 80 °C, the *cis*-1,4 content of the polymer decreased from 97.9% to 79.3%, while the *trans*-1,4- and 1,2-contents increased gradually. As shown in **Table 3**, a similar tendency was observed in **7b.** It is noteworthy that the thermal stability of the active species generated by **7b** was even higher than **6b**; the polymer yield was still up to 87% even at a high temperature of 80 °C. This result is in contrast to most late transition metal-based catalysts which suffered from the decay of catalytic activity as polymerization temperature increased. For instance, in the cases of 2,6-bis(benzimidazol-2-yl)-pyridine Co(II) dichloride and 2-[1-(2,6-diisopropylphenylimino)ethyl]-6-(pyrazol-1-yl)-pyridine cobalt dichloride, the polymer yield decreased from 80.1% at 50 °C to 47.4% at 90 °C and from 72% at 25 °C to 11% at 80 °C, respectively [43,44]. The high thermal stability might be due to the rigid structure backbone which protected the active centre [45,46].

Table 2. Effects of [Al]/[Co] ratio and temperature on 1,3-butadiene polymerization with **6b**/EASC catalyst.[a]

						Microstructure[b] (%)		
Entry	[Al]/[Co]	Temp. (°C)	Yield (%)	M_n × 10^{-4}[c]	M_w/M_n[c]	*Cis*-1,4	*Trans*-1,4	1,2
13	20	20	83.1	7.0	4.0	92.2	4.8	3.0
14	60	20	88.6	7.3	3.7	92.4	4.8	2.8
15	100	20	93.3	7.4	3.3	92.3	5.5	2.2
16	150	20	93.3	7.1	3.4	93.6	4.4	2.1
17	20	0	2.7	11.5	1.7	97.9	1.6	0.6
18	20	40	83.8	3.0	7.3	84.4	9.3	6.4
19	20	60	81.7	2.8	6.5	80.8	11.2	8.0
20	20	80	79.6	2.6	6.6	79.3	12.4	8.3

[a] Polymerization in toluene for 15 min, precatalyst: 9.26 μmol, [BD]/[Co] = 2000.

[b] Determined by ^{1}H NMR and FT-IR.

[c] Determined by GPC against polystyrene standards.

Table 3. Effects of [Al]/[Co] ratio and temperature on 1,3-butadiene polymerization with **7b**/EASC catalyst.[a]

Entry	[Al]/[Co]	Temp. (°C)	Yield (%)	M_n × 10^{-4c}	M_w/M_n[c]	Microstructure[b] (%)		
						Cis-1,4	*Trans*-1,4	1,2
21	20	20	87.5	11.5	3.3	95.1	3.2	1.7
22	60	20	89.2	10.1	3.0	95.3	3.2	1.6
23	100	20	91.3	10.1	2.9	95.9	2.8	1.3
24	150	20	88.4	10.2	3.0	95.1	3.4	1.6
25	20	0	4.5	14.1	1.6	98.9	0.5	0.6
26	20	40	90.7	7.7	4.0	88.2	7.2	4.7
27	20	60	88.2	6.6	5.5	85.0	9.7	5.2
28	20	80	87.4	5.7	7.0	82.5	11.5	6.0

[a] Polymerization in toluene for 15 min, precatalyst: 9.26 μmol, [BD]/[Co] = 2000.

[b] Determined by ^{1}H NMR and FT-IR.

[c] Determined by GPC against polystyrene standards.

3.2.3. Effect of cocatalyst on 1,3-butadiene polymerization

The effect of cocatalyst type on 1,3-butadiene polymerization were examined (**Table 4**). The polymerization with EASC-based catalyst gave polybutadiene in high yield within 15 min, while alkylaluminum ($AlEt_3$ and Al(*i*-Bu)$_3$)-based systems could not polymerize 1,3-butadiuene. In the case of MAO-based system, it is worth noting that 1,3-butadiene polymerization proceeded even at a low MAO level ([Al]/[Co] = 50) to afford polymer in 73.9% yield. When the [Al]/[Co] ratio further increased to 100, the polymer yield reached 88.6%. This catalytic system is more active than

$CoCl_2$/MAO; the latter gave polybutadiene in a low yield of 29% at [Al]/[Co]=100 [40].

Table 4. Effect of cocatalysts on polymerization behaviors with **6b** and **7b** catalyst system.[a]

							Microstructure[b] (%)		
Entry	Cat.	Cocat.	Al/Co	Yield(%)	$M_n \times 10^{-4c}$	M_w/M_n^c	*Cis*-1,4	*Trans*-1,4	1,2
29	**6b**	EASC	20	83.1	7.0	4.0	92.2	4.8	3.0
30	**6b**	TEA	40	–	–	–	–	–	–
31	**6b**	TIBA	40	–	–	–	–	–	–
32	**6b**	MAO[d]	30	31.7	1.6	3.5	91.5	3.9	4.6
33	**6b**	MAO[d]	50	84.4	2.9	3.5	95.0	2.7	2.3
34	**6b**	MAO[d]	100	98.7	3.0	3.2	94.2	2.5	3.4
35	**7b**	EASC	20	87.5	11.5	3.3	95.1	3.1	1.8
36	**7b**	TEA	40	–	–	–	–	–	–
37	**7b**	TIBA	40	–	–	–	–	–	–
38	**7b**	MAO[d]	30	5.2	2.1	2.3	96.4	1.8	1.8
39	**7b**	MAO[d]	50	73.9	2.2	3.7	95.9	2.3	1.8
40	**7b**	MAO[d]	100	88.6	5.2	3.6	95.6	2.4	2.0

[a] Polymerization conditions: precatalyst: 9.26 μmol, [BD]/[Co] = 2000, in toluene, 20 °C, 15min. TEA: triethylaluminium; TIBA: triisobutylaluminium; MAO: methyl aluminoxane.

[b] Determined by ^{1}H NMR and FT-IR.

[c] Determined by GPC against polystyrene standards.

[d] Polymerization time: 3h.

3.2.4. Effects of PPh_3 on 1,3-butadiene polymerization

It is known that the addition of Lewis base influences both the activity and specificity of Co-based catalyst systems [10,47,48]. As reflected in **Table 5**, at [Al]/[Co] = 20, the addition of PPh_3 to the EASC-based system resulted in a decrease of polymer yield and a slight increase of 1,2-content of the resultant polymer, whereas the yield and *cis*-1,4 content did not affected at a high EASC level ([Al]/[Co] = 40). These results are presumably due to the reaction between EASC and PPh_3. In contrast, in the case of MAO-based system, the addition of PPh_3 not only increased the catalytic activity but also switched the selectivity from *cis*-1,4 to 1,2 manner. For instance, the addition of 1.0 equivalent of PPh_3 resulted in a increase of polymer yield from 84.5 to 97.9% for **6b** and from 87.6% to 97.8% for **7b**, respectively, and the 1,2 selectivity was remarkably enhanced from 2.3% and 1.8% to 81.3% and 87.8%. Based on ^{13}C NMR and DSC analyses (see Fig. S1 and S2), the 1,2- and c*is*-1,4 units in the resulting polymers were randomly distributed along the polymer chain, as observed in other cobalt/phosphine systems [44]. The mechanism of transition metal catalyzed 1,3-butadiene polymerization has been extensively studied [3,49]. It is known that 1,3-butadiene coordinates to the cobalt center either via one (η^2) or both (η^4) double bonds, resulting in an allyl ligand. In the absence of PPh_3, 1,3-butadiene coordinates to the cobalt centre predominantly with η^4 manner, followed by the C^1-insertion into the terminal π-η^3 allylic polymer chain, giving rise to *cis*-1,4 structure. In the presence of PPh_3, the change of selectivity may be attributable to that external electron donor occupies the coordination site and consequently, the coordination mode of 1,3-butadiene becomes η^2-fashion, then 1,2-enchainment is favorable [3, 10, 49-51]. Moreover, the effect of amine on the polymerization was also investigated (**Table 6.**). Fixing the MAO/Co ratio at 50, the addition of an equimolar amount of amine resulted in a slight decrease of catalytic activity, whereas the selectivity did not change.

Table 5. Effect of PPh_3 on polymerization behaviors with **6b** and **7b** catalyst system.[a]

							Microstructure[b] (%)		
Entry	Cat.	Cocat.	PPh_3/Co	Yield(%)	M_n[c] ×10^{-4}	M_w/M_n[c]	*Cis*-1,4	*Trans*-1,4	1,2
41	**6b**	EASC	–	83.1	7.0	4.0	92.2	4.8	3.0
42	**6b**	EASC	1	74.0	6.5	3.3	93.6	2.9	3.5
43	**6b**	EASC	3	42.4	1.4	2.0	81.5	4.2	14.3
44	**6b**	EASC[d]	3	92.1	3.1	4.9	91.6	4.4	4.0
45	**6b**	EASC[e]	3	94.4	4.2	5.0	94.2	3.1	2.7
46	**6b**	MAO[f]	–	84.4	2.9	3.5	95.0	2.7	2.3
47	**6b**	MAO[f]	0.1	84.5	3.7	3.0	36.7	1.1	62.2
48	**6b**	MAO[f]	0.2	91.4	4.7	3.0	25.4	1.1	73.5
49	**6b**	MAO[f]	0.5	94.3	4.9	2.7	20.0	1.4	78.6
50	**6b**	MAO[f]	1.0	97.9	5.1	2.6	19.4	0.8	79.8
51	**6b**	MAO[f]	3	98.1	5.7	2.3	18.6	0.1	81.3
52	**7b**	EASC	–	87.5	11.5	3.3	95.1	3.1	1.8
53	**7b**	EASC	1	55.0	16.4	2.3	95.7	2.5	1.8
54	**7b**	EASC	3	18.8	2.1	1.8	83.5	4.0	12.5
55	**7b**	EASC[d]	3	87.2	5.1	3.9	93.3	3.3	3.4
56	**7b**	EASC[e]	3	93.7	5.4	4.5	94.1	2.9	3.0
57	**7b**	MAO[f]	–	73.9	2.2	3.7	95.9	2.3	1.8
58	**7b**	MAO[f]	0.1	87.6	6.4	3.8	25.7	0.7	73.6
59	**7b**	MAO[f]	0.2	90.9	6.8	3.2	18.6	0.4	81.1

60	**7b**	MAO[f]	0.5	93.1	6.9	2.7	16.8	0.3	83.0
61	**7b**	MAO[f]	1	97.8	6.9	2.6	11.8	0.4	87.8
62	**7b**	MAO[f]	3	97.7	7.3	2.2	11.1	0.3	88.6

[a] Polymerization conditions: precatalyst: 9.26 μmol, [BD]/[Co] = 2000, [Al]/[Co] = 20, MAO/Co = 50, in toluene, 20 °C, 15 min.

[b] Determined by ^{1}H NMR and FT-IR.

[c] Determined by GPC against polystyrene standards.

[d] [Al]/[Co] = 40.

[e] [Al]/[Co] = 60.

[f] Polymerization time: 3h.

Table 6. Effect of amines on polymerization behaviors with **6b** and **7b** catalyst system.[a]

						Microstructure[b] (%)		
Entry	Cat.	Amine	Yield(%)	M_n[c] $\times 10^{-4}$	M_w/M_n[c]	*Cis*-1,4	*Trans*-1,4	1,2
63	**6b**	aniline	80.9	2.1	3.2	94.0	3.2	2.8
64	**6b**	triethylamine	78.4	3.2	3.5	94.5	2.8	2.8
65	**7b**	aniline	72.8	9.1	2.7	95.5	2.4	2.1
66	**7b**	triethylamine	71.9	7.0	3.6	96.1	1.9	2.0

[a] Polymerization conditions: precatalyst: 9.26 μmol, [BD]/[Co] = 2000, MAO/Co = 50, [Amine]/[Co] = 1, in toluene, 20 °C, 3h.

[b] Determined by ^{1}H NMR and FT-IR.

[c] Determined by GPC against polystyrene standards.

4. Conclusion

In summary, several cobalt complexes bearing pyridine-oxazoline and quinoline-oxazoline ligands were synthesized and characterized. Single crystal X-ray analysis revealed that **6a** and **7c** adopted distorted octahedron and trigonal bipyramidal, respectively, and **6b** existed as an ion pair of $[CoL_2][CoCl_4]$, in which the cobalt center was surrounded by the two [NN] ligands in the cationic moiety and adopted distorted octahedronal geometry, and the tetrahedral $[CoCl_4]^{2-}$ anion existed as the counterion. Activated by EASC or MAO, these complexes exhibited high activity for 1,3-butadiene polymerization. The resulting polymers had high molecular weights ($M_n > 4.3 \times 10^4$) and high *cis*-1,4 contents. In particular, **6b** and **7b** afforded polymers in high yields (79.6% and 87.4%, respectively) even at a relatively high polymerization temperature of 80 °C, indicating the high thermal stability. In the case of MAO-based system, the addition of PPh_3 could enhance catalytic activity and switch the selectivity from *cis*-1,4 to 1,2-enchainment.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/xx.xxxx/ xxxx.xx.xxx.

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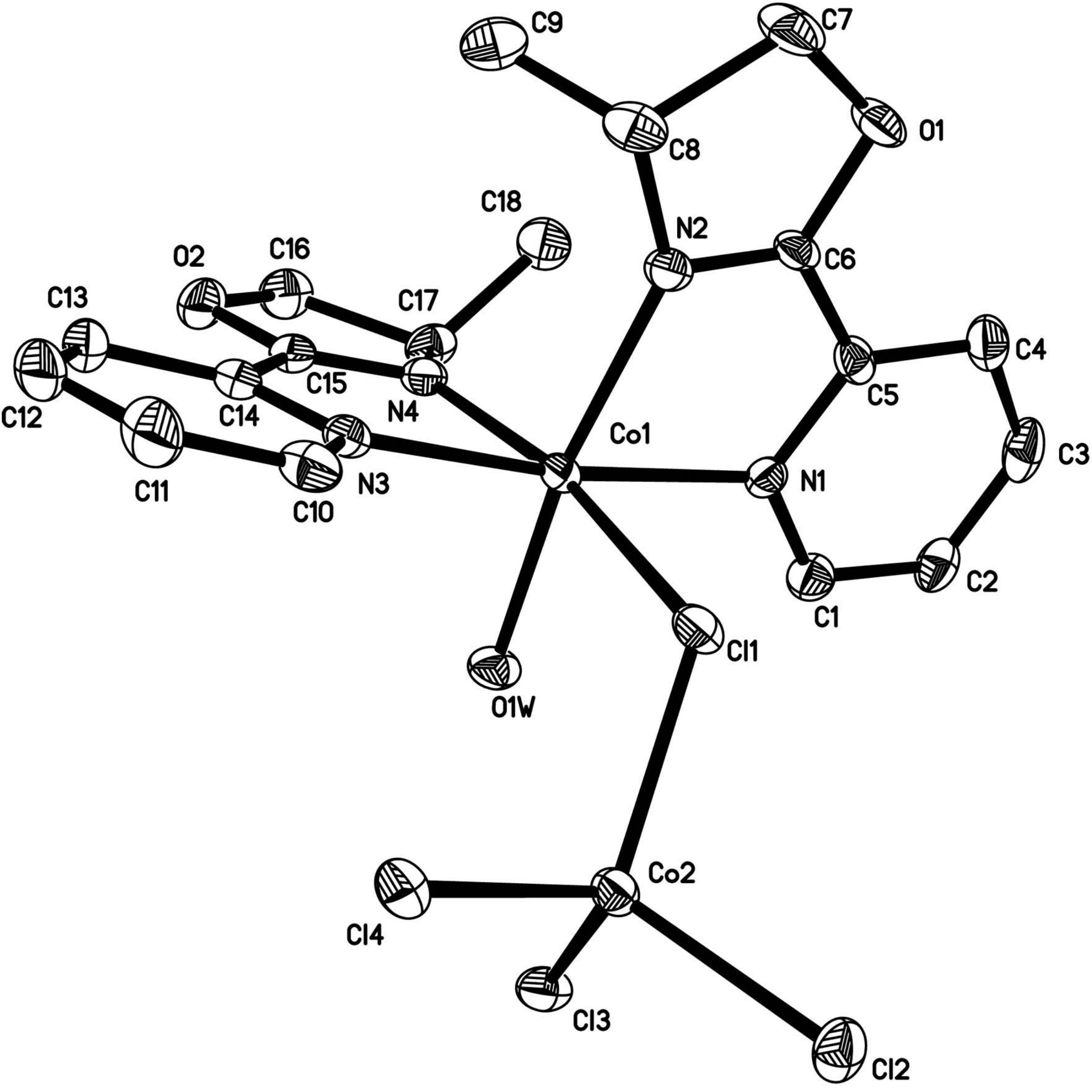
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Pyridine-oxazoline and Quinoline-oxazoline Ligated Cobalt Complexes: Synthesis, Characterization, and 1,3-Butadiene Polymerization Behaviors

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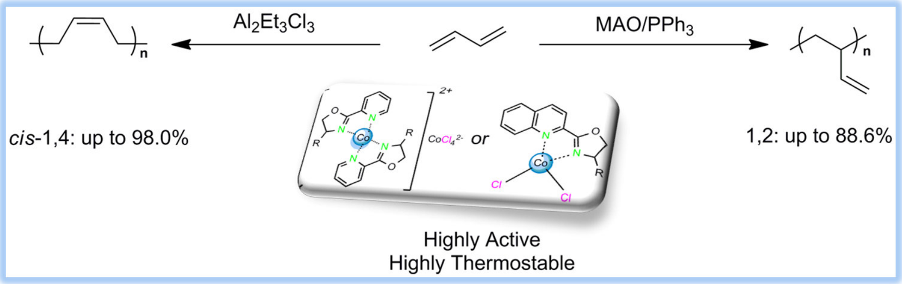
Graphical Abstract



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Graphical Abstract

Cobalt complexes supported by pyridine-oxazoline (Pyox) and quinoline-oxazoline (Quox) were synthesized and polymerized 1,3-butadiene to give polymers with high *cis*-1,4 contents. The selectivity of the catalytic system could be switched from *cis*-1,4 to 1,2-fashion via the addition of PPh_3.

Pyridine-oxazoline and Quinoline-oxazoline Ligated Cobalt Complexes: Synthesis, Characterization, and 1,3-Butadiene Polymerization Behaviors

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Highlights

- Co(II) complexes bearing pyridine-oxazoline and quinoline-oxazoline ligands were successfully synthesized.
- The complexes displayed high activity, cis-1,4 selectivity, and relative high thermostability for 1,3-butadiene polymerization.
- The addition of PPh_3 could switch the selectivity from *cis*-1,4 to 1,2-manner.