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Synthesis, characterization and 1,3-butadiene polymerization behaviors of cobalt complexes bearing 2-pyrazolyl-substituted 1,10-phenanthroline ligands

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A series of cobalt(II) complexes containing tridentate 2-pyrazolyl-substituted 1,10-phenanthroline ligands (L) with the general formula [$LCoCl_2$] have been successfully synthesized and fully identified by IR spectroscopy, elemental analysis and mass spectroscopy. Cobalt complexes Co4–Co8 were further confirmed by X-ray crystallographic analysis, and all the complexes adopted distorted trigonal pyramid geometries around the cobalt center. In combination with methylaluminoxane, the complexes exhibit high *cis*-1,4-selectivity for 1,3-butadiene polymerization. The catalytic activities of the complexes mainly depend on the nature of the substituent and its position at the pyrazolyl ring of the ligand. Complexes having a bulkier substituent on the pyrazolyl ring of the ligand show lower catalytic activity and the incorporation of electron-withdrawing substituent enhances the activity. Polymerization behaviors were almost not affected with varying [Al]/[Co] ratio, but both activity and the *cis*-1,4 content decrease slightly as polymerization temperature increasing. Copyright © 2013 John Wiley & Sons, Ltd.

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Keywords: cobalt(II) complex; 1,10-phenanthroline; 1,3-butadiene

Introduction

The regio- and stereoselective polymerization of 1,3-butadiene is a subject of intense interest because of the extensive and diverse practical applications of polybutadienes.[1] The properties of the polymer mainly depend on their microstructures, including *cis*-1,4, *trans*-1,4, and 1,2 isomers, generated during polymerization. Therefore, numerous catalysts based on transition metals (Ti, Ni, Co, etc.)[2–6] and rare earth metal have been developed to polymerize 1,3-butadiene in a selective fashion.[7–11] Among them, cobalt-based catalysts have attracted special attention because polymers with versatile microstructures can be produced depending on the catalyst formulation.[12] For instance, cobalt halides and carboxylates activated with methylaluminoxane (MAO) produce high *cis*-1,4-polybutadienes.[13–15] In addition, external donors such as CS_2 and PPh_3[16,17] have been widely documented as effective regulators in the catalytic systems, $Co(acac)_3/AlEt_3/CS_2$[18] and $Co(acac)_2/AlEt_3/H_2O/PPh_3$,[19,20] for 1,2-selective polymerization of 1,3-butadiene.

Catalytic activity and chemo- and stereoselectivity of the catalyst systems mainly depend on the steric and electronic nature of the active site. To gain a deeper understanding of how the ligand structure affects the activity and specificity of the catalyst, recent studies have focused on well-defined homogeneous single-site catalysts based on transition metal complexes. Based on the pioneering work of the highly active cobalt(II) and iron(II) complexes supported by 2,6-bis(arylimino) pyridine ligands for ethylene polymerization/oligomerization,[21–24] various well-defined late transition metal complexes bearing tridentate ligands, such as NNO,[25,26] NSN[27] and NNN,[28–30] have been widely employed as precursors for olefin polymerization. Although the attractive progress of such catalysts in olefin polymerization has led to an acceleration of research efforts in 1,3-butadiene polymerization, their extension for 1,3-butadiene polymerization has still been limited until now. Endo *et al.* reported (salen)Co(II) complexes for *cis*-1,4 selective polymerization and found that the introduction of a *t*-butyl group into the ligand can increase the activity and *cis*-1,4 selectivity simultaneously.[15] Cariou *et al.* reported that bis (benzimidazole)-supported Co(II) complexes exhibited high *cis*-1,4 selectivity towards 1,3-butadiene polymerization.[31,32] Appukuttan *et al.* prepared a series of Co(II) complexes supported by bis(benzimidazolyl)amine and 2,6-bis(benzimidazolyl)pyridine, and found

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high *cis*-1,4 selectivity for 1,3-butadiene polymerization with the assistance of ethylaluminum sesquichloride (EASC).[33,34] Jie and co-workers[35–37] found that Co(II) complexes ligated by PNP, NNO and NO ligands are effective for producing high *cis*-1,4 polybutadienes. In our previous study,[38,39] it was found that the incorporation of an electron-withdrawing group into the imino group of the ligand can enhance both activity and selectivity of bis(imino)pyridine cobalt(II)/MAO catalyst for the polymerization of 1,3-butadiene. As mentioned above, it could be concluded that both the steric and electronic properties of substituents adjacent to the metal center influence the polymerization behaviors.

1,10-Phenanthroline and its derivatives are well-known ligands for late transition metal complexes because of its ease in tuning their steric and electronic properties by modifying the parent ligand.[40–46] However, the metal complexes supported by such ligands as catalyst precursors for 1,3-butadiene polymerization are scarce. In the present study, in order to study suitable new chelating cobalt complexes for the selective polymerization of 1,3-butadiene, we reported the synthesis and characterization of a new family of cobalt complexes bearing tridentate 2-pyrazolyl substituted 1,10-phenanthroline ligands and their catalytic behaviors for 1,3-butadiene polymerization. Furthermore, the influences of the substituent of the ligand and polymerization conditions on the polymerization of 1,3-butadiene were investigated in detail.

Experimental

General Considerations

3-Phenyl-1*H*-pyrazole and 3-(4-fluorophenyl)-1*H*-pyrazole were purchased from Aldrich. 3,5-Dimethyl-1*H*-pyrazole and 5-methyl-3-(trifluoromethyl)-1*H*-pyrazole were purchased from TCI Co. 2-Chloro-1,10-phenanthroline was purchased from J&K. Other substituted pyrazoles and anhydrous $CoCl_2$ were obtained from Alfa and used without further purification unless otherwise mentioned. MAO was available from Akzo Noble. Toluene and THF were freshly distilled in the presence of sodium and benzophenone. DMF was purified by vacuum distillation under N_2 atmosphere. Polymerization-grade butadiene was supplied by Jinzhou Petrochemical Corporation and purified by passing through columns packed with 4 Å molecular sieves and KOH.

^1H NMR (400 MHz) was measured on a Varian Unity spectrometer in $CDCl_3$ at room temperature. Elemental analyses were recorded on an elemental Vario EL spectrometer. IR spectra were performed on a Bruker Vertex-70 FT-IR spectrophotometer. Mass spectrometric detection was carried out on a Xevo TQ 151 mass spectrometer (Waters Corp., Milford, MA, USA) with a 152 electrospray ionization (ESI) source. The proportion of 1,2, *cis*-1,4 and *trans*-1,4 units of polymer were determined by IR and ^1H NMR spectra.[47,48] The molecular weights (M_n) and molecular weight distributions (M_w/M_n) of polymer were measured at 30°C by gel permeation chromatography (GPC) utilizing 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^{-1}. The values of M_n and M_w/M_n were calculated using polystyrene calibration.

X-Ray Structure Determinations

Crystals suitable for X-ray analyses were obtained as described in the Experimental 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 ($\lambda = 0.71073$ Å). The determination of crystal class and unit cell parameters was carried out using the SMART program package. The raw frame data were processed using SAINT and SADABS to yield the reflection data file. The structures were solved using the SHELXTL program. Refinement was performed on 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 887490–887494 for complexes 2**d–h** contain supplementary crystallographic data for this paper and can be obtained free of charge from www.ccdc.ac.uk/data-requesst/cif.

Polymerization Procedure

Solution polymerization of 1,3-butadiene was carried out in a glass reactor connected to a rubber plug. A certain amount of cobalt complex and 1,3-butadiene/toluene solution was added to a glass reactor under dried nitrogen atmosphere. Polymerization started by injecting the prescribed amount of co-catalyst. After polymerization in a water bath at a given temperature for the given time, the mixture was poured into a large amount of ethanol containing 2,6-di-*t*-butyl-4-methylphenol (1.0 wt%) to precipitate the polymer. The polymer was washed with ethanol repeatedly and dried under vacuum at 40°C to constant weight. Polymer yield was calculated by gravimetry.

Syntheses and Characterization of Ligands and Complexes

The tridentate 2-pyrazolyl-substituted 1,10-phenanthroline ligands (**L1–L8**) were synthesized by the reaction of 2-chloro-1,10-phenanthroline and the corresponding pyrazoles using a similar procedure to 2,6-bis(*N*-pyrazolyl)pyridine,[49] and the corresponding cobalt complexes (**Co1–Co8**) were readily prepared via the reaction of anhydrous $CoCl_2$ with the corresponding ligands in THF solution at room temperature.

*2-(Pyrazol-1-yl)-1,10-phenanthroline Cobalt(II) chloride (**Co1**)*

A mixture of **L1** (0.4 g, 1.63 mmol) and anhydrous $CoCl_2$ (0.21 g, 1.63 mmol) was stirred in THF (8 ml) for 12 h at room temperature. The blue product precipitated was collected by filtration and washed with 3 × 5 ml cold THF. The desired product (0.56 g, 91.8 %) was obtained after drying under vacuum at 40°C for 12 h. IR (KBr, cm^{-1}): 3056, 2927, 1621, 1588, 1531, 1506, 1468, 1437, 1397, 1361, 1348, 1151, 1035, 951, 877, 851, 733, 646. Anal. Calcd for $C_{15}H_{10}N_4CoCl_2$: C, 47.90; H, 2.68; N, 14.90; Cl, 18.85. Found: C, 48.45; H, 2.89; N, 15.07; Cl, 18.98. ESI-MS for $C_{15}H_{10}N_4CoCl_2$ (relative ratio): (*m/z*) ($[M - Cl]^+$ 342).

*2-(3-Methylpyrazol-1-yl)-1,10-phenanthroline Cobalt(II) chloride (**Co2**)*

This complex was prepared by the same method as for **Co1** using **L2** instead of **L1** to give **Co2** as a blue powder in 87.8% yield. IR (KBr, cm^{-1}): 3064, 2929, 1621, 1586, 1546, 1512, 1471, 1457, 1393, 1348, 1330, 1052, 958, 876, 852, 790, 733, 645. Anal. Calcd for $C_{16}H_{12}N_4CoCl_2$: C, 49.26; H, 3.10; N, 14.36; Cl, 18.17. Found: C, 50.05; H, 3.28; N, 14.63; Cl, 18.36. ESI-MS for $C_{16}H_{12}N_4CoCl_2$ (relative ratio): (*m/z*) ($[M - Cl]^+$ 356).

*2-(3-Phenylpyrazol-1-yl)-1,10-phenanthroline Cobalt(II) chloride (**Co3**)*

This complex was prepared by the same method as for **Co1** using **L3** instead of **L1** to give **Co3** as a blue powder in 76.2% yield. IR

(KBr, cm^{-1}): 3059, 2927, 1609, 1588, 1537, 1514, 1470, 1454, 1431, 1392, 1367, 1331, 1157, 1039, 961, 878, 851, 768, 732, 687, 647. Anal. Calcd for $C_{21}H_{14}N_4CoCl_2$: C, 55.78; H, 3.12; N, 12.39; Cl, 15.68. Found: C, 55.96; H, 3.44; N, 12.75; Cl, 15.79. ESI-MS for $C_{21}H_{14}N_4CoCl_2$ (relative ratio): (*m/z*) ([M − Cl]$^+$ 418).

*2-(3-(4-Fluorophenyl) pyrazol-1-yl)-1,10-phenanthroline Cobalt(II) chloride (**Co4**)*

This complex was prepared by the same method as for **Co1** using **L4** instead of **L1** to give **Co4** as a blue powder in 95.4% yield. IR (KBr, cm^{-1}): 3071, 2927, 1606, 1589, 1544, 1517, 1450, 1430, 1390, 1333, 1238, 1163, 1049, 963, 856, 735, 646, 628. Anal. Calcd for $C_{21}H_{13}FN_4CoCl_2$: C, 53.64; H, 2.79; N, 11.92; Cl, 15.08. Found: C, 53.50; H, 3.01; N, 12.19; Cl, 15.18. ESI-MS for $C_{21}H_{13}FN_4CoCl_2$ (relative ratio): (*m/z*) ([M − Cl]$^+$ 436).

*2-(3,5-Dimethylpyrazol-1-yl)-1,10-phenanthroline Cobalt(II) chloride(**Co5**)*

This complex was prepared by the same method as for **Co1** using **L5** instead of **L1** to give **Co5** as a blue powder in 85.6% yield. IR (KBr, cm^{-1}): 3054, 2927, 2863, 1621, 1586, 1565, 1511, 1498, 1429, 1405, 1384, 1365, 1342, 1130, 1068, 984, 851, 772, 735, 647. Anal. Calcd for $C_{17}H_{14}N_4CoCl_2$: C, 50.52; H, 3.49; N, 13.86; Cl, 17.54. Found: C, 50.45; H, 3.78; N, 14.26; Cl, 17.72. ESI-MS for $C_{17}H_{14}N_4CoCl_2$ (relative ratio): (*m/z*) ([M − Cl]$^+$ 370).

*2-(3,5-Diisopropyl pyrazol-1-yl)-1,10-phenanthroline Cobalt(II) chloride(**Co6**)*

This complex was prepared by the same method as for **Co1** using **L6** instead of **L1** to give **Co6** as a blue powder in 76.3% yield. IR (KBr, cm^{-1}): 3057, 2935, 2871, 1584, 1561, 1509, 1498, 1464, 1428, 1384, 1375, 1332, 1061, 1029, 1011, 851, 735, 646. Anal. Calcd for $C_{21}H_{22}N_4CoCl_2$: C, 54.80; H, 4.82; N, 12.17; Cl, 15.41. Found: C, 54.82; H, 5.18; N, 12.56; Cl, 15.59. ESI-MS for $C_{21}H_{22}N_4CoCl_2$ (relative ratio): (*m/z*) ([M − Cl]$^+$ 426).

*2-(3,5-Diphenylpyrazol-1-yl)-1,10-phenanthroline Cobalt(II) chloride(**Co7**)*

This complex was prepared by the same method as for **Co1** using **L7** instead of **L1** to give **Co7** as a blue powder in 89.5% yield. IR (KBr, cm^{-1}): 3057, 2872, 1619, 1586, 1560, 1508, 1497, 1464, 1430, 1397, 1363, 1331, 1151, 1063, 976, 959, 859, 770, 757, 701, 648. Anal. Calcd for $C_{27}H_{18}N_4CoCl_2$: C, 61.38; H, 3.43; N, 10.60; Cl, 13.42. Found: C, 61.74; H, 3.89; N, 10.87; Cl, 13.55. ESI-MS for $C_{27}H_{18}N_4CoCl_2$ (relative ratio): (*m/z*) ([M − Cl]$^+$ 494).

*2-(3-Methyl-5-(trifluoromethyl)pyrazol-1-yl)-1,10-phenanthroline Cobalt(II) chloride (**Co8**)*

This complex was prepared by the same method as for **Co1** using **L8** instead of **L1** to give **Co8** as a blue powder in 78.4% yield. IR (KBr, cm^{-1}): 3053, 2932, 1623, 1587, 1511, 1485, 1431, 1402, 1372, 1343, 1238, 1154, 1135, 1062, 1004, 977, 887, 854, 738, 648. Anal. Calcd for $C_{17}H_{11}F_3N_4CoCl_2$: C, 44.57; H, 2.42; N, 12.23; Cl, 15.48. Found: C, 44.97; H, 2.96; N, 12.71; Cl, 15.65. ESI-MS for $C_{17}H_{11}F_3N_4CoCl_2$ (relative ratio): (*m/z*) ([M − Cl]$^+$ 424).

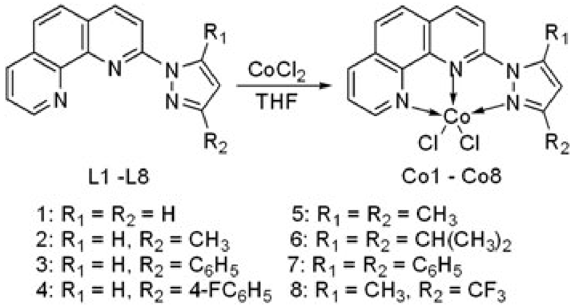
Results and Discussions

Synthesis and Characterization of the Complexes

Ligands **L1–L8** were prepared in good yields by the reaction of 2-chloro-1,10-phenanthroline and the corresponding pyrazoles according to reported literature. Cobalt complexes **Co1–Co8** were obtained in high yields by the treatment of the corresponding ligands with 1.0 equiv. of anhydrous $CoCl_2$ in THF at room temperature (Scheme 1). The obtained cobalt complexes were characterized by elemental analysis, IR spectroscopy and ESI mass spectroscopy. Fortunately, single crystals of cobalt complexes **Co4–Co8** suitable for X-ray diffraction analysis were gained by slow diffusion of diethyl ether into their DMF solutions. The molecular structures of complexes **Co1–Co8** are shown in Figs 1–5 respectively and the selected bond lengths and angles crystallographic data are listed in Tables 1 and 2.

The coordination geometry around the cobalt atom in complex **Co4** can be described as a distorted bipyramid, in which one nitrogen atom (N2) of 1,10-phenanthroline and two chlorines (Cl(1) and Cl(2)) form the equatorial plane, with the total value of three equatorial angles, N(2)−Co(1)−Cl(2) (130.09(11)°), N(2)−Co(1)−Cl(1) (114.13(10)°) and Cl(2)−Co(1)−Cl(1) (115.75(5)) equal to 360°. The bond lengths of Co(1)−N(1) and Co(1)−N(2) are 2.181(3) and 2.033(3) Å, respectively, which are much shorter than that of Co(1)−N(3) (2.302(4) Å). The deviation of the cobalt atom from the plane N(1)−N(2)−N(3) is 0.049 Å, indicating that the four atoms are coplanar. The pyrazole ring twists slightly from the phenanthroline plane (dihedral angle 3.48°), and the dihedral angle between the pyrazolyl ring and *para*-fluorophenyl plane is 15.84°.

The crystal structures of complexes **Co5–Co8** having alkyl substituent at the 3- and 5-position of the pyrazolyl ring of the ligand are similar to that of **Co4**, and the coordination geometries



Scheme 1. Syntheses of cobalt complexes **Co1–Co8**.

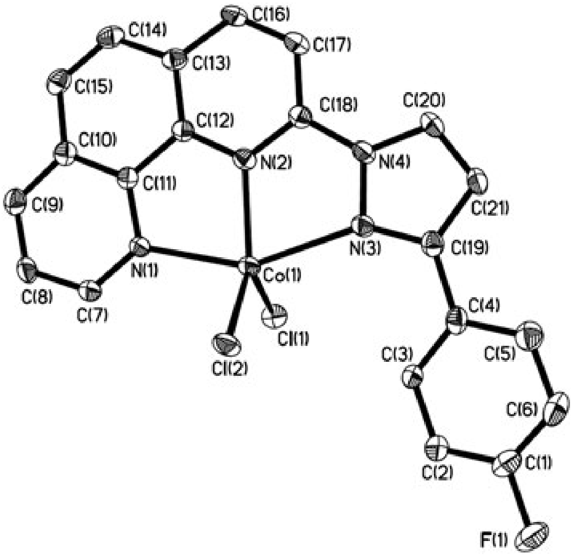


Figure 1. ORTEP view of complex **Co4**, drawn at 30% of probability. Hydrogen atoms and one DMF molecule are omitted for clarity.

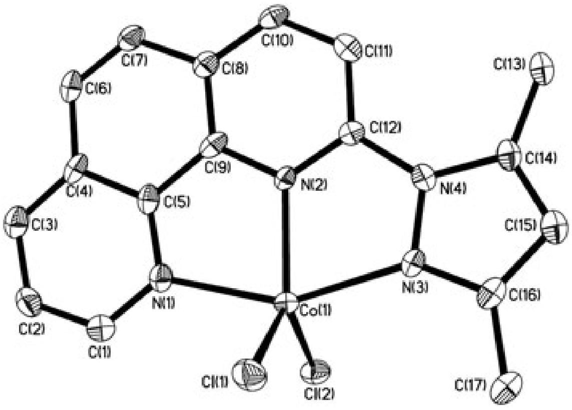


Figure 2. ORTEP view of complex **Co5**, drawn at 30% of probability. Hydrogen atoms and DMF molecule are omitted for clarity.

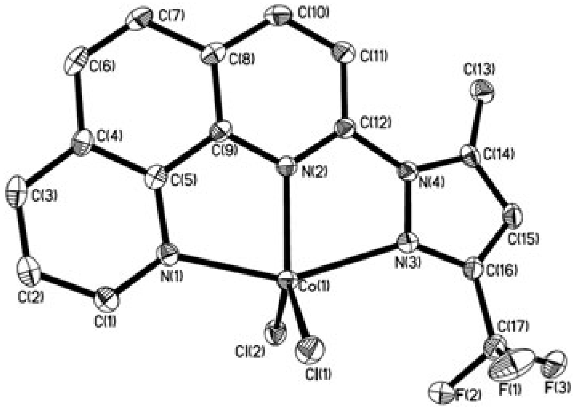


Figure 5. ORTEP view of complex **Co8**, drawn at 30% of probability. Hydrogen atoms are omitted for clarity.

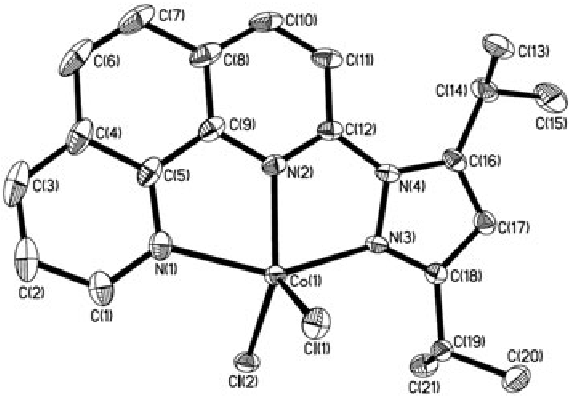


Figure 3. ORTEP view of complex **Co6**, drawn at 30% of probability. Hydrogen atoms are omitted for clarity.

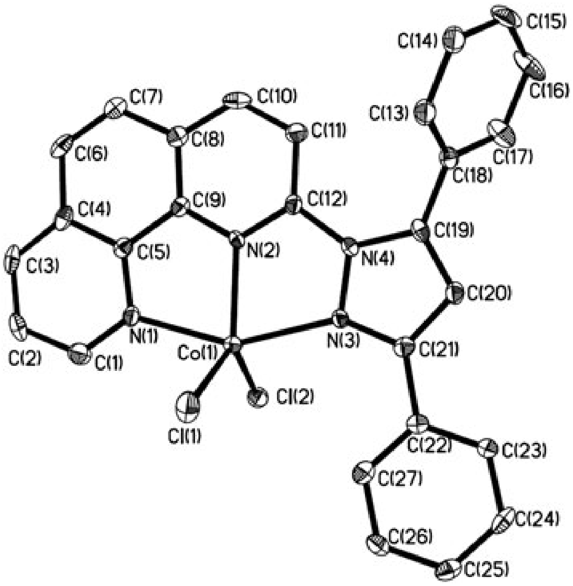


Figure 4. ORTEP view of complex **Co7**, drawn at 30% of probability. Hydrogen atoms are omitted for clarity.

of these complexes also exhibit distorted trigonal bipyramid structures. The deviations of the cobalt atom from the equatorial plane (N(1)–N(2)–N(3)) are 0.026, 0.150, 0.001 and 0.169 Å, respectively. The bond length of Co(1)–N(2) is shorter than that of Co(1)–N(1) and Co(1)–N(3), which is in accordance with complex **Co4** and nickel analogous.[30] It is notable that substituents and positions of the ligand do have a certain influence on the molecular structure. As the substituent at the 3- and 5-positions of the pyrazolyl ring changes from methyl group (**Co5**) to bulky isopropyl (**Co6**) and phenyl group (**Co7**), the Co(1)–N(3) bond length increases gradually (**Co5**: 2.163(3) Å; **Co6**: 2.1653(18) Å; **Co7**: 2.208(6) Å). The longest Co(1)–N(3) bond (2.283(2) Å) is found in complex **Co8** ($R_1 = CF_3$, $R_2 = CH_3$), suggesting that the strong electron-withdrawing trifluoromethyl group at the 3-position of the pyrazolyl ring reduces the electron density of coordinated N (3) atom. In addition, the pyrazole plane twists towards the phenanthroline plane with the dihedral angle in the follow order: **Co5** (2.31°) > **Co6** (6.24°) > **Co7** (6.39°) > **Co8** (15.98°).

Effects of Substituent on the pyrazolyl Ring of the Catalyst on 1,3-Butadiene Polymerization

Complexes **Co1–Co8** activated by MAO were examined for the polymerization of 1,3-butadiene as summarized in Table 3. All the complexes gave polybutadienes having predominantly *cis*-1,4 contents in the range 91.0–95.1%, while the polymer yields were appreciably affected by the substituent on the pyrazolyl ring of the complex ranging from 34% to 94.3%. Complex **Co1** without substituent on the pyrazolyl ring ($R_1 = H$, $R_2 = H$) afforded polymer in 74% yield (Scheme 1). When R_2 was changed to methyl (**Co2**), phenyl (**Co3**) and *para*-fluorophenyl (**Co4**) on the pyrazolyl ring, respectively, the activity exhibited in the order **Co2** (methyl) > **Co4** (*para*-fluorophenyl) > **Co3** (phenyl). Comprehensively, the methyl group (**Co2**) with hyperconjugation to the pyrazolyl ring gave the highest activity (yield 94.3%), while with **Co3**, though having a stronger conjugation to the pyrazolyl ring, bulkiness of the phenyl group might inhibit coordination of monomer, giving rise to the lowest activity (34%), and in **Co4**, though still bulky, the electron-withdrawing *para*-fluorophenyl group enhanced the Lewis acid nature of metal center and consequently facilitated the coordination of the monomer,[38] leading to better activity (51.5%) than that of **Co3**. Furthermore, when both R_1 and R_2 of the pyrazolyl ring were changed to methyl (**Co5**), i-propyl (**Co6**) and phenyl (**Co7**) respectively, the catalytic activity of complexes was in the order of iPr > Me > Ph, which is consistent with the distance of deviation of the cobalt atom from the equatorial plane [N(1)–N(2)–N(3)] of these

Table 1. Crystal data and structure refinements of complexes **Co4–Co8**

	Co4.DMF	**Co5**.DMF	**Co6**	**Co7**	**Co8**
Formula	$C_{24}H_{20}FN_5O$ $CoCl_2$	$C_{20}H_{21}N5O$ $CoCl_2$	$C_{21}H_{22}N_4$ $CoCl_2$	$C_{27}H_{18}N_4$ $CoCl_2$	$C_{17}H_{11}F_3N_4$ $CoCl_2$
Molecular weight	543.28	477.25	460.26	528.28	458.13
Crystal system	Triclinic	Monoclinic	Monoclinic	Triclinic	Monoclinic
Space group	P-1	P21/c	P21/c	P-1	P21/n
a (Å)	10.1027 (7)	11.3856 (8)	9.6134 (6)	9.1735 (9)	11.0731 (13)
b (Å)	10.3879 (8)	23.4281 (17)	8.2383 (6)	11.5613 (11)	9.4321 (11)
c (Å)	12.4120 (9)	8.0127 (6)	26.0362 (18)	21.700 (2)	17.690 (2)
α (deg)	83.8940 (10)	90.00	90.00	90.158 (2)	90.00
β (deg)	69.4020 (10)	101.7500 (10)	100.1350 (10)	90.226 (2)	108.24°
γ (deg)	74.5240 (10)	90.00	90.00	93.814 (2)	90.00
V (Å^3)	1174.99 (15)	2092.5 (3)	2029.8 (2)	2296.3 (4)	1754.7 (4)
Z	2	4	4	4	4
D_{calcd} (mg/m^3)	1.536	1.515	1.506	1.528	1.734
Absorp. coeff. (mm^{-1})	0.993	1.10	1.12	1.00	1.32
F(000)	554.0	980.0	948.0	1450	1125
Crystal size (mm)	0.22 × 0.19 × 0.16	0.19 × 0.13 × 0.08	0.20 × 0.18 × 0.12	0.24 × 0.21 × 0.15	0.20 × 0.16 × 0.12
θ range (°)	1.75–26.08	1.74–26.06	1.59–26.03	1.77–26.04	1.94–26.03
No. of reflns collected	6529	13 278	12 549	12 331	10 147
No. of indep. reflns	4581	4 112	3 983	8 856	3 451
R_{int}	0.0229	0.0240	0.0265	0.0372	0.0341
No. of data/restraint/params	4581/0/309	4 112/0/266	3 983/0/257	8 856/0/613	3 451/0/245
GOF on F^2	1.065	1.069	1.045	1.153	1.007
$R_1(I > 2\sigma(I))$	0.0578	0.0455	0.0343	0.0918	0.0374
wR_2	0.1716	0.1105	0.0885	0.1791	0.0827

Table 2. Selected bond length (Å) and angles (°) for complexes **Co4–Co8**

	Co4.DMF	**Co5**.DMF	**Co6**	**Co7**	**Co8**
Bond distance (Å)					
Co1—N1	2.181(3)	2.193(3)	2.2145(19)	2.176(6)	2.178(2)
Co1—N2	2.033(3)	2.045(2)	2.0703(18)	2.039(5)	2.042(2)
Co1—N3	2.302(4)	2.163(3)	2.1653(18)	2.208(6)	2.283(2)
Co1—Cl1	2.2626(14)	2.2726(9)	2.2697(6)	2.271(2)	2.2561(8)
Co1—Cl2	2.2695(12)	2.2748(9)	2.2791(6)	2.264(2)	2.2683(8)
Bond angle (°)					
N1—**Co1**—N3	150.93(13)	151.94(10)	149.01(7)	152.0(2)	150.20(9)
N1—**Co1**—N2	77.11(13)	77.75(10)	76.15(7)	77.3(2)	78.37(9)
N3—**Co1**—N2	73.87(13)	74.21(9)	73.41(7)	74.7(2)	72.54(8)
N1—**Co1**—Cl2	96.28(10)	96.03(7)	95.32(6)	95.94(17)	100.12(6)
N3—**Co1**—Cl2	100.88(9)	98.40(7)	101.49(5)	97.74(17)	96.78(6)
N2—**Co1**—Cl2	130.09(11)	119.12(7)	133.89(5)	119.54(17)	112.34(6)
N1—**Co1**—Cl1	95.62(10)	94.34(7)	100.10(6)	90.52(17)	95.18(6)
N3—**Co1**—Cl1	97.79(10)	98.99(7)	98.01(5)	103.47(16)	95.96(6)
N2—**Co1**—Cl1	114.13(10)	120.76(7)	115.33(5)	120.15(18)	124.52(6)
Cl2—**Co1**—Cl1	115.75(5)	120.08(3)	110.77(2)	119.92(9)	122.98(3)

complexes (0.150 Å (iPr), 0.026 Å (Me) and 0.001 Å (Ph)). Reasonably, a longer distance between metal atom and coordinated plane [N(1)—N(2)—N(3)] resulted in a more open spatial structure of the metal center, facilitating monomer coordination to the metal center, and consequently leading to the higher activity.[38] As expected, there being a greater distance of the cobalt atom from the equatorial plane [N(1)—N(2)—N(3)] than that of **Co5** (0.026 Å) and **Co6** (0.150 Å), **Co8** (0.169 Å) with an electron-withdrawing group gave higher activity than that of both **Co5** ($R_1 = R_2 = Me$) and **Co6** ($R_1 = R_2 = iPr$).

Variation of [Al]/[Co] and Temperature on 1,3-Butadiene Polymerization Behaviors

In general, excess MAO has to be used for obtaining polymer in high yield for metallocene or late transition metal-based

Table 3. Polymerization of 1,3-butadiene with **Co1–Co8** activated by MAO

Run[a]	Cat.	Yield (%)	Microstructure[b] (%)			M_n[c] ($\times 10^{-4}$)	M_w/M_n[c]
			cis-1,4	*trans*-1,4	1,2		
1	Co1	74.0	91.0	6.4	2.6	2.1	3.6
2	Co2	94.3	93.9	3.4	2.7	6.7	3.0
3	Co3	33.5	92.6	4.5	2.9	0.97	3.8
4	Co4	51.5	90.5	6.7	2.8	0.75	1.9
5	Co5	65.9	94.7	3.3	2.0	2.0	2.9
6	Co6	72.5	95.1	2.7	2.2	15.2	2.8
7	Co7	49.2	91.4	5.8	2.8	1.2	1.9
8	Co8	84.7	92.3	5.0	2.8	1.0	2.1

[a] Polymerization conditions: in toluene at 20°C for 4 h, [Co] = 1.32 mM, [BD]/[Co] = 2000, [Al]/[Co] = 100.

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

[c] Determined by GPC (THF, PSt calibration).

Table 4. Effects of [Al]/[Co] on the polymerization of 1,3-butadiene with **Co2**/MAO

Run[a]	Al/Co	Yield (%)	Microstructure[b] (%)			M_n[c] ($\times 10^{-4}$)	M_w/M_n[c]
			cis-1,4	*trans*-1,4	1,2		
11	25	—	—	—	—	—	—
12	50	52.3	94.5	3.1	2.4	4.2	2.6
13	100	94.3	93.9	3.4	2.7	6.7	3.0
14	150	95.8	93.6	3.2	3.2	6.9	2.8
15	200	96.7	93.2	3.2	3.6	7.1	2.7
16	300	98.5	93.4	3.5	3.1	6.5	2.6

[a] Polymerization conditions: in toluene at 20°C for 4 h, [Co] = 1.32 mM, [BD]/[Co] = 2000.

[b] Determined by ^{1}H NMR and FTIR.

[c] Determined by GPC (THF, PSt calibration).

Table 5. Effects of temperature on the polymerization of 1,3-butadiene with **Co2**/MAO

Run[a]	*T* (°C)	Yield (%)	Microstructure[b] (%)			M_n[c] ($\times 10^{-4}$)	M_w/M_n[c]
			cis-1,4	*trans*-1,4	1,2		
17	−20	—	—	—	—	—	—
18	0	50.6	94.6	3.2	2.2	4.2	2.7
19	20	93.9	93.9	3.4	2.7	6.7	3.0
20	40	92.5	91.8	3.2	5.0	5.4	2.7
21	60	91.8	90.6	3.7	5.7	3.8	2.8

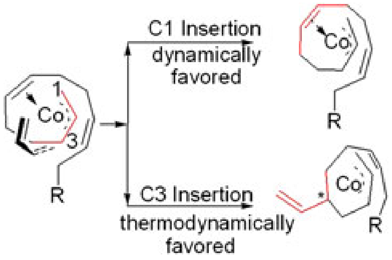
[a] Polymerization conditions: in toluene for 4 h, [Co] = 1.32 mM, [BD]/[Co] = 2000, [MAO]/[Co] = 100.

[b] Determined by ^{1}H NMR and FTIR.

[c] Determined by GPC (THF, PSt calibration).

catalysts, and it is true for cobalt-based catalyst in 1,3-butadiene polymerization. Currently, the complex **Co2** activated by MAO reached high-yield 1,3-butadiene polymerization only at [Al]/[Co] = 100 – much lower than that of reported Co complex (Table 4).[31,32] With the variation of [Al]/[Co] ratio, stereoregularity of the polymer was maintained almost consistent with *cis*-1,4 content around 94%, while molecular weight and molecular weight distribution of the resultant polymer only fluctuated slightly.

As with most late transition metal-based catalysts, the Co complexes also suffered from the decay of catalytic activity as polymerization temperature increased.[34,50] In the case of **Co2** activated by MAO, although polymerization yield also decreased as temperature increased, promisingly, the decrease was only from 93.9% to 91.8% when the temperature increased from 20°C to 60°C (Table 5), implying improvement of the thermal stability of the Co-based catalyst in the present work. With the increment of temperature, *cis*-1,4 content of the resultant polymer decreased simultaneously, with slightly increased *trans*-1,4 content and obviously increased 1,2 content. In principle, coordinated monomer can insert into the π–η^3-allyl in two ways (Scheme 2); insertion to less steric C1of π–η^3-allyl is dynamically favored, resulting in the formation of 1,4 units, while the more bulky C3 of π–η^3-allyl is thermodynamically favored, leading to the formation of 1,2 structure. Thus, comprehensively, much increased 1,2 content with increasing temperature was explainable according to Scheme 2.



Scheme 2. Proposed mechanism of C1 insertion and C3 insertion.

Effects of Co-catalyst Type on 1,3-Butadiene Polymerization by Co2

With complex **Co2** as a precursor, the effects of co-catalyst type on butadiene polymerization behavior were investigated (Table 6). All the co-catalysts examined displayed high activities, and the polymer yield reached 93.5% or above. Evidently, MAO

Table 6. Effects of co-catalyst type on the polymerization of 1,3-butadiene with **Co2**

Run[a]	Co-catalyst	[Al]/[Co]	Yield (%)	Microstructure[b] (%)			M_n[c] ($\times10^{-4}$)	M_w/M_n[c]
				Cis-1,4	*Trans*-1,4	1,2		
22	MAO	50	52.3	94.5	3.1	2.4	4.2	2.6
23	MAO	100	94.3	93.9	3.4	2.7	6.7	3.0
24	$Al_2Et_3Cl_3$	50	91.2	93.4	4.4	2.2	6.7	2.8
25	$Al_2Et_3Cl_3$	100	93.5	93.5	4.5	2.3	6.4	2.9
26	$AlEt_2Cl$	50	93.7	83.0	8.8	8.2	1.8	4.7
27	$AlEt_2Cl$	100	94.5	85.1	8.2	6.7	2.4	5.1
28	$AliBu_2Cl$	50	92.8	84.8	7.8	7.4	2.1	4.3
29	$AliBu_2Cl$	100	93.9	85.3	7.9	6.8	2.3	4.5

[a] Polymerization conditions: in toluene at 20°C for 4 h, [Co] = 1.32 mM, [BD]/[Co] = 2000.

[b] Determined by ^1H NMR and FTIR.

[c] Determined by GPC (THF, PSt calibration).

is more favorable in producing high *cis*-1,4 polymer (*cis*-1,4: 93.9%, [Al]/[Co] = 100), slightly higher than that of EASC (*cis*-1,4: 93.5%, [Al]/[Co] = 100) and remarkably higher than that of $AlEt_2Cl$ (*cis*-1,4: 85.1%, [Al]/[Co] = 100) and $AlBu_2Cl$ (*cis*-1,4: 85.3 %, [Al]/[Co] = 100). Since MAO leads to the formation of a cationic metal center, EASC may diminish the electron density of the metal center by $AlEtCl_2$ bridging through the aluminum atom. The enhanced Lewis acidity of the metal center activated with MAO and EASC may enhance the 'back-bite' of the last double bond of the molecular chain to the metal center, facilitating the formation of *cis*-1,4 unit. In addition, the enhanced 'back-bite' stabilizes the active site and solidifies the architecture around the active site, and as a consequence the polymer obtained by using MAO and EASC as co-catalysts have higher M_n and narrower M_w/M_n than with using $AlEt_2Cl$ and Al^iBu_2Cl.

Conclusion

A series of new cobalt(II) complexes supported by tridentate 2-pyrazolyl-substituted 1,10-phenanthroline ligands have been synthesized and fully characterized. Determined by X-ray crystallographic analysis, complexes **Co1–Co8** all exhibit distorted trigonal pyramid geometry around the cobalt atom. Activated by MAO, the complexes afford polybutadiene with mainly *cis*-1,4 content (up to 95.1%) in yields ranging from 33.5% to 94.3%. The catalytic activity varies with the variation of the steric and electronic nature of the substituent on the pyrazole ring of the ligand. Differentiating from the most transition metal-based catalysts, with increasing polymerization temperature, the activity of the catalyst decreases only slightly, indicating the catalyst system features much superior thermal tolerance to its analogues.

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