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Polymerization of 1,3-Butadiene Catalyzed by Cobalt(II) and Nickel(II) Complexes Bearing Pyridine-2-imidate Ligands[*]

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Abstract Cobalt and nickel complexes (**1a**–**1d** and **2a**–**2d**, respectively) supported by 2-imidate-pyridine ligands were synthesized and used for 1,3-butadiene polymerization. The complexes were characterized by IR and element analysis, and complex **1a** was further characterized by single-crystal X-ray diffraction. The solid state structure of complex **1a** displayed a distorted tetrahedral geometry. Upon activation with ethylaluminum sesquichloride (EASC), all the complexes showed high activities toward 1,3-butadiene polymerization. The cobalt complexes produced polymers with high *cis*-1,4 contents and high molecular weights, while the nickel complexes displayed low *cis*-1,4 selectivity and the resulting polymers had low molecular weights. The catalytic activities of the complexes highly depended on the ligand structure. With the increment of polymerization temperature, the *cis*-1,4 content and the molecular weight of the resulting polymer decreased.

Keywords: 1,3-Butadiene; Late-transition metal; *Cis*-1,4-polybutadiene; Pyridine-2-imidate.

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INTRODUCTION

Polydienes are an important class of polymers and find applications in various fields. Since the pioneer work by Natta, a variety of transition metal- and lanthanide- based catalytic systems have been developed for 1,3-diene polymerization[1–19], and some of them, such as $TiCl_4/I_2/Al^iBu_3$[20], $CoCl_2$/pyridine/$AlEt_2Cl$[21], $Ni(OCOR)_2/BF_3\cdot OEt_2/AlEt_3$[22], and $Nd(OCOR)_3/Al_2Et_3Cl_3/AlH^iBu_2$[23], have been realized for industrial production. In spite of these achievements, due to the nature of multiple ill-defined active species generated by the above-mentioned systems, the molecular weight and polydispersity of the resulting polymers could not be well-controlled, complicating therefore the mechanism study. In order to gain a better control in polymerization performance and better understand the polymerization mechanism, much effort has been focused on developing well-defined single-site catalysts. For instance, Ricci and coworkers reported that phosphorus-containing ligands supported transition metal complexes (Cr, Co, Fe, *etc.*) led to polybutadienes with high 1,2- contents[24–26]; Cui *et al.* reported that lanthanide complexes supported by various nitrogen-bearing ligands were highly active and *cis*-1,4 selective for 1,3-butadiene polymerization[27, 28]; Gibson and Grassi reported that $CrCl_3$- and VCl_3-

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based complexes were efficient precatalysts for *trans*-1,4- polymerization of 1,3-butadiene[29, 30].

Our group has been engaged in developing new single-site imine-based transition metal complexes for selective polymerization of 1,3-dienes[31–36]. In a recent work, we developed a series of imidoylchloride-based complexes, which displayed higher activities for 1,3-butadiene polymerization than their chloride-free counterparts due to the electro-withdrawing characteristic of chlorine atom[37, 38]. Besides, imidoylchloride group shares similar properties with acyl chloride which can be easily attacked by nucleophilic reagents and subsequently undergo nucleophilic substitution[39–41]. As an extension of our previous study, in the present study, a series of *N*,*N*-bidentate imidate-based late-transition metal complexes were synthesized and explored in 1,3-butadiene polymerization, the influences of the ligand structure and polymerization parameters on the polymerization were investigated in detail.

EXPERIMENTAL

General Considerations

All manipulations of air and/or moisture sensitive compounds were carried out under a dry and oxygen-free argon atmosphere by using Schlenk techniques or under a nitrogen atmosphere in a glove box. The solvents were refluxed over CaH_2 or sodium-benzophenone and distilled prior to use. 1,3-Butadiene was obtained from Jinzhou Petrochemical Company. $CoBr_2$ and $NiBr_2 \cdot DME$ were purchased from Alfa Aesar. Ethylaluminum sesquichloride (EASC), diethylaluminum chloride (DEAC) and methyl aluminoxane (MAO) were purchased from Akzo Noble and used as received. PPh_3, Phen (1,10-phenanthroline), and Bipy (2,2'-bipyridine) were purchased from Alladin company. The imidoylchloride-based ligands were synthesized in a similar method according to a previous report[38].

^{1}H-NMR (400 MHz) and ^{13}C-NMR (100 MHz) were recorded on a Varian Unity spectrometer in $CDCl_3$ at ambient temperature using tetramethylsilane as internal standard. FTIR spectra were recorded on Bruker Vertex-70 FTIR spectrometer. Elemental analysis was performed on an elemental Vario EL spectrophotometer. The proportion of *cis*-1,4 and *trans*-1,4 units of polymer were determined using FTIR spectra, ^{1}H-NMR, and ^{13}C-NMR. The molecular weights (M_n) and molecular weight distributions (M_w/M_n) 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. Tetrahydrofuran was used as eluent at a flow rate of 1.0 mL/min. The values of M_n and M_w/M_n were determined using polystyrene calibration.

Crystals for X-ray analysis 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 ($\lambda = 0.071073$ nm). 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 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 1037946, 1037947 for ligand **a** and complex **1a**, and supplementary crystallographic data for this paper can be obtained free of charge from the Cambridge Crystallographic Data Centre through www.ccdc.cam.ac.uk/data_request/cif.

Synthesis and Characterization of the Ligands and Complexes

General procedures for the synthesis of imidate-based ligands

All the imidate-based ligands were prepared in a similar manner using 2-(*N*-diisopropylphenyl carboximidoylchloride)-6-bromide-pyridine precursor which was synthesized in a similar method according to a previous report[38]. A typical synthesis procedure for ligand **a** is described as follows:

To a 100 mL round-bottom flask was added 20 mL of THF and 0.192 g of methanol (6 mmol) under nitrogen atmosphere, the flask was then put into ice bath and 0.14 g of sodium (6 mmol) was carefully added into the flask (a lot of hydrogen gas bubbled out!). The mixture was stirred for 2 h at room temperature and then refluxed for another 2 h. Then 2-(*N*-diisopropylphenylcarboximidoylchloride)-6-bromo-pyridine (0.75 g, 2 mmol) in 20 mL of THF was added dropwise, and the solution was further refluxed for 12 h. After that, 10 mL water and 30 mL of CH_2Cl_2 was added, and the mixture was washed with 100 mL of water for three times. The organic layer was collected and dried over anhydrous magnesium sulfate. The solvent was evaporated under reduced pressure, and the residue was purified by column chromatography on silica (eluent: petroleum ether/ethyl acetate 10:1) to give a yellow solid.

*Ligand 2-[methyl (N-diisopropylphenylcarboximidate)]-6-methoxyl pyridine (**a**)* Yield: 75.0%. ^{1}H-NMR (400 MHz, $CDCl_3$, δ): 7.54 (t, 1H, $H_{pyridine\text{-}4}$), 7.34 (d, 1H, $H_{pyridine\text{-}3}$), 6.99(d, 2H, H_{Ar}), 6.88 (d, 1H, H_{Ar}), 6.62 (d, 1H, $H_{pyridine\text{-}5}$), 4.02 (s, 3H, $-OCH_3$), 3.09 (s, 3H, $-OCH_3$), 2.86 (m, 2H, $-CH^{*}(CH_3)_2$), 1.15 (d, 6H, $-CH_3$), 0.88 (d, 6H, $-CH_3$). ^{13}C-NMR (100 MHz, $CDCl_3$, δ): 162.8, 152.4, 146.2, 144.5, 138.8, 135.9, 122.5, 121.7, 116.6, 112.5, 53.7, 52.9, 28.2, 23.2, 22.6. FTIR (KBr; cm^{-1}): 3076 (w), 2964 (m), 2870 (m), 1673 (s), 1592 (m), 1461 (m), 1411 (m), 1382 (m), 1323 (m), 1271 (m), 1219 (m), 1144 (m), 1108 (m), 1032 (m), 986 (m), 914 (m), 860 (m), 817 (m), 758 (m), 746 (m). Anal. Calc. for $C_{20}H_{26}N_2O_2$ (326.2): C, 73.59; N, 8.58; H, 8.03. Found: C, 73.51; N, 8.54; H, 7.99.

*Ligand 2-[ethyl (N-diisopropylphenylcarboximidate)]-6-ethoxylpyridine (**b**)* Yield: 62.9%. ^{1}H-NMR (400 MHz, $CDCl_3$, δ): 7.53 (t, 1H, $H_{pyridine\text{-}4}$), 7.36 (d, 1H, $H_{pyridine\text{-}3}$), 6.98 (d, 2H, H_{Ar}), 6.88 (t, 1H, H_{Ar}), 6.58 (d, 1H, $H_{pyridine\text{-}5}$), 4.48 (q, 2H, $-OCH^{*}_2CH_3$), 3.41 (q, 2H, $-OCH^{*}_2CH_3$), 2.86 (m, 2H, $-CH^{*}(CH_3)_2$), 1.47 (t, 3H, $-OCH_2CH^{*}_3$), 1.15 (d, 6H, $-CH_3$), 0.99 (t, 3H, $-OCH_2CH^{*}_3$), 0.87 (d, 6H, $-CH_3$). ^{13}C-NMR (100 MHz, $CDCl_3$, δ): 162.4, 152.0, 146.4, 144.6, 138.7, 135.9, 122.4, 121.4, 116.4, 112.5, 61.9, 61.18, 28.2, 23.3, 22.6, 14.5, 14.3. FTIR (KBr, cm^{-1}): 3074 (w), 2956 (m), 2867 (m), 1676 (s), 1589 (m), 1445 (m), 1365 (m), 1316 (m), 1269 (m), 1163 (m), 1109 (m), 1041 (m), 970 (m), 895 (m), 814 (m), 756 (m), 743 (m). Anal. Calc. for $C_{22}H_{30}N_2O_2$ (354.2): C, 74.54; N, 7.90; H, 8.53. Found: C, 74.59; N, 7.88; H, 8.51.

*Ligand 2-[phenyl (N-diisopropylphenylcarboximidate)]-6-bromidepyridine (**c**)* Yield: 69.9%. ^{1}H-NMR (400 MHz, $CDCl_3$, δ): 7.72 (1H, $H_{pyridine\text{-}3}$), 7.62 (t, 1H, $H_{pyridine\text{-}4}$), 7.55 (d, 1H, $H_{pyridine\text{-}5}$), 7.07–7.40 (m, 8H, H_{Ar}), 3.04 (m, 2H, $-CH^{*}(CH_3)_2$), 1.19 (s, 12H, $-CH_3$). ^{13}C-NMR (100 MHz, $CDCl_3$, δ): 153.9, 150.8, 150.0, 141.8, 141.2, 138.8, 138.4, 136.7, 129.4, 129.1, 125.6, 124.5, 123.4, 123.1, 122.6, 120.9, 28.4, 23.0. FTIR (KBr, cm^{-1}): 3072 (m), 2959 (m), 2867 (m), 1683 (s), 1590 (m), 1566 (m), 1485 (m), 1432 (m), 1405 (m), 1385 (m), 1287 (m), 1250 (m), 1204 (m), 1162 (m), 1134 (m), 989 (m), 929 (m), 840 (m), 813 (m), 765 (m), 688 (m). Anal. Calc. for $C_{24}H_{25}BrN_2O$ (436.1): C, 65.91; N, 6.40; H, 5.76. Found: C, 65.90; N, 6.43; H, 5.80.

*Ligand 2-[4-chlorophenyl (N-diisopropylphenylcarboximidate)]-6-bromidepyridine (**d**)* Yield: 78.5%. ^{1}H-NMR (400 MHz, $CDCl_3$, δ): 7.62 (1H, $H_{pyridine\text{-}3}$), 7.51 (t, 1H, $H_{pyridine\text{-}4}$), 7.46 (d, 1H, $H_{pyridine\text{-}3}$), 6.98–7.31 (m, 7H, H_{Ar}), 2.88 (m, 2H, $-CH^{*}(CH_3)_2$), 1.09 (d, 12H, $-CH_3$). ^{13}C-NMR (100 MHz, $CDCl_3$, δ): 152.4, 150.9, 149.4, 141.5, 141.3, 138.9, 138.5, 136.6, 129.9, 129.1, 125.8, 123.6, 123.1, 122.7, 28.4, 23.1. FTIR (KBr, cm^{-1}): 3077 (w), 2970 (m), 2867 (m), 1679 (s), 1566 (m), 1487 (m), 1405 (m), 1380 (m), 1289 (m), 1246 (m), 1209 (m), 1163 (m), 1136 (m), 1092 (m), 1013 (m), 988 (m), 914 (m), 826 (m), 776 (m), 753 (m), 667 (m). Anal. Calc. for $C_{24}H_{24}BrClN_2O$ (470.1): C, 61.10; N, 5.94; H, 5.13. Found: C, 61.15; N, 5.99; H, 5.17.

General procedures for the synthesis of the complexes

All the complexes were prepared in a similar method, and a typical synthetic procedure for complex **1a** is described as follows:

Ligand **a** (0.16 g, 0.5 mmol) in 2 mL of THF was added dropwise to a suspension of anhydrous $CoBr_2$ (0.11 g, 0.5 mmol) in 2 mL of THF, the reaction mixture was stirred for 10 h. Partial THF was removed under reduced pressure, and a large amount of ether (or hexane) was added, and plenty of precipitate formed. The precipitate was filtered and dried under vacuum at 40 °C.

*Complex 2-[methyl (N-diisopropylphenylcarboximidate)]-6-methoxylpyridine CoBr$_2$ (**1a**)* Yield: 75.5%. FTIR (KBr, cm^{-1}): 2964 (m), 2872 (w), 1627 (m), 1595 (m), 1483 (m), 1454 (m), 1429 (m), 1344 (m), 1285 (m), 1217 (m), 1058 (m), 877 (m), 806 (m), 752 (m). Anal. Calc. for $C_{20}H_{26}Br_2CoN_2O_2$ (543.0): C, 44.06; N, 5.14; H, 4.81. Found: C, 44.10; N, 5.19; H, 4.83.

*Complex 2-[ethyl (N-diisopropylphenylcarboximidate)]-6-ethoxylpyridine CoBr$_2$ (**1b**)* Yield: 75.8%. FTIR (KBr, cm^{-1}): 2964 (m), 2858 (w), 1619 (m), 1587 (m), 1459 (m), 1382 (m), 1329 (m), 1269 (m), 1161 (m), 1108 (m), 1041 (m), 812 (m), 743 (m). Anal. Calc. for $C_{22}H_{30}Br_2CoN_2O_2$ (571.0): C, 46.10; N, 4.89; H, 5.28. Found: C, 46.13; N, 4.93; H, 5.31.

*Complex 2-[phenyl (N-diisopropylphenylcarboximidate)]-6-bromidepyridine CoBr$_2$ (**1c**)* Yield: 82.1%. FTIR (KBr, cm^{-1}): 2970 (m), 2867 (w), 1612 (m), 1569 (m), 1489 (m), 1412 (m), 1385 (m), 1325 (m), 1264 (m), 1202 (m), 1164 (m), 1011 (m), 929 (m), 799 (m), 760 (m). Anal. Calc. for $C_{24}H_{25}Br_3CoN_2O$ (652.9): C, 43.93; N, 4.27; H, 3.84. Found: C, 43.95; N, 4.33; H, 3.87.

*Complex 2-[4-chlorophenyl (N-diisopropylphenylcarboximidate)]-6-bromidepyridine CoBr$_2$ (**1d**)* Yield: 69.9%. FTIR (KBr, cm^{-1}): 2961 (m), 2867 (w), 1626 (m), 1570 (m), 1485 (m), 1433 (m), 1404 (m), 1322 (m), 1207 (m), 1163 (m), 1087 (m), 1013 (m), 912 (m), 825 (m), 793 (m). Anal. Calc. for $C_{24}H_{24}Br_3ClCoN_2O$ (686.85): C, 41.74; N, 4.06; H, 3.50. Found: 41.79; N, 4.11; H, 3.46.

*Complex 2-[methyl (N-diisopropylphenylcarboximidate)]-6-methoxylpyridine NiBr$_2$ (**2a**)* Yield: 47.9%. FTIR (KBr, cm^{-1}): 2962 (m), 2868 (w), 1629 (m), 1602 (m), 1484 (m), 1457 (m), 1346 (m), 1285 (m), 1217 (m), 1061 (m), 810 (m), 749 (m). Anal. Calc. for $C_{20}H_{26}Br_2N_2NiO_2$ (542.0): C, 44.08; N, 5.14; H, 4.81. Found: C, 44.12; N, 5.19; H, 4.79.

*Complex 2-[ethyl (N-diisopropylphenylcarboximidate)]-6-ethoxylpyridine NiBr$_2$ (**2b**)* Yield: 58.3%. FTIR (KBr, cm^{-1}): 2962 (m), 2865 (w), 1624 (m), 1595 (m), 1461 (m), 1447 (m), 1334 (m), 1268 (m), 1214 (m), 1111 (m), 1058 (m), 810 (m), 743 (m). Anal. Calc. for $C_{22}H_{30}Br_2N_2NiO_2$ (570.0): C, 46.12; N, 4.89; H, 5.28. Found: C, 46.19; N, 4.93; H, 5.31.

*Complex 2-[phenyl (N-diisopropylphenylcarboximidate)]-6-bromidepyridine NiBr$_2$ (**2c**)* Yield: 73.7%. FTIR (KBr, cm^{-1}): 2969 (m), 2864 (w), 1637 (m), 1586 (m), 1485 (m), 1463 (m), 1443 (m), 1415 (m), 1383 (m), 1322 (m), 1258 (m), 1205 (m), 1168 (m), 1101 (m), 1025 (m), 926 (m), 864 (m), 762 (m), 746 (m). Anal. calc. for $C_{24}H_{25}Br_3N_2NiO$ (651.90): C, 43.95; N, 4.27; H, 3.84. Found: C, 43.97; N, 4.31; H, 3.79.

*Complex 2-[4-chlorophenyl (N-diisopropylphenylcarboximidate)]-6-bromidepyridine NiBr$_2$ (**2d**)* Yield: 50.3%. FTIR (KBr, cm^{-1}): 2956 (m), 2868 (m), 1625 (m), 1560 (m), 1483 (m), 1402 (m), 1282 (m), 1205 (m), 1167 (m), 1088 (m), 1015 (m), 912 (m), 827 (m), 778 (m). Anal. Calc. for $C_{24}H_{24}Br_3ClN_2NiO$ (685.9): C, 41.76; N, 4.06; H, 3.50. Found: C, 41.81; N, 4.04; H, 3.43.

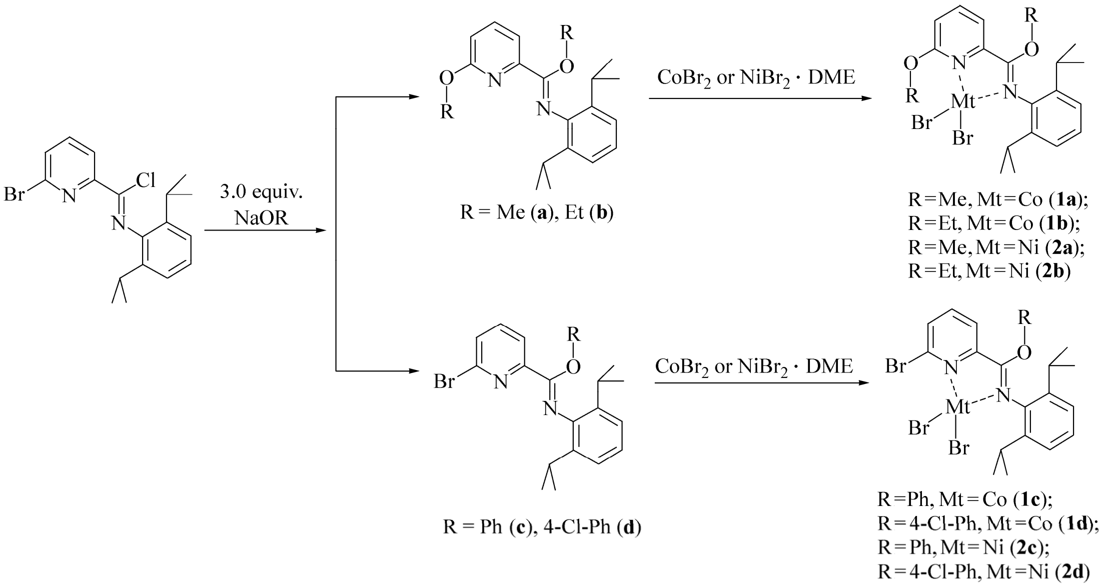
General procedures for 1,3-butadiene polymerization

A typical procedure for the polymerization is as follows (Run 15 in Table 2): a toluene solution of 1,3-butadiene (5 mL, 0.1 g/mL) was added to a moisture-free ampule preloaded with complex **1a** (4.6 μmol), then EASC (0.23 mmol) was injected to initiate the polymerization at 50 °C. After 30 min, ethanol containing 2,6-ditertbutyl-4-methylphenol (1.0 wt%) as a stabilizer was added to quench the polymerization. The precipitated polymer was washed with ethanol, and then dried under vacuum at 40 °C to constant weight. Polymer yield was determined by gravimetry.

RESULTS AND DISCUSSION

Synthesis and Characterization of the Ligands and Complexes

By reacting 2-(*N*-diisopropylphenylcarboximidoylchloride)-6-bromo-pyridine with three different NaOR, *N*,*N*-bidentate imidate-based ligands were obtained (Scheme 1). Due to the strong nucleophilicity of NaOR (R = Me, Et), alkoxyl substituted pyridine-2-imidate ligands, instead of 6-bromo-2-imidatepyridine, were obtained. The corresponding complexes were synthesized by treatment of the ligands with 1.0 equivalent of anhydrous $CoBr_2$ or $NiBr_2 \cdot DME$ in THF. All the ligands and complexes were characterized by NMR, IR, and elemental analysis. In the IR spectra, the absorption bands of the C═N groups in complexes **1a**–**1d** and **2a**–**1d** appear at 1612–1637 cm^{-1}, which are obviously red-shifted compared to the corresponding ligands (1673–1683 cm^{-1}), indicating that the nitrogen atom of imidate coordinates to the central metal. The molecular structures of ligand **a** and complex **1a** were further characterized by single-crystal X-ray diffraction. The molecular structures are shown in Figs. 1 and 2, selected bond distances and bond angles are listed in Table S1 in the supporting information.



Scheme 1 Synthesis of complexes **1a**–**1d** and **2a**–**2d**

Crystal of ligand **a** consists of two independent molecules in the asymmetric unit. The two molecules have similar geometry, and each has phenyl ring and pyridinyl ring located on the same side of the C═N double bond. This is different from the previously reported molecules, in which the phenyl ring and the quinolinyl or pyridinyl ring are on the opposite side, displaying *E* conformations[42, 43]. For these two molecules, the dihedral angles formed between the phenyl ring and the pyridine ring are 61.57° and 70.01°, respectively, which are much smaller than those in previous reported analogs, in which the aryl rings are approximately perpendicular to the pyridine rings[42, 43].

Crystals of **1a** were obtained by slow diffusion of diethyl ether into its CH_2Cl_2 solution. As the structure shown in Fig. 2, **1a** adopts a distorted tetrahedral geometry, which was built up by the two bromide and two nitrogen atoms. This is a different coordination geometry from that previously reported for 2,6-bis(imidate)pyridiene $CoCl_2$ complexes, in which distorted square pyramidal was displayed[34]. In **1a**, the two planes formed by Br(1)-Co(1)-Br(2) and N(1)-Co(1)-N(2) are almost perpendicular to each other with an angle of 79.43°. The bond angles of Br(1)-Co(1)-Br(2), Br(1)-Co(1)-N(1), Br(1)-Co(1)-N(2), Br(2)-Co(1)-N(1), and Br(2)-Co(1)-N(2) are 117.941(17)°, 104.78(6)°, 117.71(5)°, 121.46(6)°, and 108.91(5)°, respectively, which are about the same as the regular tetrahedron bond angle (109.47°). The bite angle of N(1)-Co(1)-N(2) is only 81.00(8)°, which plays an important role in distorting the tetrahedral geometry. The diisopropyl substituted phenyl ring is oriented approximately perpendicular to the pyridine plane with a dihedral angle of 84.38°. The two oxygen atoms, nitrogen (C═N) atom, and the cobalt atom are nearly coplanar with the pyridine ring, from which they deviate by 0.0036, 0.0194, 0.0154, 0.0364, respectively. The Co(1)-N(1) and Co(1)-N(2) bond distances are almost same (0.2046 and 0.2068 nm, respectively), and the Co-N(C=N) bond is much shorter than those in the tridentate 2,6-bis(imidate)pyridine Co(II) complexes, in which the Co-N(C=N) bonds are approximate 0.215 nm.

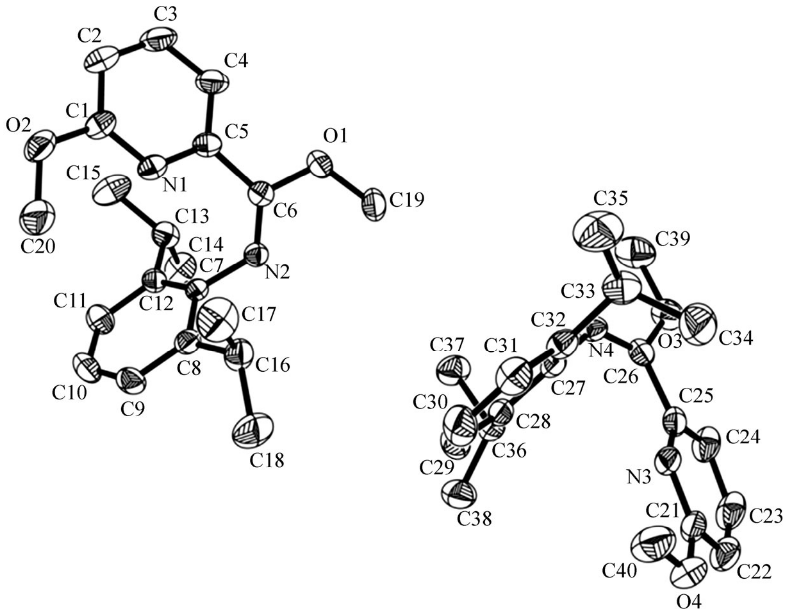


Fig. 1 Molecular structure of ligand **a**

Hydrogen atoms have been omitted for clarity. Selected bond lengths (nm) and angles (°): C(6)-N(2) 0.1269 (3), C(6)-O(1) 0.1348 (3), C(6)-C(5) 0.1500 (4), N(2)-C(7) 0.1413 (3), C(5)-C(6)-O(1) 110.4 (2), N(2)-C(6)-O(1) 120.8 (2), C(5)-C(6)-N(2) 128.8 (3), C(6)-N(2)-C(7) 125.1 (2).

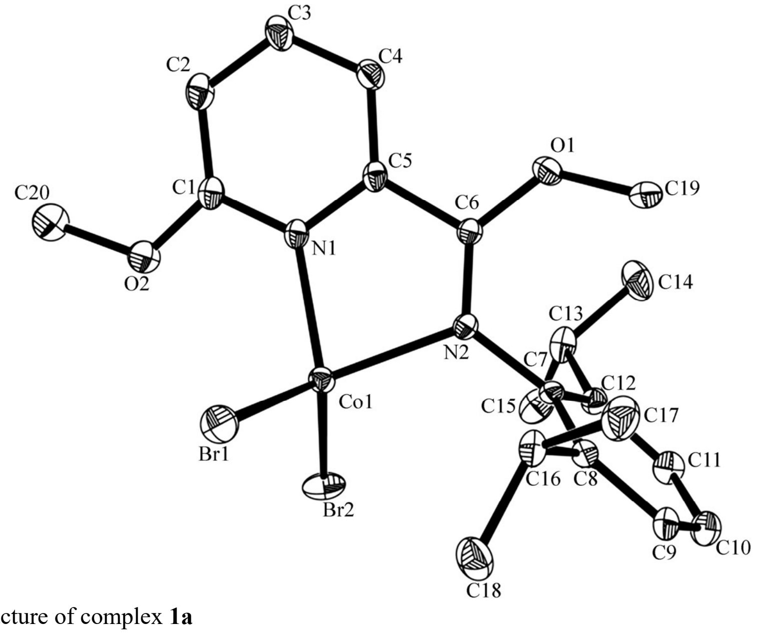


Fig. 2 Molecular structure of complex **1a**

Hydrogen atoms are omitted for clarity. Selected bond lengths (nm) and angles (°): Co(1)-N(1) 0.2046 (2), Co(1)-N(2) 0.2068 (2), C(6)-N(2) 0.1280 (3), C(6)-O(1) 0.1323 (3), C(6)-C(5) 0.1501 (3), Co(1)-Br(1) 0.23482 (4), Co(1)-Br(2) 0.23462 (4), N(2)-C(7) 0.1451 (3), N(1)-Co(1)-N(2) 81.00 (8), N(1)-Co(1)-Br(1) 104.78 (6), N(1)-Co(1)-Br(2) 121.46 (6), Br(1)-Co(1)-Br(2) 117.941, Br(1)-Co(1)-N(2) 117.71 (5), Br(2)-Co(2)-N(2) 108.91 (5).

1,3-Butadiene Polymerization

The cobalt and nickel complexes activated by EASC were applied in 1,3-butadiene polymerization. Firstly, complex **1a** was investigated as precatalyst to optimize the polymerization conditions, and the results are summarized in Table 1. The polymerization accelerated with an increase in reaction temperature from 0 °C to 50 °C. The polymer yield at 0 °C was less than 33%, it went up to 89% at 50 °C. Increasing temperature further to 70 °C resulted in a slight decrease in polymer yield (85%). This is different from the previously reported transition metal catalysts, where catalytic activities decreased significantly as polymerization temperature increased due to the decomposition of the generated active species at high temperatures[4, 44]. Polymerization temperature also influenced the catalyst selectivity. The *cis*-1,4 content of the resulting polymer decreased from 97.8% to 78.1% and the *trans*-1,4 content increased from 1.5% to 17.3% when the temperature increased from 0 °C to 70 °C. This tendency might be ascribed to the facilitated *anti*-*syn* isomerization through π-σ rearrangement at high temperatures. In principle, the terminal π-allylic unit of the polymer chain can be coordinated *via* the *anti*- or *syn*-conformation to the metal centre (Fig. 3), the former one forms first, and it will transfer to the thermodynamically stable *syn* form at elevated temperatures, thus giving rise to more *trans*-1,4 units. Meanwhile, the molecular weight of the resulting polymer decreased and the molecular weight distributions became broader due to the accelerated chain transfer reaction at elevated temperatures.

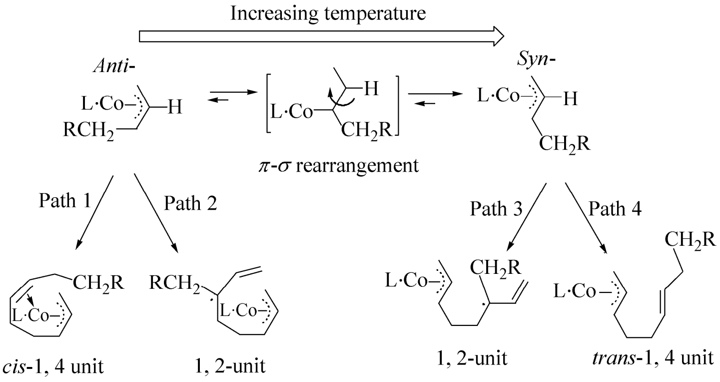


Fig. 3 Proposed scheme for 1,3-butadiene polymerization

Complex **1a** activated by other cocatalysts, MAO and DEAC, for 1,3-butadiene polymerization was further examined. MAO and DEAC were also efficient cocatalysts to activate the complex, and the produced polybutadienes possessed *cis*-1,4 contents of 94.3% and 83.9%, respectively, whereas TEA-based system could not initiate the polymerization under identical conditions. Since the EASC-based system exhibited the highest catalytic activity, EASC was used in the following study.

In order to understand the influence of ligand structure on the catalytic performance, other cobalt complexes were used for 1,3-butadiene polymerization. Complexes **1a** with methoxyl on imine group of the ligand exhibited almost the same activity as ethoxyl-substituted **1b**. This might be attributed to that these substituents located at a relatively long distance from the metal centre, and thereby displaying little impact on the catalytic behavior. Phenoxyl-substituted complex 1c afforded polymer in the yield of 84.8%, which was somewhat lower than those from **1a** and **1b**. Further introducing chlorine on para-position of phenyl ring led to an increase in the catalytic activity (**1d** versus **1c**). This is ascribed to the enhanced electropositivity of the central metal caused by the electron-withdrawing effect. It is worthy to mention that all the Co(II) complexes exhibited higher activities than the $CoCl_2$-based system, which was done in our previous reports and led to very low polymer yield[37].

The addition of nitrogen and phosphine-containing electron donors to cobalt-mediated 1,3-butadiene polymerization system has been reported to remarkably increase 1,2-content of the resulting polymers[21, 38–41]. Therefore, polymerizations of 1,3-butadiene were carried out in the presence of five equivalents of phosphine-containing donors by using **1a** as a precatalyst. As can been seen from Table 1 (Runs 12–14) for **1a**/EASC system, the addition of PPh_3, Phen, and Bipy resulted in slight decrease in catalytic activities compared with donor-free system. This might be due to that coordination of external donors to the cobalt centers leaves less vacant sites for 1,3-butadiene monomers, making therefore **1a**/EASC system less active. Meanwhile, the addition of these donors showed little influence on the selectivity of the present catalytic system. This result is different from that in the previous reports, in which the addition of phosphine-containing donors switched the selectivity of the Co(II)-based catalysts from *cis*-1,4- to 1,2- manner[41, 42]. The specific reason for the above phenomenon was still unclear yet. In addition, the molecular weight distributions of the resulting polybutadienes, obtained with **1a**/Donor/EASC system, were much broader than that obtained with the donor-free system, this might be attributable to that the coordination of donors to the metal centers generates multiple active species.

Table 1. 1,3-Butadiene polymerization with Co(II) complexes

Run [a]	Cat.	Polymerization		Yield (%)	$M_n \times 10^{-4}$	M_w/M_n [d]	Microstructure [e] (%)		
		Al [c]	*T* (°C)				*Cis*-1,4	*Trans*-1,4	1,2-
1	**1a**	EASC	0	32.2	6.01	2.5	97.8	1.5	0.7
2	**1a**	EASC	20	74.0	5.09	2.6	95.4	3.2	1.4
3	**1a**	EASC	50	89.2	4.58	4.2	85.5	11.9	2.6
4	**1a**	EASC	70	85.0	2.19	6.2	78.1	17.3	4.6
5	**1a**	MAO	50	68.0	4.23	2.0	94.3	3.5	2.2
6	**1a**	TEA [b]	50	trace					
7	**1a**	DEAC	50	74.4	2.41	2.5	83.9	7.4	8.7
9	**1b**	EASC	50	87.8	4.67	3.6	87.5	10.3	2.2
10	**1c**	EASC	50	84.8	6.33	3.3	89.2	8.6	2.5
11	**1d**	EASC	50	92.6	5.28	3.5	88.9	8.5	2.6
12 [f]	**1a**	EASC	50	80.3	2.32	5.1	89.4	4.0	6.6
13 [e]	**1a**	EASC	50	79.5	4.92	6.7	91.1	6.1	2.8
14 [e]	**1a**	EASC	50	88.1	6.31	5.9	89.6	6.1	4.3

[a] Polymerization conditions: [Bd]/[Co] = 2000, [Al]/[Co] = 50, [Bd] = 0.1 g/mL, toluene, 5 mL, 30 min; [b] Polymerization time: 4 h; [c] EASC: ethylaluminum sesquichloride; MAO: methyl aluminoxane; TEA: triethylaluminum; DEAC: diethylaluminum chloride; [d] Determined by GPC eluted with THF (polystyrenes as standards); [e] Determined by IR and NMR; [f] In Runs 12–14, external donors PPh_3, Phen, Bipy were used respectively, [Donor]/[Co] = 5.

Our previous study showed that the nature of central metal remarkably influenced the catalytic performances[31]. Thus, the nickel complexes were investigated for 1,3-butadiene polymerization, and the results are summarized in Table 2. Generally speaking, the nickel complexes exhibited lower activities than their cobalt counterparts. For example, nickel complex **2a** afforded polymer in the yield of 53.8%, which was much lower than its cobalt counterpart **1a** (89.2%). To achieve a high yield, polymerization time was elongated to 60 min in the following studies. It was observed that, for the nickel complexes, the influence of ligand structure on the

Table 2. 1,3-Butadiene polymerization with Ni(II) complexes

Run [a]	Cat.	*T* (°C)	Yield (%)	$M_n \times 10^{-4}$	M_w/M_n [c]	Microstructure [d] (%)		
						Cis-1,4-	*Trans*-	1,2-
15 [b]	**2a**	50	53.8	0.82	2.1	86.2	11.2	2.6
16	**2a**	50	74.6	0.92	1.9	83.5	13.6	2.9
17	**2b**	50	81.2	0.84	2.2	83.9	11.9	4.2
18	**2c**	50	85.7	0.93	3.0	83.0	14.3	2.7
19	**2d**	50	91.0	1.11	1.8	82.3	16.3	1.3
20	**2a**	0	68.6	1.62	2.1	91.1	4.9	4.0
21	**2a**	20	76.7	1.12	2.3	87.8	8.2	4.0
22	**2a**	70	81.8	0.51	2.8	80.7	16.8	2.5

[a] Polymerization conditions: [Bd]/[Co] = 2000, EASC, [Al]/[Co] = 50, [Bd] = 0.1 g/mL, 5 mL, toluene, 60 min; [b] Polymerization time, 30 min; [c] Determined by GPC eluted with THF (polystyrenes as standards); [d] Determined by IR and NMR

catalytic activity was almost the same as their cobalt counterparts, and a similar trend in the change of selectivity against polymer temperature was observed, that is, as the polymerization temperature increased, the *cis*-1,4-content of the resulting polymer decreased and simultaneously the *trans*-1,4- and 1,2- contents increased. On the other hand, the polymers obtained with nickel-based catalyst had much lower molecular weights. In addition, the nickel complexes displayed lower *cis*-1,4 selectivity than their cobalt counterparts; the *cis*-1,4 contents of the nickel-based polybutadienes were about 5%–10% lower than those obtained with the cobalt complexes.

CONCLUSIONS

A series of cobalt and nickel complexes ligated by 2-imidate-pyridine ligands were synthesized and investigated for 1,3-butadiene polymerization. In combination with EASC, both cobalt and nickel complexes were found to be highly active for the polymerization of 1,3-butadiene. The cobalt complexes as precatalysts afforded polybutadienes with predominant *cis*-1,4 contents and high molecular weights, while their Ni(II) counterparts displayed lower *cis*-1,4 selectivity and produced polymers with relatively lower molecular weights. The substituent at imidate-carbon of the ligand influenced catalytic activity due to steric and/or electronic reasons. The *cis*-1,4 selectivity of both cobalt and nickel complexes decreased with an increase in polymerization temperature owing to the facilitated *anti-syn* isomerization at elevated temperatures. While in some cases the observed catalysis behaviors might be explained by polymerization conditions and complex structure, further exploration of the related systems is needed to well understand the structure/performance relationship of these complexes.

REFERENCES

1 Thiele, S.K.H. and Wilson, D.R.J., Macromol. Sci. Polym. Rev., 2003, C43(4): 581
2 Miyazawa, A., Kase, T. and Soga, K., Macromolecules, 2000, 33(8): 2796
3 Tobisch, S., Macromolecules, 2003, 36(16): 6235
4 Appukuttan, V., Zhang, L., Ha, J.Y., Chandran, D., Bahuleyan, B. K., Ha, C.S. and Kim, I., J. Mol. Catal. A: Chem., 2010, 325(1–2): 84
5 Nath, D.C.D., Shiono, T. and Ikeda, T., Macromol. Chem. Phys., 2002, 203(4): 756
6 Jie, S., Ai, P. and Li, B., Dalton Trans., 2011, 40(41): 10975
7 Chandran, D., Kwak, C.H., Ha, C.S. and Kim, I., Catal. Today, 2008, 131(1–4): 505
8 Gao, B., Luo, X., Gao, W., Huang, L., Gao, S., Liu, X., Wu, Q. and Mu, Y., Dalton Trans., 2012, 41(9): 2755
9 Nishii, K., Kang, X., Nishiura, M., Luo, Y. and Hou, Z., Dalton Trans., 2013, 42(25): 9030
10 Zhang, J., Gao, W., Lang, X., Wu, Q., Zhang, L. and Mu, Y., Dalton Trans., 2012, 41(32): 9639
11 Annunziata, L., Pragliola, S., Pappalardo, D., Tedesco, C. and Pellecchia, C., Macromolecules, 2011, 44(7): 1934
12 Miyazawa, A., Kase, T., Hashimoto, K., Choi, J., Sakakura, T. and Jin, J., Macromolecules, 2004, 37(24): 8840
13 Jiang, X., Wen, X., Sun, W.H. and He, A., J. Polym. Sci., Part A: Polym. Chem., 2014, 52(17): 2398
14 Liu, B., Liu, D., Li, S., Sun, G. and Cui, D., Chinese J. Polym. Sci., 2015, 34(1): 104
15 Li, G., Ren, C., Dong, W., Jiang, L., Zhang, X. and Wang, F., Chinese J. Polym. Sci., 2010, 28(2): 157
16 Wen, J., Zhang, X. and Dai, Q., Chinese J. Polym. Sci., 2015, 33(3): 475
17 Liu, W., Pan, W., Wang, P., Li, W., Mu, J., Weng, G., Jia, X., Gong, D. and Huang, K.W., Inorg. Chim. Acta, 2015, 436(1): 132
18 Gong, D., Wang, B., Jia, X. and Zhang, X., Dalton Trans., 2014, 43(10): 4169
19 Gong, D., Jia, W., Chen, T. and Huang, K.W., Appl. Catal. A, 2013, 464–465(15): 35
20 VanAmerongen, G.J., "Transition metal catalyst systems for polymerizing butadiene and isoprene", American Chemical Society, 1966, Vol. 52, p. 136
21 Porri, L., Giarrusso, A. and Ricci, G., Prog. Polym. Sci., 1991, 16(2-3): 405

22 Furukawa, J. Pure Appl. Chem., 1975, 42(4): 495

23 Oehme, A., Gebauer, U., Gehrke, K. and Lechner, M.D., Die Angew. Makromol. Chem., 1996, 235(1): 121

24 Ricci, G., Sommazzi, A., Masi, F., Ricci, M., Boglia, A. and Leone, G., Coord. Chem. Rev., 2010, 254(5-6): 661

25 Ricci, G., Forni, A., Boglia, A. and Sonzogni, M., Organometallics, 2004, 23(15): 3727

26 Ricci, G., Forni, A., Boglia, A., Motta, T., Zannoni, G., Canetti, M. and Bertini, F., Macromolecules, 2005, 38(4): 1064

27 Jian, Z., Tang, S. and Cui, D., Chem. Eur. J., 2010, 16(47): 14007

28 Gao, W. and Cui, D., J. Am. Chem. Soc., 2008, 130(14): 4984

29 Colamarco, E., Milione, S., Cuomo, C. and Grassi, A., Macromol. Rapid Commun., 2004, 25(2): 450

30 Cariou, R., Chirinos, J., Gibson, V. C., Jacobsen, G., Tomov, A.K. and Elsegood, M.R.J., Macromolecules, 2009, 42(5): 1443

31 Gong, D., Wang, B., Bai, C., Bi, J., Wang, F., Dong, W., Zhang, X. and Jiang, L., Polymer, 2009, 50(26): 6259

32 Wang, B., Gong, D., Bi, J., Dai, Q., Zhang, C., Hu, Y., Zhang, X. and Jiang, L., Appl. Organomet. Chem., 2013, 27(4): 245

33 Gong, D., Jia, X., Wang, B., Zhang, X. and Jiang, L., J. Organomet. Chem., 2012, 702(1): 10

34 Gong, D., Wang, B., Cai, H., Zhang, X. and Jiang, L., J. Organomet. Chem., 2011, 696(8): 1584

35 Guo, J., Wang, B., Bi, J., Zhang, C., Zhang, H., Bai, C., Hu, Y. and Zhang, X., Polymer, 2015, 59(24): 124

36 Guo, J., Liu, H., Bi, J., Zhang, C., Zhang, H., Bai, C., Hu, Y. and Zhang, X., Inorg. Chim. Acta, 2015, 435(24): 305

37 Liu, H., Jia, X., Wang, F., Dai, Q., Wang, B., Bi, J., Zhang, C., Zhao, L., Bai, C., Hu, Y. and Zhang, X., Dalton Trans., 2013, 42(37): 13723

38 Liu, H., Wang, F., Jia, X., Liu, L., Bi, J., Zhang, C., Zhao, L., Bai, C., Hu, Y. and Zhang, X., J. Mol. Catal. A: Chem., 2014, 391: 25

39 Smit, T.M., Tomov, A.K., Gibson, V.C., White, A.J.P. and Williams, D.J., Inorg. Chem., 2004, 43(21): 6511

40 Smit, T.M., Tomov, A.K., Britovsek, G.J.P., Gibson, V.C., White, A.J.P. and Williams, D., J. Catal. Sci. Technol., 2012, 2(3): 643

41 Liu, H., Wang, F., Han, C., Zhang, H., Bai, C., Hu, Y. and Zhang, X., Inorg. Chim. Acta, 2015, 434(1): 135

42 Sun, W., Tang, X., Gao, T., Wu, B., Zhang, W. and Ma, H., Organometallics, 2004, 23(21): 5037

43 Nienkemper, K., Kotov, V.V., Kehr, G., Erker, G. and Fröhlich, R., Eur. J. Inorg. Chem., 2006, 2006(2): 366

44 Ai, P., Chen, L., Guo, Y., Jie, S. and Li, B.G., J. Organomet. Chem., 2012, 705: 51