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Metal dependent control of *cis*-/*trans*-1,4 regioselectivity in 1,3-butadiene polymerization catalyzed by transition metal complexes supported by 2,6-bis[1-(iminophenyl)ethyl]pyridine

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ABSTRACT

Fe(III), Cr(III), Fe(II), Co(II) and Ni(II) chloride complexes supported by 2,6-bis[1-(iminophenyl)ethyl]pyridine have been synthesized and characterized along with single crystal X-ray diffraction. These complexes, in combination with MAO, have been examined in butadiene polymerization. The catalytic activity and regioselectivity are strongly controlled by metal center and cocatalyst (MAO/Co ratio dependent in the case of Co(II) complex). The activity decreases in the order of Fe(III) > Co(II) > Cr(III) ≈ Ni (II) complexes, in consistent with the space around the metal center. Polybutadiene with different microstructure content, from high *trans*-1,4 units (88–95% for iron(III) and Cr(III)), medium *trans*-1,4 and *cis*-1,4 units (55% and 35%, respectively, for iron(II)) to high *cis*-1,4 units 79% for Co(II) and 97% for Ni(II) can be easily achieved by varying of the metal center. In addition, mechanism speculation is also presented to elucidate the dependence of catalytic behaviors on metal and cocatalyst.

1. Introduction

Investigation of catalysts conducting regio- and/or stereoselective polymerization of butadiene to afford polybutadiene with controlled microstructure has been a fascinating and challengeable subject over the past decades. Approaches to this target, to date, mainly involved adjusting the sterical and electronic properties of ligand or donor in the applied catalyst system. Jang found the microstructure of polybutadiene, within a wide range, from *cis*-1,4 (96.6%) to high 1,2 (95.8%) content, could be gradually tuned by modifying the electronic and sterical properties of substituted groups on PPh_3 in Co(2-ethyl hexanoate)$_2$/$AlEt_3$/H_2O/PPh_3-derivatives system [1]. In the meantime, addition of external donors such as CS_2 [2], PPh_3 [3], and phosphites [4] were widely documented as effective regulators of selectivity. Cocatalyst, referring to varying their structures and feeding amount, were also claimed to be a powerful tool as reported by Natta, Ricci and Hou [5]. Controlling of stereoselectivity by changing polymerization parameters such as temperature and solvent were recorded as well, but to a less extent [5d,6]. Nevertheless, metal-dependent control of selectivity, as a potential alternative, has not been recognized to date, probably due to the distinguishing intrinsic natures among the central metals. An effective ligand as a support in one metal for butadiene polymerization usually became invalid for another in terms of catalytic activity under the comparable polymerization conditions [7,8].

The past decade has witnessed a tremendous growth in interest in the development and application of new ligands as supports for transition metal complexes in olefin polymerization and oligomerization areas. Particularly, encouraged by the innovative finding of the highly active 2,6-bis(arylimino)pyridine ligated iron(II) and cobalt(II) complexes [9], numerous analogous ligand frameworks, as well as their associated metal complexes have been developed [10]. Reports to date for these complexes have been limited mainly to that of ethylene, studies on the polymerization of diolefins, such as isoprene and butadiene, however, remained scarce [10b,11], even though polydiene is a material that finds extensive and diverse applications in tire industry. We have been interested in transition metal supported by 2,6-bis(arylimino)pyridyl ligands with non-substituents on iminophenyl rings. This attention, on one hand, stems from the least bulkiness around the metal center, which can facilitate the coordination of relative bulky butadiene molecule, on the other hand, from the metal center restrained by *N*,*N*,*N*-tridentate ligand

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framework, which probably exclusively specify one coordination mode, forming high regio-selective active site. Herein, we intend to report the syntheses of transition metal (iron(III), chromium(III), iron(II), cobalt(II) and nickel(II)) complexes ligated with 2,6-bis[1-(phenylimino)ethyl]pyridine, and their catalytic behaviors in butadiene polymerization. Experimental data demonstrate that the activity and regio-specificity are well controlled by the central metal and MAO/Co (in the case of Co(II) complex) and polybutadienes having microstructures from high *trans*-1,4 (95%) to high *cis*-1,4 (96%) can be readily obtained by altering the central metal of complexes. Explanations, from correlation between structure of complexes and the corresponding regio-specificity, are also presented to elucidate the metal and cocatalyst dependent catalytic behaviors.

2. Experimental

2.1. Materials

$FeCl_3$, $CrCl_3(THF)_3$, $FeCl_2\cdot 4H_2O$, $CoCl_2$ and $NiCl_2$ were purchased from Alfa Aesar. 2,6-Diacetylpyridine and aniline were purchased from Aldrich. Methylaluminoxane (MAO, 10 wt% in toluene) was commercially available from Akzo Nobel Chemical Inc. Toluene and tetrahydrofuran (THF) were freshly distilled in the presence of sodium and benzophenone. Polymerization grade butadiene was supplied from Jinzhou Petrochemical Corporation, purified by passing through four columns packed with 4 Å molecular sieves and solid KOH before use. 2,6-Bis[1-(phenylimino)ethyl]pyridine [9] and complexes **a** [12], **b** [13], **c** [10e], **d** [14], and **e** [15] were prepared according to the published or modified methods (Scheme 1). Other chemicals were used as received unless otherwise noted.

2.2. Instrumentation

^1H NMR (400 MHz) and ^{13}C NMR (100 MHz) were recorded on a Varian Unity spectrometer in $CDCl_3$ at room temperature. IR spectra were performed on BRUKE Vertex-70 FIR spectrophotometer. Elemental analyses were recorded on an elemental Vario EL spectrometer. The proportions of 1,2, *cis*-1,4 and *trans*-1,4 units of polymer were determined by IR spectra and ^1H NMR [16]. 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) 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 M_n and M_w/M_n were determined using the polystyrene calibration. DSC measurements were performed on a Perkin–Elmer Diamond differential scanning calorimeter at a heating rate of 10 °C/min.

Crystals 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 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-713160 for **a** and CCDC-701490 for **d** contain supplementary crystallographic data for this article and can be obtained free of charge from www.ccdc.ac.uk/data-request/cif [or from the Cambridge crystallographic Data Centre, 12 Union Road, Cadbridge CB21EZ, United Kingdom; fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk].

2.3. Preparation and characterization of ligand and complexes

2.3.1. Synthesis of 2,6-bis[1-(phenylimino)ethyl]pyridine

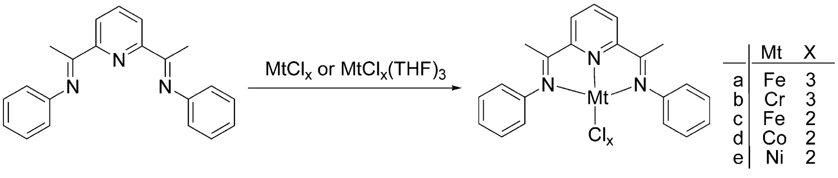
2,6-Diacetylpyridine (4.0 g, 24.5 mmol) and aniline (9.1 g, 97.8 mmol) were added to a flask containing 100 mL CH_2Cl_2. Na_2SO_4 (15.0 g) and formic acid (0.3 mL) were then added. The mixture was stirred at 25 °C for two days. Na_2SO_4 and CH_2Cl_2 were then removed, finally, 60 mL cold methanol was added. The flask was placed in the freezer at −30 °C and a yellow solid precipitated after several days. The desired product (6.1 g, 79.4%) was identified by ^1H NMR, IR and elemental analysis. ^1H NMR (400 MHz, $CDCl_3$, δ, ppm): 8.35 (d, 2H, $J = 7.60$ Hz, H_{pyr}), 7.88 (t, 1H, $J = 7.80$ Hz, H_{pyr}), 7.39 (t, 4H, $J = 7.80$ Hz, H_{aryl}), 7.13 (t, 2H, $J = 7.40$ Hz, H_{aryl}), 6.85 (d, 4H, $J = 7.90$ Hz, H_{aryl}), 2.41 (s, 6H, $-N{=}C-CH_3$). IR (KBr, cm^{-1}): 3070, 1637 ($\nu_{C=N}$), 1592, 1483, 1447, 1363, 1217, 1078, 823, 774, 708. Anal. Calcd. For $C_{21}H_{19}N_3$: C, 80.48; H, 6.11; N, 13.41. Found: C, 80.25; H, 6.00; N, 13.65.

2.3.2. Synthesis of {2,6-bis[1-(phenylimino)ethyl]pyridine}$FeCl_3$ (*a*)

Anhydrous iron(III) chloride powder (0.16 g, 1.0 mmol) and 2,6-bis[1-(phenylimino)ethyl]pyridine (0.31 g, 1.0 mmol) were added to a flask containing cold THF (8 mL). The reaction temperature was kept at 0 °C to suppress the reduction of iron(III) to iron(II). Stirring for 1 h, the red precipitate was collected and then washed with heptane (3 × 5 mL). The desired product (0.46 g, 97.9%) was obtained after dried in *vacuo*. IR (KBr, cm^{-1}): 3079, 1626 ($\nu_{C=N}$), 1586, 1486, 1372, 1266, 1229, 1027, 777, 694. Anal. Calcd. For $C_{21}H_{19}N_3FeCl_3$: C, 53.03; H, 4.03; N, 8.84. Found: C, 53.26; H, 3.89; N, 9.17.

2.3.3. Synthesis of {2,6-bis[1-(phenylimino)ethyl]pyridine}$CrCl_3$ (*b*)

To a solution of 2,6-bis[1-(phenylimino)ethyl]pyridine (0.31 g, 1.0 mmol) in CH_2Cl_2 (8 mL), was added $CrCl_3(THF)_3$ (0.37 g, 1.0 mmol). The resultant solution was stirred at 25 °C for 12 h giving a green suspension. The reaction volume was reduced to about 2 mL by *vacuo*, next, 20 mL Et_2O was added and a green precipitate immediately formed. The solid was filtered and then washed with heptane (3 × 10 mL). The desired product (0.36 g, 76.4%) was obtained after dried under *vacuo*. IR (KBr, cm^{-1}): 3080, 1614 ($\nu_{C=N}$), 1528, 1487, 1373, 1273, 1233, 780, 697. Anal. Calcd. For $C_{21}H_{19}N_3CrCl_3$: C, 53.47; H, 4.06; N, 8.91. Found: C, 53.20; H, 3.85; N, 8.66.



Scheme 1. Syntheses of Fe(III), Cr(III), Fe(II), Co(II) and Ni(II) complexes.

2.3.4. *Synthesis of {2,6-bis[(1-(phenylimino)ethyl]pyridine)}FeCl$_2$ (**c**)*

2,6-Diacetylpyridine (0.31 g, 1.0 mmol) was added to a solution of $FeCl_2 \cdot 4H_2O$ (0.20 mg, 1.0 mmol) in THF (15 mL) at 25 °C with rapid stirring. The solution turned deep purple immediately. The dark purple product precipitated from the solution after several minutes. The reaction volume was reduced to about 6 mL after stirring for 12 h. The remaining mixture was allowed to stand at room temperature for overnight, and then the supernatant liquid was removed. The product was washed with 4 × 5 mL of Et_2O and dried in *vacuo*. The desired product (0.39 g, 88.6%) was obtained as a dark purple powder. IR (KBr, cm^{-1}): 3392, 3063, 1618 ($\nu_{\mathrm{C=N}}$), 1590, 1528, 1484, 1449, 1440, 1379, 731, 701. Anal. Calcd. For $C_{21}H_{19}N_3FeCl_2$: C, 57.30; H, 4.35; N, 9.55. Found: C, 57.02; H, 4.56; N, 9.68.

2.3.5. *Synthesis of {2,6-bis[1-(phenylimino)ethyl]pyridine}CoCl$_2$ (**d**)*

2,6-Bis[1-(phenylimino)ethyl]pyridine (0.31 g, 1.0 mmol) and anhydrous $CoCl_2$ (0.13 g, 1.0 mmol) were added to a flask containing THF (30 mL). The mixture was stirred at 20 °C for 12 h, during which time, a yellow green suspension formed. Et_2O was then added to precipitate product. The precipitate was collected by filtration and washed with 4 × 5 mL of heptane. The desired product (0.42 g, 95.5%) was obtained after dried in *vacuo* at 40 °C. IR (KB, cm^{-1}): 3079, 1628 ($\nu_{\mathrm{C=N}}$), 1594, 1487, 1372, 1261, 1229, 1027, 779, 696. Anal. Calcd. For $C_{21}H_{19}N_3CoCl_2$: C, 56.91; H, 4.32; N, 9.48. Found: C, 56.68; H, 4.20; N, 9.29.

2.3.6. *Synthesis of {2,6-bis[1-(phenylimino)ethyl]pyridine}NiCl$_2$ (**e**)*

Anhydrous $NiCl_2$ (0.13 g, 1.0 mmol) was added to a solution of 2,6-bis[1-(phenylimino)ethyl]pyridine (0.31 g, 1.0 mmol) in acetonitrile (CH_3CN, 40 mL). The mixture was stirred at 20 °C overnight. Solvent was evaporated and the product was recrystallized from CH_3CN/THF. The desired product (0.35 g, 81.8%) was obtained after dried in *vacuo*. IR (KBr, cm^{-1}): 3080, 1623 ($\nu_{\mathrm{C=N}}$), 1591, 1482, 1441, 1372, 1267, 1234, 1039, 786, 771, 704. Anal. Calcd. For $C_{21}H_{19}N_3NiCl_2$: C, 56.94; H, 4.32; N, 9.49. Found: C, 56.68; H, 4.44; N, 9.28.

2.4. *Procedure for butadiene polymerization*

A typical procedure for the polymerization is as follows (entry 2 in Table 1): a toluene solution of butadiene (5 mL, 2.0 mol/L) was added to a moisture free ampere bottle preloaded with complex **a** (4.8 mg, 0.01 mmol). MAO (Al, 0.5 mmol) was then injected to initiate the polymerization at 20 °C. After 4 h, methanol was added to quench the polymerization. The mixture was poured into a large quantity of methanol containing 2,6-di-*tert*-butyl-4-methylphenol (1.0 wt%) as a stabilizer. Filtered and dried under vacuum at 40 °C, polybutadiene was resulted at a constant weight (0.54 g, 100%).

3. Results and discussions

3.1. *Synthesis and characterization of ligand and complexes*

2,6-Bis[1-(phenylimino)ethyl]pyridine can be readily prepared by condensation of aniline with 2,6-diacetylpyridine in CH_2Cl_2 in the presence of a catalytic amount of formic acid [9]. Complexes **a**–**e** are synthesized by reaction of the corresponding metal chlorides or its THF complex ($CrCl_3(THF)_3$) with 2,6-bis[1-(phenylimino)ethyl]pyridine in THF or CH_2Cl_2. The obtained solid compounds are air and moisture stable. For synthesis of complex **a**, reaction temperature is lowered down to 0 °C in our experiment for preventing undesirable reduction of iron(III) to iron(II) by α-hydrogen abstracted from THF molecule [17]. The elemental analyses results reveal that the components of all complexes are in accord with the formula $MtLCl_x$,(Mt = Fe(III), Cr, $x = 3$; Mt = Fe(II), Co, Ni, $x = 2$; L = 2,6-bis[1-(phenylimino)ethyl]pyridine). The IR spectrum of the pristine ligand shows that the C=N stretching frequencies appears at 1637 cm^{-1}, while in the complexes **a**–**e**, the C=N stretching vibrations shift toward lower frequencies between 1614 and 1628 cm^{-1} and are greatly reduced in intensity, which indicate the coordination interaction between the imino nitrogen atoms and the metal ions. Complexes **a** and **d** are further characterized by X-ray crystallography.

Table 1
Polymerization results with complexes (Fe(III), Cr(III), Fe(II), Co(II) and Ni(II)) carrying 2,6-bis[1-(iminophenyl)ethyl]pyridine.

Entry[a]	Precursor[b]	MAO/Mt[c] (equiv)	Yield (%)	M_n ($\times 10^{-4}$)	M_w/M_n	Microstructure (%)			T_m[d]
						Cis-1,4	*Trans*-1,4	1,2	
1	$FeCl_3$	100	0	–	–	–	–	–	–
2	$FeCl_3L$	50	100	2.9	2.0	0	95.3	4.7	101
3	$FeCl_3L$	100	100	2.7	1.9	0	94.6	5.4	103
4	$CrCl_3$	100	0	–	–	–	–	–	–
5	$CrCl_3L$	50	38	4.9	2.0	9.5	90.2	0.3	87
6	$CrCl_3L$	100	46	4.1	2.2	11.5	88.1	0.4	85
7	$FeCl_2L$	100	0	–	–	–	–	–	–
8	$FeCl_2L$	50	69	3.7	1.7	35.5	55.1	9.4	–
9	$FeCl_2L$	100	82	3.5	1.7	34.8	54.9	10.3	–
10	$CoCl_2$	100	24	2.6	1.8	98.1	1.6	0.3	–
11	$CoCl_2L$	25	0	–	–	–	–	–	–
12	$CoCl_2L$	50	39	1.0	1.7	0	94.4	5.6	96
13	$CoCl_2L$	75	86	4.8	4.9	78.8	18.2	3.0	–
14	$CoCl_2L$	100	100	5.2	7.0	79.2	18.0	2.8	–
15	$NiCl_2$	100	24	2.4	3.9	90.1	6.1	4.1	–
16	$NiCl_2L$	50	33	1.3	2.2	95.1	1.1	3.8	–
17	$NiCl_2L$	100	42	1.4	2.9	96.2	2.1	1.7	–
18	$NiCl_2L$	200	39	1.6	2.6	96.9	2.0	1.1	–

[a] Polymerization conditions: precursor, 0.01 mmol; butadiene, 0.01 mol; toluene, 5 mL; time, 4 h; temperature, 20 °C.

[b] $FeCl_3L$, $CrCl_3L$, $FeCl_2L$, $CoCl_2L$ and $NiCl_2L$ denote complexes **a**, **b**, **c**, **d** and **e**, respectively.

[c] MAO/precursor molar ratio.

[d] Melting temperature, determined by DSC.

Crystal of complex **a** suitable for X-ray structural determination is obtained by slowly evaporation of dichloromethane/benzene solution containing the corresponding complex. The molecular structure is shown in Fig. 1. The geometry around the iron atom can be described as a distorted octahedron, with the equatorial plane formed by three nitrogen atoms and one chlorine atom (Cl(1)), and the two axial Fe–Cl bonds. The iron center deviates by only 0.0039 Å from this equatorial plane. The equatorial angles range is between 72.9(2) and 109.37(14)°, and the two axial Fe–Cl bonds subtend an angle of 171.05(7)°. The planes of two phenyl rings are oriented essentially orthogonal to each other (89.06°) and also to the coordination plane formed by three coordinated nitrogen atoms with angles about 86.53 and 81.89°. Three chlorine ligands are in a meridional geometry. The Fe–Cl bond distance located at *trans* position (Fe–Cl(1), 2.2427(19) Å) to pyridine is shorter than those at *cis* position to pyridine (Fe–Cl(2), 2.361(2) Å and Fe–Cl(3), 2.321(2) Å). The Fe–N(pyridyl) bond distance (Fe–N(1) = 2.117(5) Å) is shorter than the Fe–N(imino) bond distances (2.155(5) Å, Fe–N(2) and 2.152(5) Å, Fe–N(3)). The Cl–Fe–Cl and N–Fe–N angles are 171.05(7), 95.81(7), 93.05(7)° and 72.9(2), 73.5(2), 146.13(19)°, respectively. The two imino C=N bonds in **a** have typical double-bond character with C=N bond lengths of 1.283(7) and 1.277(7) Å.

Crystal of complex **d** suitable for X-ray structural determination is grown from a slow diffusion of diethyl ether into a dichloromethane solution of the corresponding complex. Compound **d** crystallizes with two independent molecules per asymmetric unit, which differ in the orientation of the phenyl groups [C(8)–C(9)–N(3)–Co(1) 75.06° and C(16)–C(17)–N(2)–Co(1) 59.24° for one

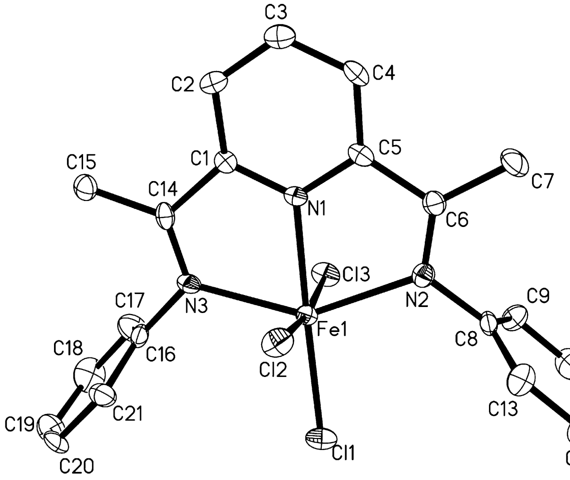


Fig. 1. Molecular structure of complex **a** with 35% probability of thermal ellipsoids. Hydrogen atoms and benzene molecule are omitted for clarity. Selected bond lengths (Å) and bond angles (°): Fe(1)–N(1) 2.118(5), Fe(1)–N(2) 2.155(5), Fe(1)–N(3) 2.151(5), Fe(1)–Cl(1) 2.2427(19), Fe(1)–Cl(2) 2.361(2), Fe(1)–Cl(3) 2.321(2), N(1)–Fe(1)–N(3) 72.9(2), N(1)–Fe(1)–N(2) 73.5(2), N(3)–Fe(1)–N(2) 146.13(19), N(1)–Fe(1)–Cl(1) 176.00(16), N(3)–Fe(1)–Cl(1) 109.37(14), N(2)–Fe(1)–Cl(1) 104.42(14), N(1)–Fe(1)–Cl(3) 87.57(14), N(3)–Fe(1)–Cl(3) 86.74(14), N(2)–Fe(1)–Cl(3) 87.62(14), Cl(1)–Fe(1)–Cl(3) 95.81(7), N(3)–Fe(1)–Cl(2) 83.63(14), N(2)–Fe(1)–Cl(2) 89.13(15), N(1)–Fe(1)–Cl(2) 91.41(15), Cl(1)–Fe(1)–Cl(2) 93.05(7), Cl(3)–Fe(1)–Cl(2) 171.05(7).

molecule; C(37)–C(38)–N(5)–Co(2) 88.75° and C(29)–C(30)–N(6)–Co(2) 79.70° for the other molecule] with respect to the plane defined by the three nitrogen atoms. Due to the fact that the bond distances and angles are similar in the two independent molecules, reference can be made to the molecule identified by Co(1). The molecular structure of Co(1) is shown in Fig. 2. The molecule possesses a structure with approximate C_s symmetry about a plane containing the cobalt atom, the two chlorine atoms, and the pyridyl nitrogen atom. The geometry at the cobalt center can be better described as distorted trigonal bipyramidal, with the equatorial plane formed by the pyridyl nitrogen atom and the two chlorine ligands, and the two axial Co–N bonds. The metal center lies 0.0183 Å out of the equatorial plane. Three equatorial angles are very close to each other (Cl(1)–Co(1)–Cl(2), 117.84(3)°, N(1)–Co(1)–Cl(1), 118.36(5)° and N(1)–Co(1)–Cl(2), 123.78(5)°), and the two axial Co–N bonds subtend an angle of 150.88(7)°. The dihedral angle between two phenyl rings is 78.03°, and those between the phenyl rings and the plane formed by three coordinated nitrogen atoms are 70.06 and 59.09°. The Co–N(pyridyl) bond distance (2.0310(18) Å) is also shorter than those of two Co–N(imino) (2.2217(18), 2.2129(18) Å). The two imino C=N bonds have distinctive double-bond character, with C–N distances of 1.282(3) and 1.281(3) Å.

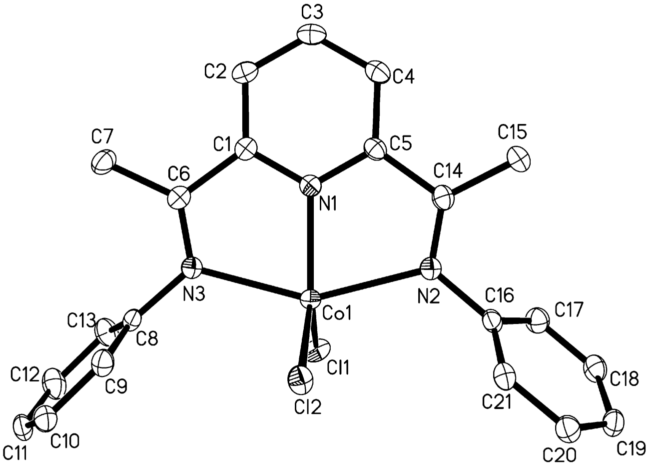


Fig. 2. Molecular structure of complex **c** with 35% probability of thermal ellipsoids. Hydrogen atoms and methylene chloride molecule are omitted for clarity. Selected bond lengths (Å) and bond angles (°): Co(1)–N(1) 2.0310(18), Co(1)–N(2) 2.2217(18), Co(1)–N(3) 2.2129(18), Co(1)–Cl(1) 2.2680(6), Co(1)–Cl(2) 2.2613(6), N(1)–Co(1)–N(3) 75.29(7), N(1)–Co(1)–N(2) 75.64(7), N(3)–Co(1)–N(2) 150.88(7), N(1)–Co(1)–Cl(2) 123.78(5), N(3)–Co(1)–Cl(2) 95.86(5), N(2)–Co(1)–Cl(2) 98.80(5), N(1)–Co(1)–Cl(1) 118.36(5), N(3)–Co(1)–Cl(1) 97.85(5), N(2)–Co(1)–Cl(1) 97.31(5), Cl(2)–Co(1)–Cl(1) 117.84(3).

3.2. *Butadiene polymerization*

Complexes **a**, **b**, **c**, **d**, and **e** are employed to initiate the polymerization of butadiene in toluene under the polymerization conditions ([Bd]/[Mt] = 1000, [MAO]/[Mt] = 0–200, temperature = 20 °C). The polymerization results are tabulated in Table 1. For comparison, the corresponding metal chlorides $FeCl_3$, $CrCl_3$, $FeCl_2$, $CoCl_2$ and $NiCl_2$ are also individually tested as initiator for polymerization of butadiene with activation of MAO. $FeCl_3$, $CrCl_3$, $FeCl_2$ systems are completely inert, while $CoCl_2$/MAO and $NiCl_2$/MAO displayed *cis*-1,4 selectivity.

As seen from the Table 1, the distinguishing catalytic behaviors, in terms of activity, selectivity and molecular weight of polymer, between metal chlorides and their corresponding complexes indicate the bisiminopyridine ligand is attached to the metal center during polymerization process rather than eliminated from the metal center.

3.2.1. *Activity*

From Table 1, polymerization activity is basically governed by the metal center, decreasing in the following order of Fe(III) > Co(II) > Cr(III) ≈ Ni(II), in accordance with decreasing sterical environment of the metal center pinched by three nitrogen atoms. Fe(II) complex, having the iron pair structure differentiating from that of metal center examined, is not included. Presumably, the longer the mean Mt–N bond distance (Fe(III)–N ≈ Co–N > Cr–N [13] ≈ Ni–N [15]) is and the smaller the angle N(imino)–Mt–N(imino) (N_2–Fe–N_3 (146.1°) < N_2–Co–N_3 (150.9°) < N_2–Cr–N_3 (155.3°) [13] ≈ N_2–Ni–N_3 (155.7°) [15]) is, the larger the space around metal center is, which ultimately leads to much higher activity.

3.2.2. *Regioselectivity*

Complex **a** in combination with MAO, shows excellent catalytic behaviors, completely converting butadiene to *trans*-1,4 polybutadiene (*trans*-1,4 = 95%, *cis*-1,4 = 0, entries 2 and 3 in Table 1 and Fig. 3(a)) with molecular weight of $2.7–2.9 \times 10^4$ and molecular weight distribution about 2.0. Complex **b**, activated by MAO, exhibits good catalytic activity as well, which yields polybutadiene with *trans*-1,4 units about 90% and *cis*-1,4 units about 10% (entries 5 and 6 in Table 1). The unique high *trans*-1,4 selectivity observed in the Fe(III) and Cr(III) catalysts may be attributed to the incorporation of tridentate bisiminopyridine ligand into the corresponding metal chlorides, shifting monomer coordination mode with the metal center. As diene polymerization mechanism proposed by Tobish [18] and Brookhart [19], tridentate ligated Fe(III) and Cr(III) complexes with one less coordination site in the metal center than that of the corresponding metal with bidentated counterparts, such as $FeCl_2$(bipyridine)$_2$ [7d], $FeEt_2$(bipyridine)$_2$ [20] and $CrCl_2(P\cap P)_2$($P\cap P$: bidentate phosphine ligand) [7a–c], may exclusively facilitate the single-*trans*-η^2 coordination with butadiene (Scheme 2), due to the less vacant site and more crowded sterical space of the former complexes than the later, and accordingly, the syn-π-allyl transition state may be dominant. As a consequence, highly *trans*-1,4 selectivity of tridentate ligated Fe(III) and Cr(III) complexes is observed (Scheme 2, path 2).

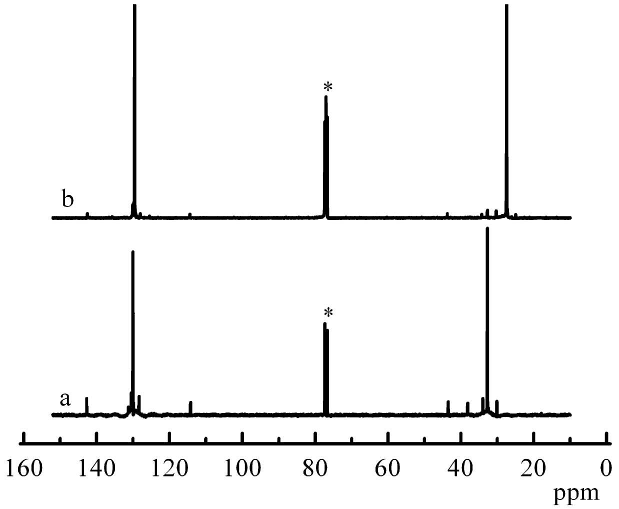
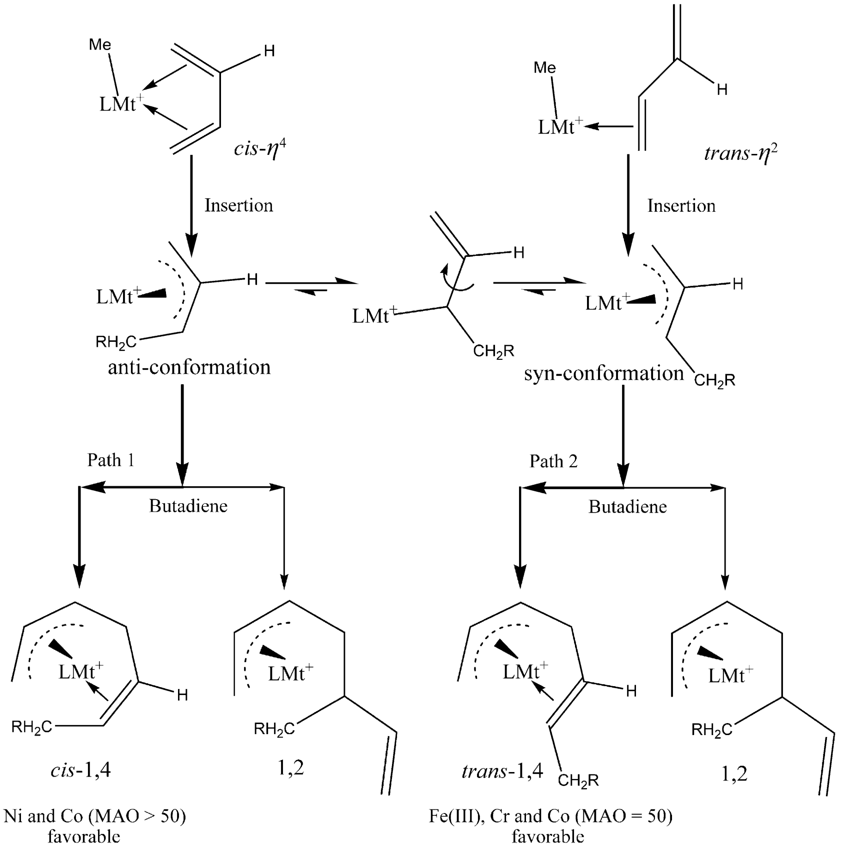


Fig. 3. The ^{13}C NMR of polybutadiene (a, *trans*-1,4 polybutadiene from entry 2 in Table 1; b, *cis*-1,4 polybutadiene from entry 18 in Table 1; *, $CDCl_3$).

The *trans*-1,4 selectivity is reduced to 55% (*cis*-1,4 units is about 35%) when iron(II) complex is employed (entries 8 and 9 in Table 1). Probably, the distinguishing solid-state structures can shed light on the different selectivity from that of Fe(III) counterpart. Fe(II)Cl_2L complex with alkyl free substituent at *ortho*-positions on iminophenyls were reported to exist as an ion pair, $[FeL_2]^{2+}[FeCl_4]^{2-}$ with one iron atom coordinated with two ligand and another with four chlorine atoms [10e], which is completely different from the structure of Fe(III)Cl_3L as illustrated in Fig. 1. The much higher activity observed in Fe(III) can be argued with a stronger Lewis acidic character of the Fe(III) center than that of an Fe(II) center, therefore, an increased affinity to coordinate an electron rich butadiene molecule.

Co(II) complex is surprisingly special among the metal analogues examined, which shows unusual polymerization behaviors never observed before [1–4,21], i.e. both activity and selectivity are strongly dependent on MAO/Co molar ratio. When the molar ratio of 50 is used (entry 12 in Table 1), the polymer obtained is essentially *trans*-1,4 units about 94.4%, with molecular weight about 1.0×10^4. Interestingly, increment of MAO loading (MAO/Co = 75, 100, entries 13 and 14 in Table 1) leads to a dramatic increase of *cis*-1,4 selectivity, reaching 79.0%, as a whole in expense of *trans*-1,4 selectivity, decreasing to 18.0%. The M_n of polymer increases substantially and the molecular weight distribution becomes much broadened. From the mechanistic study [18,19,22], two types of active species may be formed, which undergo different polymerization mechanisms (Path 1 and 2 in Scheme 2). It seems that, at lower MAO/Co ratio, one coordinated nitrogen atom in the complex is probably displaced. and *trans*-η^2 coordination mode may be favorable (Path 2 in Scheme 2) which leads to syn-π-allyl intermediate for *trans*-1,4 polymer. While the abstraction of other nitrogen atom(s) from the Co center by further increasing MAO/Co ratio results in more vacant sites permitting *cis*-η^4-coordination (Path 1 in Scheme 2), and accordingly, facilitating the formation of anti-π-allyl intermediate and giving rise to *cis*-1,4 enriched polymer (79.0%). However, the ligand is still attached to the metal center as demonstrated by the obvious different polymerization behaviors between $CoCl_2L$/MAO and ligand-free $CoCl_2$/MAO systems. As reported [23,24], the presence of syn-π-allyl intermediate resulted from anti-syn-isomerization or *trans*-η^2 coordination mode may account for 20% *trans*-1,4 structure in the final polymer chains.



Scheme 2. The proposed two intermediates responsible for *cis*-1,4 and *trans*-1,4 polymer, respectively.

Among the metal analogues examined, nickel(II) complex yields the highest *cis*-1,4 selectivity, up to 96%, (entries 16–18 in Table 1, Fig. 3(b)). Probably, monomer insertion speed is much higher than that of anti-syn-rearrangement. It should be mentioned that, comparing with heterogeneous $NiCl_2$/MAO system (entry 15 in Table 1), the higher catalytic activity as well as lower molecular weight and narrower molecular weight distribution of polymer observed in the $NiCl_2L$/MAO system indicate that bisiminopyridine ligand is not eliminated from the Ni center, and exerts beneficial effects on catalytic activity and selectivity.

Further investigations on polymerization performance by the modifying the backbone and substituents of ligand in the iron(III) and cobalt catalyst systems are in progress and the results will be presented later.

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