

Syntheses of iron, cobalt, chromium, copper and zinc complexes with bulky bis(imino)pyridyl ligands and their catalytic behaviors in ethylene polymerization and vinyl polymerization of norbornene

Jianxin Chen*, Yuanbiao Huang, Zhongshui Li, Zhichun Zhang,
Chunxia Wei, Tingyan Lan, Wenjie Zhang

College of Chemistry and Materials Science, Fujian Normal University, Fuzhou, Fujian 350007, PR China

Received 18 February 2006; received in revised form 4 May 2006; accepted 7 June 2006

Available online 24 July 2006

Abstract

The syntheses, characterization, and ethylene and norbornene polymerization behaviors of iron, cobalt, chromium, copper and zinc complexes (**3–7b**) bearing chelating bulky 2,6-bis[1-(2,6-diisopropylphenylimino)ethyl]pyridine ligand (**1**) or 2,6-bis[1-(2,5-ditertbutylphenylimino)ethyl]pyridine ligand (**2**) are reported. X-ray diffraction study of the cobalt complex (**4**) shows the geometry of the cobalt center to be distorted trigonal bipyramid. Treatment of the iron, cobalt 2,6-bis[1-(2,5-ditertbutylphenylimino)ethyl]pyridine complexes (**3** and **4**) with methylaluminoxane (MAO) lead to a highly active ethylene polymerization catalysts converting ethylene to highly linear polyethylene (PE), while the corresponding chromium complex (**5**) is disclosed as moderate catalytic activity for the polymerization of ethylene. The specific catalytic activities were evaluated at different temperature and Al/M (M = Fe, Co and Cr) ratio. In addition, the complexes **3–5** and corresponding compounds of FeCl₂, CoCl₂(THF)_{1.5} and CrCl₃(THF)₃ can also catalyze vinyl polymerization of norbornene activated with MAO and show good activities. However, the copper and zinc complexes (**6a–7b**) showed no active in ethylene and norbornene polymerization in the presence of MAO. © 2006 Elsevier B.V. All rights reserved.

Keywords: Ethylene and norbornene polymerization; Bis(imino)pyridyl ligands; Iron; Cobalt; Chromium; Copper; Zinc

1. Introduction

Non-metallocene complexes have been shown to be important catalysts in the polymerization of olefins [1]. One of the most effective catalyst are Fe(II), Co(II) and Cr(II or III) *N,N,N*-bis(imino)pyridyl-type complexes [2]. Treatment of these complexes LMX_n (M = Fe, Co, Cr) with methylaluminoxane (MAO) leads to highly active ethylene polymerization catalysts converting ethylene to highly linear polyethylene (PE) or oligomerization. Several modifications of the bis(imino)pyridine backbone, which have already been described in the literature [1b,3–5], mostly lead to a decrease in catalytic activity. Recently, simultaneous polymerization and Schulz–Flory oligomerization of ethylene made possible by activation with MAO of a C₁-symmetric [2,6-bis(arylimino)pyridyl]iron dichloride pre-

cursor were described [6], as were bis(imino)pyridine complexes containing dendritic wedges [7] and metalodendrimer [8].

The NBE (norbornene) addition polymer displays a characteristic rigid random coil conformation, which shows restricted rotation about the main chain and exhibits strong thermal stability (*T_g* > 350 °C). In addition, it has excellent dielectric properties, optical transparency and unusual transport properties. Therefore, it has been attracted many chemists to study the NBE vinyl polymerization. In recent years, the vinyl-type polynorbornene (PNB) can be prepared by nickel-based complexes and other metal complexes [9–15]. Yasuda et al. [16] reported several cobalt complexes bearing substituted terpyridine ligands for vinyl norbornene polymerization. Frédéric et al. [17] reported polymerization of NBE with CoCl₂ and pyridine bisimine cobalt(II) complexes activated with MAO. Janiak and co-workers [18] reported dihalogeno(diphosphane)metal(II) complexes (metal = Co, Ni, Pd) as pre-catalysts for the vinyl/addition polymerization of norbornene-elucidation of

* Corresponding author. Tel.: +86 591 83448669.
E-mail address: jxchen.1964@163.com (J. Chen).

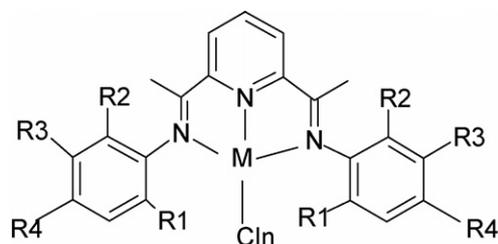


Fig. 1. Iron, cobalt and chromium bis(imino)pyridyl precatalysts for the polymerization of ethylene.

the activation process with $B(C_6F_5)_3/AlEt_3$ or $Ag[closo-1-CB_{11}H_{12}]$. Janiak and co-workers [19] also reported novel polynuclear cage complexes as precatalysts in the vinyl or addition polymerization of norbornene activated with MAO as well as with $B(C_6F_5)_3$, in combination with or without $AlEt_3$ and correlated with the results of the known mononuclear precatalysts $M(acac)_x$ ($M=Ni^{II}$, Co^{III} , Cr^{III} and Fe^{III} , $acac$ = acetylacetonate, $x=2$ or 3).

The nature of the metal center has a large influence on catalyst productivity. In general, Fe catalysts are more active than the corresponding Co analogues. It is well known that the position and steric bulk of the substituents on the imino nitrogen donors of the bis(imino)pyridyl catalysts (Fig. 1) play a pivotal role in determining the selectivity of the catalyst. The *ortho* substituents (R_1 and R_2) have been identified as being particularly important. If only one of the *ortho* substituents R_1 or R_2 on each ring is an alkyl group and the other is a hydrogen or halogen [4], then the catalyst is selective for the oligomerization of ethylene to linear 1-alkenes with a Schultz–Flory chain length distribution. If both the *ortho* substituents R_1 and R_2 groups are bulky alkyl substituents such as *iso*-propyl groups, then the catalysts are selective for the production of high molecular weight polymers from ethene.

To date, reports on olefin polymerization catalysts based on copper are scarce [1b]. The α -diimine Cu^{II} complex produces very high-molecular-weight PE with moderate activity [20]. Although there have been no reports of single-site olefin polymerization catalysts based on Group 12 metals, it has recently been shown that transition metal catalysts can catalyze PE chain growth on zinc centers, affording linear alkanes or α -olefins with a Poisson distribution [21]. The effect of substituents in the *meta*-position has been less studied [4,5d]. Here we report the syntheses, structures and ethylene and norbornene additional polymerization behaviors of iron, cobalt, chromium, copper and zinc complexes bearing bulky bis(imino)pyridyl ligands with 2,6-diisopropylphenyl or 2,5-ditertbutylphenyl substituents. We also report the effects observed on variation of the reaction conditions, such as the concentration of methylaluminoxane (MAO) and the temperature of ethylene polymerization. The results show that iron and cobalt bis(imino)pyridine complexes are highly active in the polymerization of ethylene by activation with MAO, while the corresponding chromium complex is disclosed as moderate active for the polymerization of ethylene. The iron and cobalt and chromium complexes show good active for the vinyl norbornene polymerization. However, the copper and zinc complexes almost show no active neither for the poly-

merization of ethylene nor vinyl norbornene polymerization in the presence of MAO.

2. Experimental

All manipulations of air and/or moisture-sensitive compounds were performed under an atmosphere of nitrogen using standard Schlenk techniques. Solvents were dried prior to use by refluxing over and distillation from sodium (THF, toluene, hydrocarbons) or calcium hydride (dichloromethane, chlorobenzene). Norbornene (Across) was purified by distillation over sodium and used as a solution in chlorobenzene. IR spectra were recorded using a Nicolet AV-360 spectrometer. Elemental analyses were Perkin-Elmer 2400 elemental analyzer for C, H, N. 2,6-Diacetylpyridine, 2,5-ditertbutylaniline were purchased from Aldrich; MAO (10% solution in toluene) was obtained from Witco. $CoCl_2(THF)_{1.5}$ and $CrCl_3(THF)_3$ was prepared according to a published procedure [22]. Anhydrous $CuCl_2$ and $ZnCl_2$ were obtained from the corresponding aqueous salts which heated up under vacuum condition.

2.1. Synthesis of 2,6-bis[1-(2,6-diisopropylphenylimino)ethyl]pyridine (1)

2,6-Bis[1-(2,6-diisopropylphenylimino)ethyl]pyridine was synthesized according to the public literature [2c]. IR (KBr): 3063.2, 2960.6, 2926.7, 2867.4, 1643.2 (vs, $C=N$), 1577.56, 1457.55, 1383.5, 1364.6, 1322.5, 1240.1, 1192.4, 1118.3, 1077.6, 935.9, 875.7, 825.6, 767.5 and 689.2. Anal. Calcd for $C_{33}H_{43}N_3$: C, 82.20; H, 8.93; N, 8.72. Found: C, 82.45; H, 9.01; N, 8.45.

2.2. Synthesis of 2,6-bis[1-(2,5-ditertbutylphenylimino)ethyl]pyridine (2)

To a solution of 2,6-diacetylpyridine (0.50 g, 3.07 mmol) in absolute ethanol (20 ml) was added 2,5-ditertbutylphenylaniline (1.258 g, 6.14 mmol). After the addition of a few drops of glacial acetic acid, the solution was refluxed overnight. Upon cooling to room temperature, the product crystallized from ethanol. The yellow solid formed was then filtered and washed with cold ethanol and dried under vacuum; the yield was 86%. IR (KBr): 2958.8, 2866.8, 1635.6 ($\nu_{C=N}$), 1566, 1491, 1457.7, 1385.5, 1363.6, 1297.6, 1248.9, 1205, 1119.5, 1072, 974, 927, 886, 820, 722 and 652 cm^{-1} . Anal. Calcd for $C_{37}H_{51}N_3$: C, 82.68; H, 9.49; N, 7.82. Found: C, 82.75; H, 9.52; N, 7.71.

2.3. Synthesis of 2,6-bis[1-(2,5-ditertbutylphenylimino)ethyl]pyridineiron(II) chloride (3)

Ligand **2** (107 mg, 0.2 mmol) was added to a suspension of $FeCl_2$ (25 mg, 0.2 mmol) in CH_2Cl_2 (15 ml) at room temperature with rapid stirring. The solution turned deep blue immediately. After it was stirred at room temperature for 12 h, the excess $FeCl_2$ was removed. The reaction volume was concentrated, and *n*-hexane (30 ml) was added to precipitate the product as a blue powder, which was subsequently washed

with *n*-hexane (3 × 10 ml), filtered, and dried to afford 105 mg (79%) of **3**. IR (KBr): 2960, 2868.5, 1633 ($\nu_{\text{C=N}}$), 1491, 1467.5, 1366.8, 1265.9, 1206, 1134.6, 1070, 1035, 928, 891, 820 and 733.5 cm^{-1} . Anal. Calcd for $\text{C}_{37}\text{H}_{51}\text{N}_3\text{FeCl}_2$: C, 67.89; H, 7.80; N, 6.42. Found: C, 67.93; H, 7.86; N, 6.38.

2.4. Synthesis of 2,6-bis[1-(2,5-ditertbutylphenylimino)ethyl]pyridinecobalt(II) chloride (**4**)

A suspension of **2** (107 mg, 0.2 mmol) in *n*-butanol was added to a solution of CoCl_2 (25 mg; 0.2 mmol) in *n*-butanol (20 ml) at 80 °C to yield a grass green solution. After being stirred at 80 °C for 30 min, the reaction was allowed to cool to room temperature. The reaction volume was concentrated, and *n*-hexane (30 ml) was added to precipitate the product as a grass green powder, which was subsequently washed with *n*-hexane (3 × 10 ml), filtered, and dried to afford 116 mg (85%) of **3**. Grass green crystals of the product **3** formed in THF/*n*-hexane solution at 0 °C for several days. IR (KBr): 2959.7, 2868, 1630 ($\nu_{\text{C=N}}$), 1590, 1497, 1464, 1367.6, 1264.5, 1210, 1135, 1068, 1027, 927, 891 and 823 cm^{-1} . Anal. Calcd for $\text{C}_{37}\text{H}_{51}\text{N}_3\text{CoCl}_2 \cdot \text{H}_2\text{O}$: C, 64.82; H, 7.74; N, 6.13. Found: C, 64.76; H, 7.68; N, 6.24.

2.5. Synthesis of 2,6-bis[1-(2,5-ditertbutylphenylimino)ethyl]pyridinechromium(III) chloride (**5**)

A solution of $\text{CrCl}_3(\text{THF})_3$ (75 mg, 0.2 mmol) and **2** (107 mg, 0.2 mmol) in acetone (10 ml) was refluxed overnight, giving a tan suspension. The reaction volume was concentrated, and diethyl ether was added to afford a jade-green solid, which was washed repeatedly with diethyl ether and dried in vacuum. Yield: 128 mg (92%). IR (KBr): 2963, 1631, 1501, 1471, 1368.6, 1269.2, 1081, 1044 and 816 cm^{-1} . Anal. Calcd for $\text{C}_{37}\text{H}_{51}\text{N}_3\text{CrCl}_3$: C, 63.76; H, 7.32; N, 6.03. Found: C, 64.36; H, 7.41; N, 5.91.

2.6. Synthesis of 2,6-bis[1-(2,6-diisopropylphenylimino)ethyl]pyridinecopper(II) chloride (**6a**)

A solution of ligand **1** (50 mg) and anhydrous CuCl_2 (14 mg) in THF (10 ml) was stirred at room temperature for 24 h. The reaction volume was concentrated, and diethyl ether was added to afford a brown solid, which was washed three with diethyl ether and dried in vacuum. IR (KBr): 2962.6, 2918.4, 2863.2, 1630.4, 1582.2, 1463.8, 1383.3, 1260.3, 1205.9, 1054.3, 800.6 and 561.5 cm^{-1} . Anal. Calcd for $\text{C}_{33}\text{H}_{43}\text{N}_3\text{CuCl}_2$: C, 64.21; H, 6.97; N, 6.81. Found: C, 64.38; H, 7.01; N, 6.74.

2.7. Synthesis of 2,6-bis[1-(2,5-ditertbutylphenylimino)ethyl]pyridinecopper(II) chloride (**6b**)

The procedure as above in (2.6) using **2** and CuCl_2 gave complex **6b** as a brown solid. IR (KBr): 2961.4, 2871.1, 1626.5, 1586.1, 1467.2, 1427.7, 1384.1, 1267.6, 1067.6, 822.3 and 556.7 cm^{-1} . Anal. Calcd for $\text{C}_{37}\text{H}_{51}\text{N}_3\text{CuCl}_2$: C, 65.99; H, 7.58; N, 6.24. Found: C, 66.03; H, 7.61; N, 6.18.

2.8. Synthesis of 2,6-bis[1-(2,6-diisopropylphenylimino)ethyl]pyridinezinc(II) chloride (**7a**)

A solution of ligand **1** (50 mg) and anhydrous ZnCl_2 (50 mg) in THF (10 ml) was stirred at room temperature for 24 h. The reaction volume was concentrated, and *n*-hexane was added to afford a light yellow solid, which was washed three with *n*-hexane and dried in vacuum. IR (KBr): 2965.2, 2926.3, 2867.6, 1634.4, 1587.0, 1463.0, 1329.2, 1253.8, 1203.4, 1100.1, 1056.6, 1024.7, 937.6, 820.6, 798.4 and 776.8 cm^{-1} . Anal. Calcd for $\text{C}_{33}\text{H}_{43}\text{N}_3\text{ZnCl}_2$: C, 64.06; H, 6.96; N, 6.79. Found: C, 64.01; H, 6.99; N, 6.59.

2.9. Synthesis of 2,6-bis[1-(2,5-ditertbutylphenylimino)ethyl]pyridinezinc(II) chloride (**7b**)

The procedure as above in (2.8) using **2** and ZnCl_2 gave complex **7b** as a light yellow solid. IR (KBr): 2956.9, 2903.5, 2866.2, 1642.3, 1600.6, 1568.2, 1491.4, 1448.1, 1387.3, 1363.6, 1296.6, 1249.5, 1208.1, 1118.5, 1073.8, 977.6, 925.7, 885.8, 819.9, 741.1 and 720.9 cm^{-1} . Anal. Calcd for $\text{C}_{37}\text{H}_{51}\text{N}_3\text{ZnCl}_2$: C, 65.89; H, 7.57; N, 6.23. Found: C, 65.91; H, 7.62; N, 6.15.

2.10. X-ray structure determination

Data collection for complex **4** were performed at 293 K on a Rigaku R-AXIS RAPID Weissenberg IP diffractometer equipped with a graphite-monochromatized Mo $\text{K}\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$). Lorentz-Polarization corrections and empirical absorption correction were applied to the data. The structures were solved by direct methods with SHELXS-97 [23] and refined on F^2 using full-matrix least-squares calculations with SHELXL-97 [24]. All non-hydrogen atoms were refined with anisotropic thermal parameters, and all the hydrogen atoms were placed at the idealized positions with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ and $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{C})$ for aromatic and methyl H atoms, respectively. Crystal data and processing parameters for complex **4** are summarized in Table 1. The crystallographic data for complex **4** has been deposited at the Cambridge Crystallographic Data Centre and allocated the deposition number CCDC 290535. Copies of the data can be obtained free from the Director, CCDC, 12 Union Road, Cambridge CB2 1EZ (fax: C44 1223 336 033; e-mail: deposit@ccdc.cam.ac.uk or <http://www.ccdc.cam.ac.uk>).

2.11. Ethylene polymerization

The precatalyst was dissolved in toluene and MAO (10 wt% in toluene) added to the solution. The flamedried Schlenk flask was placed in a water bath and purged with ethylene, and the contents were magnetically stirred and maintained under ethylene (1 atm) for 1 h. The polymerization was terminated by the addition of 10% (by mass) acidified ethanol. The solid PE was recovered by filtration, washed with ethanol and dried under vacuum at 70 °C overnight.

Table 1
Crystallographic data and structure refinement for complex **4**

Formula	C ₃₇ H ₅₃ ON ₃ CoCl ₂
Formula weight	685.65
Crystal system	Monoclinic
Space group	<i>P</i> 2(1)/ <i>c</i>
<i>a</i> (Å)	11.6063(4)
<i>b</i> (Å)	26.2498(10)
<i>c</i> (Å)	16.0347(5)
α (°)	90
β (°)	108.8538(11)
γ (°)	90
<i>V</i> (Å ³)	4623.1(3)
<i>Z</i>	4
<i>D</i> _{calc} (Mg m ⁻³)	0.985
Crystal size (mm)	0.72 × 0.63 × 0.54
μ (mm ⁻¹)	0.512
<i>F</i> (0 0 0)	1460
θ_{\max} , θ_{\min} (°)	27.48, 1.55
Index range	
<i>h</i>	0 → 15
<i>k</i>	0 → 34
<i>l</i>	-20 → 19
<i>R</i> _{int}	0.0548
No. of independent reflections	10081
No. of observed reflections	5917
No. of variables	396
<i>R</i>	0.0658
<i>wR</i>	0.1696
GOF	0.982
Largest difference peak ^a (hole) (e Å ⁻³)	0.577 (-0.369)
Δ/σ	0.000, 0.000

$$R = \frac{\sum ||F_o| - |F_c||}{\sum |F_o|}; wR = \left\{ \frac{\sum [w(F_o^2 - F_c^2)^2]}{\sum w(F_o^2)} \right\}^{1/2}$$

^a Largest peak (hole) in difference Fourier map.

2.12. Vinyl polymerization of norbornene

In a typical procedure, the precatalyst (3.07 μmol) was added in a Schlenk tube in 11.12 ml chlorobenzene and 2.88 ml chlorobenzene solution of norbornene (1 g/ml, 2.88 g) was added via syringe. The polymerization was initiated by adding 1 ml toluene solution of MAO (10%) at 30 °C. After 12 h, the polymerization was terminated by injecting 50 ml 10% acidic ethanol into the reactor. The PNB was isolated by filtration, washed with ethanol, dried in vacuum at 100 °C for 48 h.

2.13. Polymer characterization

The intrinsic viscosity [η] of polymer solution in decalin was determined using a modified Ubbelohde viscosimeter at 135 °C and the one-point intrinsic viscosity method [25]. SEM study on polymer morphology was carried out on a KYKY-1000B facility. The viscosity-average molar masses (M_v) of the polyethylene were calculated using the Mark-Houwink equation [26]:

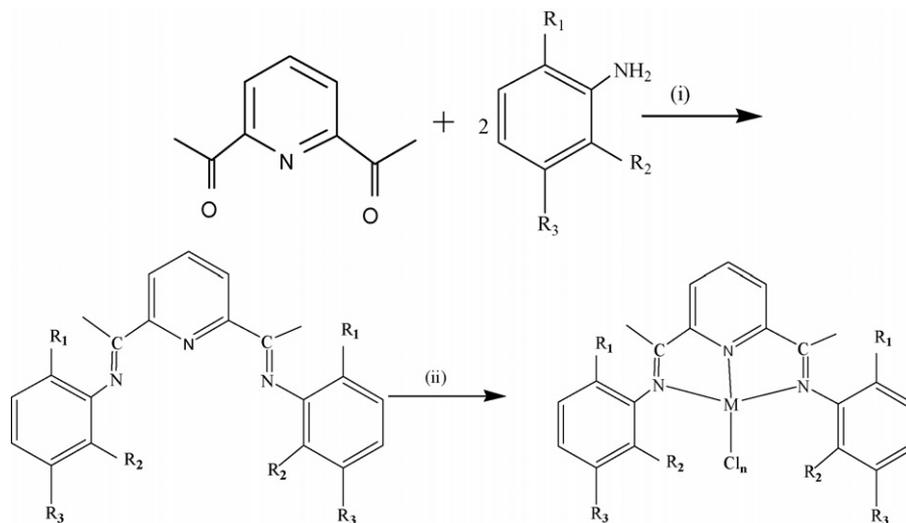
$$[\eta] = 6.77 \times 10^{-2} M_v^{0.67}$$

The thermal characteristics of the polymers were examined using a DSC-822 instrument (Mettler toledo) with a heating rate of 10 °C/min, in the range from 50 to 200 °C. The crystallinity of the polyethylene was calculated using the following equation [27]:

$$\chi_c (\%) = \frac{\Delta H}{\Delta H_0} \times 100\%$$

($\Delta H_0 = 287.3$ J/g for completed crystal polyethylene).

The viscosity-average molar masses (M_v) of the PNB were obtained using the Mark-Houwink coefficients [28,29]: $\alpha = 0.56$, $K = 7.78 \times 10^{-4}$ dl/g.



Scheme 1. Synthesized iron, cobalt, chromium, copper and zinc bis(imino)pyridyl complexes; reagents and conditions: (i) EtOH, H⁺ and (ii) **3**, FeCl₂, R₁ = R₃ = tertbutyl, R₂ = H, CH₂Cl₂; **4**, CoCl₂, R₁ = R₃ = tertbutyl, R₂ = H, *n*-BuOH, Δ; **5**, CrCl₃(THF)₃, R₁ = R₃ = tertbutyl, R₂ = H, acetone, Δ; **6a**, CuCl₂, R₁ = R₂ = isopropyl, R₃ = H, THF; **6b**, CuCl₂, R₁ = R₃ = tertbutyl, R₂ = H, THF, Δ; **7a**, ZnCl₂, R₁ = R₂ = isopropyl, R₃ = H, THF, Δ; **7b**, ZnCl₂, R₁ = R₃ = tertbutyl, R₂ = H, THF, Δ.

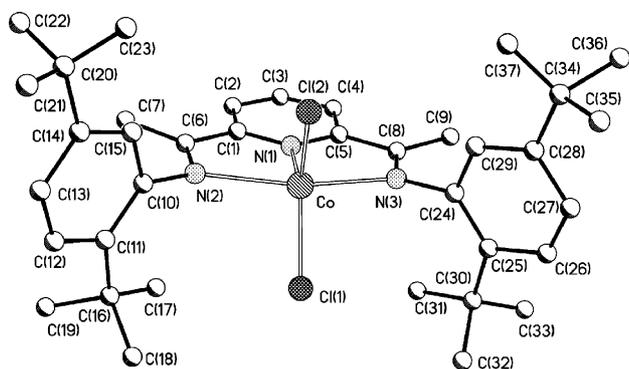


Fig. 2. Molecular structure of the cobalt complex **4** (One H₂O molecule in the lattice is not included).

3. Results and discussion

3.1. Syntheses and structures of complexes

The ligands **1** and **2** were prepared in high yield from the condensation of two equivalents of appropriate aniline with one equivalent of 2,6-diacetylpyridine (Scheme 1). Ligands **1** and **2** was characterized by elemental analyses, IR spectroscopy (see Section 2). The complexes **3–7b** were synthesized in good yield by treating MCl_{*n*} (*M* = Fe, Co, Cr, Cu and Zn; *n* = 2, 3) with the ligands **1** or **2** in different solvent (Scheme 1). All the complexes, **3–7b**, were characterized by elemental analyses, IR spectroscopy (see Section 2). The elemental analysis results revealed that the components of all complexes were in accord with the formula MCl_{*n*} (*n* = 2, 3), and one molecule of H₂O in **4**. The IR spectra of the ligands **1** and **2** show that the C=N stretching frequency appear at 1643 and 1635.6 cm⁻¹, respectively. In complexes **3–7b**, the C=N stretching vibrations shift toward lower frequencies and were greatly reduced in intensity, which indicated the coordination interaction between the imino nitrogen atoms and the metal ions. In addition, the cobalt complex **4** was subject to single-crystal X-ray diffraction study. The molecular structure of the cobalt complex **4** is shown in Fig. 2, and selected bond lengths and angles are presented in Table 2.

The complex **4** displays an approximate C₂ symmetry about a plane containing the cobalt atom, the two chloro atoms, and the pyridyl nitrogen atom. The Co–N (pyridyl) bond (2.033(2) Å) is significantly shorter than the Co–N (imino) bonds (2.250(2) and 2.294(2) Å), but the bond lengths Co–N (pyridyl) and Co–N (imino) are very similar to that of three related

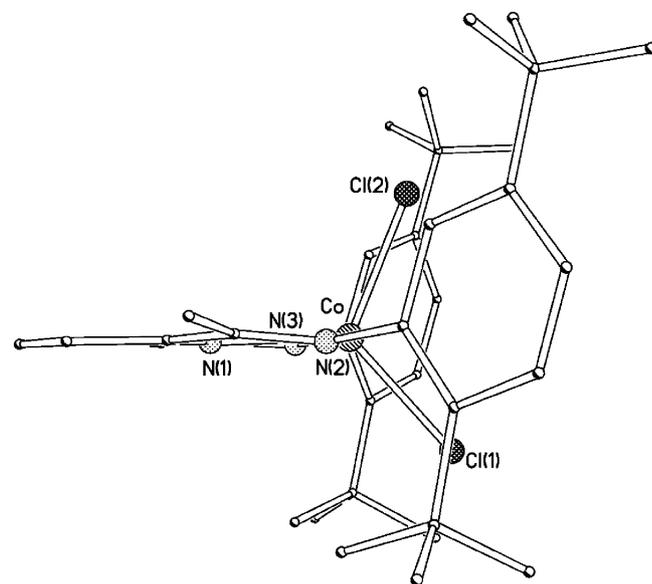


Fig. 3. Side-on view, perpendicular to the plane of the three ligand nitrogen atoms of the complex **4**, showing the pronounced differences in coordination geometry and the deviation of the metal centers from the ligand plane.

Co analogues [2b,2c,2g]. In addition, in the complex **4**, the two imino C=N bonds have distinctive double-bond character, with C=N distances in the range 1.273(4) and 1.276(3) Å. Although the substitutes on the bis(imino)pyridine ligand backbone is bulky 2,5-ditertbutylphenyl, the planes of the phenyl rings are oriented essentially orthogonal to the plane of the backbone (ranging between 83.29(14)° and 87.77(11)°) which is coplanar to within 0.0029–0.0067 Å. The cobalt atom deviates by 0.0882(28) Å from the plane formed by three coordinated nitrogen atoms. The Cl(1)–Co–Cl(2) angle is 116.20(4)°. Two N(1)–Co–Cl angles are unsymmetrical: one is 113.43(8)°, while the other is 130.31(8)°. The “axial” Co–N bonds subtend an angle of 149.83(8)°, which is near to that of 2,6-dimethylphenyl substituted Co complex (150.42(17)°) [2g], but wider than that of 2,6-diisopropylphenyl [2c] and 2-terbutyl [2b] substituted Co complexes (141.3(7)°, 142.1(4)°). Inspection of the space-filling model reveals a bulky steric interactions created by the 2,5-tertbutyl of the phenyl within the cobalt center (Fig. 4). The coordination geometry of the central cobalt can be best described as distorted trigonal bipyramidal, with the pyridyl nitrogen atom and the two chloro atoms forming the equatorial plane (Fig. 3), which is similar to that of 2,6-dimethylphenyl substituted Co complex [2g]. However, the 2,6-diisopropylphenyl [2c] and 2-terbutyl substituted Co complexes [2b] can be regarded as distorted square pyramidal geometry.

Table 2
Selected bond lengths (Å) and angles (°) for complex **4**

Co–N(1)	2.033(2)	Co–N(2)	2.294(2)
Co–N(3)	2.250(2)	Co–Cl(1)	2.233(10)
Co–Cl(2)	2.260(10)	N(2)–C(6)	1.276(3)
N(3)–C(8)	1.273(4)		
N(1)–Co–N(2)	74.81(9)	N(1)–Co–N(3)	75.19(9)
N(3)–Co–N(2)	149.83(8)	Cl(1)–Co–N(3)	98.82(7)
Cl(1)–Co–Cl(2)	116.20(4)	N(1)–Co–Cl(2)	113.43(8)
Cl(1)–Co–N(2)	98.02(7)	N(3)–Co–Cl(2)	99.16(7)
Cl(2)–Co–N(2)	95.59(7)	N(1)–Co–Cl(1)	130.31(8)

3.2. Ethylene polymerization experiments

All the complexes (**3–7b**) are generated in situ in toluene by the addition of methylaluminumoxane as activator in the presence of ethylene. The chromium complex **5** was previously dissolved and preactivated in a methylaluminumoxane/toluene solution for 60 min, which helps to solubilize the poorly soluble complex and performs the actual catalytic species [2e]. The activity results

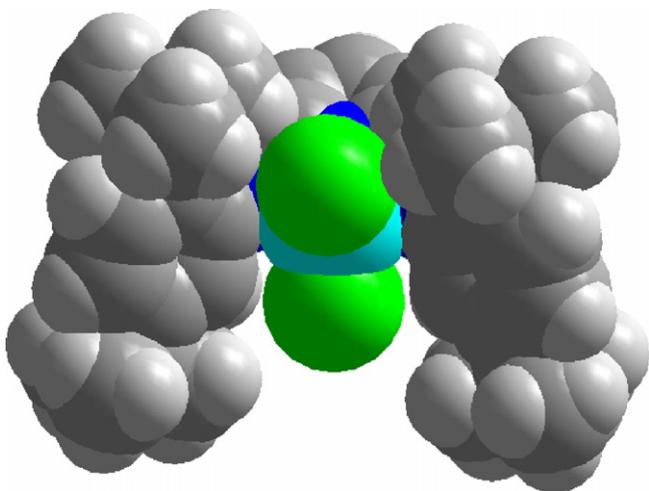


Fig. 4. Space-filling model of the complex 4.

and molecular weights with diverse sets of conditions are given in Figs. 5–8 and Table 3.

In order to investigate detailed polymerization behavior of the complexes (3–5), polymerizations were carried out at various MAO concentrations. The $[Al]/[M]$ ratios in complexes 3 and 4 can have a significant effect on the activity and molecular weights (Figs. 5 and 6). When $[Al]/[Fe] = 1500$, the catalytic activity of the complex 3 achieved the maximum value (2.33×10^6 g PE/mol Fe h) (see Fig. 5). As the $[Al]/[Fe]$ still rising, the activity and the molecular weights possess decrease trend. Similarly, the Co complex 4 obtained the maximum activity value 1.15×10^6 g PE/mol Co h (see Fig. 5) as the $[Al]/[Co]$ is 2000. First, increasing the MAO concentration results in higher activity may be due to an increase in the number of active sites. However, excess MAO concentrations will block the contact of the ethylene and the active sites. On the other hand, the trimethylaluminum (TMA) of the MAO will reduce the active sites. The MAO concentrations affect unobvious on the activity and molecular weights of the chromium complex 5. The poorly solu-

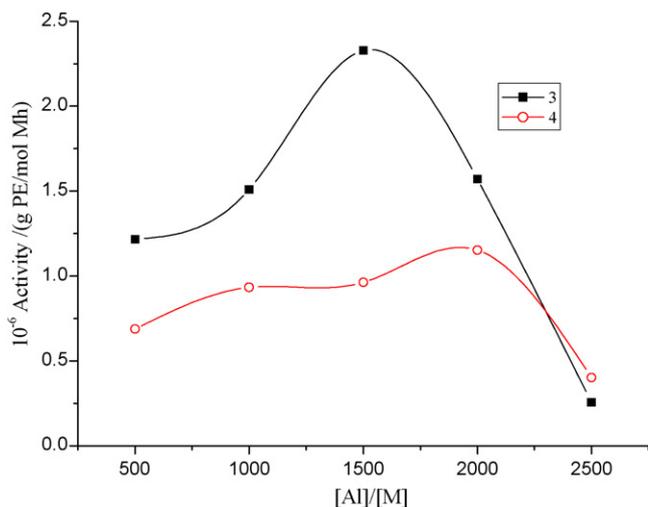


Fig. 5. Influence of the $[Al]/[M]$ ($M = Fe, Co$) ratio on the activity of complexes 3 and 4. General conditions: $3.0 \mu\text{mol}$ of M , 100 ml of toluene, 1 atm, 35°C , 60 min.

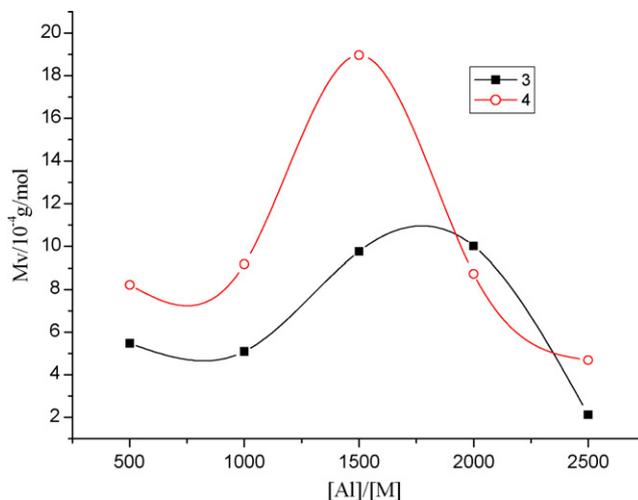


Fig. 6. Effect of the $[Al]/[M]$ ($M = Fe, Co$) ratio on the viscosity average molecular weight using complexes 3 and 4. General conditions: $3.0 \mu\text{mol}$ of M ($M = Fe, Co$), 100 ml of toluene, 1 atm, 35°C , 60 min.

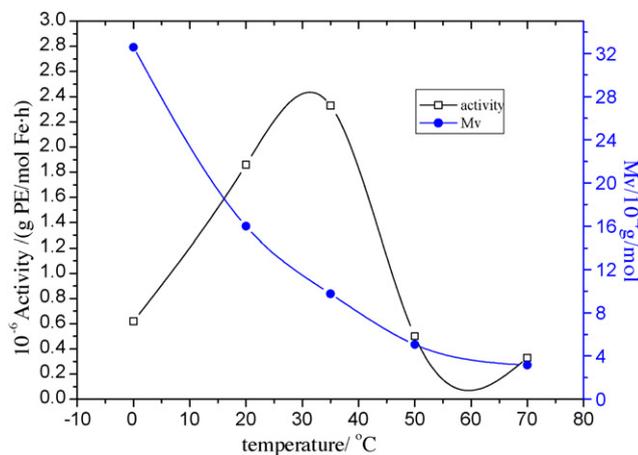


Fig. 7. Dependence of the activity and the viscosity average molecular weight on temperature for complex 3. General conditions: $3.0 \mu\text{mol}$ of Fe , $[Al]/[Fe] = 1500$, 100 ml of toluene, 1 atm, 60 min.

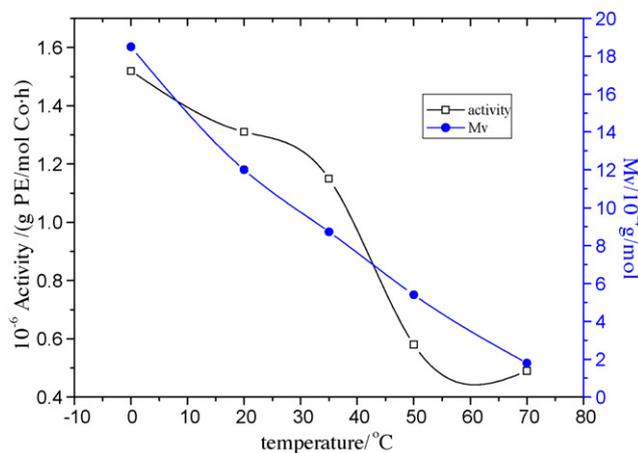


Fig. 8. Dependence of the activity and the viscosity average molecular weight on temperature for complex 4. General conditions: $3.0 \mu\text{mol}$ of Co , $[Al]/[Co] = 2000$, 100 ml of toluene, 1 atm, 60 min.

Table 3
The results of ethylene polymerization by complex **5** in the presence of MAO^a

Entry	Catalyst (μmol)	[Al]/[Cr]	T ($^{\circ}\text{C}$)	PE (g)	Activity ^b	M_v ($\times 10^4$ g/mol)
1	2.87	200	30	0.090	3.10×10^4	18.2
2	2.58	500	30	0.085	3.29×10^4	13.4
3	2.87	1000	30	0.123	4.31×10^4	25.6
4	3.70	1500	30	0.207	5.60×10^4	10.8
5 ^c	2.87	2000	30	0.256	8.91×10^4	9.8
6	2.87	2000	30	0.344	11.9×10^4	11.1
7	2.29	2500	30	0.154	6.75×10^4	6.2
8	2.87	2000	0	0.048	1.67×10^4	12.3
9	1.58	2000	50	0.015	0.95×10^4	9.0
10	1.43	2000	75	0.091	6.34×10^4	5.6

^a Polymerization conditions: run time = 60 min, 50 ml of toluene, $T_p = 30^{\circ}\text{C}$, $P_{\text{C}_2\text{H}_4} = 1.0$ atm.

^b g/mol Cr h.

^c Using 50 ml of CH_2Cl_2 instead of toluene.

ble chromium complex may be responsible for the result. When using CH_2Cl_2 instead of toluene as solvent in entry 5 (Table 3), the activity increases to 11.9×10^4 g/mol Cr h.

Figs. 7 and 8; Table 3 show the results of polymerizations performed at various temperatures between 0 and 80°C employing the three complexes. For the three complexes, a significant reduction in the activity and the molecular weights as the temperature rising. However, the activity of the complex **3** first increases and reaches max at about 35°C then decline, while chromium complex **5** increases again when the temperature at 75°C . Elevated temperatures will result in higher chain propagation and chain-transfer rates, which would be expected to afford higher activity and lower molecular weight product. The other hand a decrease in ethylene solubility at higher temperatures will lead to reduced productivity and result in higher rates of catalyst deactivation. It is a combination of these effects that is likely to account for the observed temperature dependence [2c]. The solubility of the complex **5** increases when at higher temperature may be explain the activity increase at 75°C .

The nature of the metal center has a significant effect on catalyst activity. The Fe complex **3** (2.33×10^6 g/mol Fe h) is more active than the corresponding Co complex **4** (1.52×10^6 g/mol Co h) (see Fig. 8), while the chromium complex **5** is only 1.19×10^5 g/mol Cr h, which is in accordance with the previously reported results [2]. The copper and zinc

Table 4
The PE results of DSC

Complex	χ_c (%)	T_m ($^{\circ}\text{C}$)	T_c ($^{\circ}\text{C}$)
3 ^a	79.70	136.76	106.91
4 ^b	71.02	145.42	120.45
5 ^c	49.26	128.75	100.01

^a Conditions: 3.0 μmol of Fe, [Al]/[Fe] = 1500, 100 ml of toluene, 1 atm, 60 min, $T_p = 0^{\circ}\text{C}$.

^b Conditions: 3.0 μmol of Co, [Al]/[Co] = 2000, 100 ml of toluene, 1 atm, 60 min, $T_p = 0^{\circ}\text{C}$.

^c Conditions: 2.87 μmol of Cr, [Al]/[Cr] = 2000, 50 ml of toluene, 60 min, 1.0 atm, $T_p = 30^{\circ}\text{C}$.

complexes (**6a–7b**) showed almost no active for ethylene polymerization in the presence of MAO. The metal center also influences molecular weight. Fe precatalyst yield M_v in the range of 2.1×10^4 – 32.6×10^4 (see Figs. 6 and 7). The Co-based complex polymer's M_v are in the range of 1.8×10^4 – 18.5×10^4 (see Figs. 6 and 8), which is lower than complex **3**. Similarly, the chromium complex **5** yield M_v in the range of 5.6×10^4 – 25.6×10^4 (see Table 3). According to the results of the differential scanning calorimetry (DSC) (Table 4), the polymer samples obtained by the **3** and **4** complexes showed sharp single melting peaks and very high crystallinities, demonstrating they are highly linear chains, which is different from

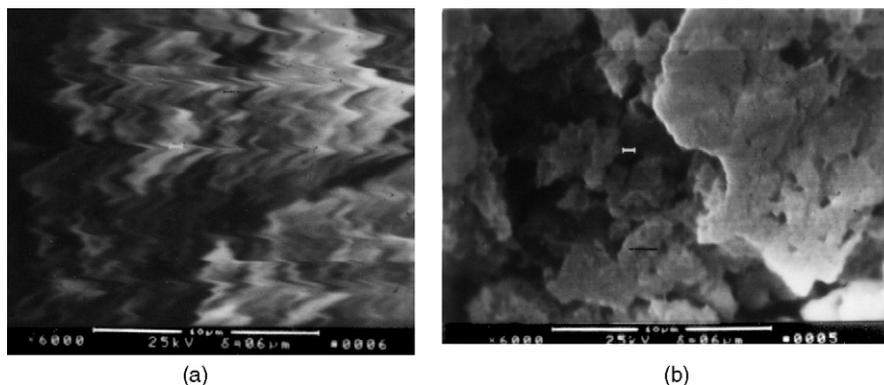


Fig. 9. The SEM of the PE obtained from (a) complex **3**, 3.0 μmol of Fe, [Al]/[Fe] = 1500, 100 ml of toluene, 1 atm, 60 min, $T_p = 0^{\circ}\text{C}$ and (b) complex **4**, 3.0 μmol of Co, [Al]/[Co] = 2000, 100 ml of toluene, 1 atm, 60 min, $T_p = 0^{\circ}\text{C}$.

the branching polymer obtained by the Ni(II) and Pd(II) diimine catalysts [30], whereas the PE obtained from the complex **5** possesses moderate linear chain. The SEM study shows the PE with the different morphology obtained from the complexes **3** and **4** (Fig. 9).

The reason for the different performance of the iron, cobalt and chromium complexes, **3–5**, bearing 2,5-ditertbutylphenyl may be the differences of the electronic environments [2,31] and chain-transfer mechanisms [2]. The Fe(II) complex possesses four unpaired electrons while the Co(II) complex has three unpaired electrons. The chain-transfer in Fe complex involves a combination of β -H transfer and chain transfer to aluminum. In contrast, the Co complex is characteristic of chain transfer exclusively by β -H transfer. The Cr complex may occur several chain transfer fasion: β -H transfer to the monomer and chain transfer to MAO. The near full d-orbit for copper center and full d-orbit zinc center may be responsible for the complexes (**6a–7b**) showing almost no active for ethylene polymerization.

The complexes, **3–5**, with 2,5-ditertbutyl in each aryl ring are compared to that with 2-*tert*-butyl in the literatures [2b,2e] under the similar conditions. The results show that the iron and cobalt complexes with 2,5-di-*tert*-butyl substitutes have a slight decrease activity than the complexes with 2-*tert*-butyl {Fe (25 °C): 2.65×10^6 g/mol Fe h; Co (0 °C): 1.63×10^6 g/mol Co h} [2b], while the chromium complex **5** shows a high activity relative to the 2-*tert*-butyl complex [2d]. The relationship between the different activity and the presence of an additional *tert*-butyl group in the 5-position of the aryl rings may be that the additional *tert*-butyl group increases the steric bulky hindrance in another face of the pyridyl ring. The other reason may be the additional *tert*-butyl group in the 5-position of the aryl rings which increases the net charge in the lower charge area and reduce the net charge in the higher area [29]. The increase of the bond length of Co–N(2), Co–N(3) indicates that the density of electron cloud of the metallic center decrease [5a].

3.3. Norbornene polymerization

The iron, cobalt and chromium complexes showed high activity for ethylene polymerization, there will be active for norbornene polymerization [17]. The catalysis of the complexes **3–7b** and the corresponding salts or the complex of tetrahydrofuran for the polymerization of norbornene were also investigated in the presence of MAO as a cocatalyst (Table 5). Without a cocatalyst, these complexes showed no catalytic activity. The complexes (**3–5**) showed good activities, in particular, the cobalt complex **4** showed the highest activity 11.4×10^3 g PNB/(mol Co h). In addition, to our best knowledge, it is the first time that FeCl₂, CoCl₂(THF)_{1.5} and CrCl₃(THF)₃ are shown to be active catalysts for the addition polymerization of norbornene. Interestingly, the activity of CrCl₃(THF)₃ is higher than the complex **5**, and the activity of FeCl₂ is higher than the CoCl₂(THF)_{1.5} [17]. These complexes are as active as the recently described nickel- and palladium-based complexes activated with MAO [32,33], but less active than some others exhibiting activities up to 5×10^7 g/mol h

Table 5

The results of PNB with the precatalysts in the presence of MAO^a

Precatalyst	Activity ($\times 10^3$ g PNB/(mol M h))	M_v ($\times 10^4$ g/mol)
Complex 3	9.25	1.9
Complex 4	11.4	1.2
Complex 5	0.35	41.7
FeCl ₂	0.65	1.7
CoCl ₂ (THF) _{1.5}	0.60	4.6
CrCl ₃ (THF) ₃	0.73	8.4

Reaction time, 12 h; chlorobenzene; total volume, 15 ml; norbornene/M = 10000:1.

^a Polymerization condition: 3.07 μ mol of precatalyst; [Al:M] = 500:1; T_p = 30 °C.

[9b–15,18,19]. In the same condition, similar to the ethylene polymerization behavior, the copper and zinc complexes show almost no active for NBE additional polymerization. All the polymers obtained have been characterized by IR spectra. The IR spectra prove the absence of a double bond, as no peaks appeared between 1620 and 1680 cm^{-1} . This further ensures the occurrence of vinyl-type polymerization. The polymers molecular mass M_v are between 1.2×10^4 and 8.4×10^4 g/mol except the polymer (41.7×10^4) which obtained from complex **5**.

4. Conclusions

In summary, the syntheses and characterization of three new iron-, cobalt- and chromium-based precatalysts (**3–5**) with bulky 2,6-bis[1-(2,5-ditertbutylphenylimino)ethyl] pyridine ligand (**1**) and copper and zinc complexes (**6a–7b**) bearing bulky 2,6-bis[1-(2,6-diisopropylphenylimino)ethyl]pyridine or 2,6-bis[1-(2,5-ditertbutylphenylimino)-ethyl]pyridine ligand (**2**) have been described. Activation with MAO the complexes **3** and **4** produce highly active catalysts converting ethylene to highly linear polyethylene (PE), while the corresponding chromium complex **5** is disclosed as moderate active for the polymerization of ethylene. And their catalytic activity were evaluated at different temperature and Al/M (M = Fe, Co and Cr) ratio. The complexes **3–5** and FeCl₂, CoCl₂(THF)_{1.5} and CrCl₃(THF)₃ can catalyse vinyl polymerization of norbornene activated with MAO and show good activity. However, the copper and zinc complexes show almost no active for ethylene and NBE polymerization.

Acknowledgements

Project supported by the Natural Science Foundation of Fujian Province (E0310016) and the Education Committee Foundation of Fujian Province (JB05309).

References

- [1] (a) S.D. Ittle, L.K. Johnson, M. Brookhart, Chem. Rev. 100 (2000) 1169; (b) V.C. Gibson, S.K. Spitzmesser, Chem. Rev. 103 (2003) 283, and references cited therein; (c) F. Speiser, P. braunstein, L. Saussine, Acc. Chem. Res. 38 (2005) 784–793.

- [2] (a) B.L. Small, M. Brookhart, *J. Am. Chem. Soc.* 120 (1998) 7143–7144;
(b) B.L. Small, M. Brookhart, A.M.A. Bennett, *J. Am. Chem. Soc.* 120 (1998) 4049–4050;
(c) G.J.P. Britovsek, M. Bruce, V.C. Gibson, *J. Am. Chem. Soc.* 121 (1999) 8728–8740;
(d) B.L. Small, M.J. Carney, D.M. Holman, *Macromolecules* 37 (2004) 4375–4386;
(e) M.A. Esteruelas, A.M. López, L. Méndez, *Organometallics* 22 (2003) 395–406;
(f) C.K. Liu, G.X. Jin, *Acta. Chim. Sin.* 60 (2002) 157–161;
(g) C.K. Liu, G.X. Jin, *New J. Chem.* 26 (2002) 1485–1489;
(h) T.M. Kooistra, K.F.W. Hekking, Q. Knijnenburg, B.d. Bruin, P.H.M. Budzelaar, R.d. Gelder, J.M.M. Smits, A.W. Gal, *Eur. J. Inorg. Chem.* (2003) 648–655.
- [3] (a) W.H. Sun, X.B. Tang, T. Gao, B. Wu, W. Zhang, H. Ma, *Organometallic* 23 (2004) 5037–5047;
(b) T.M. Smit, A.K. Tomov, V.C. Gibson, A.J.P. White, D.J. Williams, *Inorg. Chem.* 43 (2004) 6511–6512;
(c) K.P. Tellmann, V.C. Gibson, A.J.P. White, D.J. Williams, *Organometallics* 24 (2005) 280–286.
- [4] (a) Y. Chen, C. Qian, J. Sun, *Organometallics* 22 (2003) 1231–1236;
(b) Y. Chen, R. Chen, C. Qian, X. Dong, J. Sun, *Organometallics* 22 (2003) 4312–4321.
- [5] (a) J.Y. Liu, Y. Zheng, Y.G. Li, L. Pan, Y.S. Li, N.H. Hu, *J. Organomet. Chem.* 690 (2005) 1233–1239;
(b) J. Cámpora, A.M. Naz, P. Palma, E. Alvarez, *Organometallics* 24 (2005) 4878–4881;
(c) I.S. Paulino, U. Schuchardt, *J. Mol. Catal. A: Chem.* 211 (2004) 55–58;
(d) I. Kim, B.H. Han, Y. Ha, C. Ha, D. Park, *Catal. Today* 93–95 (2004) 281–285;
(e) T. Zhang, W.H. Sun, T. Li, X. Yang, *J. Mol. Catal. A: Chem.* 218 (2004) 119–124;
(f) R. Schmidt, M.B. Welcha, R.D. Knudsen, S. Gottfried, H.G. Alt, *J. Mol. Catal. A: Chem.* 222 (2004) 17–25;
(g) R. Schmidt, P.K. Das, M.B. Welch, R.D. Knudsen, *J. Mol. Catal. A: Chem.* 222 (2004) 27–45;
(h) K.P. Tellmann, V.C. Gibson, A.J.P. White, D.J. Williams, *Organometallics* 24 (2005) 280–286.
- [6] C. Bianchini, G. Giambastiani, I.R. Guerrero, A. Meli, E. Passaglia, T. Gragnoli, *Organometallics* 23 (2004) 6087–6089.
- [7] M.J. Overtt, R. Meijboom, J.R. Moss, *Dalton Trans.* (2005) 551–555.
- [8] Z.J. Zheng, J. Chen, Y.S. Li, *J. Organomet. Chem.* 689 (2004) 3040–3045.
- [9] (a) C. Janiak, P.G. Lassahn, *J. Mol. Catal. A: Chem.* 166 (2001) 193–209;
(b) B. Berchtold, V. Lozan, P.G. Lassahn, C. Janiak, *J. Polym. Sci. A* 40 (2002) 3604.
- [10] Y.Z. Zhu, J.Y. Liu, Y.S. Li, Y.J. Tong, *J. Organomet. Chem.* 689 (2004) 1295.
- [11] J.X. Hou, W.H. Sun, D.H. Zhang, L.Y. Chen, *J. Mol. Catal. A: Chem.* 231 (2005) 221–233.
- [12] G.Q. Gui, F. Bao, H.Y. Gao, F.M. Zhu, Q. Wu, *Appl. Organomet. Chem.* 19 (2005) 627–632.
- [13] F. Bao, X.Q. Lu, Y.Q. Qiao, G.Q. Gui, H.Y. Gao, Q. Wu, *Appl. Organomet. Chem.* 19 (2005) 957–963.
- [14] F. Chang, D. Zhang, G.Y. Xu, H.J. Yang, J.T. Li, H.B. Song, W.H. Sun, *J. Organomet. Chem.* 689 (2004) 936–946.
- [15] H. Suzuki, S. Matsumura, Y. Satoh, K. Sogoh, H. Yasuda, *React. Funct. Polym.* 58 (2004) 77–91.
- [16] H. Yasuda, Y. Nakayama, Y. Sato, *J. Organomet. Chem.* 689 (2004) 744–750.
- [17] P. Frédéric, J.L. Pierre, W. Marcel, K. Jacky, *Macromol. Rapid Commun.* 24 (2003) 768–771.
- [18] P.-G. Lassahn, V. Lozan, B. Wu, A.S. Weller, C. Janiak, *Dalton Trans.* (2003) 4437–4450.
- [19] P.-G. Lassahn, V. Lozan, G.A. Timco, P. Christian, C. Janiak, R.E.P. Winpenny, *J. Catal.* 222 (2004) 260.
- [20] V.C. Gibson, A. Tomov, D.F. Wass, A.J.P. White, D.J.J. Williams, *Dalton Trans.* (2002) 2261–2262.
- [21] G.J.P. Britovsek, S.A. Cohen, V.C. Gibson, P.J. Maddox, M. van Meurs, *Angew. Chem., Int. Ed.* 41 (2002) 489–491.
- [22] J. Shamir, *Inorg. Chim. Acta* 156 (1989) 163–164.
- [23] G.M. Sheldrick, SHELXL-97, Program for X-ray Crystal Structure Refinement, University of Göttingen, Göttingen, Germany, 1997.
- [24] G.M. Sheldrick, SHELXS-97, Program for X-ray Crystal Structure Solution, University of Göttingen, Göttingen, Germany, 1997.
- [25] J.H. Elliott, K.H. Horowitz, T. Hoddock, *J. Appl. Polym. Sci.* 19 (1970) 2947–2963.
- [26] R.J. Chiang, *Polym. Sci.* 36 (1959) 91–103.
- [27] B. Wunderlich, C.M. Cormier, *J. Polym. Sci. (Part A-2)* 5 (1967) 987.
- [28] M. Christian, K. Matthias, D. Kurt, G. Andreas, *Macromol. Rapid Commun.* 20 (1999) 232–235.
- [29] W.H. Wang, G.X. Jin, *Inorg. Chem. Commun.* 8 (2005) 109–112.
- [30] L.K. Johnson, C.M. Killian, M. Brookhart, *J. Am. Chem. Soc.* 117 (1995) 6414–6415.
- [31] T.Z. Zhang, W.H. Sun, T. Li, X.Z. Yang, *J. Mol. Catal. A: Chem.* 218 (2004) 119–124.
- [32] X.F. Li, Y.S. Li, *J. Polym. Chem.* 40 (2002) 2680.
- [33] P.G. Lassahn, C. Janiak, J.S. Oh, *Macromol. Rapid Commun.* 23 (2002) 16.