Journal of Organometallic Chemistry 658 (2002) 62–70

Journal of Organometallic Chemistry

www.elsevier.com/locate/jorganchem

Late transition metal complexes bearing 2,9-bis(imino)-1,10-phenanthrolinyl ligands: synthesis, characterization and their ethylene activity

Leyong Wang [a], Wen-Hua Sun [a,*], Lingqin Han [a,b], Haijian Yang [a], Youliang Hu [a], Xianglin Jin [c]

[a] *State Key Laboratory of Engineering Plastics and Center for Molecular Sciences, Institute of Chemistry, The Chinese Academy of Sciences, Beijing 100080, People's Republic of China*

[b] *College of Chemistry and Environmental Science, Hebei University, Baoding 071002, People's Republic of China*

[c] *Institute of Physical Chemistry, Peking University, Beijing 100871, People's Republic of China*

Received 5 March 2002; received in revised form 1 April 2002; accepted 25 May 2002

Abstract

A series of iron, cobalt and nickel halide complexes, LMX_2 ($M = Fe$, $X = Cl$; $M = Co$, $X = Cl$; $M = Ni$, $X = Br$) bearing 2,9-bis(imino)-1,10-phenanthrolinyl ligands [$L = 2,9\text{-}(ArNCH)_2C_{12}H_6N_2$] were synthesized. The solid-state structures of **4** and **7** have been determined by single-crystal X-ray diffraction study. Treatment of the complexes LMX_2 with methylaluminoxane (MAO) leaded to activate ethylene as oligomerization catalysts. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Iron; Cobalt; Nickel; Phenanthrolinyl ligands; Crystal structures

1. Introduction

Olefin polymerization and oligomerization catalyzed by transition metal complexes have attracted great attentions in both academic and industrial research [1,2]. Driven by industry for increasing control over microstructures of olefin polymerization along with advances in the understanding of homogeneous polymerization systems, the development of option has observed from heterogeneous systems of the classical Ziegler–Natta technology to more sophisticated single-site catalysts, such as Group 4 metallocenes and 'constrained geometry' catalysts [3–6]. The development of non-metallocene transition metal catalysts, particularly the discovery of highly active systems based with late-transition metal complexes, have signposted the way forward to further develop in catalytic olefin polymerization. The disclosure by the group of Brookhart in 1995, in which they produced high molecular weight polyethylene for the first time with cationic Ni(II) α-diimine complexes, has revived the investigation of late transition metal complexes as potential catalyst precursors [7–10]. These catalyst systems incorporated polar monomers such as methyl acrylate into ethylene and propylene copolymers along with relatively good productivities [11,12].

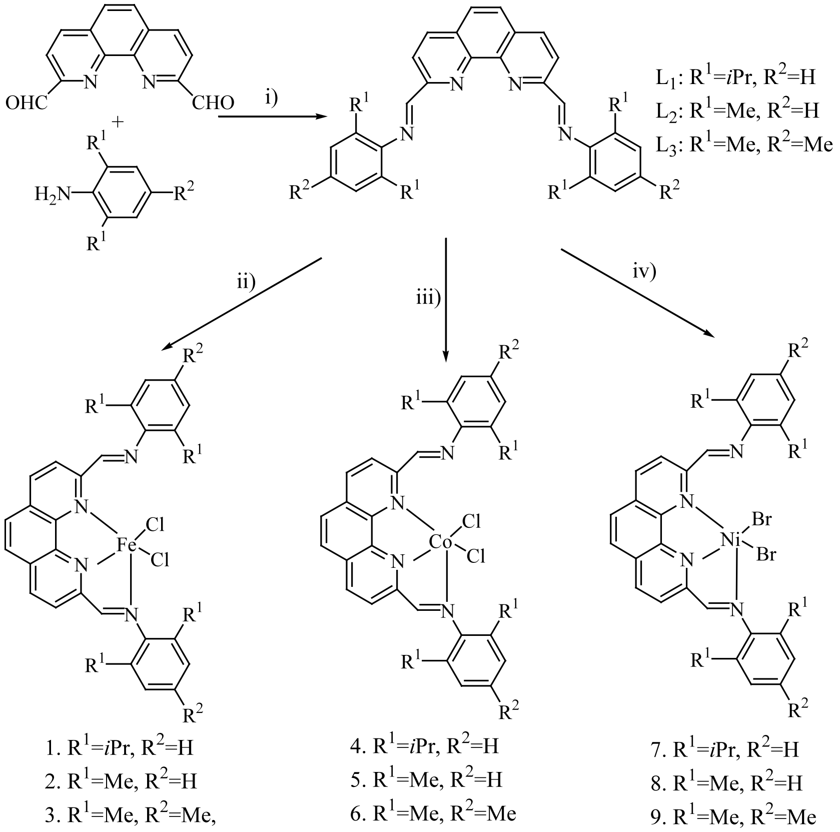
The idea that metal complexes could process polymerization has stimulated a search for late transition metal complexes as polymerization catalysts. Laine group reported pyridinylimino-based nickel(II), cobalt(II) and palladium(II) complexes as alkene polymerization catalyst [13–15]. Brookhart [16] and Gibson group [17] have reported highly active ethylene polymerization catalysts based on iron(II) and cobalt(II) complexes bearing 2,6-bis(imino)pyridyl ligands. Modification of substituents on their aryl (Ar) and imino groups resulted in dramatic changes for the productivity and physical properties of the corresponding polyolefin materials [18–22]. In addition, we were interested in exploring and synthesizing some new ligands in order to develop new late-transition metal complexes as catalysts in olefin polymerization and oligomerization [23]. Here we de-

---

* Corresponding author. Tel.: +86-10-6255-7955; fax: +86-10-6255-9373

E-mail address: whsun@infoc3.icas.ac.cn (W.-H. Sun).

PII: S0022-328X(02)01623-6



Scheme 1. Synthesis of compounds **1**–**9**. Reagents and conditions: (i) EtOH, HAc; (ii) $FeCl_2$, THF; (iii) $CoCl_2$, EtOH; (iv) (DME)$NiBr_2$, CH_2Cl_2.

scribe the synthesis of a novel series of iron, cobalt and nickel complexes bearing 2,9-bis(imino)-1,10-phenanthrolinyl ligands (Scheme 1). Their nickel and cobalt complexes, with the assistance of methylaluminoxane (MAO), could activate ethylene for oligomerization to produce oligomers.

2. Results and discussion

2.1. Synthetic aspects

2,9-Bis(imino)-1,10-phenanthrolinyl ligands L_1, L_2, L_3 were prepared in good yields by the condensation reaction of two equivalents of the appropriate aniline with one equivalent of 2,9-dialdehyde-1,10-phenanthroline (Scheme 1), yielding pale yellow crystalline products after being purified through re-crystallization in ethanol. The L_1, L_2, L_3 were characterized by microanalysis, ^{1}H-NMR spectra and mass spectrometry.

The complexes **1**–**6** were synthesized in reasonable yields by treating MCl_2 (M = Fe, Co) with the corresponding 2,9-bis(inimo)-1,10-phenanthrolinyl ligand in appropriate solvents (Fe, THF; Co, ethanol) at elevated temperature, while the nickel(II) dibromide complexes **7**–**9** were prepared with the corresponding ligands by reacting of a slight excess of the diimino ligand with (1,2-dimethoxyethane)nickel(II) bromide in dichloromethane (Scheme 1). Their resulting solutions were concentrated, and diethyl ether was added to make the products precipitated. The products were purified by washing with diethyl ether for removing non-reacted ligand. Complexes **1**–**9** are air-stable in solid, and insoluble in saturated hydrocarbons, whereas they are soluble in polar organic solvents, such as CH_2Cl_2, $CHCl_3$, ethanol and acetonitrile.

The complexes obtained were fully characterized by IR, FABMS and elemental analysis. In the FABMS spectra of complexes **1**–**9**, although ion peak of complex was not observed (except for complex **1**), fairly intensive fragments were obtained upon elimination of one and two halide and then $FeCl_2$ ($CoCl_2$, $NiBr_2$). To confirm their structures, complexes **4**, **7** were subjected to single-crystal X-ray diffraction studies.

2.2. X-ray crystallography

Crystals of complexes **4**, **7** suitable for X-ray structural determination were grown by vapor diffusion of Et_2O into the acetonitrile–dichloromethane solution (**4**) and acetonitrile solution (**7**), respectively. The molecular structure of complex **4** is shown in Fig. 1. In this complex, the structure consists of a metal atom surrounded by one ligand L_1 and two chlorine atoms

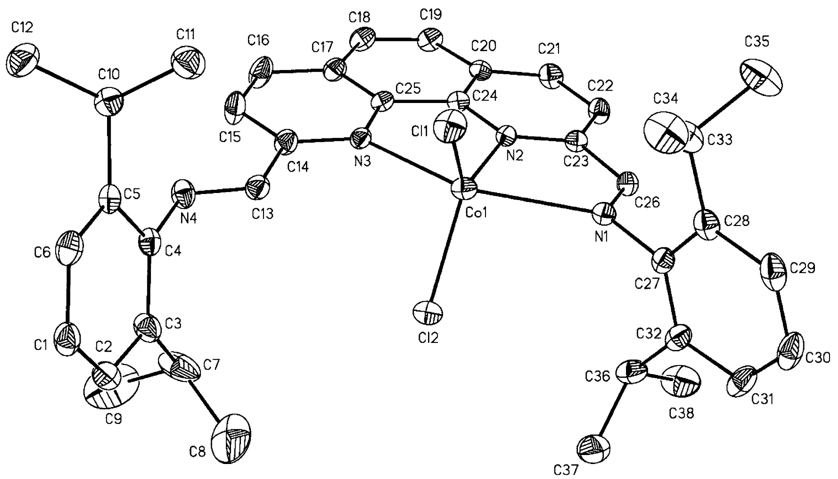


Fig. 1. Crystal structure of complex **4** with 30% probability displacement ellipsoids.

in a distorted trigonal–bipyramidal geometry. The axial positions are occupied by cobalt with two nitrogen atoms N(1) and N(3) [N(1)–Co–N(3) = 149.83(6)°]. The equatorial plane is made by the two chlorine atoms and a nitrogen atom N(2) of the phenanthroline fragment. The equatorial plane and the axial plane make a dihedral angle of 88.4°. The metal center is coordinated with N(2), N(3) in the rigid ring of **1**, 10-phenanthroline and N(1) of the imino group for forming two fused five-membered rings with acute N–M–N angles: N(3)–Co–N(2) = 76.82(7)°, N(2)–Co–N(1) = 73.08(6)°. The Co–N(2) and Co–N(3) bonds are significantly shorter than the Co–N(1) (imino) bonds, with the formed double bond character of the imino linkage N(1)–C(26) have been retained [C=N distances in 1.276(2) Å]. The 2,6-diisopropylphenyl substituents C(27)–C(28)–C(29)–C(30)–C(31)–C(32) are oriented ca. orthogonal to the basal coordination plane N(1)–C(26)–C(3)–N(2)–C(24)–C(25)–N(3)–Co(1), with the ca 85.2° twist about the N(1)–C(27) bond. Selected bond lengths and angles of complex **4** are presented in Table 1.

Table 1
Selected bond lengths (Å) and angles (°) for complex **4**

Bond lengths (Å)			
Co(1)–N(2)	2.0428(17)	Co(1)–Cl(2)	2.2299(8)
Co(1)–Cl(1)	2.2501(8)	Co(1)–N(3)	2.2503(18)
Co(1)–N(1)	2.4352(18)	N(1)–C(26)	1.276(2)
N(1)–C(27)	1.449(2)	N(2)–C(23)	1.331(2)
N(2)–C(24)	1.351(2)	N(3)–C(14)	1.329(3)
N(3)–C(25)	1.370(2)	N(4)–C(13)	1.259(3)
N(4)–C(4)	1.433(3)	C(13)–C(14)	1.486(3)
C(23)–C(26)	1.469(3)		
Bond angles (°)			
N(2)–Co(1)–Cl(2)	121.37(5)	N(2)–Co(1)–Cl(1)	123.19(5)
Cl(2)–Co(1)–Cl(1)	115.42(3)	N(2)–Co(1)–N(3)	76.82(7)
Cl(2)–Co(1)–N(3)	97.82(5)	Cl(1)–Co(1)–N(3)	97.14(5)
N(2)–Co(1)–N(1)	73.08(6)	Cl(2)–Co(1)–N(1)	95.97(5)
Cl(1)–Co(1)–N(1)	100.93(5)	N(3)–Co(1)–N(1)	149.83(6)

In complex **7**, Br(1) was disordered into two positions, and C(39) of acetonitrile lies in a special position ($x = 0.000$; $y = -0.2391(5)$; $z = 0.2500$), that is to say that C(39) of acetonitrile is in the 2-fold rotation axis, therefore X-ray analysis of complex Ni reveals that the crystal contains not only 5-coordinated species (Fig. 2) that is often observed in similar Ni complexes but also 6-coordinated ones (Fig. 3). The 6-coordinate structure consists of a metal atom surrounded by one ligand **L_1**, two bromine atoms and one CH_3CN linked by the N atoms, in a distorted octahedral geometry. The metal center is coordinated to N(2) and N(3) of the rigid 1,10-phenanthroline and N(1) of one imino group forming two fused 5-membered rings (Table 2) with acute N–Ni–N angles: N(1)–Ni–N(2) = 77.42(12)°; N(2)–Ni–N(3) = 77.95(11)°. These three nitrogen atoms occupy

Table 2
Selected bond lengths (Å) and angles (°) for complex **7**

Bond lengths (Å)			
Br(1A)–Ni(1)	2.3039(11)	Br(1B)–Ni(1)	2.5311(9)
Br(2)–Ni(1)	2.4944(7)	Ni(1)–N(2)	1.969(3)
Ni(1)–N(1)	2.187(3)	Ni(1)–N(3)	2.188(3)
Ni(1)–N(5)	2.195(5)	N(1)–C(13)	1.279(4)
N(1)–C(1)	1.441(4)	N(2)–C(25)	1.327(4)
N(2)–C(14)	1.330(4)	N(3)–C(23)	1.343(4)
N(3)–C(24)	1.362(4)	N(4)–C(26)	1.248(4)
N(4)–C(27)	1.436(4)	N(5)–C(40)	1.160(7)
C(13)–C(14)	1.486(3)	C(23)–C(26)	1.469(3)
Bond angles (°)			
N(2)–Ni(1)–N(1)	77.42(12)	N(2)–Ni(1)–N(3)	77.95(11)
N(1)–Ni(1)–N(3)	155.02(11)	N(2)–Ni(1)–N(5)	170.75(15)
N(1)–Ni(1)–N(5)	93.52(15)	N(3)–Ni(1)–N(5)	110.93(14)
N(2)–Ni(1)–Br(1A)	113.46(8)	N(1)–Ni(1)–Br(1A)	94.59(8)
N(3)–Ni(1)–Br(1A)	91.39(7)	N(5)–Ni(1)–Br(1A)	64.91(13)
N(2)–Ni(1)–Br(2)	92.60(8)	N(1)–Ni(1)–Br(2)	99.37(8)
N(3)–Ni(1)–Br(2)	85.82(7)	N(5)–Ni(1)–Br(2)	90.70(13)
Br(1A)–Ni(1)–Br(2)	152.62(4)	N(2)–Ni(1)–Br(1B)	95.38(8)
N(1)–Ni(1)–Br(1B)	88.98(8)	N(3)–Ni(1)–Br(1B)	89.24(7)
N(5)–Ni(1)–Br(1B)	82.46(13)	Br(2)–Ni(1)–Br(1B)	169.54(3)

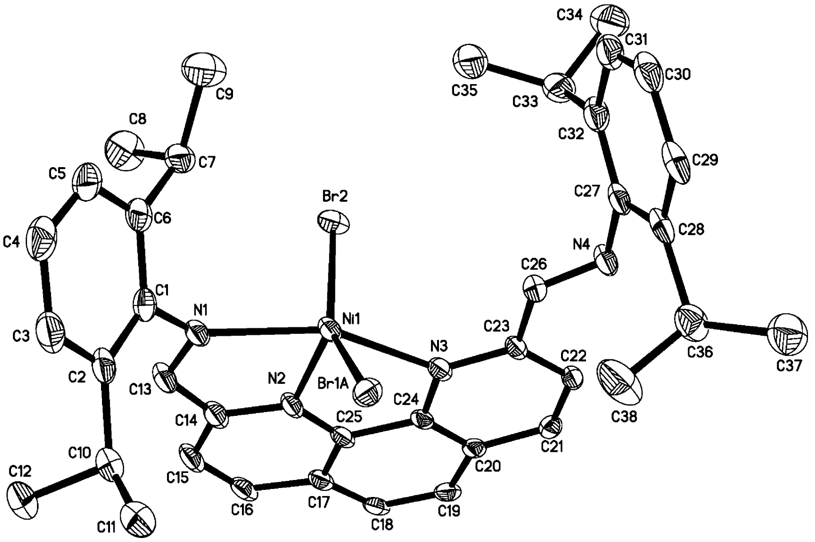


Fig. 2. Crystal structure of complex **7** in which Ni is 5-coordinated, with 30% probability displacement ellipsoids.

the equatorial plane which also contains the N(5) atom of the acetonitrile, whereas the axial position are occupied by nickel with two bromine. All the atoms of 1,10-phenanthroline ligand and the C(13), N(1), C(26) and N(4) of the imino groups as well as the Ni(1) atom and N(5) of CH_3CN make an almost perfect plane, with the largest deviation from the plane being 0.0776 Å at C(14). The 2,6-diisopropylphenyl substituents C(27)–C(28)–C(29)–C(30)–C(31)–C(32) are oriented ca. orthogonal to the basal coordination plane N(1)–C(13)–C(14)–N(2)–C(25)–C(24)–N(3)–Ni(1) (ca 104°); however the 2,6-diisopropylphenyl group C(1)–C(2)–C(3)–C(4)–C(5)–C(6) is oriented to the basal coordination plane N(1)–C(13)–C(14)–N(2)–C(25)–C(24)–N(3)–Ni(1), with the ca 64.6° twist about the N(1)–C(1) bond. Selected bond lengths and angles for complex **7** are presented in Table 2.

In this complex **7**, the 5-coordinate structure (Fig. 2) consists of a metal atom surrounded by one ligand $\mathbf{L_1}$ and two bromine atoms in a distorted trigonal–bipyramidal geometry. The axial positions are occupied by nickel with two nitrogen atoms N(1) and N(3) [N(1)–Ni–N(3) = 155.02(11)°]. The equatorial plane is made by the two bromine atoms and a nitrogen atom N(2) of the phenanthroline fragment. The equatorial plane and the axial plane make a dihedral angle of 87.1°.

2.3. Oligomerization of ethylene

Upon treatment with methylaluminoxane(MAO), at **1** bar pressure, no activity was found for all complexes **1**–

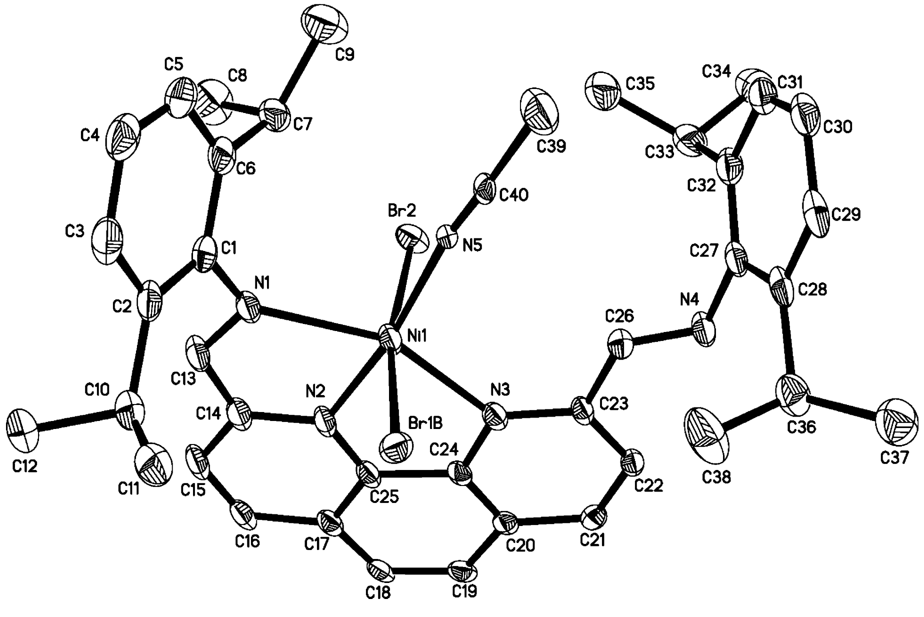


Fig. 3. Crystal structure of complex **7** in which Ni is 6-coordinated, with 30% probability displacement ellipsoids.

9. Increasing the pressure of ethylene to **10** bar, as seen from Table 3, the nickel and cobalt complexes **4**–**9** are active for ethylene oligomerization. Catalyst activities were calculated on the base of GC–MS analysis, and Table 3 listed their activity and distribution of oligomers in the oligomerization with nickel and cobalt precatalysts **4**–**9**. Table 4 shows the structures and ratios of product C_4 and C_6, however, it is not clear about the double bond immigration, especially for the rearrangement of oligomers. During the oligomerization reaction, a decrease in activity is notified with the final activity being typically 10–15% of the initial activity. The nature of the metal center has a major influence on catalytic activity. In general, Ni catalysts are more active than the corresponding Co(II) analogues in our research condition. The most active Ni(II) catalyst is complex **7** (3.3×10^6 g mol^{-1} h), while the most active Co(II) complexes is complex **6** (9.3×10^5 g mol^{-1} h) for oligomerization of ethylene. As seen from Table 3, in addition to the toluene-soluble fraction of oligomers, catalysts **4**–**7** and **9** also yield a small toluene-insoluble PE fraction, which was confirmed by DSC. However, the iron complexes **1**–**3** show almost no activity for ethylene oligomerization, although some consumption of ethylene was observed during the reaction, but small amount of solid polyethylene (run 2) was found. It appears that compared with iron(II) and cobalt(II) complexes bearing 2,6-bis(imino)pyridyl ligands [16,17,22], the active site of the present complexes might too wide to suppress undesired β-H elimination.

3. Experimental

3.1. General

All manipulations were carry out under an atmosphere of nitrogen using standard Schlenk and cannula techniques. Solvents were refluxed over an appropriate drying agent and distilled and degassed prior to use. Elemental analyses were performed on a Hezaeous CHN-RAPID microanalyzer. NMR spectra were recorded on a Bruker DMX-300 spectrometer, with TMS as the internal standard. IR spectra were obtained as KBr pellets on a Perkin–Elmer FTIR 2000 Spectrometer. Mass spectra were measured on a Kratos AEI MS-50 instrument using fast atom bombardment (FAB) or electron impact (EI) technology. T_m of PE was measured on a Perkin–Elmer DSC-7A Spectrometer. Melting points were determined with a digital electrothermal apparatus without furher correction. Distribution for the oligomerization was recorded on a HP5890 Series II gas chromatogram spectrometer.

Compound **1**, 10-phenanthroline-2,9-dicarboaldehyde was prepared according to an established procedure [24,25], while MAO (1.4 mol l^{-1}) solution in toluene was purchased from Albemarle Corp (USA); $(DME)NiBr_2$ and all of the anilines were purchased from Aldrich Chemical Co. or Acros Chemical Co. All other chemicals were obtained commercially without purification unless stated otherwise.

3.2. Preparations of 2,9-bis(imino)-1,10-phenanthrolinyl ligands

3.2.1. 2,9-Diformyl-1,10-phenanthrolinebis(2,6-diisopropylanil) (*L_1*)

To a refluxing solution of **1**, 10-phenanthroline-2,9-dicarboaldehyde (1.0 g, 4.2 mmol) and a few drops of glacial acetic acid in anhydrous ethanol (120 ml) was added 2,6-diisopropylaniline (4.0 g, 20 mmol) in anhydrous ethanol (50 ml) over a period of 30 min with stirring. Then the mixture was refluxed for further 5 h. Upon cooling to room temperature (r.t.), the solution was evaporated to 30 ml under vacuum, and the product was crystallized from ethanol. After filtration, the

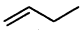
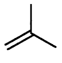
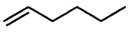
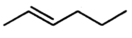
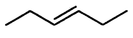
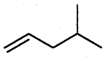
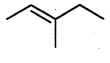
Table 3
Complexes activity and distribution of oligomers [a]

Run	Precat (μmol)	MAO (mmol per equiv)	P (bar)	Activity (g mol^{-1} h^{-1})	Mass of PE (mg)	T_m [b] of PE (°C)	Distribution of the oligomerization			
							C_4 (g)	C_6 (g)	C_8 (g)	C_{10} (g)
1	1(8.4)	10(1190)	20							
2	2(16)	10(625)	20		80	133.13				
3	3(10)	10(1000)	20							
4	4(10)	10(1000)	10	7.0×10^5	30	133.75	3.5			
5	5(10)	10(1000)	10	7.1×10^5	480	124.78	2.54	0.54		
6	6(10)	10(1000)	20	9.3×10^5	30	125.56	4.2	0.26	0.18	
7	7(14)	10(710)	20	3.3×10^6	230	120.27	4.0	11.1	5.4	2.0
8	8(17)	10(590)	20	2.1×10^6			11.0	5.8	0.96	
9	9(10)	10(1000)	10	2.0×10^6	105	117.97	3.60	5.2	1.23	

[a] Toluene solvent, reaction time 0.5 h.

[b] Determined by DSC.

Table 4
The structures and ratios of product C_4 and C_6

Run	C_4(mol%)		C_6 (mol%)				
							
4	100%	--	--	--	--	--	--
5	100%	--	84%	16%	--	--	--
6	100%	--	53%	32%	15%	--	--
7	--	100%	12%	29%	32%	4%	23%
8	--	100%	8%	61%	14%	3%	14%
9	--	100%	6%	73%	--	2%	19%

yellow solid was washed with cold ethanol and dried to give yellow crystal 1.56 g in 62% yield. M.p. 269–270 °C; IR(KBr): 3063 (s), 2962 (s), 1639 (vs), 1586 (s), 1550, 1499, 1462 (m), 1383, 1363, 1251, 1182, 1086, 933 (m), 860, 756 (s) cm^{-1}; ^{1}H-NMR ($CDCl_3$): δ 1.18 (24H, d, $J = 10.2$Hz), 3.05 (4H, m), 7.15–7.23 (6H, m), 7.99 (2H, s), 8.47 (2H, d, $J = 7$Hz), 8.75 (2H, d, $J = 7$Hz), 8.78 (2H, s); EIMS (*m/z*): 554 (M^+, 88.7%), 553 (23.0%), 539 (22.1%), 511 (10.8%), 381 (13.4%), 369 (31.4%), 364 (12.4%), 352 (15.6%), 208 (18.9%), 207 (13.5%), 194 (100.0%), 193 (15.1%), 186 (24.9%), 181 (40.5%), 176 (20.8%), 146 (13.8%); Anal. Calc. for $C_{38}H_{42}N_4$: C, 82.27; H, 7.63; N, 10.10. Found: C, 81.98; H, 7.90; N: 9.72%.

3.2.2. 2,9-Diformyl-1,10-phenanthrolinebis(2,6-dimethylanil) (**L₂**)

By using similar procedure described in synthesis of Ligand $\mathbf{L_1}$, we obtained $\mathbf{L_2}$ as yellow crystal in 58% yield. M.p. 132–133 °C; IR(KBr): 3449 (m), 3325 (m), 3018 (m), 2969, 2918 (m), 1636 (vs), 1591, 1550 (s), 1500, 1474, 1442 (s), 1192, 1088 (s), 861, 762 (s) cm^{-1}; ^{1}H-NMR ($CDCl_3$): δ 2.18 (12H, s), 6.94–7.14 (6H, m), 8.05 (2H, s), 8.42–8.52 (2H, d), 8.75–8.86 (4H, m); EIMS (*m/z*): 442 (M^+, 100%), 441 (39.5%), 427 (14.9%), 424 (16.7%), 337 (28.4%), 324 (18.2%), 323 (53.2%), 322 (14.1%), 311 (25.2%), 310 (64.7%), 309 (14.3%), 308 (11.4%), 296 (14.1%), 295 (10.5%),132 (13.5%); Anal. Calc. for $C_{30}H_{26}N_4 \cdot 1/2H_2O$: C, 79.79; H, 6.03; N, 12.41. Found: C, 79.86; H, 6.41; N, 12.13%.

3.2.3. 2,9-Diformyl-1,10-phenanthrolinebis(2,4,6-trimethylanil) (**L₃**)

By using similar procedure described in synthesis of Ligand $\mathbf{L_1}$, we obtained $\mathbf{L_3}$ as yellow crystal in 77% yield. M.p. 166–167 °C; IR(KBr): 3394 (br), 1724 (s), 1633 (vs), 1553 (m), 1499, 1480 (s), 1208 (s), 854 (s) cm^{-1}; ^{1}H-NMR ($CDCl_3$): δ 2.06 (12H, s), 2.23 (6H, s), 6.85 (4H, m), 7.90 (2H, s), 8.38 (2H, d), 8.43–8.86 (4H, m); FABMS (*m/z*): 471($M^+ + 1$); Anal. Calc. for $C_{32}H_{30}N_4H_2O \cdot H_2O$: C, 78.66; H, 6.60; N, 11.47. Found: C, 78.29; H, 6.31; N, 11.06%.

3.3. Complexation with MCl_2 ($M = Fe, Co$) and DME $NiBr_2$

3.3.1. Preparation of [2,9-diformyl-1,10-phenanthrolinebis(2,6-diisopropylanil)]$FeCl_2$ (**1**)

A solution of 2,9-diformyl-1,10-phenanthroline(2,6-diisopropylanil) (197 mg, 0.33 mmol) in THF (10 ml) was added dropwise at 60 °C to a solution of $FeCl_2 \cdot 4H_2O$ (60 mg, 0.30 mmol) in THF (5 ml) to yield a blue solution. After stirring at 60 °C for 18 h, the reaction mixture was allowed to cool to r.t. The reaction volume was concentrated, and diethyl ether (10 ml) was added to precipitate the product as a green power, which was subsequently washed with diethyl ether (3 × 10 ml), filtered, and dried in vacuo to afford 135 mg (65%) of 2,9-diformyl-1,10-phenanthroline(2,6-diisopropylanil) $FeCl_2$. M.p. > 320 °C; IR(KBr): 3441 (br), 2963 (s), 2868 (m), 1633, 1503, 1461 (s) cm^{-1}; FABMS (*m/z*): 680 (M^+), 646 ($M^+ - Cl$), 610 ($M^+ - 2Cl$); Anal. Calc. for $C_{38}H_{42}N_4$ $FeCl_2 \cdot H_2O$: C, 65.24; H, 6.34; N, 8.01. Found: C, 65.12; H, 6.38; N, 7.80%.

3.3.2. Preparation of [2,9-diformyl-1,10-phenanthrolinebis(2,6-dimethylanil)]$FeCl_2$ (**2**)

By using same procedure described above in synthesis of complex **1**, the reaction of $\mathbf{L_2}$ and $FeCl_2$ $4H_2O$ gave **2** as green powder in 87% yield. M.p. > 320 °C; IR(KBr): 3403 (br), 2959 (s), 1641, 1617 (vs), 1508, 1468 (s), 1381, 1304 (s), 1223, 1177 (s), 862, 776 (s) cm^{-1}; FABMS (*m/z*): 534 ($M^+ - Cl$), 498 ($M^+ - 2Cl$); Anal. Calc. for $C_{30}H_{26}N_4$ $FeCl_2$ H_2O: C, 50.46; H, 3.95; N, 7.85. Found: C, 50.86; H, 3.65; N, 7.44%.

*3.3.3. Preparation of [2,9-diformyl-1,10-phenanthrolinebis(2,4,6-trimethylanil)]FeCl$_2$ (**3**)*

By using same procedure described above in synthesis of complex **1**, the reaction of **L$_3$** and $FeCl_2 \cdot 4H_2O$ gave **3** as green powder in 91% yield. M.p. > 320 °C; IR(KBr): 1610(s), 1570(s), 1502, 1479(s), 862(s) cm^{-1}; FABMS (*m*/*z*): 561 ($M^+ -Cl$), 526 ($M^+ -2Cl$); Anal. Calc. for $C_{32}H_{30}N_4$ $FeCl_2 \cdot H_2O$: C, 62.46; H, 5.24; N, 9.10. Found: C, 62.04; H, 4.90; N, 8.65%.

*3.3.4. Preparation of [2,9-diformyl-1,10-phenanthrolinebis(2,6-diisopropylanil)]CoCl$_2$ (**4**)*

A suspension of 2,9-diformyl-1,10-phenanthroline(2,6-diisopropylanil) (179 mg, 0.30 mmol) in ethanol (60 ml) was added dropwise at 60 °C to a solution of $CoCl_2$ (70 mg, 0.30 mmol) in ethanol (5 ml) to yield a blue solution. After stirring at 60 °C for 8 h, the reaction mixture was cooled to r.t. The reaction volume was concentrated, and diethyl ether (10 ml) was added to precipitate the product as a green power, which was subsequently washed with diethyl ether (3 × 10 ml), filtered, and dried in vacuum to afford 130 mg (60%) of 2,9-diformyl-1,10-phenanthroline(2,6-diisopropylanil) $CoCl_2$. M.p. > 320 °C; IR(KBr): 2961, 2866 (s), 1639, 1615, 1586, 1566 (s), 1505, 1461 (s) cm^{-1}; FABMS (*m*/*z*): 648 ($M^+ -Cl$), 614 ($M^+ -2Cl$); Anal. Calc. for $C_{38}H_{42}N_4$ $CoCl_2$: C, 66.67; H, 6.18; N, 8.18. Found: C, 66.22; H, 5.71; N, 8.10%. Crystals of complexes **4** suitable for X-ray structural determination was grown by vapor diffusion of Et_2O into acetonitrile–dichloromethane solutions.

*3.3.5. Preparation of [2,9-diformyl-1,10-phenanthrolinebis(2,6-dimethylanil)]CoCl$_2$ (**5**)*

By using same procedure described above in synthesis of complex **4**, the reaction of **L$_2$** and $CoCl_2 \cdot 6H_2O$ gave **5** as green powder in 73% yield. M.p. > 320 °C; IR(KBr): 1604, 1574 (vs), 1381 (vs), 1064 (s) cm^{-1}; FABMS (*m*/*z*): 536 ($M^+ -Cl$), 501 ($M^+ -2Cl$); Anal. Calc. for $C_{30}H_{26}N_4$ $CoCl_2$: C, 62.95; H, 4.58; N 9.79. Found: C, 62.72; H, 4.67; N 9.34%.

*3.3.6. Preparation of [2,9-diformyl-1,10-phenanthrolinebis(2,4,6-trimethylanil)]CoCl$_2$ (**6**)*

By using same procedure described above in synthesis of complex **4**, the reaction of **L$_3$** and $CoCl_2 \cdot 6H_2O$ gave **6** as green powder in 73% yield. M.p. > 320 °C; IR(KBr): 3425 (br), 1612 (s), 1564, 1502, 1477 (s) cm^{-1}; FABMS (*m*/*z*): 564 ($M^+ -Cl$), 529 ($M^+ -2Cl$); Anal. Calc. for $C_{32}H_{30}N_4$ $CoCl_2$ H_2O: C, 62.15; H, 5.22; N 9.06. Found: C, 62.30; H, 4.98; N, 8.90%.

*3.3.7. Preparation of [2,9-diformyl-1,10-phenanthrolinebis(2,6-diisopropylanil)]NiBr$_2$ (**7**)*

(DME)$NiBr_2$ (77 mg, 0.25 mmol) and 2,9-diformyl-1,10-phenanthroline(2,6-diisopropylanil) (**L$_1$**) (179 mg, 0.30 mmol) were combined in a Schlenk flask under N_2 atmosphere. CH_2Cl_2 (10 ml) was added, and the reaction mixture was stirred at r.t. for 18 h. The reaction solution was concentrated into its half volume, and diethyl ether (10 ml) was added to precipitate the product as a green power, which was subsequently washed with diethyl ether (3 × 10 ml), filtered, and dried to give **7** as orange powder 185 mg, yield: 86%. M.p. > 320 °C; IR(KBr): 3407(Br), 2963 (s), 1631, 1608, 1584 (s), 1503, 1401 (s) cm^{-1}; FABMS (*m*/*z*): 693 ($M^+ -Br$), 612 ($M^+ -2Br$); Anal. Calc. for $C_{38}H_{42}N_4NiBr_2 \cdot CH_2Cl_2$: C, 54.58; H, 5.17; N, 6.53. Found: C, 54.09; H, 4.86; N, 6.23%. Crystals of complexes **7** suitable for X-ray structural determination was grown by vapor diffusion of Et_2O into acetonitrile solutions.

*3.3.8. Preparation of [2,9-diformyl-1,10-phenanthrolinebis(2,6-dimethylanil)]NiBr$_2$ (**8**)*

By using same procedure described above in synthesis of complex **7**, the reaction of **L$_2$** and DME $NiCl_2$ gave **8** as orange powder in 78% yield. M.p. > 320 °C; FABMS: 582 ($M^+ -Br$), 501 ($M^+ -2Br$); Anal. Calc. For $C_{30}H_{26}N_4NiBr_2$ CH_2Cl_2: C, 49.91; H, 3.78; N, 7.51. Found: C, 49.95; H, 3.51; N, 7.50%.

*3.3.9. Preparation of [2,9-diformyl-1,10-phenanthrolinebis(2,4,6-Trimethylanil)]NiBr$_2$ (**9**)*

By using same procedure described above in synthesis of complex **7,** the reaction of **L$_3$** and $DME \cdot NiCl_2$ gave **9** as orange powder in 78% yield. M.p. > 320 °C; IR(KBr): 1629 (vs), 1569 (s) cm^{-1}. FABMS (*m*/*z*): 609 ($M^+ -Br$), 528 ($M^+ -2Br$); Anal. Calc. for $C_{32}H_{30}N_4NiBr_2$ CH_2Cl_2: C, 51.21; H, 4.17; N, 7.24. Found: C, 49.95; H, 3.57; N, 7.52%.

*3.4. X-ray crystallstructure determination of complex **4** and complex 7*

Complex **4**s intensity data sets were collected at 293 K on a Rigaku RAXIS RAPID IP diffractometer with graphite-monochromated Mo–K$_\alpha$ radiation ($\lambda =$ 0.71073 Å), while complex **7**s intensity data sets were collected at 123 (2) K on the same diffractometer with graphite-monochromated Mo–K$_\alpha$ radiation ($\lambda =$ 0.71073 Å), using the $\omega - 2\theta$ scan mode. Cell parameters were obtained by the global refinement of the positions of all collected reflections. Intensities were corrected by Lorentz and polarization effects and empirical absorptions were applied. Both structures were solved by direct method, and refined by full-matrix least-squares on F^2, using SHELX-97 package [26]. For complex **4**, all non-H atoms were refined anisotropically. For complex **7**, Br(1) was found to be disordered into two positions, these two positions were refined to occupancies of 42 and 58%, respectively, and C(39) of acetonitrile lies in a special position ($x = 0.000$; $y = -0.2391(5)$; $z = 0.2500$), that is

Table 5
Crystal data, collection parameters, and refinements for complexes **4** and **7**

Complexes	**4**	**7**
Empirical formula	$C_{38}H_{42}Cl_2N_4Co$	C_{38} H_{42} Br_2 N_4 $Ni \cdot 0.5CH_3CN$
Formula weight	684.59	793.81
Crystal color and form	Yellow, block	Green, block
Space group	$P2_1/n$	$C2/c$
Crystal system	Monoclinic	Monoclinic
a (Å)	9.7558(4)	26.9439(10)
b (Å)	14.7282(5)	12.2608(4)
c (Å)	24.9304(10)	22.4878(8)
β (°)	94.6060(9)	99.564(1)
V (Å^3)	3570.6(2)	7325.7 (5)
Z	4	8
T (K)	293(2)	123 (2)
D_{calc} (Mg m^{-3})	1.274	1.439
Absorption coefficient (mm^{-1})	0.662	2.745
F (000)	1436	3256
Crystal size (mm)	0.40 × 0.30 × 0.08	0.70 × 0.60 × 0.25
Scan mode	$\omega - 2\theta$	$\omega - 2\theta$
θ_{max} (°)	27.48	27.48
Number of collected reflections	26 218	31 955
Number of independent reflections	7963	8233
Number of parameters	415	442
Goodness-of-fit	0.730	0.686
Final R indices ($I > 2.00(\sigma(I))$)	$R = 0.0379$, $wR = 0.0585$	$R = 0.0373$, $wR = 0.0768$
R indices (all data)	$R = 0.0973$, $wR = 0.0654$	$R = 0.1022$, $wR = 0.0951$
Largest differential peak and hole (e Å^{-1})	0.332 and −0.303	0.648 and −0.593

to say that C(39) of acetonitrile is in the twofold rotation axis, therefore acetonitrile was changed to line N–C–C–C–N in cell by the symmetrical operation. This is addition of two part of disordered acetonitrile which share terminal C atom. Their crystal data, together with the diffraction data collection and structure refinement parameters are presented in Table 5.

3.5. *General procedure for ethylene oligomerization*

3.5.1. *High pressure tests*

A 100 ml autoclave was heated under vacuum at 80 °C for 3 h and cooled to the r.t. and then vacuated-filled three times by nitrogen and once ethylene. Freshly distilled toluene (50 ml) and the aluminum cocatalyst MAO were introduced into the reactor, the autoclave was sealed, and the ethylene pressure raised to required pressure, and the mixture was stirred at the r.t. for 10 min. The autoclave was then vented, the precatalyst solution/suspension was added, and the autoclave was sealed and pressurized to the desired ethylene pressure while stirring. The reaction was quenched by venting the autoclave and followed by addition of with acidified ethanol. The solid polethylene was collected through filteration (if it was observed). Quantitative GC analysis of this solution was performed using a weighed aliquot of this solution with a weighed amount of toluene as standard.

4. Supplementary material

Crystallographic data for the structures reported in this paper have been deposited in the Cambridge Crystallographic Data Centre with the deposited numbers CCDC Number169182 (Complex **4**) and 169183 (Complex **7**). Copies of the data can be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

Acknowledgements

We are grateful to the Chinese Academy of Sciences for financial support under the Fund of One Hundred Talents and Core Research for Engineering Innovation KGCX203-2. W.H.S., thank Professor Gerhard Erker of Münster University and the Alexander von Humboldt-Stiftung. L.W. thanks China Postdoctoral Science Foundation for partial financial support.

References

[1] S.D. Ittel, L.K. Johnson, M. Brookhart, Chem. Rev. 100 (2000) 1169.

[2] G.J.P. Britovsek, V.C. Gibson, D.F. Wass, Angew. Chem. Int. Ed. Engl. 38 (1999) 428.

[3] M. Bochmann, J. Chem. Soc. Dalton. Trans. (1996) 255.

[4] W. Kaminsky, J. Chem. Soc., Dalton. Trans. (1998) 1413.

[5] A.L. McKnight, R.M. Waymouth, Chem. Rev. 98 (1998) 2587.

[6] H.G. Alt, A. Köppl, Chem. Rev. 100 (2000) 1205.

[7] L.K. Johnson, C.M. Killian, M. Brookhart, J. Am. Chem. Soc. 117 (1995) 6414.

[8] L.K. Johnson, S. Mecking, M. Brookhart, J. Am. Chem. Soc. 118 (1996) 267.

[9] C.M. Killian, D.J. Tempel, L.K. Johnson, M. Brookhart, J. Am. Chem. Soc. 118 (1996) 11664.

[10] T. Schleis, T.P. Spaniol, J. Okuda, J. Heinemann, R. Mulhaupt, J. Organomet. Chem. 569 (1998) 159.

[11] S. Mecking, L.K. Johnson, L. Wang, M. Brookhart, J. Am. Chem. Soc. 120 (1998) 888.

[12] J. Heinemann, R. Mulhupt, P. Brinkmann, G. Luinstra, Macromol. Chem. Phys. 200 (1999) 384.

[13] T.V. Laine, M. Klinga, M. Leskelä, Eur. J. Inorg. Chem. (1999) 959.

[14] T.V. Laine, K. Lappalainen, J. Liimatta, E. Aitola, B. Löfgren, Macromol. Rapid Commun. 20 (1999) 487.

[15] T.V. Laine, U. Piironen, K. Lappalainen, M. Klinga, E. Aitola, M. Leskelä, J. Organomet. Chem. 606 (2000) 112.

[16] B.L. Small, M. Brookhart, A.M.A. Bennett, J. Am. Chem. Soc. 120 (1998) 4049.

[17] G.J.P. Britovsek, V.C. Gibson, B.S. Kimberley, P.J. Maddox, S.J. McTavish, G.A. Solan, A.J.P. White, D.J. Williams, Chem. Commun. (1998) 849.

[18] G.J.P. Britovsek, S. Mastroianni, G.A. Solan, S.P.D. Baugh, C. Redshaw, V.C. Gibson, A.J.D. White, D.J. Williams, M.R.J. Elsegood, Chem. Eur. J. 6 (2000) 2221.

[19] B.L. Small, M. Brookhart, J. Am. Chem. Soc. 120 (1998) 7143.

[20] G.J.P. Britovsek, M. Bruce, V.C. Gibson, B.S. Kimberley, P.J. Maddox, S. Mastroianni, S.J. McTavish, C. Redshaw, G.A. Solan, S. Strömberg, A.J.P. White, D.J. Williams, J. Am. Chem. Soc. 121 (1999) 8728.

[21] G.J.P. Britovsek, V.C. Gibson, S. Mastroianni, D.C.H. Oakes, C. Redshaw, G.A. Solan, A.J.P. White, D.J. Williams, Eur. J. Inorg. Chem. (2001) 431.

[22] Z. Ma, W.H. Sun, Z. Li, C. Shao, Y. Hu, X. Li, Polym. Int., in press

[23] (a) L. Wang, W.H. Sun, L. Han, Z. Li, Y. Hu, C. He, C. Yan, J. Organomet. Chem. 650 (2002) 59;
(b) L. Han, T. Li, W.H. Sun, L. Wang, D. Guo, C. Shao, H. Wang, Trans. Met. Chem., in press.

[24] C.J. Chandler, L.W. Deady, A. Reiss, J. Heterocycl. Chem. 18 (1981) 599.

[25] U. Lüning, M. Müller, Liebigs Ann. Chem. (1989) 367.

[26] G.M. Sheldrick, SHELXTL-97, Program for the Refinement of Crystal Structures, University of Gottingen, Germany, 1997.