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Cobalt and nickel complexes bearing 2,6-bis (imino) phenoxy ligands: syntheses, structures and oligomerization studies

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Abstract

A series of new cobalt and nickel complexes LMX_2 (M = Co, X = Cl; M = Ni, X = Br) bearing 2, 6-bis(imino)phenoxy ligands were synthesized. The solid-state structures of **1** and **4** have been determined by single-crystal X-ray diffraction study. Treatment of the complexes LMX_2 with methylaluminoxane (MAO) leads to active catalysts for oligomerization of ethylene with catalytic activities in the range of 1.2×10^5–2.1×10^5 g mol^{-1} h^{-1} atm^{-1} for Ni complexes, and $\sim 10^3$ g mol^{-1} h^{-1} atm^{-1} for Co complexes. The oligomers were olefins from C_4 to C_{16}. © 2002 Published by Elsevier Science B.V.

Keywords: Cobalt; Nickel; Ethylene oligomerization; Crystal structures

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1. Introduction

Olefin polymerization and oligomerization promoted by late transition metal complexes have drawn much attention in both academic research and industrial application [1,2]. Recent progress was made by employing cationic Ni(II) bis(imine) complexes as effective catalysts for ethylene oligomerization or polymerization [3–5]. These catalyst systems also incorporate monomers such as methyl acrylate with ethylene or propylene resulting in copolymers with considerable productivities [6,7]. The groups of Brookhart [5,6], Bennett [8] and Gibbson [9] have made great contributions in designing highly active ethylene polymerization catalysts based on iron(II) and cobalt(II) bearing 2,6-(imino)pyridyl ligands. Moreover, Grubbs [10] reported new neutral Ni(II) salicylaldiminato complexes as catalysts for the polymerization of ethylene to obtain high molecular weight polyolefins under moderate conditions. Modifications of their substituents of imino groups result in dramatic changes to the productivity of the catalyst and physical properties of the resultant polyolefin. For instance, by reducing the steric bulk of the bisiminopyridine ligands, the resultant iron catalysts oligomerized ethylene to linear olefins with remarkably high activity and selectivity [11]. In our current project, we focus on exploring the effect of changing the central pyridinyl moiety to phenol. The 2,6-bis(imino)phenoxy ligands were designed to coordinate with Co(II) and Ni(II), and the additional imino group could be varied in order to adapt the activities of the catalysts. The corresponding complexes were recognized as precursors for ethylene oligomerization using the co-catalyst methylaluminoxane(MAO). Herein, we report the syntheses and the full characterization of Co(II) and Ni(II) complexes bearing 2,6-bis(imino)phenoxy ligands, as well as their properties for the oligomerization of ethylene with MAO as co-catalyst.

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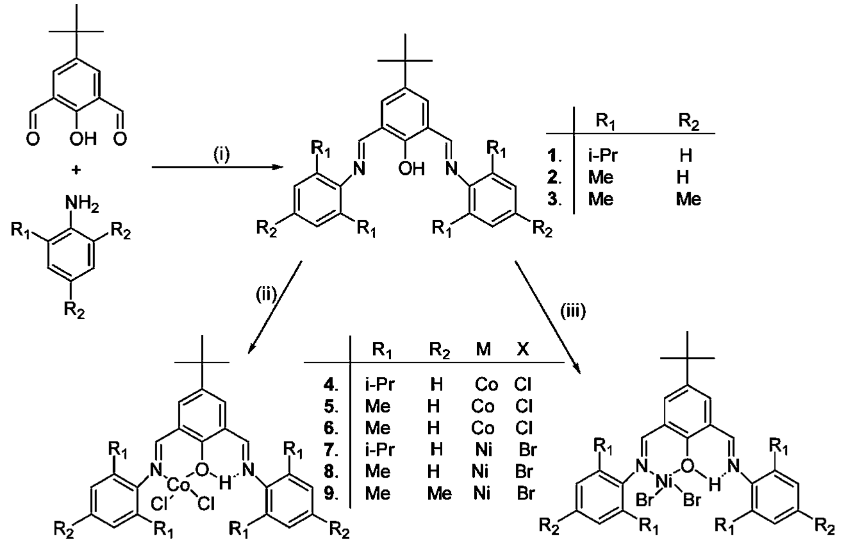

Reagents and Conditions :(i) EtOH, HAc; (ii) $CoCl_2$, EtOH; (iii) $DMENiBr_2$, CH_2Cl_2

Scheme 1.

2. Result and discussion

2.1. Synthesis and characterization

The 2,6-bis(imino)phenoxy ligands **1**–**3** were prepared as yellow solids in good yields by the condensation of two equivalents of the appropriate aniline with one equivalent of 2-hydroxy-5-*tert*-butylisophthaldehyde (Scheme 1). Compounds **1**–**3** were characterized by microanalysis, proton NMR and mass spectrometry. Ligand **1** was finally confirmed by single-crystal X-ray diffraction (Fig. 1).

The complexes **4**–**6** were synthesized in reasonable yields by treating $CoCl_2 \cdot 6H_2O$ with the corresponding 2,6-bis(inimo)phenoxy ligands in ethanol at elevated temperature, while the nickel(II) dibromide complexes **7**–**9** were prepared by reaction of a slight excess of the corresponding diimino ligand with (1,2-dimethoxyethane)nickel(II) bromide in dichloromethane (Scheme 1). Complexes **4**–**9** are stable solids and insoluble in saturated hydrocarbons, while they are soluble in polar organic solvents, including CH_2Cl_2, $CHCl_3$, acetonitrile, etc. The structure of all the complexes **4**–**9** were confirmed with elemental analyses, IR and FABMS spectroscopy. In the FABMS spectra of complexes **4** and **6**–**9**, the ion peaks of complex were not found, only fairly intense peaks from the fragments due to elimination of one or two halide and $CoCl_2(NiBr_2)$. Crystals of complex **4** suitable for X-ray structural determination were grown from its ethanol solution. The molecular structure complex **4** is shown in Fig. 2.

The structure of ligand **1** (Fig. 1) shows that this molecule possesses a transoid configuration between the imino groups, a geometry that is different from the cisoid conformation in the Co complex **4** (Fig. 2). There are strong O–H–N interactions between hydroxy group [O(1)] and imino nitrogen [N(2)], with the H–N distance 1.720 Å and the O–H–N angle 156.9°. Another conjugated imino group is flexible around the C(14)–C(13). The selected bond lengths and angles for ligand **1** were shown in Table 1.

The X-ray analysis of complex **4** shows that this molecule possesses a cisoid configuration between imino groups, and the N(1)–C(13)–C(14)–C(19)–C(18)–C(24)–N(2) component is co-planar within 0.0367 Å. The N(1)–C(13)–C(14)–C(19)–O(1)–Co(1) forms a planar, six-membered chelate ring. The geometry around the cobalt atom is a distorted tetrahedron with *cis* angles in the range of 92.79–117.55°.

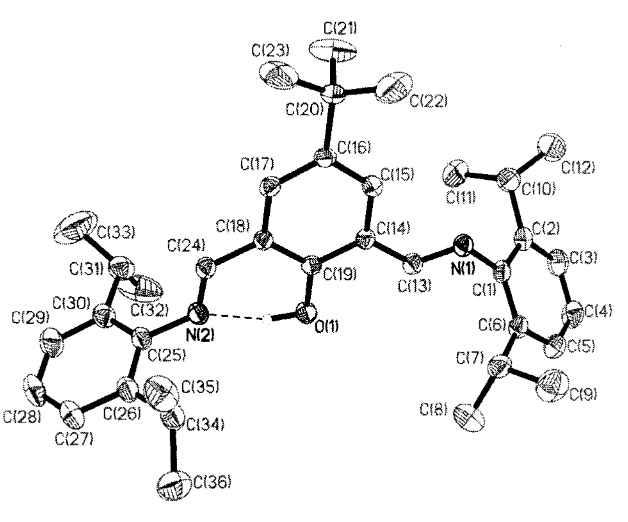

Fig. 1. Molecular structure of ligand **1**, showing 30% probability displacement ellipsoids. Hydrogen atoms are omitted for clarity.

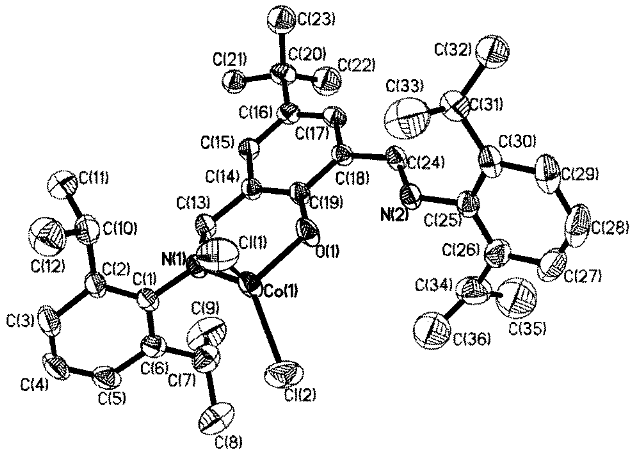

Fig. 2. Molecular structure of complex **4**, showing 30% probability displacement ellipsoids. Hydrogen atoms are omitted for clarity.

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

Bond lengths			
O(1)–C(19)	1.3477(18)	N(1)–C(13)	1.266(2)
N(1)–C(1)	1.429(2)	N(2)–C(24)	1.269(2)
N(2)–C(25)	1.435(2)	C(13)–C(14)	1.470(2)
C(18)–C(24)	1.457(2)		
Bond angles			
C(13)–N(1)–C(1)	117.31(14)	C(24)–N(2)–C(25)	120.16(14)
N(1)–C(13)–C(14)	123.00(15)	O(1)–C(19)–C(14)	119.03(13)
O(1)–C(19)–C(18)	121.67(14)	N(2)–C(24)–C(18)	122.66(14)

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

Bond lengths			
Cl(1)–Co(1)	2.2263(17)	Cl(2)–Co(1)	2.2121(15)
Co(1)–O(1)	1.951(2)	Co(1)–N(1)	2.023(3)
N(1)–C(13)	1.277(4)	N(1)–C(1)	1.443(4)
N(2)–C(24)	1.295(5)	C(13)–C(14)	1.447(4)
C(18)–C(24)	1.427(5)	O(1)–C(19)	1.299(4)
N(2)–C(25)	1.445(5)		
Bond angles			
O(1)–Co(1)–N(1)	92.79(10)	O(1)–Co(1)–Cl(2)	111.20(11)
N(1)–Co(1)–Cl(2)	117.59(10)	O(1)–Co(1)–Cl(1)	109.85(11)
N(1)–Co(1)–Cl(1)	113.47(10)	Cl(2)–Co(1)–Cl(1)	110.56(6)
C(19)–O(1)–Co(1)	127.1(2)	C(13)–N(1)–C(1)	118.0(3)
C(13)–N(1)–Co(1)	122.4(2)	C(1)–N(1)–Co(1)	119.60(19)
C(18)–C(24)–N(2)	122.7(3)	C(24)–N(2)–C(25)	126.3(3)
O(1)–C(19)–C(14)	124.0(3)	O(1)–C(19)–C(18)	119.4(3)

The 2,6-diisopropylphenyl substituted aryl ring (C(1)–C(2)–C(3)–C(4)–C(5)–C(6)) is oriented approximately orthogonally to the basal coordination plane, with a approximately 93.6° twist about the N(1)–C(1) bond. Table 2 listed the selected bond lengths and angles for complex **4**.

2.2. Oligomerization of ethylene

Upon treatment with methylaluminoxane(MAO), all of the complexes **4**–**9** are active for ethylene oligomerization. Table 3 lists their activity and molecular weight distribution of the oligomers produced by nickel and cobalt catalysts. The nature of the metal center has a major influence on catalytic activities. In general, Ni catalysts are more active than their corresponding Co(II) analogues under our conditions. The most active Ni(II) catalyst is complex **9** (2.1×10^5 g mol^{-1} h^{-1} atm^{-1}), while the Co(II) complexes are less active than 10^3 g mol^{-1} h^{-1} atm^{-1} for oligomerization.

The metal core of complexes also influence the molecular weight distribution of oligomers. Cobalt catalysts **4**, **5** and **6** yield butylene, while Ni complexes **7**, **8** and **9** gave higher olefins such as 1-hexene and 1-octene along with 1-butylene. Stereochemistry of the ligands affected their catalytic activities. Ni-based catalysts **7**–**9** revealed that a reduction of steric bulk at the *ortho*-aryl position resulted in the increase of their activities. The complex **7** contains isopropyl groups in the ortho positions of the aryl rings and display an activity of 1.2×10^5 g mol^{-1} atm^{-1} h^{-1}, approximately complex **8** with dimethyl on the aryl ring with an activity of 1.9×10^5 g mol^{-1} atm^{-1} h^{-1}. Methyl-substitution on the *para*-position of aryl (Complex **9**) resulted an slight increase of catalytic activity.

3. Experimental

All manipulations were carried out under an atmosphere of nitrogen using standard Schlenk and cannula techniques. Solvents were refluxed over an appropriate drying agent and distilled under nitrogen prior to use. Using HP-MOD 1106 microanalyzer performed elemental analyses. NMR spectra were recorded on a Bruker spectrometer DMX-300, 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 either fast atom bombardment (FAB) or electron impact (EI). Melting points (m.p.) were determined with a digital electrothermal apparatus without further correction. Distribution of oligomers obtained was measured on a HP5890 Series II gas chromatograph spectrometer.

Compound 2-hydroxy-5-*tert*-butylisophthaldehyde was prepared according to an established procedure [12], 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 these were used commercially without further purification unless stated otherwise.

3.1. Preparations of 2,6-bis(imino)phenoxy ligands

*3.1.1. 2,6-Diformyl-4-tetra-butyl-phenoxy(2,6-diisopropylanil) (**1**)*

To a solution of 2-hydroxy-5-*tert*-butyl-isophthaldehyde (1.76 g, 6 mmol) with a few drops of glacial acetic acid in anhydrous ethanol (25 ml) under N_2 at 50 °C was added a solution of 2,6-diisopropylaniline (2.16 g, 13.2 mmol) in anhydrous ethanol (25 ml) over a period of 30 min with stirring. Then the mixture was refluxed for additional 4 h. Upon cooling to room temperature, the volatiles were removed under vacuum, and the residue was recrystallized from ethanol at -20 °C to give the yellow crystals 2.8 g in 70% yield: m.p. 192–193 °C. IR (KBr): 3414 (m), 3063 (m), 2963, 2869 (s), 1629, 1586 (vs), 1540 (s), 1460 (s), 1360, 1313, 1282, 1227, 1179 (s), 819, 758 (s) cm^{-1}; ^1H-NMR ($CDCl_3$): δ 1.27 (24H, d, $J = 6.8$Hz), 1.49 (9H, s), 3.04–3.14 (4H, m), 7.24 (6H, m), 7.5 (1H, br), 8.37–8.80 (3H, br); EIMS (*m/z*): 524 (M^+, 7.8%), 509 (M^+–CH_3, 5.1%), 349 (M^+–NAr′, 23.6%), 348 (M^+–NAr′–H, 100%), 319 (M^+–CH_3–NAr′, 5.5%); Anal. Calc. for $C_{36}H_{48}N_2O$: C, 82.39; H, 9.22; N, 5.34. Found: C, 82.10; H, 9.29; N, 5.12%.

*3.1.2. 2,6-Diformyl-4-tetra-butyl-phenoxy-(2,6-dimethylanil) (**2**)*

By using the procedure described above for synthesis of **1**, the ligand **2** was obtained by the reaction of 2-hydroxy-5-*tert*-butyl-isophthaldehyde with 2, 6-dimethylaniline as a yellow power in 79% yield. M.p: 162–163 °C. IR (KBr): 3368 (br), 2962 (s), 1630, 1588 (s), 1469 (s), 1369 (s), 1310, 1284, 1263, 1232, 1190 (m), 1091, 1034, 1006 (m), 858, 765 (m) cm^{-1}; ^1H-NMR ($CDCl_3$): δ 1.44 (9H, s), 2.24 (12H, s), 6.95–7.14 (6H, m), 7.30–8.60 (4H, br); EIMS (*m/z*): 412 (M^+, 6.6%), 411 (4.4%), 292 (M^+–NAr′, 100%), 291 (M^+–NAr′–H, 85.4%), 290 (8.3%), 277 (M^+–CH_3–NAr′, 6.6%), 206 (5.1%), 132 (8.2%), 120 (6.9%), 105 (10.1%); Anal. Calc. for $C_{28}H_{32}N_2O$: C, 81.51; H, 7.82; N, 6.79. Found: C, 81.22; H, 8.21; N, 6.34%.

*3.1.3. 2,6-Diformyl-4-tetra-butyl-phenoxy(2,4,6-trimethylanil) (**3**)*

By using the same procedure for synthesis of **1**, the ligand **3** was obtained by the reaction of 2-hydroxy-5-*tert*-butyl-isophthaldehyde with 2, 4, 6-dimethylaniline as a yellow power in 89% yield; m.p. 106.5–107 °C. IR (KBr): 3432 (br), 2964, 2914 (m), 1630 (vs), 1592 (s), 1479 (s), 1373, 1206, 1146,1005, 856 (s), 819, 758 (s) cm^{-1}; ^1H-NMR ($CDCl_3$): δ1.45 (9H, s), 2.22 (12H, s), 2.34 (6H, s), 6.95 (4H, s), 8.63 (2H, s); EIMS (*m/z*): 440 (M^+, 12.4%), 307 (M^+–NAr′19.0%), 306 ((M^+–NAr′–H, 89.8%), 305 (M^+–NAr′–2H, 100%), 304 (10.4%), 220 (10.0%), 135 (9.6%); Anal. Calc. for $C_{30}H_{36}N_2O$: C, 81.78; H, 8.24; N, 6.36. Found: C, 81.49%; H, 8.43; N, 6.74%.

3.2. Complexation with $CoCl_2$

*3.2.1. [2,6-Diformyl-4-tetra-butyl-phenoxy(2,6-diisopropylanil)]·$CoCl_2$ (**4**)*

To a solution of Ligand **1** (104 mg, 0.2 mmol) in anhydrous ethanol (5 ml) under N_2 atmosphere at 50 °C was added a solution of $CoCl_2·6H_2O$ (47.6 mg, 0.2 mmol) in anhydrous ethanol (5 ml). After stirring at 50 °C for 2 h, the solution was cooled to room temperature. The solvent volume was concentrated to 1ml, and diethyl ether (5 ml) was added to precipitate the product as a green power. Filtration, washing with diethyl ether and drying afford of complex **4** as a green power in 76% yield. The product was recrystallized from the solution of ethanol and diethyl ether: m.p. > 300 °C. IR (KBr): 3427 (br, s), 2964 (s), 1638 (vs), 1591 (s), 1537 (s), 1463(m), 1388, 1363, 1328, 1289, 1225, 1127 (m), 1059 (m) cm^{-1}; FABMS (*m/z*): 618 (M^+–Cl), 582 (M^+–2Cl), 525 (M^+–$CoCl_2$); Anal. Calc. for: $C_{36}H_{48}N_2OCoCl_2·2H_2O$: C, 62.61; H, 7.59; N, 4.06. Found: C, 62.37; H, 7.19; N, 3.80%.

*3.2.2. [2,6-Diformyl-4-tetra-butyl-phenoxy(2, 4, 6-dimethylanil)]·$CoCl_2$ (**5**)*

Using the procedure described in Section 3.2.1, the reaction of ligand **2** and $CoCl_2·6H_2O$ gave complex **5** in

Table 3
Activity and distribution for the oligomerization

Catalyst		MAO (mmol)	Activity[a]	Distribution of the oligomerization (%)						
Complex	(μmol)			C_4	C_6	C_8	C_{10}	C_{12}	C_{14}	C_{16}
4	10	14	$\sim 10^3$	100						
5	10	14	$\sim 10^3$	100						
6	10	14	$\sim 10^3$	100						
7	5	7	1.2×10^5	49.5	28.2	14.6	3.4	1.9	1.4	1.0
8	5	7	1.9×10^5	77	23					
9	5	7	2.1×10^5	69	31					

Toluene solvent, 1 atm of ethylene, reaction time 0.5 h.

[a] $g\ mol^{-1}\ h^{-1}\ atm^{-1}$.

75% yield as a green powder: m.p. > 300 °C. IR (KBr): 3434 (m), 2963 (s), 1638 (s), 1620 (s), 1539 (s), 1471(m), 1397, 1381, 1363, 1327, 1290 (w), 1236, 1184 (m) cm^{-1}; FABMS (*m*/*z*): 541 (M^+), 506 (M^+–Cl), 470 (M^+–2Cl), 412 (M^+–$CoCl_2$); Anal. Calc. for $C_{28}H_{32}N_2O\cdot CoCl_2$: C, 62.00; H, 5.95; N, 5.16. Found: C, 61.65; H, 5.89; N, 4.90%.

3.2.3. [2,6-Diformyl-4-tetra-buthyl-phenoxy (2,4,6-trimethylanil)]$CoCl_2$ (**6**)

Similarly, ligand **3** reacted with $CoCl_2\cdot 6H_2O$ to give complex **6** in 45% yield as a green powder: m.p. > 300 °C. IR (KBr): 3435 (br, s), 2960, 2915 (m), 1638 (s), 1591 (s), 1539 (m), 1479 (m), 1239, 1201, 1148(m), 1063, 1028(m) cm^{-1}; FABMS (*m*/*z*): 534 (M^+–Cl), 498 (M^+–2Cl), 441 (M^+–$CoCl_2$); Anal. Calc. for $C_{30}H_{36}N_2O\cdot CoCl_2$: C, 63.16; H, 6.36; N, 4.91. Found: C, 62.80; H, 6.23; N, 4.91%.

3.3. Complexation with (DME)$NiBr_2$

3.3.1. [2,6-Diformyl-4-tetra-butyl-phenoxy(2,6-diisopropylanil)]$NiBr_2$ (**7**)

(DME)$NiBr_2$ (77 mg, 0.25 mmol) and 2,6-diformyl-4-tetra-butyl-phenoxy (2,6-diisopropylanil) (167 mg, 0.32 mmol) were combined in a Schlenk flask under an N_2 atmosphere. CH_2Cl_2 (10 ml) was added, and the reaction mixture was stirred at room temperature for 24 h. The supernatant liquid was removed, and the product was filtrated, washed with 3 × 4 ml of Et_2O and dried to give 139 mg of **7** in 73% yield: m.p. 238 °C (dec.). IR (KBr): 3389 (br), 2964 (m), 1637 (s), 1538 (s), 1463 (m), 1390 (m), 1363, 1328,1289, 1234, 1177 (m), 1060 (m) cm^{-1}; FABMS (*m*/*z*): 663 (M^+–Br), 582 (M^+–2Br), 525 (M^+–$NiBr_2$); Anal. Calc. for $C_{36}H_{48}N_2ONiBr_2\cdot H_2O$: C, 56.80; H, 6.62; N, 3.68. Found: C, 56.80; H, 6.37; N, 3.52%.

3.3.2. [2,6-Diformyl-4-tetra-butyl-phenoxy(2,6-dimethylanil)]$NiBr_2$ (**8**)

The procedure described as above Section 3.3.1 by using ligand **2** and (DME)$NiBr_2$ gave a complex **8** in 85% yield as a light brown powder: m.p. 208 °C (Dec). IR (KBr): 3391 (br), 2961 (m), 1640 (s), 1535 (s), 1472 (s), 1400, 1364, 1334, 1292 (w), 1238, 1182 (m) cm^{-1}; FABMS (*m*/*z*): 551 (M^+–Br), 471 (M^+–2Br), 414 (M^+–$NiBr_2$); Anal. Calc. for: $C_{28}H_{32}N_2ONiBr_2\cdot H_2O$: C, 51.81; H, 5.28; N, 4.32. Found: C, 51.47; H, 5.62; N, 3.97%.

3.3.3. 2,6-Diformyl-4-tetra-butyl-phenoxy(2, 4, 6-trimethylanil) $NiBr_2$ (**9**)

Similarly, the reaction of ligand **3** and (DME)$NiBr_2$ gave a complex **9** in 85% yield as a light brown powder: m.p. 202 °C (Dec). IR (KBr): 3380 (br), 2960 (m), 1638 (s), 1536 (s), 1364, 1330, 1292 (w), 1239, 1200 (m), 1143(w), 1064, 1024(s), 853(s) cm^{-1}; FABMS (*m*/*z*): 579 (M^+–Br), 498 (M^+–2Br), 441 (M^+–$NiBr_2$); Anal. Calc. for $C_{30}H_{36}N_2ONiBr_2\cdot H_2O$: C, 53.21; H, 5.66; N, 4.14. Found: C, 53.58; H, 5.29; N, 4.48%.

3.4. X-ray crystal structure determination of ligand **1** and complex **4**

Both intensity data sets were collected at 293K on a Nonius KappaCCD diffractometer with graphite-monochromated Mo–K_α radiation ($\lambda = 0.71073$ Å). 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 absorption. Both structures were solved by direct method, and refined by full-matrix least-squares on F^2, using SHELX-98 package [13]. For ligand **1**, all non-H atoms were refined anisotropically. The hydrogen atom was found from the different Fourier map. For complex **4**, several methyl carbon atoms, C21, C22, C32, C35, C36 were assigned into two positions, the two type structures were refined to occupancies of 0.56(1) and 0.44(1), respectively. In addition, C23 was also assigned into two positions with occupancies of 0.70(1) and 0.30(1), respectively. The hydrogen atoms of the water molecules were found from the different Fourier map, however, refined using riding model. Crystallographic parameters for ligand **1** and complex **4** are collected in Table 3. Detail crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited at the Cambridge Crystallographic Data Centre and allocated the deposition numbers CCDC 167796 and 167797.

3.5. General procedure for ethylene oligomerization

A flame dried three-neck round flask was vacuated-filled three times by nitrogen. Then ethylene was charged with 50 ml of freshly distilled toluene and stirred. At the room temperature, the aluminum cocatalyst MAO was added via syringe. The solution was stirred for 10 min, then the precatalyst complex (**4**–**9**, in 5 ml toluene) was added to the reaction mixture via syringe. The reaction mixture was stirred under 1 atm ethylene pressure for 30 min, and the oligomerization was terminated with acidified ethanol. An aliquot of the reaction mixture was analyzed by GCMS. Their activity and distribution for the oligomers were collected in the Tables 3 and 4.

4. Supplementary material

Full information on the crystal structure can be ordered from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-1223-336-033; e-mail: de-

Table 4
Crystal Data, collection parameters, and refinements for $C_{36}H_{48}N_2O$ (**1**) and $C_{36}H_{48}N_2O \cdot CoCl_2 \cdot 2H_2O$ (**4**)

	Ligand **1**	Complex **4**
Empirical formula	$C_{36}H_{48}N_2O$	$C_{36}H_{48}N_2O \cdot CoCl_2 \cdot 2H_2O$
Formula weight	524.76	689.62
Space group	$P2_1/n$	$P2_12_12_1$
Crystal system	monoclinic	orthorhombic
a (Å)	9.9570(2)	14.5582(3)
b (Å)	17.4138(3)	16.5895(4)
c (Å)	19.0076(4)	16.8190(2)
β (°)	99.5295(3)	90
V (Å^3)	3250.23(11)	4062.0(14)
Z	4	4
Crystal dimensions (mm)	$0.40 \times 0.40 \times 0.17$	$0.17 \times 0.35 \times 0.40$
Crystal color	Yellow	Green
D_{calc} (g cm^{-3})	1.072	1.128
Absorption coefficient (mm^{-1})	0.063	0.586
θ_{max} (°)	27.51	29.16
Diffractometer	NONIUS KappaCCD	NONIUS KappaCCD
T (K)	293(2)	293(2)
Independent reflections	7380	10 833
Reflections collected	48396	74 180
Independent reflections observed [$I > 2\sigma(I)$]	5559	7473
Wave length (Å)	0.71073	0.71073
R (F)	0.0649	0.0597
wR	0.1719	0.1587
Goodness-of-fit on F^2	1.018	1.024
$\Delta\rho_{max}$ (e Å^{-3})	0.346	0.652
$\Delta\rho_{min}$ (e Å^{-3})	−0.296	−0.439

posit@ccdc.cam.ac.uk or www:http://www.ccdc.ac.uk), upon request, quoting the deposition number CCDC 167796 and 167797.

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