

A series of new zirconium complexes bearing bis(phenoxyketimine) ligands: Synthesis, characterization and ethylene polymerization

Shangtao Chen^{a,b}, Xiaofan Zhang^{a,b}, Hongwei Ma^a, Yingying Lu^{a,*},
Zhicheng Zhang^{a,b}, Huayi Li^{a,b}, Zhanxia Lu^{a,b}, Nannan Cui^{a,b}, Youliang Hu^a

^a Joint Laboratory of Polymer Science and Materials, Key Laboratory of Engineering Plastics, Institute of Chemistry, the Chinese Academy of Sciences, Beijing 100080, China

^b Graduate School of the Chinese Academy of Sciences, Beijing 100039, China

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Abstract

A series of new zirconium complexes bearing bis(phenoxyketimine) ligands, bis((3,5-di-*tert*-butyl-C₆H₂-2-O)R₁C=N (2-R₂-C₆H₄))ZrCl₂ {R₁ = Me, R₂ = H (**2a**); R₁ = Et, R₂ = H (**2b**); R₁ = Ph, R₂ = H (**2c**); R₁ = 2-Me-Ph, R₂ = H (**2d**); R₁ = 2-F-Ph, R₂ = H (**2e**); R₁ = 2-Cl-Ph, R₂ = H (**2f**); R₁ = 2-Br-Ph, R₂ = H (**2g**); R₁ = Ph, R₂ = Me (**2h**); R₁ = Ph, R₂ = F (**2i**)}, have been prepared, characterized and tested as catalyst precursors for ethylene polymerization. Crystal structure analysis reveals that complex **2c** has a six coordinate center in a distorted octahedral geometry with *trans*-O, *cis*-N, *cis*-Cl arrangement which possesses approximate C₂ symmetry. When activated with methylaluminumoxane (MAO), complexes **2a–2i** exhibited high ethylene polymerization activities of 10⁶–10⁸ g PE (mol M h)⁻¹. Compared with the bis(phenoxyimine) zirconium analogues bis((3,5-di-*tert*-butyl-C₆H₂-2-O)CH=NC₆H₅)ZrCl₂ (**3**), the introduction of substituent on the carbon atom of the imine double bond enhanced the catalytic activity and molecular weight of prepared polyethylene. Especially, when the H atom at the carbon atom of the imine double bond was replaced by 2-fluoro-phenyl with strong electronic-withdrawing property, complex **2e** displayed the highest catalytic activity, and the polyethylene obtained possessed the highest molecular weight and melt point.

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1. Introduction

Olefin polymerization by well-defined single-site transition metal catalysts has attracted considerable attention in the fields of organometallic chemistry and polymer chemistry both for academic and industrial interests [1]. During the past two decades for development of new homogeneous transition metal complex,

ligand design and modification played a key role for optimizing polymerization activity as well as polymer microstructure [2]. Advances in the understanding of homogeneous polymerization mechanism have resulted in the design and development of highly active single component non-metallocene [3].

Recently, much attention has been focused on the early and late transition metal non-metallocene complexes incorporating [N,O] based multidentate ligands [4]. Grubbs and co-workers [4a,4b] discovered Ni metal complexes bearing phenoxyimine moieties which exhibited high activity for ethylene copolymerization with

* Corresponding author. Tel.: +86 10 6256 2697; fax: +86 10 6255 4061.

E-mail address: yylu@iccas.ac.cn (Y. Lu).

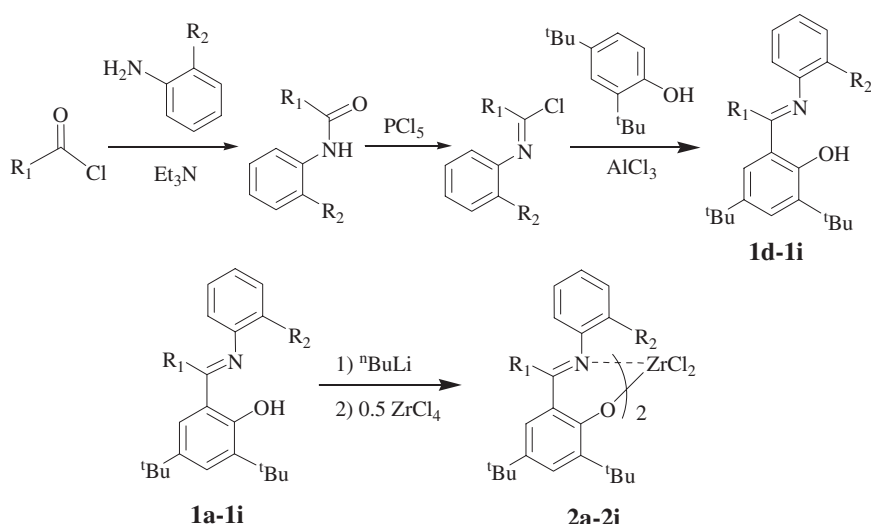
polar monomer to produce functional polyolefin. Almost at the same time, scientists at Mitsui Chemicals developed a series of group IV transition metal complexes bearing bis(phenoxyimine) ligands for α -olefin polymerization [5,6]. The independent work of them and other groups [7] indicated that these complexes were very active catalysts for olefin polymerization and copolymerization. The catalytic activity of these catalysts was highly dependent on the property of the substituents in the *ortho*-position of the phenoxy ring and on the nitrogen atom of the imine double bond. The great variety of these complexes conveniently obtained by changing the substituents of the phenol and aniline moieties of the phenoxyimine ligand allows significant modifications in the steric and electronic features of catalyst. We expected that the substituent on the carbon atom of the imine double bond also affects the catalytic performance of the phenoxy-based complexes. To the best of our knowledge, there have been very few examples focused on the effect of substituents at the carbon atom of the imine double bond on the catalytic activity. Coates and co-workers [8] found that titanium complexes bearing bis(phenoxyketimine) ligands without fluorine-containing substituent in the aniline moiety were active for living ethylene polymerization. Kettunen et al. [9] prepared nickel metal complex supported by phenoxyketimine ligand, but no result of these complexes for olefin polymerization was reported. In this paper, nine new zirconium complexes bearing bis(phenoxyketimine) ligands, where there are alkyl or aryl groups (R_1) on the

carbon atom of the imine double bond, have been synthesized and used for ethylene polymerization. The steric bulk and electronic effects caused by substituents on the carbon atom of the imine double bond (R_1) on catalytic activities of ethylene polymerization were investigated. The preliminary work showed that all these new zirconium complexes were highly active catalysts for ethylene polymerization.

2. Results and discussion

2.1. Synthesis and characterization of ligands and corresponding zirconium complexes

The synthesis of phenoxyketimine ligand and corresponding zirconium complexes was summarized in Scheme 1. The ligands **1d–1i** were prepared in a similar way as published in [8]. Amides used for the ligand synthesis were prepared by treating equimolar amounts of acid chloride, aniline, and triethylamine in methylene chloride at 0 °C and recrystallized before use. The desired ligand was prepared through Friedel-Crafts reaction of imidoyl chlorides generated in situ by the reaction of amides and PCl_5 with 2,4-di-*tert*-butylphenol in moderate to good yield. This method was more efficient for the introduction of aryl or electron-withdrawing containing group onto the carbon atom of the imine double bond compared with the condensation method between 2-hydroxyl-phenone and aniline



	a	b	c	d	e	f	g	h	i	3
R_1	Me	Et	Ph	2-Me-Ph	2-F-Ph	2-Cl-Ph	2-Br-Ph	Ph	Ph	H
R_2	H	H	H	H	H	H	H	Me	F	H

Scheme 1. Synthesis of phenoxyketimine ligands and corresponding zirconium complexes.

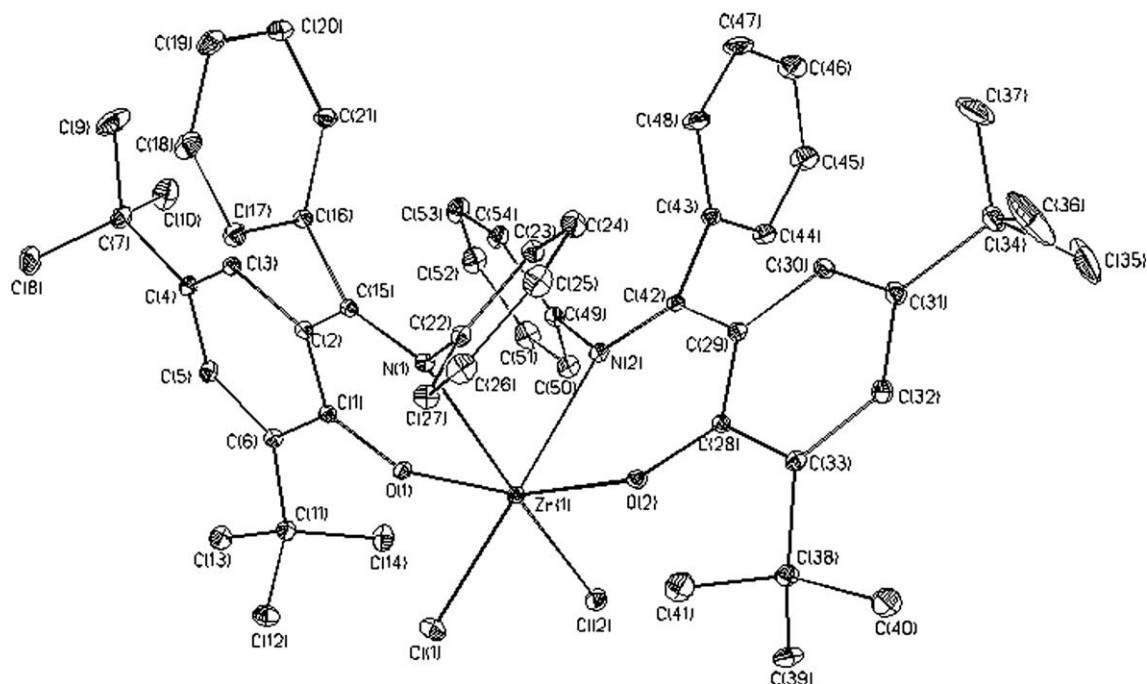


Fig. 1. Thermal ellipsoid drawing of complex **2c**. Hydrogen atoms are omitted for clarity.

reported in the literature [9]. Treatment of lithium salt of the ligand with 0.5 equivalent $ZrCl_4$ in ether gave the bis(phenoxyketimine) zirconium complex in moderate yield. Ligands **1d–1i** have been well characterized by 1H NMR, ^{13}C NMR, mass spectrometry and elemental analysis. The formation of the corresponding metal complexes was supported very well by 1H NMR and elemental analysis. 1H NMR studies showed that these complexes existed as isomeric mixtures in solution, which has already been observed by Coates and co-workers [8] for bis(phenoxyketimine) titanium complexes and by Fujita and co-workers [10] for bis(phenoxyimine) group IV complexes. The crystal structure of **2c** has been further studied by X-ray diffraction analysis. Thermal ellipsoid diagram of complex **2c** was presented in Fig. 1. The data collection and structure refinement of the analysis were listed in Table 1. The crystallography study revealed that molecule **2c** in solid state has a six coordinate center in a distorted octahedral geometry with *trans*-O, *cis*-N, *cis*-Cl arrangement which possesses approximate C_2 symmetry. The configuration of **2c** closely resembles its bis(phenoxyketimine) titanium [8] and bis(phenoxyimine) zirconium [11] analogues. For complex **2c**, the phenyl ring of the aniline moiety (Ph3) and the phenyl (Ph2) on carbon atom of the imine double bond orient themselves nearly perpendicular to the phenol plane (Ph1) with dihedral angle as 74.8° and 78.2° respectively, while the two phenyl rings Ph3 and Ph2 tilt to each other at an angle of 56.4° . The Zr1–O1–Ph1–C15–N1 combination of **2c** is almost coplanar with an average deviation from the mean plane of 0.09 \AA . The Cl–Zr–Cl angle is 99.14° (Table 2). The

cis-location site of the chlorine atoms around the metal center in the complex indicated its potential as catalyst precursor for olefin polymerization [12].

Table 1
Crystal data and structure refinement of complex **2c**

Empirical formula	$C_{54}H_{60}Cl_2N_2O_2Zr$
F_w	931.16
Temperature (K)	293(2)
Crystal size (mm)	$0.722 \times 0.672 \times 0.591$
Cryst system	Orthorhombic
Space group	$P2_12_12_1$
a (Å)	16.235(3)
b (Å)	17.165(3)
c (Å)	18.097(4)
α (°)	90
β (°)	90
γ (°)	90
V (Å ³)	5043.2(17)
Z , calculated density (Mg/m ³)	4, 1.226
Absorption coefficient (mm ⁻¹)	0.364
θ Range for data collection (°)	1.73–27.48
Limiting indices	$-18 \leq h \leq 21$, $-20 \leq k \leq 22$, $-23 \leq l \leq 23$
Reflections collected/unique	43268/6239
Completeness to θ maximum	98.1%
Absorption correction	Empirical
Refinement method	Full-matrix least-squares on F^2
Number of data/restraints/parameters	6239/0/551
Goodness-of-fit on F^2	1.008
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0311$, $wR_2 = 0.0765$
R indices (all data)	$R_1 = 0.0372$, $wR_2 = 0.0859$
Largest difference peak and hole (e Å ⁻³)	0.381 and -0.401

Table 2
Selected bond distances (Å) and angles (°) for complex **2c**

Bond distances (Å)	
Zr(1)–O(2)	1.973(2)
Zr(1)–O(1)	1.973(2)
Zr(1)–N(1)	2.349(2)
Zr(1)–N(2)	2.381(3)
Zr(1)–Cl(2)	2.422(1)
Zr(1)–Cl(1)	2.427(1)
O(1)–C(1)	1.333(3)
O(2)–C(28)	1.328(3)
N(1)–C(15)	1.305(4)
N(1)–C(22)	1.457(3)
N(2)–C(42)	1.306(4)
N(2)–C(49)	1.454(4)
Bond angles (°)	
O(2)–Zr(1)–O(1)	164.38(9)
O(2)–Zr(1)–N(1)	92.74(8)
O(1)–Zr(1)–N(1)	75.53(8)
O(2)–Zr(1)–N(2)	75.32(8)
O(1)–Zr(1)–N(2)	92.21(9)
N(1)–Zr(1)–N(2)	79.66(8)
O(2)–Zr(1)–Cl(2)	95.31(7)
O(1)–Zr(1)–Cl(2)	94.40(6)
N(1)–Zr(1)–Cl(2)	166.30(6)
N(2)–Zr(1)–Cl(2)	91.68(6)
O(2)–Zr(1)–Cl(1)	94.79(6)
O(1)–Zr(1)–Cl(1)	95.72(7)
N(1)–Zr(1)–Cl(1)	91.19(7)
N(2)–Zr(1)–Cl(1)	166.03(6)
Cl(2)–Zr(1)–Cl(1)	99.14(4)

2.2. Polymerization of ethylene by complexes **2a–2i**

The catalytic properties of complexes **2a–2i** for ethylene polymerization were evaluated using MAO as cocatalyst. The polymerization was performed in toluene at atmospheric pressure and the results were listed in Table 3. Bis(phenoxyimine) zirconium complex **3**, bearing a hydrogen at the R₁ position yielded polyethylene with an M_w of 12,000 and an activity of 1.6 kg PE (mmol Zr h)⁻¹ at 20 °C. Compared with bis(phenoxyimine) complex **3**, the introduction of substituent into the carbon atom of the imine double bond greatly enhanced

the catalytic activity of ethylene polymerization and the molecular weight of products as shown in Table 3. When the methyl substituent was introduced, complex **2a** gave higher molecular weight polyethylene (M_w 89,000) with greatly increased catalytic activity of 12.9 kg PE (mmol Zr h)⁻¹. The introduction of ethyl group led to further increased catalytic activity of 41.1 kg PE (mmol Zr h)⁻¹. For steric consideration of the substituents H (**3**) < Me (**2a**) < Et (**2b**) of R₁, the catalytic activity followed the order **3** < **2a** < **2b**, while the molecular weight of PE followed **3** < **2b** < **2a**. There was no direct relationship between the catalytic performance and the steric bulk of the R₁ substituent. This might be due to the complicated electronic structures between the complexes resulting from the introduction of R₁ substituent.

From the ethylene polymerization result listed in Table 3, the substituent in the *ortho*-position of the phenyl group of R₁ exhibited significant effect on catalytic activity. Compared with **2c**, the introduction of methyl in the *ortho*-position of R₁ (**2d**) resulted in dramatic decrease of catalytic activity to 3.4 kg (mmol Zr h)⁻¹, while the introduction of fluorine group (**2e**) led to a significant increase of catalytic activity to 216.3 kg (mmol Zr h)⁻¹. This enhancement in activity might be due to the increased positive charge of the metal center caused by the electron-withdrawing effect of the fluorine containing substituent which favored the coordination of ethylene monomer with the metal center. As the decrease of the electron-withdrawing effect of groups from F, Cl to Br, the catalytic activity and molecular weight of polyethylene obtained decreased accordingly. The steric and electronic effects could be combined together to account for this. These results indicated that the introduction of electronic withdrawing group led to the increase of catalytic activity for ethylene polymerization.

The effect of the substituent in the *ortho*-position of the aniline moiety on catalytic activity has also been investigated. On the one hand, the introduction of alkyl group in the *ortho*-position of the aniline moiety resulted

Table 3
Ethylene polymerization results by complexes **2a–2i** in toluene activated with MAO^a

Run	Complex	Yield (g)	Activity (kg (mmol Zr h) ⁻¹)	T _m (°C)	ΔH _f (J/g)	M _w ^b	M _w /M _n ^b
1	3 /0.2 μmol	0.053	1.6	127	220.8	12000	1.43
2	2a /0.2 μmol	0.431	12.9	134	207.6	89000	1.97
3	2b /0.2 μmol	1.373	41.2	133	194.0	40000	2.07
4	2c /0.2 μmol	0.670	20.1	133	200.9	31000	1.72
5	2d /0.2 μmol	0.112	3.4	134	226.4	41000	1.92
6	2e /0.02 μmol ^c	0.721	216.3	135	170.4	165000	2.43
7	2f /0.2 μmol	1.320	39.6	132	181.4	53000	1.94
8	2g /0.2 μmol	0.407	12.2	134	191.9	32000	2.03
9	2h /0.2 μmol	0.057	1.7	132	213.1	104000	3.84
10	2i /0.2 μmol	1.129	33.9	133	200.6	71000	2.76

^a Conditions: 20 °C, V_{total} = 100 mL, Al/Zr = 6000, 0.1 MPa ethylene pressure, polymerization time: 10 min.

^b Determined by GPC relative to polystyrene standard.

^c 2.12 g polyethylene was produced for 2 min when 0.2 μmol complex was used. In order to eliminate the problem of mass transfer, the amount of complex **2e** was changed to 0.02 μmol.

Table 4
Ethylene polymerization results by complexes **2b**, **2c** and **2e** at different temperature^a

Run	Complex	Yield (g)	T_p (°C)	Activity (kg (mmol Zr h) ⁻¹)
1	2b /0.2 μmol	1.052	0	31.6
2	2b /0.2 μmol	1.373	20	41.2
3	2b /0.2 μmol	0.310	40	9.3
4	2b /0.2 μmol	0.021	60	0.6
5	2c /0.2 μmol	0.418	0	12.5
6	2c /0.2 μmol	0.670	20	20.1
7	2c /0.2 μmol	0.174	40	5.2
8	2c /0.2 μmol	0.012	60	0.36
9	2e /0.02 μmol	0.366	0	109.8
10	2e /0.02 μmol	0.721	20	216.3
11	2e /0.02 μmol	0.234	40	70.2
12	2e /0.02 μmol	0.038	60	11.4
13	2e /0.02 μmol	0.010	80	3.0

^a Conditions: toluene ($V_{\text{total}} = 100$ mL), 10 min, Al/Zr = 6000, 0.1 MPa ethylene pressure.

in the significant decrease of the catalytic activity. On the other hand, if the hydrogen atom at the R_2 position was replaced with a fluorine atom, the catalytic activity was increased to 33.9 kg PE (mmol Zr h)⁻¹. The catalytic increase might be attributed to the stability of metal center favored by the introduction of substituent with strong electronic-withdrawing property.

It is interesting to compare the polymerization results of complex **2e** and **2i**, whose substituents on carbon atom and nitrogen atom of the imine double bond were exchanged between phenyl and 2-fluoro-phenyl. When 2-fluoro-phenyl was on the N atom and phenyl was on the C atom, complex **2i** exhibited an activity as high as 33.9 kg PE (mmol Zr h)⁻¹ and the M_w of product was 71,000. When the two groups were exchanged, complex **2e** possessed six times higher catalytic activity and two times higher M_w of polyethylene than **2i**. This result might suggest that the attachment of electron-withdrawing group in the carbon atom of the imine double resulted in more significant enhancement on the catalytic properties than that in the nitrogen atom for these bis(phenoxyketimine) zirconium complexes.

The polymerization of complex **2b**, **2c** and **2e** for ethylene polymerization has been studied at different temperatures. The results were collected in Table 4. All three catalysts showed the highest catalytic activity at about 20 °C. Then activity decreased rapidly as the temperature increased which may be due to the decomposition of the complexes at high temperature. More detailed work of these bis(phenoxyketimine) zirconium complexes for olefin polymerization is still under investigation.

3. Conclusion

In summary, nine new bis(phenoxyketimine) zirconium complexes **2a–2i** bearing bis(phenoxyketimine)

ligands have been synthesized and characterized as designed. The catalytic activities of these compounds for ethylene polymerization at atmospheric pressure have been investigated using MAO as the cocatalyst. All complexes showed high catalytic activities for ethylene polymerization especially at 20 °C. The introduction of substituent into the R_1 position of the phenoxy-based ligand enhanced the catalytic activity of the complex and the molecular weight of polyethylene produced. The attachment of electron-withdrawing containing group onto the carbon atom of the imine double bond led to significant increase in catalytic activity of the complexes and molecular weight of prepared polyethylene. Especially, the introduction of 2-fluoro-phenyl group into the R_1 position gave the highest catalyst activity for ethylene polymerization and the highest molecular weight and melting point of the obtained polymers.

4. Experimental

All manipulations of air- and/or moisture sensitive compounds were carried out using drybox procedures or standard Schlenk techniques. ¹H NMR (300 MHz) and ¹³C NMR (75 MHz) spectra were performed on a Bruker DMX-300 spectrometer. Mass spectra were carried out with an electron impact (EI) instrument (Kratos AEI MS-50). Elemental analyses were obtained using Carlo Erba 1106 and ST02 apparatus. Molecular weights (M_w and M_n) and polydispersities (M_w/M_n) were determined by high temperature gel-permeation chromatography (GPC) on a PL-GPC220 instrument at 140 °C in trichlorobenzene and the data were analyzed relative to polystyrene standards. Melting temperatures (T_m) of polyethylene were measured by a Perkin–Elmer differential scanning calorimetry (DSC) operating at a heating rate of 10 °C/min and determined in the second scan.

Ethylene for polymerization was obtained from Yanshan Petro-chemical Company SINOPEC China. Methylaluminoxane (MAO) solution (1.4 M) in toluene was purchased from Albemarle. ⁿBuLi (1.6 M) in hexane was purchased from Acros. Ligand **1a–1c** [8] and complex **3** [13] were prepared according to published procedures. Amides for the ligand syntheses were prepared by treating equimolar amounts of acid chloride, aniline, and triethylamine in methylene chloride at 0 °C. The amides were recrystallized from hot toluene and dried before use. All other chemicals were commercially available and used as received. Toluene, tetrahydrofuran, hexane, and ether were refluxed over sodium-benzophenone and degassed under argon. Methylene chloride was vigorous degassed to remove oxygen and then distilled from P₂O₅. All glasswares were flame dried before use.

4.1. Synthesis of ligands **1d–1i**

Ligands **1d–1i** were prepared in a way similar to established procedure [8]. The synthetic route is depicted in Scheme 1. Typically, amide (1 equiv.) and PCl_5 (1 equiv.) were combined in a Schlenk flask under argon, dry methylene chloride was slowly added at 0 °C. The cold bath was removed, the solution was stirred for 5 h at room temperature. After removing the solvent under vacuum, the solid residue was dissolved in methylene chloride and filtered through a celite pad. The resulting clear solution was transferred via cannula to a Schlenk flask filled with a slurry of AlCl_3 (1.2 equiv.) in methylene chloride at 0 °C. The solution was stirred for 10 min before 10 mL methylene chloride solution of 2,4-di-*tert*-butylphenol (0.95 equiv.) was added. The reaction mixture was stirred at room temperature for 24 h. Pouring the resulting solution to ice water, the organic layer was separated and then washed with water, 1.0 M Na_2CO_3 and brine, and dried over Na_2SO_4 . After filtration and solvent removal, the residual yellow or orange solid was chromatographed on silica (10% ethyl acetate/hexane). The solution obtained was concentrated and placed at –30 °C overnight. The ligand was obtained as crystal solid in moderate to good yield (based on phenol employed).

(3,5-Di-*tert*-butyl- C_6H_2 -2-OH)(2-Me- C_6H_4) $\text{C}=\text{NC}_6\text{H}_5$ (**1d**): bright yellow solid, yield (64%), ^1H NMR (CDCl_3 , 300 MHz): δ 14.94 (1H, b, OH), 7.44 (1H, d, $^4J = 1.2$ Hz), 7.23 (1H, t, $^3J = 7.8$ Hz), 7.15–7.07 (5H, m), 6.96 (1H, t, $^3J = 7.4$ Hz), 6.82–6.78 (3H, m), 2.10 (3H, s) (Ph- CH_3), 1.52 (9H, s, $\text{C}(\text{CH}_3)_3$), 1.12 (9H, s, $\text{C}(\text{CH}_3)_3$); ^{13}C NMR (CDCl_3 , 75 MHz): δ 174.0 (N=C), 159.5 (ArC-OH), 146.4, 138.7, 136.9, 134.8, 134.4, 129.7, 128.5, 128.0, 127.7, 125.8, 124.9, 124.3, 121.9, 118.3, 35.0, 33.8, 31.0, 29.3, 19.7; MS (EI): 399 (53, M^+), 384 (100, $\text{M}^+ - 15$), 356 (19, $\text{M}^+ - 43$); Anal. Calc. for $\text{C}_{28}\text{H}_{33}\text{NO}$: C, 84.17; H, 8.32; N, 3.51. Found: C, 84.10; H, 8.36; N, 3.48%.

(3,5-Di-*tert*-butyl- C_6H_2 -2-OH)(2-F- C_6H_4) $\text{C}=\text{NC}_6\text{H}_5$ (**1e**): bright orange solid, yield (71%), ^1H NMR (CDCl_3 , 300 MHz): δ 14.70 (1H, s, OH), 7.47 (1H, d, $^4J = 2.1$ Hz), 7.36 (1H, m), 7.13–6.91 (6H, m), 6.87 (1H, s), 6.80 (2H, d, $J = 7.8$ Hz), 1.51 (9H, s, $\text{C}(\text{CH}_3)_3$), 1.15 (9H, s, $\text{C}(\text{CH}_3)_3$); ^{13}C NMR (CDCl_3 , 75 MHz): δ 169.0 (N=C), 159.3, 158.0 (d, $^1J_{\text{CF}} = 247.5$ Hz), 147.0, 139.0, 137.1, 130.8 (d, $J_{\text{CF}} = 7.5$ Hz), 130.0 (d, $J_{\text{CF}} = 7.5$ Hz), 128.2 (d, $J_{\text{CF}} = 15.1$ Hz), 125.6, 124.4, 123.6 (d, $J_{\text{CF}} = 7.5$ Hz), 122.7 (d, $J_{\text{CF}} = 15.1$ Hz), 121.3, 118.2, 115.3 (d, $J_{\text{CF}} = 22.5$ Hz), 35.1, 33.9, 31.1, 29.4; MS (EI): 403 (53, M^+), 388 (100, $\text{M}^+ - 15$), 360 (26, $\text{M}^+ - 43$); Anal. Calc. for $\text{C}_{27}\text{H}_{30}\text{FNO}$: C, 80.36; H, 7.49; N, 3.47. Found: C, 80.31; H, 7.52; N, 3.40%.

(3,5-Di-*tert*-butyl- C_6H_2 -2-OH)(2-Cl- C_6H_4) $\text{C}=\text{NC}_6\text{H}_5$ (**1f**): bright yellow solid, yield (69%), ^1H NMR (CDCl_3 , 300 MHz): δ 14.68 (1H, s, OH), 7.45 (1H, s), 7.34 (1H,

d, $J = 7.8$ Hz), 7.26–7.08 (5H, m), 6.96 (1H, t, $J = 7.5$ Hz), 6.86 (2H, d, $J = 7.7$ Hz), 6.75 (1H, s), 1.51 (9H, s, $\text{C}(\text{CH}_3)_3$), 1.14 (9H, s, $\text{C}(\text{CH}_3)_3$); ^{13}C NMR (CDCl_3 , 75 MHz): δ 169.9, 158.1, 145.6, 137.8, 135.8, 133.0, 130.9, 128.7, 127.9, 127.0, 126.8, 125.1, 124.4, 123.2, 120.2, 116.5, 33.9, 32.7, 29.9, 28.2; MS (EI): 419 (58, M^+), 404 (100, $\text{M}^+ - 15$), 376 (22, $\text{M}^+ - 43$); Anal. Calc. for $\text{C}_{27}\text{H}_{30}\text{ClNO}$: C, 77.21; H, 7.20; N, 3.34. Found: C, 77.15; H, 7.16; N, 3.36%.

(3,5-Di-*tert*-butyl- C_6H_2 -2-OH)(2-Br- C_6H_4) $\text{C}=\text{NC}_6\text{H}_5$ (**1g**): orange solid, yield (73%), ^1H NMR (CDCl_3 , 300 MHz): δ 14.73 (1H, s, OH), 7.59 (1H, d, $J = 7.8$ Hz), 7.51 (1H, s), 7.27 (1H, t, $J = 7.4$ Hz), 7.22–7.12 (4H, m), 7.01 (1H, t, $J = 7.3$ Hz), 6.95 (2H, d, $J = 7.8$ Hz), 6.80 (1H, s), 1.57 (9H, s, $\text{C}(\text{CH}_3)_3$), 1.19 (9H, s, $\text{C}(\text{CH}_3)_3$); ^{13}C NMR (CDCl_3 , 75 MHz): δ 171.5, 159.0, 146.3, 138.6, 136.6, 135.9, 131.9, 129.7, 129.6, 127.8, 127.5, 126.4, 125.5, 124.1, 121.2, 117.2, 34.7, 33.5, 30.7, 29.1; MS (EI): 463 (62, $\text{M}^+ - \text{H}$), 448 (100, $\text{M}^+ - \text{H} - 15$), 420 (25, $\text{M}^+ - \text{H} - 43$). Anal. Calc. for $\text{C}_{27}\text{H}_{30}\text{BrNO}$: C, 69.82; H, 6.51; N, 3.02. Found: C, 69.80; H, 6.49; N, 3.04%.

(3,5-Di-*tert*-butyl- C_6H_2 -2-OH)Ph $\text{C}=\text{N}$ (2-Me- C_6H_4) (**1h**): yellow crystal, yield (62.8%), ^1H NMR (CDCl_3 , 300 MHz): δ 15.15 (1H, s, OH), 7.52 (1H, d, $^4J(\text{H,H}) = 2.3$ Hz), 7.32 (3H, m), 7.19–7.11 (3H, m), 7.00 (1H, d, $^4J(\text{H,H}) = 2.3$ Hz), 6.92 (2H, m), 6.50 (1H, m), 2.34 (3H, s, CH_3), 1.57 (9H, s, $\text{C}(\text{CH}_3)_3$), 1.20 (9H, s, $\text{C}(\text{CH}_3)_3$); ^{13}C NMR (CDCl_3 , 75 MHz): δ 174.1, 160.1, 146.2, 138.8, 137.3, 134.9, 130.0, 129.8, 128.8, 128.4, 128.0, 127.9, 126.8, 125.8, 124.3, 121.7, 118.6, 35.3, 34.2, 31.4, 29.6, 18.6; MS (EI): 399 (59, M^+), 384 (100, $\text{M}^+ - 15$), 356 (23, $\text{M}^+ - 43$). Anal. Calc. for $\text{C}_{28}\text{H}_{33}\text{NO}$: C, 84.17; H, 8.32; N, 3.51. Found: C, 83.98; H, 8.29; N, 3.57%.

(3,5-Di-*tert*-butyl- C_6H_2 -2-OH)Ph $\text{C}=\text{N}$ (2-F- C_6H_4) (**1i**): yellow crystal, yield (53%), ^1H NMR (CDCl_3 , 300 MHz): δ 14.65 (1H, s, OH), 7.51 (1H, d, $^4J(\text{H,H}) = 1.4$ Hz), 7.33 (3H, m), 7.23 (2H, m), 6.94 (4H, m), 6.77 (1H, m), 1.55 (9H, s, $\text{C}(\text{CH}_3)_3$), 1.18 (9H, s, $\text{C}(\text{CH}_3)_3$); ^{13}C NMR (CDCl_3 , 75 MHz): δ 176.9, 159.9, 153.2 (d, $^1J_{\text{CF}} = 244.5$ Hz), 139.0, 137.4, 135.6 (d, $^2J_{\text{CF}} = 12.1$ Hz), 135.1, 128.8, 128.5 (d, $^3J_{\text{CF}} = 9.1$ Hz), 128.1, 127.8, 127.0 (d, $^4J_{\text{CF}} = 4.5$ Hz), 125.5 (d, $^3J_{\text{CF}} = 7.5$ Hz), 123.9, 123.7, 118.5, 115.6 (d, $^2J_{\text{CF}} = 19.6$ Hz), 35.3, 34.1, 31.2, 29.6; MS (EI): m/z 403 (32, M^+), 388 (100, $\text{M}^+ - 15$), 360 (13, $\text{M}^+ - 43$); Anal. Calc. for $\text{C}_{27}\text{H}_{30}\text{FNO}$: C, 80.36; H, 7.49; N, 3.47; Found: C, 80.34; H, 7.50; N, 3.51%.

4.2. Synthesis of the complex **2a–2i**

To a stirred solution of phenoxyketimine ligand (1 equiv.) in dried diethyl ether (5 mL) at –78 °C, $n\text{BuLi}$ (1 equiv.) was added dropwise over 5 min. The solution was allowed to be warmed up to room temperature and

stirred for 3 h. The resulting solution was added slowly over a 10 min to a slurry of $ZrCl_4$ (0.5 equiv.) in 10 mL diethyl ether at $-78^\circ C$ via cannula. The cold bath was removed and the reaction mixture was stirred at room temperature overnight. Evaporation of the solvent in vacuum yielded a crude product. Methylene chloride (10 mL) was added to the resulting solid, and the mixture was stirred for 10 min and centrifugated for 30 min. The above clear solution was transferred. The organic filtrates were concentrated in vacuum. The resulting product was washed with hexane (10 mL \times 3) and dried to afford the desired complex in moderate yield.

Bis((3,5-di-*tert*-butyl- C_6H_2-2-O)MeC=NC $_6H_5$)ZrCl $_2$ (**2a**): yellow powder, yield (55%), 1H NMR (CDCl $_3$, 300 MHz): isomers, δ 7.60 (d, $J = 12.6$ Hz), 7.51 (d, $J = 3.9$ Hz), 7.47–7.34 (m), 7.23–7.15 (m), 6.96 (d, $J = 7.2$ Hz), 6.88 (t, $J = 7.2$ Hz), 6.79 (t, $J = 7.2$ Hz), 6.48 (d, $J = 7.2$ Hz), 6.09 (d, $J = 7.2$ Hz), 5.97 (d, $J = 7.2$ Hz), 2.40, 2.23, 2.15, 2.03 (s), 1.58–1.29 (m), integral ratio of total aliphatic vs. total aromatic region is 3.2 (expected: 3.0); Anal. Calc. for C $_{44}H_{56}Cl_2N_2O_2Zr \cdot CH_2Cl_2$: C, 60.59; H, 6.55; N, 3.14. Found: C, 59.82; H, 6.45; N, 3.21%.

Bis((3,5-di-*tert*-butyl- C_6H_2-2-O)EtC=NC $_6H_5$)ZrCl $_2$ (**2b**): yellow powder, yield (67%), 1H NMR (CDCl $_3$, 300 MHz): isomers, δ 7.60 (s), 7.56–7.46 (m), 7.42 (s), 7.37 (m), 7.23–7.16 (m), 6.92–6.85 (m), 6.77 (t, $J = 7.5$ Hz), 6.55 (d, $J = 7.8$ Hz), 6.24 (d, $J = 7.8$ Hz), 6.06 (d, $J = 7.8$ Hz), 3.07 (q), 2.74 (q), 2.62 (q), 2.49 (m), 2.35 (m), 1.55, 1.47, 1.42, 1.36 (s), 1.32 (m), 1.25 (m), 1.15 (t), 1.01 (t), 0.88 (m); integral ratio of total aliphatic vs. total aromatic region is 3.4 (expected: 3.3); Anal. Calc. for C $_{46}H_{60}Cl_2N_2O_2Zr \cdot CH_2Cl_2$: C, 61.36; H, 6.79; N, 3.04. Found: C, 60.74; H, 6.85; N, 2.96%.

Bis((3,5-di-*tert*-butyl- C_6H_2-2-O)PhC=NC $_6H_5$)ZrCl $_2$ (**2c**): bright yellow powder, yield (48%). Single crystals suitable for X-ray diffraction analysis were grown by layer diffusion of hexane into a CH $_2Cl_2$ solution of complex **2c** at room temperature over a few days. 1H NMR (CDCl $_3$, 300 MHz): major C $_2$ isomer only, δ 7.50 (2H, s), 7.33 (6H, m), 7.15–7.20 (8H, m), 7.02 (2H, t), 6.93 (2H, s), 6.85 (4H, d), 1.55 (18H, s), 1.18 (18H, s). Anal. Calc. for C $_{54}H_{60}Cl_2N_2O_2Zr$: C, 69.65; H, 6.49; N, 3.01. Found: C, 69.46; H, 6.42; N, 2.97%.

Bis((3,5-di-*tert*-butyl- C_6H_2-2-O)(2-Me-Ph)C=NC $_6H_5$)ZrCl $_2$ (**2d**): yellow powder, yield (43%), 1H NMR (CDCl $_3$, 300 MHz): isomers, δ 7.50 (m), 7.43 (d, $J = 2.4$ Hz), 7.35 (m), 7.27–6.60 (m), 6.49 (d), 6.47 (d), 6.40 (d), 6.32 (t), 6.99 (d), 5.87 (d), 2.16 (s), 2.09 (s), 1.98 (s), 1.88 (s), 1.62 (s), 1.51 (s), 1.48 (s), 1.29 (s), 1.12 (s), 1.05 (s), 1.00 (s), integral ratio of total aliphatic vs. total aromatic region is 2.0 (expected: 1.9); Anal. Calc. for C $_{56}H_{64}Cl_2N_2O_2Zr$: C, 70.12; H, 6.72; N, 2.92. Found: C, 69.51; H, 6.84; N, 2.88%.

Bis((3,5-di-*tert*-butyl- C_6H_2-2-O)(2-F-Ph)C=NC $_6H_5$)ZrCl $_2$ (**2e**): yellow solid, yield (62%), 1H NMR (CDCl $_3$,

300 MHz): isomers, δ 7.62, 7.58, 7.46, 7.38 (m), 7.17–6.42 (m), 1.61 (s), 1.50 (s), 1.45 (s), 1.42 (s), 1.25 (s), 1.22 (s), 1.20 (s), 1.14 (s), 1.08 (s), 1.06 (s), integral ratio of total aliphatic vs. total aromatic region is 1.7 (expected: 1.6); Anal. Calc. for C $_{54}H_{58}Cl_2F_2N_2O_2Zr \cdot CH_2Cl_2$: C, 62.79; H, 5.75; N, 2.66. Found: C, 62.35; H, 5.76; N, 2.66%.

Bis((3,5-di-*tert*-butyl- C_6H_2-2-O)(2-Cl-Ph)C=NC $_6H_5$)ZrCl $_2$ (**2f**): yellow solid, yield (35%), 1H NMR (CDCl $_3$, 300 MHz): major C $_2$ isomer only, δ 7.45 (2H, d, $J = 1.4$ Hz), 7.35 (2H, d, $J = 7.9$ Hz), 7.29–7.09 (10H, m), 6.98 (2H, t, $J = 7.2$ Hz), 6.89 (4H, d, $J = 7.5$ Hz), 6.74 (2H, d, $J = 1.7$ Hz), 1.52 (18H, s), 1.14 (18H, s). Anal. Calc. for C $_{54}H_{58}Cl_4N_2O_2Zr$: C, 64.85; H, 5.85; N, 2.80. Found: C, 64.56; H, 5.80; N, 2.75%.

Bis((3,5-di-*tert*-butyl- C_6H_2-2-O)(2-Br-Ph)C=NC $_6H_5$)ZrCl $_2$ (**2g**): yellow solid, yield (44%), 1H NMR (CDCl $_3$, 300 MHz): isomers, δ 7.58 (m), 7.42 (d), 7.32 (m), 7.28 (m), 7.14–5.80 (m), 1.60, 1.59, 1.48, 1.45, 1.35, 1.23, 1.16, 1.10, 1.06, 1.04, 1.00 (s), integral ratio of total aliphatic vs. total aromatic region is 1.65 (expected: 1.6); Anal. Calc. for C $_{54}H_{58}Br_2Cl_2N_2O_2Zr$: C, 59.56; H, 5.37; N, 2.57. Found: C, 58.91; H, 5.42; N, 2.52%.

Bis(3,5-di-*tert*-butyl- C_6H_2-2-O)PhC=N(2-Me- C_6H_4)ZrCl $_2$ (**2h**): yellow powder, yield (47%), 1H NMR (CDCl $_3$, 300 MHz): major C $_2$ isomer only, δ 7.53 (2H, s), 7.32 (6H, m), 7.14 (6H, m), 6.95 (2H, s), 6.90 (4H, m), 6.54 (2H, m), 2.33 (6H, CH $_3$), 1.56 (18H, s), 1.19 (18H, s). Anal. Calc. for C $_{56}H_{64}Cl_2N_2O_2Zr$: C, 70.12; H, 6.72; N, 2.92. Found: C, 69.85; H, 6.64; N, 2.84%.

Bis(3,5-di-*tert*-butyl- C_6H_2-2-O)PhC=N(2-F- C_6H_4)ZrCl $_2$ (**2i**): yellow powder, yield (65%), 1H NMR (CDCl $_3$, 300 MHz): isomers, δ 7.48 (d, $J = 2.5$ Hz), 7.46 (m), 7.36 (d, $J = 2.4$ Hz), 7.31 (m), 7.25 (m), 7.21–7.10 (m), 6.96–6.90 (m), 6.83 (d, $J = 7.7$ Hz), 6.78 (m), 6.69 (t), 6.64 (d, $J = 2.4$ Hz), 6.61 (d, $J = 8.6$ Hz), 6.58 (d, $J = 2.4$ Hz), 6.45 (d, $J = 2.4$ Hz), 6.41 (t, $J = 7.2$ Hz), 6.28 (t, $J = 9.6$ Hz), 6.18 (m), 1.52 (s), 1.36 (s), 1.25 (s), 1.24 (s), 1.15 (s), 1.06 (s), 1.04 (s), 1.02 (s), integral ratio of total aliphatic vs. total aromatic region is 1.8 (expected: 1.6); Anal. Calc. for C $_{54}H_{58}Cl_2F_2N_2O_2Zr$: C, 67.06; H, 6.04; N, 2.90. Found: C, 66.94; H, 5.89; N, 2.87%.

4.3. X-ray crystallography

Crystals of **2c** coated with vaseline were mounted onto the goniometer and placed on a Rigaku RAXIS RAPID IP diffractometer with graphite monochromated Mo K α radiation ($\lambda = 0.71073 \text{ \AA}$) at 293 K. The structures were solved by direct methods (SHELXS-97) [14] and refined against all F^2 data (SHELXL-97). All non-hydrogen atoms were refined with anisotropic thermal parameters. The hydrogen atoms were treated as idealized contributions.

4.4. Ethylene polymerization under atmospheric pressure

Ethylene polymerization was carried out in toluene using a 250 mL glass reactor with magnetic stir bar. The pressure of ethylene was maintained by an electromagnetic valve. Toluene was introduced into the ethylene purged reactor. The reaction system was kept at a prescribed temperature until the solution was saturated with ethylene. Polymerization was initiated by the addition of a toluene solution of MAO and then a toluene solution of a complex via syringe. After a prescribed time, ethanol was added to terminate the polymerization, the mixture was added acidic ethanol, the polymer was filtered, washed with ethanol, and dried at 70 °C under vacuum to constant weight.

5. Supplementary information available

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Center, CCDC 244438 for the complex **2c**. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK, fax: +44 1223 336033; e-mail: eposit@ccdc.cam.ac.uk or www: <http://ccdc.cam.ac.uk>.

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