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Highly Thermally Stable Eight-Coordinate Dichloride Zirconium Complexes Supported by Tridentate [ONN] Ligands: Syntheses, Characterization, and Ethylene Polymerization Behavior

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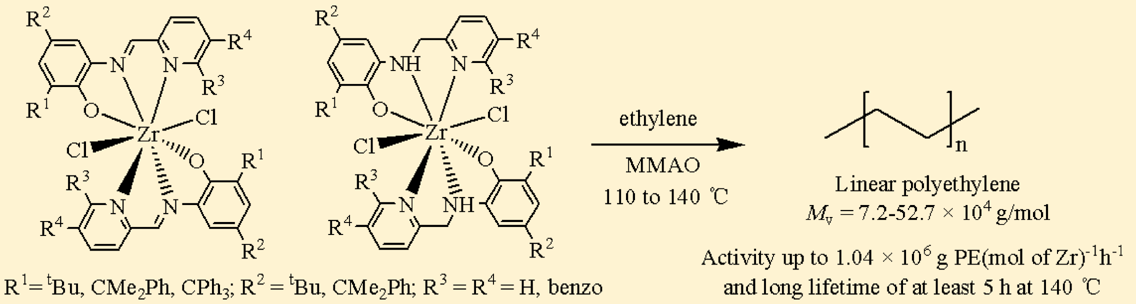
Supporting Information



ABSTRACT: A series of novel eight-coordinate dichloride zirconium complexes with the general formula L_2ZrCl_2 supported by two tridentate [ONN] ligands have been synthesized by the reaction of $ZrCl_4 \cdot 2THF$ with 2 equiv of the corresponding ligands (tridentate phenoxy-imine ligands (**L^{1}H−L^{4}H**) or tridentate phenoxy-amine ligands (**L^{5}H** and **L^{6}H**)). These complexes were characterized by NMR and elemental analyses. The molecular structures of representative zirconium complexes **C2** and **C6** were confirmed by single-crystal X-ray diffraction and revealed that the metal center is eight-coordinated by two tridentate [ONN] ligands and two chlorides in a distorted-square-antiprismatic geometry. When **C1−C6** were activated by modified methylaluminoxane (MMAO), the resultant catalysts displayed notable thermal stability and high activities toward ethylene polymerization. The ligand substituents, the metal coordination environment, and the reaction conditions had a profound effect on the polymerization. The catalytic activity increases consistently with increasing polymerization temperature, and the highest activity of 1.04×10^6 g of PE (mol of Zr)$^{-1}$ h^{-1} was achieved in *o*-xylene at 140 °C. A catalytic lifetime of nearly 5 h was observed for the **C5**/MMAO catalyst system at 140 °C.

INTRODUCTION

In recent years, the nonmetallocene single-site catalysts have drawn considerable attention in both academic and industrial fields due to their high catalyst efficiencies and ability to provide greater control of molecular weight distributions and polymer microstructures.[1−8] Among the most significant results in this field are highly active catalysts based on Pd(II) and Ni(II) α-diimine complexes,[9−14] Fe(II) and Co(II) pyridine diimine complexes,[15−17] salicylaldiminato-based nickel catalysts,[18−20] bis(phenoxy-imine) group 4 complexes,[6−8] and tridentate and tetradentate metal complexes.[21−30] Despite the fact that these catalysts exhibit excellent catalytic properties, their industrial utility is generally limited by their thermal instability at elevated temperatures. Moreover, the mean molecular weight of the polyethylene product generally decreases as the reaction temperature increases.[7,24]

From the aspect of industrial applications, the thermal stability of olefin polymerization catalysts is very important, because performing a solution polymerization at high temperature can reduce the viscosity of the reaction system, thus leading to better mass transportation.[31] Therefore, the development of new catalysts that are stable and maintain high activity at elevated temperatures is quite desirable. To date, there are only a few examples of catalysts that are thermally stable and active at temperatures close to or higher than 100 °C among the many reports in the literature.[6,31−41] In 2000, Yoshifuji and co-workers reported a dimethylpalladium complex based on a phosphorus bidentate ligandl when it was activated with $H(OEt_2)_2BAr_4$, the generated active species showed high thermal stability and moderate activity toward ethylene polymerization (9.07×10^4 g of PE (mol of Pd)$^{-1}$ h^{-1}) at 100 °C.[32] The author proposed that this remarkable behavior may be attributed to the coordination of the phosphorus-based ligand with the palladium center. In 2002, Fujita and co-workers reported that bis(phenoxy-imine) zirconium complexes possessing an electron-donating methoxy group para to the phenolic oxygen (FI catalysts) exhibited very high activities up to 1697 kg of PE (mmol of Zr)$^{-1}$ h^{-1} for ethylene polymerization at 90 °C.[6,7] Pyridyl-amide hafnium

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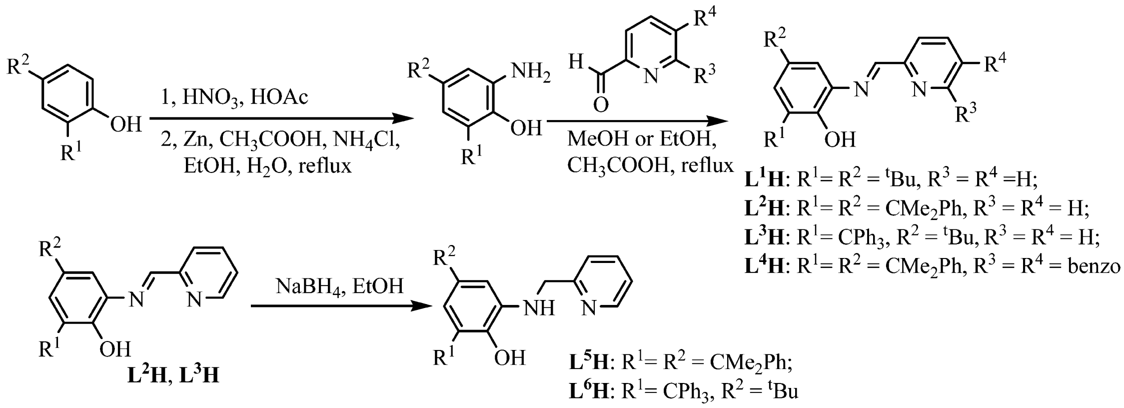
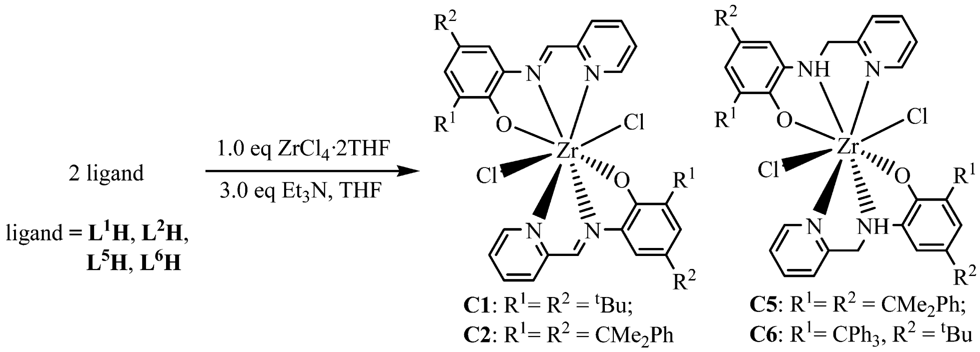
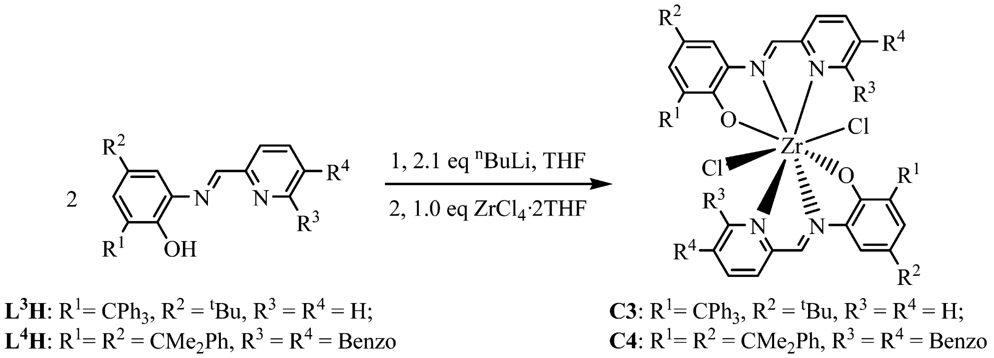
Scheme 1. General Synthetic Route of the Ligands L^1H-L^6H



Scheme 2. Synthesis of Bis(ligand) Dichloride Zirconium Complexes C1, C2, C5, and C6



Scheme 3. Synthesis of Bis(ligand) Dichloride Zirconium Complexes C3 and C4



complexes, developed by the Dow Chemical Co., are well-known to prepare olefin block copolymers and isotactic polypropylene conducted in a solution polymerization process at high temperatures (>100 °C).[35−37] This catalyst system typically generates productivities as high as 300 kg of polymer/g of Hf, equivalent to nearly two million insertions during its lifetime. Very recently, Tang developed a series of tridentate trichloride titanium complexes bearing extra pendant S and P donors on phenoxy-imine ligands,[41] which exhibited good thermal stability and high activities toward ethylene polymerization. A high activity of 1.26×10^6 g of PE (mol of Ti)$^{-1}$ h^{-1} was obtained at reaction temperatures up to 110 °C. However, after 30 min beyond the period no increase in polymer yield was observed.

On the other hand, it is worth noting that the formation of eight-coordinate geometry dichloride group 4 complexes supported by tridentate ligands is rarely observed.[40] Herein, we first report the syntheses and characterization of a series of novel eight-coordinate dichloride zirconium complexes supported by two tridentate [ONN] ligands. When these complexes were activated with modified methylaluminoxane (MMAO), the resultant catalyst species showed notable thermal stabilities and high activities for ethylene polymerization at temperatures ranging from 110 to 140 °C. The **C5**/MMAO catalyst system displayed the highest activity of 1.04×10^6 g of PE (mol of Zr)$^{-1}$ h^{-1} with a lifetime of at least 5 h at 140 °C. Modification of the ligand architecture has a strong influence on the catalytic activity and the molecular weight of the resultant polymers. The effects of the polymerization conditions are discussed in detail.

■ RESULTS AND DISCUSSION

Synthesis and Characterization of Ligands L^1H-L^6H and Complexes C1−C6. The general synthetic routes for

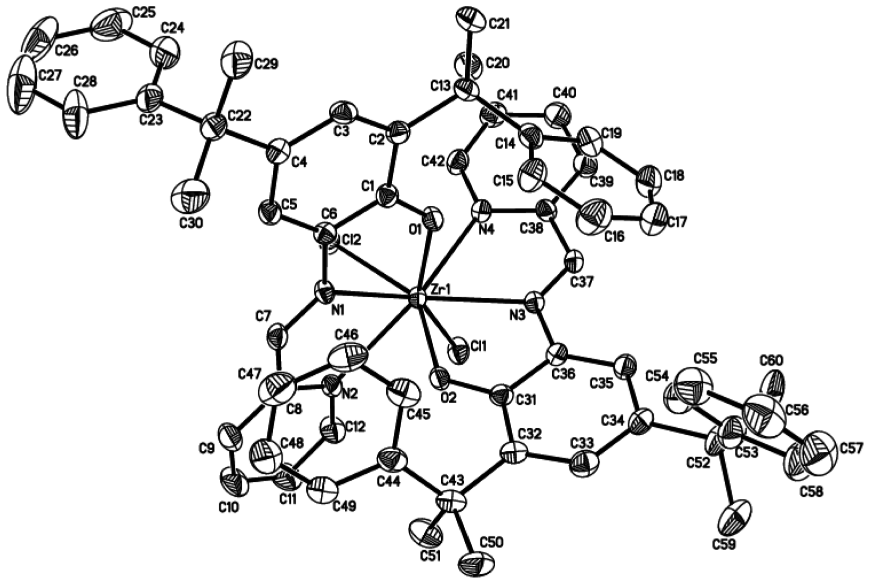


Figure 1. ORTEP drawing of the molecular structure of **C2**. Thermal ellipsoids are at the 50% probability level. All hydrogen atoms and uncoordinated toluene solvent molecules are omitted for clarity. Selected bond lengths (Å) and angles (deg): Zr1−O1 = 2.059(3), Zr1−O2 = 2.050(3), Zr1−N1 = 2.369(3), Zr1−N2 = 2.521(4), Zr1−N3 = 2.376(4), Zr1−N4 = 2.495(4), Zr1−Cl1 = 2.5427(13), Zr1−Cl2 = 2.5342(15), N1−C7 = 1.265(6), N3−C37 = 1.280(5); O1−Zr1−N1 = 69.79(12), N1−Zr1−N2 = 65.80(12), N2−Zr1−Cl1 = 79.23(9), O1−Zr1−Cl1 = 145.18(9), Cl1−Zr1−Cl2 = 91.83(5), O1−Zr1−O2 = 98.52(13), N1−Zr1−N3 = 129.54(13), N2−Zr1−N4 = 144.83(13), O1−Zr1−Cl2 = 95.10(10), N1−Zr1−Cl2 = 75.64(10), N2−Zr1−Cl2 = 76.29(10), N1−Zr1−Cl1 = 144.66(9).

tridentate [ONN] ligands are shown in Scheme 1. Ligands **L^{1}H−L^{4}H** were synthesized by the Schiff base condensation of corresponding substituted *o*-aminophenol with pyridine-2-aldehyde or quinoline-2-aldehyde using acetic acid as catalyst. Ligands **L^{5}H** and **L^{6}H** were obtained easily in high yield by reduction of the corresponding tridentate phenoxy-imine derivatives **L^{2}H** and **L^{3}H** with excess $NaBH_4$ in ethanol. They have been well characterized by elemental analyses and ^{1}H and ^{13}C NMR. ^{1}H NMR analysis of ligands **L^{5}H** and **L^{6}H** revealed no signals for imine C*H*═N protons, whereas a new resonance appeared for the C*H*$_2$NH protons at 4.32 and 4.42 ppm for **L^{5}H** and **L^{6}H**, respectively. These results indicate that C*H*═N (imine) has been transformed into C*H*$_2$NH (amine).

The bis(ligand) dichloride zirconium complexes **C1, C2, C5,** and **C6** were synthesized from $ZrCl_4$·2THF and 2 equiv of the corresponding ligands in the presence of triethylamine in good yields (70.7−77.2%), as shown in Scheme 2. These compounds were recrystallized from tetrahydrofuran (THF) or toluene solution. Alternatively, the corresponding zirconium analogues, **C3** and **C4**, were prepared by the reaction of $ZrCl_4$·2THF with 2 equiv of the corresponding lithium salt of **L^{3}H** and **L^{4}H** in THF (Scheme 3). Purification of **C3** and **C4** was performed by recrystallization from dichloromethane solution upon cooling to −30 °C. It is worth noting that only the bis(ligand) dichloride complexes were isolated, even when only 1 equiv of ligand was used. Zirconium complexes **C1**−**C6** were characterized by elemental analyses and NMR spectroscopy; the molecular structures of **C2** and **C6** were determined by single-crystal X-ray diffraction analysis.

In the ^{1}H NMR spectra of the tridentate phenoxy-imine ligated zirconium complexes **C1**−**C4**, the chemical shifts of the phenoxy protons in the corresponding ligands (at 7.77, 7.45, 7.37, and 7.48 ppm for ligands **L^{1}H**−**L^{4}H**, respectively) disappeared and the chemical shifts of the imine C*H*═N proton resonances were shifted upfield by 0.12−1.80 ppm relative to those of the corresponding free ligand. Furthermore, the signals observed for the protons *ortho* to the pyridine (**C1**−**C3**) or quinoline group (**C4**) shifted dramatically downfield by 1.12−1.75 ppm relative to those of the free ligands. These results indicate that the ligands are bound to the zirconium center in a tridentate fashion by the phenolate and the imine group and the nitrogen atom from the pyridine or quinoline moiety. In addition, the ^{1}H NMR spectra showed one set of resonances for the ligands in **C1**−**C4** in chloroform-*d*, consistent with the formation of a single isomer with two symmetry-related tridentate ligands. For example, the ^{1}H NMR spectra of **C1** showed two singlets for the four *tert*-butyl groups at 1.25 and 0.82 ppm and a singlet for the two imine C*H*═N groups at 8.75 ppm. The signals for the eight C*H* protons of the two pyridyl groups were observed at 10.20, 8.00, 7.87, and 7.50 ppm.

As observed for **C1**−**C4**, zirconium complex **C6** also existed as a single isomer with two symmetry-related tridentate phenoxy-amine ligands. The two protons of the CH$_2$N*H* groups were observed as a triplet at 4.82 ppm. The chemically inequivalent methylene protons of the C*H*$_2$NH moiety appeared as separate doublets of doublets centered at 4.28 and 3.39 ppm (*J* = 13.1, 4.1 Hz).

Interestingly, all regions of the ^{1}H NMR spectra of tridentate phenoxy-amine ligated zirconium complex **C5** revealed the presence of a minor amount of isomers at a level of about 9% in chloroform-*d* solution. However, it was found that the chemical shifts and the multiplicity are very similar between the two isomers. In the ^{1}H NMR spectra of **C5**, the four methylene protons of C*H*$_2$NH appeared as two separated doublets of doublets at 4.17 and 3.41 ppm (*J* = 14.3, 4.0 Hz) for the major isomer and at 4.07 and 3.35 ppm (*J* = 12.0, 3.5 Hz) for the minor isomer, respectively. The CH$_2$N*H* groups were detected as a triplet at 4.72 ppm (*J* = 13.2 Hz) for the major isomer and at 4.81 ppm (*J* = 12.8 Hz) for the minor isomer. These results indicate that the minor isomer appears to be structurally similar to the major isomer. In solution, FI catalysts often exist as a

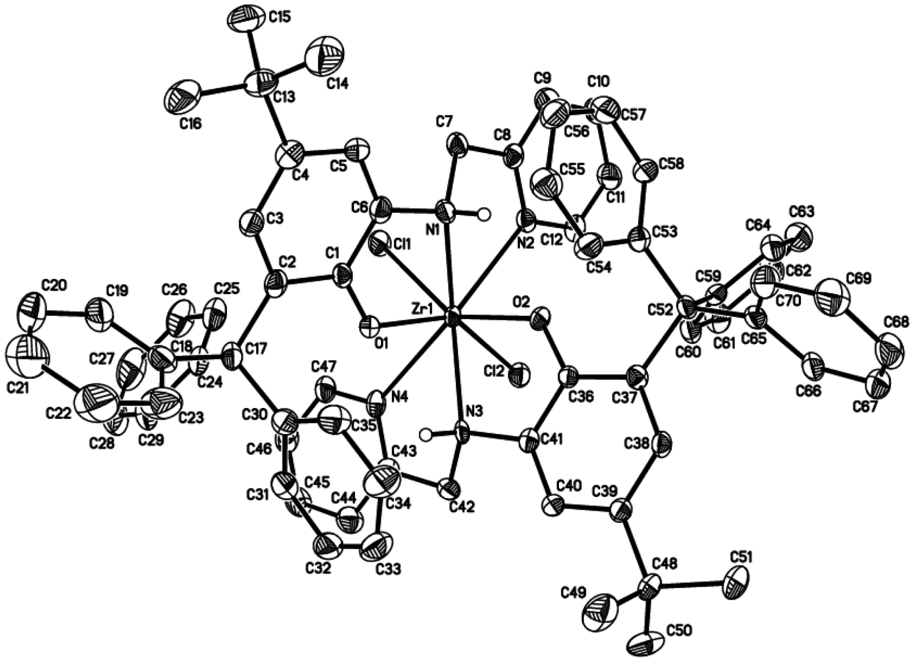


Figure 2. ORTEP drawing of the molecular structure of **C6**. Thermal ellipsoids are at the 50% probability level. All hydrogen atoms (except those on N1 and N3) and uncoordinated THF solvent molecules are omitted for clarity. Selected bond lengths (Å) and angles (deg): Zr1−O1 = 2.066(3), Zr1−O2 = 2.063(3), Zr1−N1 = 2.403(3), Zr1−N2 = 2.521(4), Zr1−N3 = 2.417(3), Zr1−N4 = 2.498(3), Zr1−Cl1 = 2.5415(11), Zr1−Cl2 = 2.5406(11), N1−C7 = 1.470(5), N3−C42 = 1.473(6); O1−Zr1−N1 = 70.25(11), N1−Zr1−N2 = 65.61(11), N2−Zr1−Cl2 = 80.36(8), O1−Zr1−Cl2 = 144.65(8), Cl1−Zr1−Cl2 = 99.90(4), O1−Zr1−N2 = 134.82(11), O1−Zr1−O2 = 102.04(11), N1−Zr1−N3 = 119.97(11), N2−Zr1−N4 = 139.27(11), O1−Zr1−Cl1= 89.52(8), N1−Zr1−Cl1 = 79.79(8), N2−Zr1−Cl1 = 74.00(8), N1−Zr1−Cl2 = 144.81(8).

mixture of configurational isomers that stem from different coordination modes of the two phenoxy-imine ligands.[7] In addition, it should be noted that the trans-N/cis-O/cis-Cl isomer is preferred in FI catalysts with more bulky substituents on the imine nitrogen.[7,47] Considering what is observed in FI catalysts, we tentatively think that the isomers in complex **C5** may also stem from the different coordination modes of the two tridentate ligands.[42−46] In contrast, complex **C6**, with a more bulky triphenylmethyl group near the metal center, exists as only one isomer in solution.

X-ray Crystallographic Studies. The molecular structures of complexes **C2** and **C6** with selected bond distances and angles are shown in Figures 1 and 2, respectively. As shown in Figure 1, the X-ray structural analysis of complex **C2** shows that in the solid state the zirconium atom is bound to two tridentate [ONN] ligands and two chlorides in a distorted-square-antiprismatic geometry. The zirconium atom is located in the plane defined by three donor atoms from the same tridentate phenoxy-imine ligand and one chloride. The Zr1 atom slightly deviates from the planes constructed by the coordinated atoms (O1, N1, N2, Cl1 and O2, N3, N4, Cl2) by about 0.0373 and 0.0519 Å, respectively. The sum of the O1−Zr1−N1 = 69.79(12)°, N1−Zr1−N2 = 65.80(12)°, N2−Zr1−Cl1 = 79.23(9)°, and O1−Zr1−Cl1 = 145.18(9)° bond angles is nearly 360°. Moreover, the mean planes of the two tridentate phenoxy-imine ligands coordinated to the zirconium center are nearly orthogonal with a dihedral angle of 95.3°. The Cl1−Zr1−Cl2 angle is 91.83(5)°, indicating that the two chlorides are located in positions cis to each other, which is favorable for ethylene polymerization. The average Zr−ligand bond distances (Zr−O = 2.054(5) Å, Zr−N(imine) = 2.372(5) Å, Zr−N(pyridyl) = 2.508(4) Å, Zr−Cl = 2.5384(5) Å) are comparable to those observed in six-coordinate zirconium complexes which contain phenoxy-imine ligands or pyridyl derivatives.[21−24,48−54] In addition, in complex **C2**, the imine C═N bond has a distinctive double-bond character (N1−C7 = 1.265(6) Å, N3−C37 = 1.280(5) Å).

The molecular structure of **C6**, as shown in Figure 2, is comparable to that of **C2**. The average Zr−ligand bond distances (Zr−O = 2.064(5) Å, Zr−N(amine) = 2.410(3) Å, Zr−N(pyridyl) = 2.509(5) Å, Zr−Cl = 2.5410(5) Å) of **C6** are slightly longer than those observed for **C2**. In addition, the Cl1−Zr1−Cl2 bond angle of 99.90(4)° is significantly larger than that of 91.83(5)° in **C2**. The amine C−N bond distances (N1−C7 = 1.470(5) Å, N3−C42 = 1.473(6) Å) are in the range of carbon−nitrogen single-bond distances.

Ethylene Polymerization. The activation of **C1**−**C6** with MMAO afforded catalysts for promoting ethylene polymerization in toluene. As shown in Table 1, these Zr-based catalysts displayed notable thermal stability and high activities toward ethylene polymerization at a high temperature of 110 °C and afforded high-molecular-weight polyethylene.

The structures of the complexes have a pronounced influence on the catalytic activity and the molecular weight (M_v) of the obtained polyethylene (entries 1−6 in Table 1; see also Figure 3). The tridentate phenoxy-imine ligated zirconium complex **C1** bearing *tert*-butyl groups at the R^1 and R^2 positions of the ligand gave high-molecular-weight polyethylene ($M_v = 24.4 \times 10^4$ g/mol) with a catalytic activity of 0.53×10^6 g of PE (mol of Zr)$^{-1}$ h^{-1}. When the steric bulk of the substituents of the ligand was increased, the zirconium analogue **C2** ($R^1 = R^2 = CMe_2Ph$) exhibited relatively low catalytic activity but gave higher molecular weight polyethylene (0.32×10^6 g of PE (mol of Zr)$^{-1}$ h^{-1}, $M_v = 31.9 \times 10^4$ g/mol). Moreover, complex **C3** with a sterically bulky triphenylmethyl *ortho* to the phenoxy oxygen (R^1) showed the lowest catalytic activity (0.29×10^6 g

Table 1. Ethylene Polymerization Results Catalyzed by Zirconium Complex C1−C6/MMAO Catalytic Systems in Toluene[a]

entry	catalyst	Al/Zr (molar ratio)	temp (°C)	C_2H_4 pressure (MPa)	yield (mg)	activity[b]	M_v[c] (10^4 g/mol)
1	**C1**	5000	110	1.0	1050	0.53	24.4
2	**C2**	5000	110	1.0	645	0.32	31.9
3	**C3**	5000	110	1.0	571	0.29	42.7
4	**C4**	5000	110	1.0	1141	0.57	20.5
5	**C5**	5000	110	1.0	1191	0.60	29.5[d]
6	**C6**	5000	110	1.0	867	0.43	38.4
7	**C5**	2500	110	1.0	385	0.19	33.8
8	**C5**	7500	110	1.0	1364	0.68	21.9
9	**C5**	10000	110	1.0	1277	0.64	17.6
10	**C5**	5000	70	1.0	39	0.02	35.8
11	**C5**	5000	90	1.0	413	0.21	33.7
12	**C5**	5000	110	0.2	154	0.08	24.2
13	**C5**	5000	110	0.4	301	0.15	25.2
14	**C5**	5000	110	0.6	512	0.26	27.9
15	**C5**	5000	110	0.8	841	0.42	29.1

[a] Polymerization conditions: 2 μmol of catalyst, 60 min, toluene (total volume 25 mL). [b] Activity in 10^6 g of PE (mol of Zr)$^{-1}$ h^{-1}. [c] The intrinsic viscosity was determined in decahydronaphthalene at 135 °C, and molecular weight was calculated using the relatio: $[\eta] = (6.77 \times 10^{-4})M_v^{0.67}$. [d] M_w and M_w/M_n were determined by GPC. For entry 5, $M_w = 20.2 \times 10^4$ g/mol, $M_w/M_n = 2.61$.

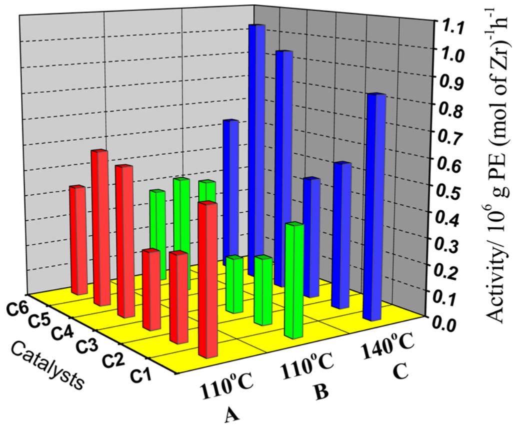


Figure 3. Catalytic activities of complexes **C1**−**C6** at different conditions. Polymerization conditions: (A) 110 °C, toluene as solvent (entries 1−6 in Table 1); (B) 110 °C, *o*-xylene as solvent (entries 16−21 in Table 2); (C) 140 °C, *o*-xylene as solvent (entries 22−27 in Table 2).

of PE (mol of Zr)$^{-1}$ h^{-1}, $M_v = 42.7 \times 10^4$ g/mol) for ethylene polymerization under the same conditions. The catalytic activity followed the order **C3** (R^1 = CPh_3, R^2 = ^{t}Bu) < **C2** (R^1 = R^2 = CMe_2Ph) < **C1** (R^1 = R^2 = ^{t}Bu). These results indicate that the catalytic activity decreases upon increasing the steric size of the R^1 group, which is presumably located near the active metal center in the corresponding catalytic species generated from its $[ONN]_2ZrCl_2$ precursor.[7,48] A similar trend was also observed for tridentate phenoxy-amine ligated zirconium complexes **C5** and **C6**. Complex **C5**, which features a CMe_2Ph group at the R^1 position, was beneficial to the catalytic activity (0.60×10^6 g of PE (mol of Zr)$^{-1}$ h^{-1}, $M_v = 29.5 \times 10^4$ g/mol) in comparison with complex **C6** (0.43×10^6 g of PE (mol of Zr)$^{-1}$ h^{-1}, $M_v = 38.4 \times 10^4$ g/mol), which has a sterically larger triphenylmethyl group at the R^1 position (entry 5 vs 6). Generally, greater steric hindrance near the active metal center is beneficial to increasing the molecular weight of polyethylene.[7,17] As investigated by Fujita and co-workers using bis(phenoxy-imine) zirconium complexes, by increasing the size of the *ortho* substituents on the aniline moiety, the molecular weight of polyethylene increases in the following order: H < Me < ^{i}Pr < ^{t}Bu. The increase in the M_v value may reflect a concomitant decrease in the β-hydride elimination rate by sterically impeding the chain transfer reactions.[48]

In comparison with complex **C2**, the analogue **C4** bearing a quinolinyl donor (R^3 = R^4 = benzo) displayed much higher catalytic activity (0.57×10^6 g of PE (mol of Zr)$^{-1}$ h^{-1}) than the corresponding catalyst with a pyridyl donor due to the difference in the pendant donors (entry 2 vs 4). Complex **C5** displayed the highest catalytic activity of 0.60×10^6 g of PE (mol of Zr)$^{-1}$ h^{-1} under the same conditions, due to the difference in the phenoxy-amine and phenoxy-imine skeletons (entry 2 vs 5). Similarly, a significant increase in catalytic activity was also observed for complex **C6** in comparison with the case of complex **C3** (entry 3 vs 6). This could be attributed to the more electron-donating nature of the phenoxy-amine ligand in comparison to that of the phenoxy-imine ligand. The introduction of an electron-donating group is beneficial to strengthen the bonds between the zirconium metal and the ligand, thus improving the stability of the catalytically active species and leading to higher activity.[56−59]

To investigate the reaction parameters affecting the polymerization of ethylene, the performance of precatalyst **C5** was investigated in detail by changing the reaction parameters such as Al/Zr molar ratio, polymerization temperature, and ethylene pressure (entries 5 and 7−15). The variation of the MMAO/Zr molar ratio had a significant influence on the catalytic activity and the molecular weight of the resultant polyethylene (entries 5 and 7−9). As the Al/Zr molar ratio increased from 2500 to 7500, the catalytic activity increased from 0.19×10^6 to 0.68×10^6 g of PE (mol of Zr)$^{-1}$ h^{-1}. However, a further increase of the Al/Zr molar ratio to 10000 resulted in a slightly reduced catalytic activity (entry 9). In addition, the M_v value of the resultant polyethylene was significantly decreased when the Al/Zr molar ratio increased, which is possibly due to the enhanced rate of chain transfer to aluminum for the termination.[60]

The catalytic activity was also influenced by reaction temperature. The catalytic activity improved appreciably from 0.02×10^6 g of PE (mol of Zr)$^{-1}$ h^{-1} at 70 °C to 0.60×10^6 g of PE (mol of Zr)$^{-1}$ h^{-1} at 110 °C (entries 5, 10, and 11). In addition, the M_v value of resultant polyethylene slightly decreased upon an increase in the temperature. This can be attributed to a facilitated chain transfer reaction at elevated temperatures.[24] When the ethylene pressure was increased, both the catalytic activity and the molecular weight increased consistently (entries 5 and 12−15).

To further examine the thermal stability of these zirconium complexes, a series of ethylene polmyerizations were carried out using *o*-xylene as solvent at much higher temperatures (110−140 °C). The results are summarized in Table 2 (see also Figure 3). Under the same conditions, **C1**−**C6** exhibited somewhat lower activities but gave higher molecular weight polyethylene in comparison to that obtained in toluene (entries 1−6 in Table 1 vs entries 16−21 in Table 2).

The thermal stability of the **C5**/MMAO catalyst system was further investigated by conducting ethylene polymerizations at 140 °C for varying polymerization times (Figure 4, entries 26

Table 2. Ethylene Polymerization Results Catalyzed by Zirconium Complex C1−C6/MMAO Catalytic Systems in *o*-Xylene[a]

entry	catalyst	temp (°C)	time (min)	yield (mg)	activity[b]	M_v[c] (10^4 g/mol)
16	**C1**	110	60	816	0.41	30.7
17	**C2**	110	60	497	0.25	37.1
18	**C3**	110	60	413	0.21	52.7
19	**C4**	110	60	931	0.47	26.8
20	**C5**	110	60	907	0.45	38.8
21	**C6**	110	60	733	0.37	50.2
22	**C1**	140	60	1675	0.84	8.3
23	**C2**	140	60	1122	0.56	12.2[d]
24	**C3**	140	60	937	0.47	15.5
25	**C4**	140	60	1891	0.95	7.7
26	**C5**	140	60	2070	1.04	9.7[e]
27	**C6**	140	60	1257	0.63	15.4[f]
28	**C5**	120	60	1339	0.67	31.3
29	**C5**	130	60	1722	0.86	17.3
30	**C5**	140	15	407	0.81	7.2
31	**C5**	140	30	925	0.93	7.5
32	**C5**	140	45	1505	1.00	8.6
33	**C5**	140	90	2471	0.82	10.3
34	**C5**	140	120	2822	0.71	10.9
35	**C5**	140	180	3532	0.59	11.2
36	**C5**	140	240	4042	0.51	11.3
37	**C5**	140	300	4182	0.42	11.3
38	**C5**	140	360	4213	0.35	11.5

[a] Polymerization conditions: 2 μmol of catalyst, *o*-xylene (total volume 25 mL), Al/Zr molar ratio 5000, ethylene pressure 1.0 MPa. [b] Activity in 10^6 g of PE (mol of Zr)$^{-1}$ h^{-1}. [c] The intrinsic viscosity was determined in decahydronaphthalene at 135 °C, and the molecular weight was calculated using the relation $[\eta] = (6.77 \times 10^{-4})M_v^{0.67}$. [d] M_w and M_w/M_n were determined by GPC. For entry 23, $M_w = 8.8 \times 10^4$ g/mol, $M_w/M_n = 2.29$. [e] For entry 26, $M_w = 6.6 \times 10^4$ g/mol, $M_w/M_n = 2.46$. [f] For entry 27, $M_w = 9.9 \times 10^4$ g/mol, $M_w/M_n = 2.08$.

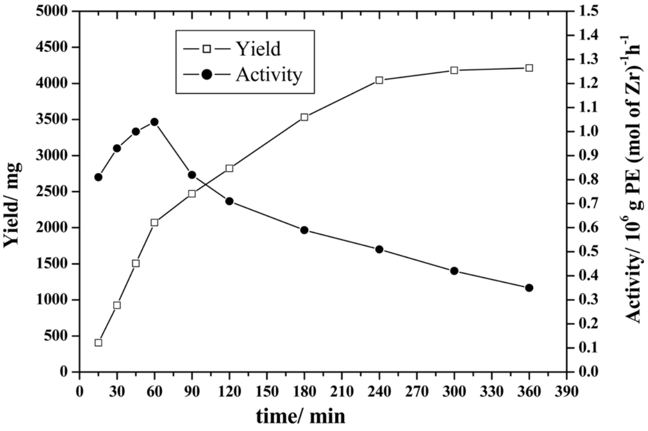


Figure 4. Plots of polymerization time versus catalytic activity (●) and polymer yield (□) of the resultant polyethylene obtained by **C5**/MMAO at 140 °C (entries 26 and 30−38 in Table 2).

and 30−38 in Table 2). When the polymerization time was prolonged, the catalytic activity increased in the early stage and then decreased slowly. The highest activity of 1.04×10^6 g of PE (mol of Zr)$^{-1}$ h^{-1} was achieved in 1 h (entry 26). However, the yield of the obtained polyethylene continuously increased from 2070 to 4182 mg with polymerization time over the range of 1−5 h, while further enhancement of the polymerization time to 6 h resulted in a very slight increase of the polymers (entry 38). This is presumably due to the limited ethylene uptake in the reaction mixture, because the polymerization mixture became more and more viscous after a long period of polymerization. These results indicate that the catalyst has a minimal lifetime of 5 h. In contrast, most of those reported six-coordinate FI catalysts generally suffer from thermal instability and their catalytic activities decayed rapidly at elevated temperatures.[6−8] These eight-coordinate zirconium complexes with remarkable thermal stability may be attributable to the good coordination ability of the two tridentate [ONN] ligands which can stabilize the active catalytic species with higher coordination numbers and sufficient steric protection better than bidentate phenoxy-imine ligands.[55,61]

^{1}H and ^{13}C NMR analysis indicated that the resultant polyethylene are highly linear with no detectable branches (Figure S25, Supporting Information). According to the results of differential scanning calorimetry (DSC), the polyethylene product showed high melting points (T_m) in the range of 135−142 °C, which also indicates that the polymer is a linear polyethylene.[62] In addition, the selected gel permeation chromatography (GPC) analysis of the resultant polyethylene revealed a narrow molecular weight distribution (M_w/M_n) (sample of entry 5, 2.61; sample of entry 23, 2.29; sample of entry 26, 2.46; sample of entry 27, 2.08), suggesting that the polymer is produced by a single active species (Figures S27−S30, Supporting Information).

■ CONCLUSIONS

In summary, a series of eight-coordinate dichloride zirconium complexes supported by two tridentate [ONN] ligands have been synthesized and well characterized. The crystal structures of complexes **C2** and **C6** were similar in that the zirconium complexes adopt a eight-coordinate distorted-square-antiprismatic geometry bearing two tridentate [ONN] ligands and two chlorides. In the presence of MMAO, these zirconium complexes showed notable thermal stability and high activities toward ethylene polymerization at high temperature. The highest catalytic activity of 1.04×10^6 g of PE (mol of Zr)$^{-1}$ h^{-1} and a long lifetime of at least 5 h were observed on the basis of the complex **C5**/MMAO catalyst system at 140 °C. This remarkable thermal stability may be attributable to the good coordination ability of the two tridentate [ONN] ligands that possessed a pyridine or quinoline group as a pendant donor which can stabilize the active catalytic species with higher coordination numbers and sufficient steric protection. Moreover, the catalytic activity and the molecular weight of the obtained polyethylene could be tuned by changing catalyst structures and polymerization conditions. Therefore, the zirconium complexes introduced in this paper have high potential in developing efficient olefin polymerization catalysts used in solution polymerization at high temperatures.

■ EXPERIMENTAL SECTION

General Considerations. All manipulations of air- and/or moisture-sensitive compounds were performed under a dry argon atmosphere using standard Schlenk techniques unless otherwise indicated. Dichloromethane and chloroform-*d* were dried over calcium hydride under argon prior to use. Toluene, *o*-xylene, petroleum ether, and tetrahydrofuran (THF) were refluxed with sodium/benzophenone ketyl and distilled under argon prior to use. Polymerization-grade ethylene was directly used. $ZrCl_4$ and modified methylaluminoxane (MMAO) (2.5 M in toluene) were purchased from Sigma-Aldrich.

^{n}BuLi (2.4 M in *n*-hexane), $NaBH_4$, SeO_2, 2-methylquinoline, pyridine-2-aldehyde, and substituted phenol were purchased from J&K Chemical Ltd. Various *o*-aminophenols with different substituents on the R^1 and R^2 positions were prepared by a procedure similar to that in the literature.[24] Quinoline-2-aldehyde and $ZrCl_4 \cdot 2THF$ were synthesized according to the published procedures.[26,63] All other chemicals were commercially available and used as received.

Measurements. NMR spectra of ligands and complexes were recorded on Bruker AVANCE-400 spectrometers with $CDCl_3$ as the solvent at ambient temperature. ^1H and ^{13}C NMR chemical shifts are reported in ppm using the residual solvent resonances or reported relative to tetramethylsilane. Elemental analyses (C, H, N) were carried out on an EA-1106 type analyzer. IR spectra were recorded on a Perkin-Elmer System 2000 FT-IR spectrometer. ^1H and ^{13}C NMR spectra of the obtained polyethylene were recorded on a Bruker ADVANCE-500 spectrometer using 1,2-dichlorobenzene-d_4 as solvent at 100 °C. Differential scanning calorimetry (DSC) traces and melting points of polyethylene were obtained from the second scanning run on a Universal V2.3C TA Instruments at a heating rate of 10 °C/min. The intrinsic viscosities (η) of the obtained polyethylene were measured with an Ubbelohde viscometer in decahydronaphthalene at 135 °C, and viscosity average molecular weights (M_v) were calculated as follows: $[\eta] = (6.77 \times 10^{-4})M_v^{0.67}$.[64] Molecular weights (M_n and M_w) and polydispersities (M_w/M_n) of the obtained polyethylene were determined by high-temperature GPC using a PL-GPC 220 instrument with 1,2,4-trichlorobenzene as the solvent at 150 °C, at a flow rate of 1.0 mL/min. The calibration was made by polystyrene standard samples.

Synthesis of 2-[(Pyridin-2-yl)methyleneamino]-4,6-di-*tert*-butylphenol (L^1H). To a stirred solution of 2-amino-4,6-di-*tert*-butylphenol (1.107 g, 5.0 mmol) in anhydrous ethanol (40 mL) were added pyridine-2-aldehyde (0.557 g, 5.2 mmol) and a catalytic amount of acetic acid. The mixture was refluxed and stirred for 6 h. When the solution was cooled to ambient temperature, a yellow solid was obtained in 87.7% yield (1.361 g). **L^1H** was characterized by comparing its NMR spectra with those reported in the literature.[65] ^1H NMR (400 MHz, $CDCl_3$): δ 8.87 (s, 1H, C*H*═N), 8.71 (d, 1H, *J* = 4.4 Hz, Py-*H*), 8.23 (d, 1H, *J* = 7.9 Hz, Py-*H*), 7.82 (td, 1H, *J* = 7.7, 1.2 Hz, Py-*H*), 7.77 (s, 1H, ArO*H*), 7.38 (td, 1H, *J* = 7.4, 1.0 Hz, Py-*H*), 7.33 (d, 1H, *J* = 2.1 Hz, Ar-*H*), 7.31 (d, 1H, *J* = 2.1 Hz, Ar-*H*), 1.46 (s, 9H, $C(CH_3)_3$), 1.33 (s, 9H, $C(CH_3)_3$). ^{13}C NMR (100 MHz, $CDCl_3$): δ 156.17, 154.74, 149.90, 149.41, 141.86, 136.89, 135.74, 133.83, 125.26, 124.71, 121.36, 110.55, 35.18, 34.80, 31.78, 29.62.

Synthesis of 2-[(Pyridin-2-yl)methyleneamino]-4,6-dicumylphenol (L^2H). To a stirred solution of 2-amino-4,6-dicumylphenol (3.455 g, 10.0 mmol) in anhydrous methanol (40 mL) were added pyridine-2-aldehyde (1.125 g, 10.5 mmol) and a catalytic amount of acetic acid. The mixture was refluxed and stirred for 6 h, and the resulting mixture was cooled to −30 °C to afford a yellow crystals in 69.3% yield (3.012 g). Mp: 38−39 °C. ^1H NMR (400 MHz, $CDCl_3$): δ 8.75 (s, 1H, C*H*═N), 8.67 (d, 1H, *J* = 4.2 Hz, Py-*H*), 8.07 (d, 1H, *J* = 8.0 Hz, Py-*H*), 7.73 (td, 1H, *J* = 7.6, 1.2 Hz, Py-*H*), 7.45 (s, 1H, ArO*H*), 7.39−7.27 (m, 11H, Ar-*H* and Py-*H*), 7.24−7.17 (m, 2H, Ar-*H*), 1.77 (s, 6H, CH_3), 1.73 (s, 6H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$): δ 156.37, 154.56, 150.83, 150.67, 149.80, 149.06, 141.49, 136.75, 135.15, 133.90, 128.23, 128.00, 126.86, 126.44, 125.90, 125.87, 125.42, 125.20, 121.14, 112.74, 43.05, 42.29, 31.19, 29.45. Anal. Calcd for $C_{30}H_{30}N_2O$: C, 82.91; H, 6.96; N, 6.45. Found: C, 82.71; H, 6.99; N, 6.39.

Synthesis of 2-[(Pyridin-2-yl)methyleneamino]-4-*tert*-butyl-6-(triphenylmethyl)phenol (L^3H). To a stirred solution of 2-amino-4-*tert*-butyl-6-triphenylmethylphenol (2.445 g, 6.0 mmol) in anhydrous ethanol (40 mL) were added pyridine-2-aldehyde (0.675 g, 6.3 mmol) and a catalytic amount of acetic acid. The mixture was refluxed and stirred for 6 h. When the solution was cooled to ambient temperature, a yellow solid was obtained in 85.2% yield (2.539 g). Mp: 161−162 °C. ^1H NMR (400 MHz, $CDCl_3$): δ 8.85 (s, 1H, C*H*═N), 8.66 (d, 1H, *J* = 4.8, Py-*H*), 8.05 (d, 1H, *J* = 7.9 Hz, Py-*H*), 7.72 (td, 1H, *J* = 7.6, 1.2 Hz, Py-*H*), 7.40 (d, 1H, *J* = 2.2 Hz, Ar-*H*), 7.37 (s, 1H, ArO*H*), 7.32 (td, 1H, *J* = 7.6, 1.2 Hz, Py-*H*), 7.28−7.15 (m, 16H, Ar-*H*), 1.20 (s, 9H, $C(CH_3)_3$). ^{13}C NMR (100 MHz, $CDCl_3$): δ 156.37, 154.55, 149.83, 149.36, 145.62, 141.67, 136.78, 134.01, 133.10, 131.24, 129.29, 127.32, 125.86, 125.25, 121.35, 111.58, 63.56, 34.73, 31.58. Anal. Calcd for $C_{35}H_{32}N_2O$: C, 84.64; H, 6.49; N, 5.64. Found: C, 84.63; H, 6.50; N, 5.59.

Synthesis of 2-[(Quinolin-2-yl)methyleneamino]-4,6-dicumylphenol (L^4H). To a stirred solution of 2-amino-4,6-dicumylphenol (1.036 g, 3.0 mmol) in anhydrous ethanol (40 mL) were added quinoline-2-aldehyde (0.495 g, 3.2 mmol) and a catalytic amount of acetic acid. The mixture was refluxed and stirred for 6 h. When the solution was cooled to ambient temperature, blue crystals were obtained in 81.7% yield (1.188 g). Mp: 154−156 °C. ^1H NMR (400 MHz, $CDCl_3$): δ 8.85 (s, 1H, C*H*═N), 8.14−8.05 (m, 3H, quino-*H*), 7.78 (d, 1H, *J* = 8.0 Hz, quino-*H*), 7.70 (t, 1H, *J* = 7.7 Hz, quino-*H*), 7.53 (t, 1H, *J* = 7.4 Hz, quino-*H*), 7.48 (s, 1H, ArO*H*), 7.32−7.29 (m, 2H, Ar-*H*), 7.27−7.20 (m, 8H, Ar-*H*), 7.18−7.10 (m, 2H, Ar-*H*), 1.70 (s, 6H, CH_3), 1.65 (s, 6H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$): δ 156.23, 154.70, 150.89, 150.69, 149.35, 148.12, 141.57, 136.81, 135.27, 133.79, 130.28, 129.70, 128.97, 128.27, 128.04, 127.97, 127.95, 126.89, 125.93, 125.89, 125.47, 118.19, 112.76, 43.11, 42.33, 31.24, 29.48. Anal. Calcd for $C_{34}H_{32}N_2O$: C, 84.26; H, 6.66; N, 5.78. Found: C, 84.13; H, 6.68; N, 5.72.

Synthesis of 2-[(Pyridin-2-yl)methylamino]-4,6-dicumylphenol (L^5H). To a stirred solution of 2-[(pyridin-2-yl)methyleneamino]-4,6-dicumylphenol (**L^2H**) (1.738 g, 4.0 mmol) in anhydrous ethanol (30 mL) was slowly added $NaBH_4$ (1.362 g, 36.0 mmol). After the mixture was stirred for 5 h at room temperature, acetone (5 mL) and water (30 mL) were added sequentially at 0 °C. The mixture was extracted with CH_2Cl_2 (3 × 60 mL), and the organic layer was dried over Na_2SO_4. Then the volatiles were removed under vacuum, and the crude product was recrystallized from a ethanol/petroleum ether mixture. The product **L^5H** was obtained as a pale red powder in 83.1% yield (1.451 g). Mp: 128−129 °C. ^1H NMR (400 MHz, $CDCl_3$): δ 8.46 (d, 1H, *J* = 4.8 Hz, Py-*H*), 7.56 (td, 1H, *J* = 7.7, 1.7 Hz, Py-*H*), 7.39−7.30 (m, 4H, Ar-*H* and Py-*H*), 7.29−7.23 (m, 5H, Ar-*H*), 7.20 (d, 1H, *J* = 7.8 Hz, Py-*H*), 7.17−7.07 (m, 2H, Ar-*H*), 6.80 (d, 1H, *J* = 2.1 Hz, Ar-*H*), 6.42 (d, 1H, *J* = 1.9 Hz, Ar-*H*), 4.78 (t, 1H, *J* = 5.4 Hz, CH_2NH), 4.60 (s, 1H, ArO*H*), 4.32 (d, 2H, *J* = 5.4 Hz, CH_2NH), 1.66 (s, 6H, CH_3), 1.63 (s, 6H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.08, 151.45, 149.14, 149.10, 142.87, 139.60, 137.79, 136.63, 134.24, 129.26, 127.94, 126.89, 126.87, 126.24, 125.45, 121.99, 121.74, 113.81, 110.78, 50.29, 42.97, 42.09, 31.16, 29.77. Anal. Calcd for $C_{30}H_{32}N_2O$: C, 82.53; H, 7.39; N, 6.42. Found: C, 82.13; H, 7.38; N, 6.23.

Synthesis of 2-[(Pyridin-2-yl)methylamino]-4-*tert*-butyl-6-(triphenylmethyl)phenol (L^6H). Ligand **L^6H** was prepared by a procedure similar to that described above for **L^5H**, using 2-[(pyridin-2-yl)methyleneamino]-4-*tert*-butyl-6-triphenylmethylphenol (**L^3H**; 1.192 g, 2.4 mmol) and $NaBH_4$ (0.817 g, 21.6 mmol). **L^6H** was obtained as a pale white powder in 75.8% yield (0.907 g). Mp: 185−187 °C. ^1H NMR (400 MHz, $CDCl_3$): δ 8.41 (d, 1H, *J* = 4.6 Hz, Py-*H*), 7.56 (td, 1H, *J* = 7.7, 1.1 Hz, Py-*H*), 7.25−7.12 (m, 16H, Ar-*H* and Py-*H*), 7.08 (t, 1H, *J* = 5.6 Hz, Py-*H*), 6.62 (d, 1H, *J* = 1.9 Hz, Ar-*H*), 6.40 (d, 1H, *J* = 1.9 Hz, Ar-*H*), 4.76 (br, 2H, CH_2NH and ArO*H*), 4.42 (s, 2H, CH_2NH), 1.03 (s, 9H, $C(CH_3)_3$). ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.30, 149.23, 144.96, 143.01, 140.06, 137.87, 136.79, 132.36, 131.26, 127.87, 126.67, 122.11, 121.83, 117.55, 109.48, 63.38, 50.70, 34.61, 31.63. Anal. Calcd for $C_{35}H_{34}N_2O$: C, 84.30; H, 6.87; N, 5.62. Found: C, 83.92; H, 6.68; N, 5.81.

Synthesis of $(L^1)_2ZrCl_2$ (C1). To a stirred solution of $ZrCl_4 \cdot 2THF$ (0.453 g, 1.2 mmol) in dried THF (40 mL) was added slowly a solution of 2-[(pyridin-2-yl)methyleneamino]-4,6-di-*tert*-butylphenol (**L^1H**; 0.745 g, 2.4 mmol) in THF (40 mL) at room temperature, and then Et_3N (0.50 mL, 0.364 g, 3.6 mmol) was added. The resulting solution was stirred overnight at ambient temperature, and then the mixture was filtered to remove the precipitated $Et_3N \cdot HCl$ salt. The final product was crystallized from THF by cooling at −30 °C, washed with petroleum ether, and dried in vacuo. Complex **C1** was obtained as red crystals in 73.3% yield (0.687 g). Mp: >300 °C (**C1** was extremely stable and did not decompose at temperatures up to 300 °C). ^1H NMR (400 MHz, $CDCl_3$): δ 10.20 (d, 2H, *J* = 4.6 Hz, Py-*H*), 8.75 (s, 2H, C*H*═N), 8.00 (td, 2H, *J* = 7.5, 1.5 Hz, Py-*H*), 7.87 (d, 2H, *J* = 7.5 Hz, Py-*H*), 7.50 (td, 2H, *J* = 7.5, 1.5 Hz, Py-*H*), 7.29 (d, 2H, *J* = 2.1 Hz, Ar-*H*), 7.11 (d, 2H, *J* = 2.1 Hz, Ar-*H*), 1.25 (s, 18H, C(CH_3)$_3$), 0.82 (s, 18H, C(CH_3)$_3$). ^{13}C NMR (100 MHz, $CDCl_3$): δ 163.67, 153.77, 152.69, 146.38, 140.12, 138.60, 137.77, 134.90, 127.20, 126.94, 125.66, 109.95, 34.66, 34.28, 31.72, 28.89. Anal. Calcd for $C_{40}H_{50}Cl_2N_4O_2Zr\cdot0.5C_4H_8O$: C, 61.74; H, 6.66; N, 6.86. Found: C, 61.91; H, 6.87; N, 6.47. The final product contains about 0.5 equiv of THF, as verified by NMR spectroscopy.

Synthesis of $(L^2)_2ZrCl_2$ (C2). The procedure was similar to the synthesis of **C1** (except that it was recrystallized from toluene), using ligand **L^2H** (1.043 g, 2.4 mmol), $ZrCl_4\cdot2THF$ (0.453 g, 1.2 mmol), and Et_3N (0.50 mL, 0.364 g, 3.6 mmol). Complex **C2** was obtained as red crystals (suitable for X-ray diffraction) in 76.1% yield (0.940 g). Mp: 136−137 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 10.00 (d, 2H, *J* = 4.7 Hz, Py-*H*), 7.92 (td, 2H, *J* = 7.6, 1.4 Hz, Py-*H*), 7.60 (s, 2H, C*H*═N), 7.58 (d, 2H, *J* = 7.6 Hz, Py-*H*), 7.40−7.14 (m, 12H, Ar-*H* and Py-*H*), 7.07 (d, 2H, *J* = 1.8 Hz, Ar-*H*), 6.92 (d, 2H, *J* = 1.8 Hz, Ar-*H*), 6.88−6.82 (m, 4H, Ar-*H*), 6.74−6.66 (m, 6H, Ar-*H*), 1.76 (s, 6H, CH_3), 1.74 (s, 6H, CH_3), 1.14 (s, 6H, CH_3), 0.70 (s, 6H, CH_3). Because of its poor solubility, ^{13}C NMR resonances were unavailable. Anal. Calcd for $C_{60}H_{58}Cl_2N_4O_2Zr\cdot C_7H_8$: C, 71.76; H, 5.93; N, 5.00. Found: C, 71.34; H, 6.12; N, 4.64. The final product contains about 1.0 equiv of toluene, as verified by NMR spectroscopy.

Synthesis of $(L^3)_2ZrCl_2$ (C3). To a stirred solution of the ligand 2-[(pyridin-2-yl)methyleneamino]-4-*tert*-butyl-6-triphenylmethylphenol (**L^3H**; 1.192 g, 2.4 mmol) in 50 mL of THF was added dropwise ^{n}BuLi (2.4 M in *n*-hexane, 1.05 mL, 2.5 mmol) at −78 °C. The mixture was stirred for an additional 3 h at ambient temperature, then $ZrCl_4\cdot2THF$ (0.453 g, 1.2 mmol) was added at −78 °C, and the reaction mixture was slowly warmed to ambient temperature and stirred overnight. Then the solvent was removed under reduced pressure and the residue was extracted with dry CH_2Cl_2 (40 mL). The mixture was filtered, and the volatiles were removed under reduced pressure. The final product was crystallized from CH_2Cl_2 by cooling at −30 °C, washed with petroleum ether, and dried in vacuo. Complex **C3** was obtained as red crystals in 25.5% yield (0.353 g). Mp: >300 °C (**C3** was extremely stable and did not decompose at temperatures up to 300 °C). ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.78 (d, 2H, *J* = 4.9 Hz, Py-*H*), 7.75 (s, 2H, C*H*═N), 7.57 (t, 2H, *J* = 7.7 Hz, Py-*H*), 7.31 (d, 2H, *J* = 7.5 Hz, Py-*H*), 7.21−6.76 (m, 34H, Ar-*H* and Py-*H*), 6.67−6.63 (m, 2H, Ar-*H*), 1.19 (s, 18H, C(CH_3)$_3$). Because of its poor solubility, the ^{13}C NMR resonance was unavailable. Anal. Calcd for $C_{70}H_{62}Cl_2N_4O_2Zr\cdot1.5CH_2Cl_2$: C, 67.05; H, 5.12; N, 4.37. Found: C, 67.04; H, 5.36; N, 4.27. The final product contains about 1.5 equiv of dichloromethane, as verified by NMR spectroscopy.

Synthesis of $(L^4)_2ZrCl_2$ (C4). The procedure was similar to the synthesis of **C3**, using ligand **L^4H** (1.163 g, 2.4 mmol), ^{n}BuLi (2.4 M in *n*-hexane, 1.05 mL, 2.5 mmol), and $ZrCl_4\cdot2THF$ (0.453 g, 1.2 mmol). Complex **C4** was obtained as a dark red solid in 29.2% yield (0.330 g). Mp: >300 °C (**C4** was extremely stable and did not decompose at temperatures up to 300 °C). ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.87 (d, 2H, *J* = 9.3 Hz, quino-*H*), 8.36 (d, 2H, *J* = 8.3 Hz, quino-*H*), 7.82−7.76 (m, 4H, quino-*H*), 7.59−7.50 (m, 4H, quino-*H*), 7.35−7.23 (m, 10H, Ar-*H*), 7.19−7.14 (m, 2H, Ar-*H*), 7.05 (s, 2H, C*H*═N), 7.01−6.96 (m, 4H, Ar-*H*), 6.94−6.80 (m, 8H, Ar-*H*), 1.71 (s, 6H, CH_3), 1.70 (s, 6H, CH_3), 1.17 (s, 6H, CH_3), 0.67 (s, 6H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$): δ 162.51, 152.88, 150.92, 150.46, 149.66, 147.81, 139.21, 138.70, 136.01, 134.77, 131.99, 129.94, 129.23, 128.83, 128.41, 128.28, 127.95, 127.15, 126.86, 126.33, 125.85, 124.90, 124.20, 114.11, 42.84, 42.19, 33.39, 31.40, 31.12, 26.28. Anal. Calcd for $C_{68}H_{62}Cl_2N_4O_2Zr\cdot0.2CH_2Cl_2$: C, 71.45; H, 5.49; N, 4.89. Found: C, 71.28; H, 5.63; N, 4.84. The final product contains about 0.2 equiv of dichloromethane, as verified by NMR spectroscopy.

Synthesis of $(L^5)_2ZrCl_2$ (C5). The procedure was similar to the synthesis of **C1** (except that it was recrystallized from toluene), using ligand **L^5H** (0.873 g, 2.0 mmol), $ZrCl_4\cdot2THF$ (0.377 g, 1.0 mmol), and Et_3N (0.42 mL, 0.303 g, 3.0 mmol). Complex **C5** was obtained as orange crystals in 77.2% yield (0.798 g). Mp: 216−218 °C. There are two isomers found in chloroform-*d* solution (the ratio between the major and minor isomers is ca. 10:1). ^{1}H NMR (400 MHz, $CDCl_3$): major isomer (91%), δ 9.80 (d, 2H, *J* = 5.5 Hz, Py-*H*), 7.81 (t, 2H, *J* = 7.5 Hz, Py-*H*), 7.42−7.15 (m, 16H, Ar-*H*), 6.80−6.71 (m, 4H, Ar-*H* and Py-*H*), 6.62 (s, 2H, Ar-*H*), 6.49 (m, 4H, Ar-*H*), 6.33 (t, 2H, *J* = 7.5 Hz, Py-*H*), 4.72 (t, 2H, *J* = 13.2, CH_2N*H*), 4.17 (dd, 2H, *J* = 14.3, 4.0 Hz, CH_2NH), 3.41 (dd, 2H, *J* = 14.3, 4.0 Hz, CH_2NH), 1.76 (s, 6H, CH_3), 1.75 (s, 6H, CH_3), 1.22 (s, 6H, CH_3), 0.93 (s, 6H, CH_3); minor isomer (9%), δ 9.66 (d, 2H, *J* = 5.6 Hz, Py-*H*), 7.72 (t, 2H, *J* = 7.2 Hz, Py-*H*), 7.21−7.17 (m, 4H, Ar-*H*), 7.09−7.04 (m, 6H, Ar-*H*), 6.98−6.85 (m, 10H, Ar-*H* and Py-*H*), 6.65 (s, 2H, Ar-*H*), 6.59−6.53 (m, 4H, Ar-*H*), 6.27 (t, 2H, *J* = 7.2 Hz, Py-*H*), 4.81 (t, 2H, *J* = 12.8, CH_2N*H*), 4.07 (dd, 2H, *J* = 12.0, 3.5 Hz, CH_2NH), 3.35 (dd, 2H, *J* = 12.0, 3.5 Hz, CH_2NH), 1.73 (s, 6H, CH_3), 1.71 (s, 6H, CH_3), 1.16 (s, 6H, CH_3), 0.95 (s, 6H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$, only resonances for the major isomer are reported): δ 158.41, 158.25, 152.57, 151.83, 151.40, 138.41, 137.77, 134.22, 128.21, 127.66, 126.94, 125.76, 125.48, 124.91, 124.55, 122.92, 122.31, 122.10, 119.96, 54.59, 42.78, 41.56, 32.71, 31.36, 31.30, 26.45. Anal. Calcd for $C_{60}H_{62}Cl_2N_4O_2Zr\cdot0.5C_7H_8$: C, 70.66; H, 6.16; N, 5.19. Found: C, 70.44; H, 6.18; N, 4.91. The final product contains about 0.5 equiv of toluene, as verified by NMR spectroscopy.

Synthesis of $(L^6)_2ZrCl_2$ (C6). The procedure was similar to the synthesis of **C1**, using ligand **L^6H** (0.798 g, 1.6 mmol), $ZrCl_4\cdot2THF$ (0.302 g, 0.8 mmol), and Et_3N (0.34 mL, 0.243 g, 2.4 mmol). Complex **C6** was obtained as orange crystals (suitable for X-ray diffraction) in 70.7% yield (0.654 g). Mp: >300 °C (**C6** was extremely stable and did not decompose at temperatures up to 300 °C). ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.30 (d, 2H, *J* = 5.2 Hz, Py-*H*), 7.50 (td, 2H, *J* = 7.6, 1.2 Hz, Py-*H*), 7.20−7.07 (m, 20H, Ar-*H*), 7.02 (d, 2H, *J* = 2.0 Hz, Ar-*H*), 6.78−6.69 (m, 12H, Ar-*H* and Py-*H*), 6.67 (d, 2H, *J* = 7.6 Hz, Py-*H*), 6.64 (d, 2H, *J* = 2.0 Hz, Ar-*H*), 4.82 (t, 2H, *J* = 13.2, CH_2N*H*), 4.28 (dd, 2H, *J* = 13.1, 4.1 Hz, CH_2NH), 3.39 (dd, 2H, *J* = 13.1, 4.1 Hz, CH_2NH), 1.18 (s, 18H, (CH_3)$_3$). ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.71, 157.15, 151.54, 146.46, 138.60, 136.71, 133.92, 131.95, 131.05, 127.24, 126.81, 125.60, 122.51, 120.90, 119.27, 62.84, 56.07, 34.48, 31.89. Anal. Calcd for $C_{70}H_{66}Cl_2N_4O_2Zr\cdot0.4C_4H_8O$: C, 72.49; H, 5.88; N, 4.72. Found: C, 72.30; H, 5.80; N, 4.74. The final product contains about 0.4 equiv of THF, as verified by NMR spectroscopy.

X-ray Crystallographic Studies. Single-crystal X-ray diffraction studies for complexes **C2** and **C6** were carried out on a Bruker AXS D8 diffractometer with graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). All data were collected at 25 °C (for **C2**) or −133 °C (for **C6**) using the ω-scan technique. Unit cell dimensions were obtained with least-squares refinements. Intensities were corrected for Lorentz and polarization effects and empirical absorption. The structures were solved by direct methods[66] and refined by full-matrix least squares on F^2.[67] All calculations were carried out with the SHELXTL program. All non-hydrogen atoms were refined anisotropically, and the hydrogen atoms were included in idealized positions. The crystal data and structure refinement parameters are given in Table S1 (Supporting Information).

Polymerization of Ethylene. Ethylene polymerization was carried out in a 100 mL autoclave equipped with a magnetic stirrer. The autoclave was heated at 100 °C under vacuum for 30 min and then thermostatted to the desired temperature and filled with ethylene. The proper amounts of modified methylaluminoxane (MMAO) solution and toluene were added to the autoclave, which was then filled with ethylene for 15 min at the reaction temperature. After the proper amount of a toluene solution of the zirconium complex was injected into the reactor, ethylene at the desired pressure was introduced to start the polymerization. The reaction mixture was stirred vigorously for a designated time, and the ethylene pressure in the autoclave was slowly vented. Then 10 mL of ethanol was added to terminate the polymerization. The resulting mixture was poured into 3% HCl in ethanol (50 mL). The polymer was collected by filtration, washed with ethanol (30 mL × 2), and then dried for 16 h in a vacuum oven at 60 °C to constant weight.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Figures, a table, and CIF files giving NMR spectra of ligands **L^1H–L^6H** and zirconium complexes **C1–C6**, X-ray crystallographic data for zirconium complexes **C2** and **C6**, ^{13}C NMR and IR spectra of polyethylene obtained by **C5**/MMAO (entry 26), and selected GPC plots regarding the data of entries 5, 23, 26, and 27. This material is available free of charge via the Internet at http://pubs.acs.org. Crystallographic data for the structures reported in this paper have also been deposited with the Cambridge Crystallographic Data Centre under the numbers CCDC 944109 (for **C2**) and 951475 (for **C6**). Copies of the data can be obtained free of charge from the Cambridge Crystallographic Data Centre (www.ccdc.cam.ac.uk/data_request/cif).

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Notes

The authors declare no competing financial interest.

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