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Highly Active Ethylene Polymerization and Regioselective 1-Hexene Oligomerization Using Zirconium and Titanium Catalysts with Tridentate [ONO] Ligands

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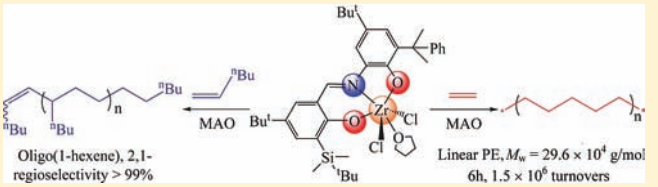
ABSTRACT: A series of tridentate dianionic ligands [4-^{t}Bu-6-R-2-(3-R′-5-^{t}Bu-2-OC_6H_2)N=CH C_6H_2O]$^{2-}$ (**L**) [R = R′ = ^{t}Bu (**L1**); R = CMe_2Ph, R′ = ^{t}Bu (**L2**); R = adamantyl, R′ = ^{t}Bu (**L3**); R = R′ = CMe_2Ph (**L4**); R = $SiMe_2{}^t$Bu, R′ = CMe_2Ph (**L5**)] were synthesized. Reactions of $TiCl_4$ with 1 equiv of ligands **L1**−**L5** in toluene afford five-coordinate titanium complexes with general formula $LTiCl_2$ [L = L1 (**1**); L2 (**2**); L3 (**3**); L4 (**4**); L5 (**5**)]. The addition of tetrahydrofuran (THF) to titanium complex **5** readily gives THF-solvated six-coordinate complex **6**, which also was obtained by reaction of $TiCl_4$ with 1 equiv of ligand **L5** in THF. Reactions of $ZrCl_4$ with 1 or 2 equiv of ligands **L1**−**L5** afford six-coordinate zirconium mono(ligand) complexes $LZrCl_2(THF)$ [L = L2 (**7**); L4 (**8**); L5 (**9**)], and bis(ligand) complexes L_2Zr [L = L1 (**10**); L4 (**11**)]. The molecular structures of complexes **2**, **8**, and **11** were established by single-crystal X-ray diffraction studies. Upon activation with methylaluminoxane, complexes **1**−**9** are active for ethylene polymerization. The activities and half-lifes of the catalyst systems based on zirconium complexes are more than 10^6 g of polyethylene (mol Zr)$^{-1}$ h^{-1} and 6 h, respectively. Complex **9** is more active and long-lived, with a turnover frequency (TOF) of 2.6×10^5 (mol C_2H_4) (mol Zr)$^{-1}$ h^{-1}, a half-life of >16 h, and a total turnover number (TON) of more than 10^6 (mol C_2H_4) (mol Zr)$^{-1}$ at 20 °C and 0.5 MPa pressure. Even at 80 °C, complex **9**/MAO catalyst system has a long lifetime ($t_{1/2}$ > 2 h), as well as high activity that is comparable with that at 20 °C. When activated with methylaluminoxane (MAO), complex **9** also show moderate catalytic activity and more than 99% 2,1-regioselectivity for 1-hexene oligomerization.



INTRODUCTION

In recent years, the nonmetallocene metal catalysts have attracted intensive attention because they can produce a variety of high performance polyolefin products, including linear low-density polyethylene,[1] isotactic polypropylene,[2] syndiotactic polypropylene,[3] isotactic polystyrene,[4] copolymers of ethylene with olefins, comprising propylene,[5] polar monomer,[6] conjugated dienes,[7] and so forth. Especially, group 4 nonmetallocene catalysts have been instrumental in studying polymerization mechanisms, searching structure−property relationships, and synthesizing polymers of tailored microstructures and desired physical properties. An important family of group 4 nonmetallocene catalysts is based on phenoxy-imine ligands developed independently by the Fujita and the Coates groups. These catalysts can be used to produce many important polyolefins, such as high molecular weigh polyethylene, isotactic, and syndiotactic polypropylene, and so forth in high catalytic activity or living polymerization fashion.[8] Therefore, the study of new group 4 metal complexes based on phenoxy-imine backbone as olefin polymerization catalysts is an ever-growing area.

Side arm effect is an efficient strategy for developing highly active catalysts for olefin polymerization. Kol et al. reported that bis(phenolate) [O^-NNO^-] group 4 metal complexes are excellent catalysts for 1-hexene polymerization,[9] and revealed that the pendant amino group of the ligand influences strongly the catalytic activity.[9a] Sudhakar and Sundararajan found that the incorporation of a pendant methoxy donor into the aminodiol ligand framework led to the resultant catalysts that were capable of 1-hexene living polymerization.[10] Gibson also described that the group 4 metal phenoxy-amide complexes[11a] and chromium phenoxy-imine complexes,[11b] bearing pendant donors, displayed higher ethylene polymerization activity than the corresponding catalysts systems without a pendant donor. Recently, Li reported that tridentate Schiff base ligands with pendant donors are beneficial to stabilize vanadium(III) catalysts in comparison with the bidentate Schiff base ligands.[11c]

On the basis of phenoxy-imine backbone and the role of side arm appended heteroatom groups in catalysis, a series of titanium complexes with tridentate monoanionic [O^-NX^R] (X = O, P, S, Se; R = alkyl, aryl) and dianionic [O^-NS^-] ligands have been reported in olefin polymerization. Titanium complexes containing monoanion tridentate ligands [O^-NX^R] (X = P, S; R = alkyl, aryl) bearing soft pendant donors were reported to be efficient in catalyzing olefin homo- and copolymerization.[12] Interestingly, when X is a hard pendant donor, such as O atom, the corresponding titanium complexes exhibited only low activities. Recently, Jin reported that dianionic tridentate ligands [O^-NS^-] titanium complexes bearing soft pendant donors showed good activities for ethylene polymerization.[13] So far, few dianionic

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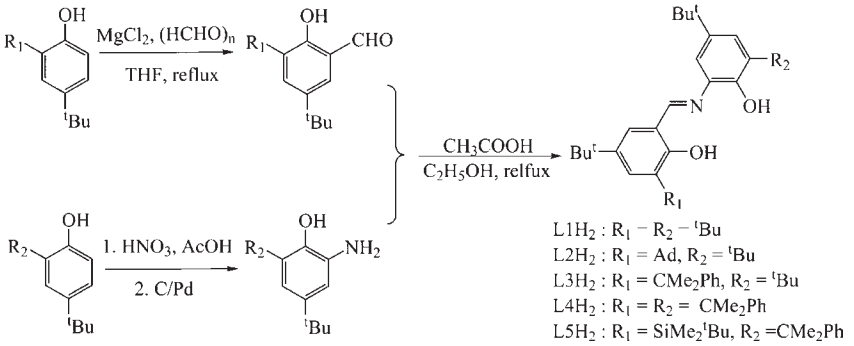
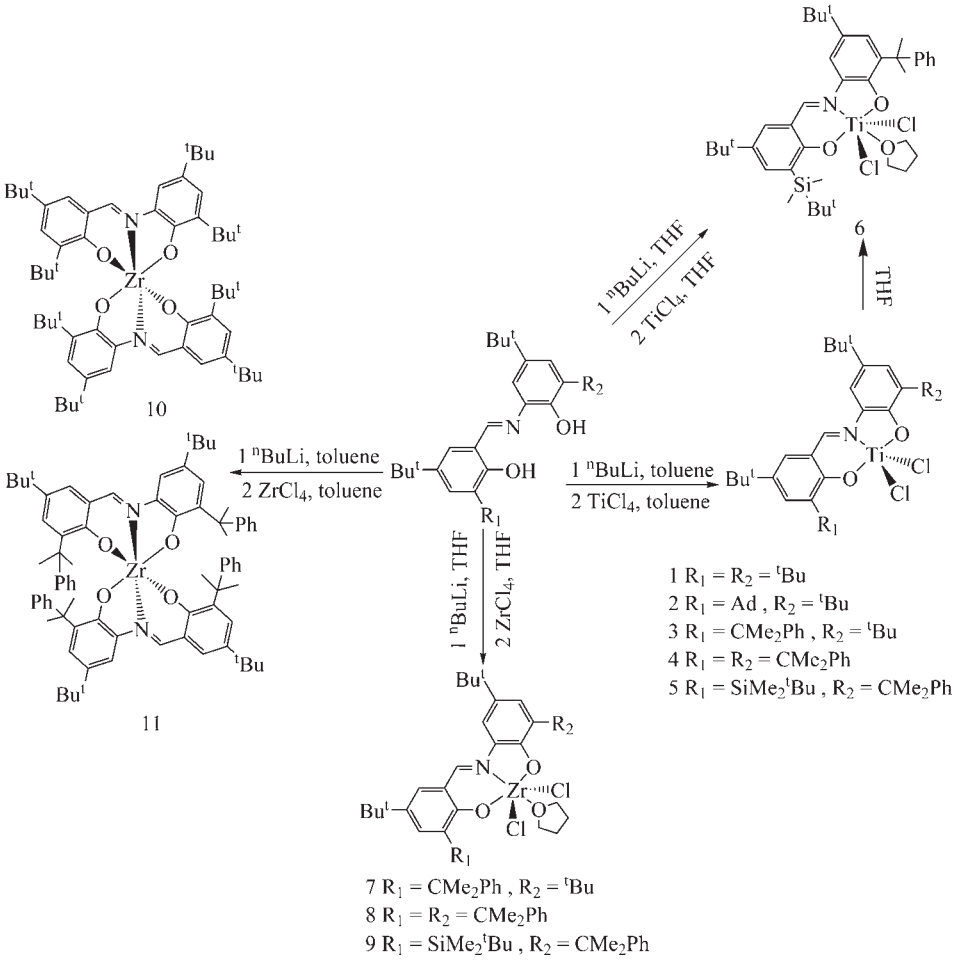
Scheme 1. Synthetic Procedures for Pro-Ligands $L1H_2$−$L5H_2$



Scheme 2. Synthetic Procedures for Complexes 1−11



tridentate [O^-NO^-] with phenoxy-imine backbone ligated group 4 metal complexes have been described.[14]

In the literatures, group 4 metal complexes supported by dianionic tridentate pyridine-based bis(phenolate) or bis(alkoxide) [O^-NO^-] ligand showed outstanding catalytic performance for olefin polymerization. For example, zirconium and titanium complexes of bis(phenoxy)pyridine, bis(alkoxy) pyridine, and bulky silyl ortho-substituted tridentate bis(naphthol)pyridine were reported to polymerize ethylene or propylene with excellent activities.[15−18] These results encouraged us to develop group 4 metal complexes containing [O^-NO^-] ligand based on phenoxy-imine backbone and investigate their catalytic behaviors for olefins polymerization. In this paper, we wish to report the synthesis and structural characterization of various zirconium and titanium complexes with [O^-NO^-] ligand, as well as their catalytic performance in the homopolymerization of olefins such as ethylene and 1-hexene.

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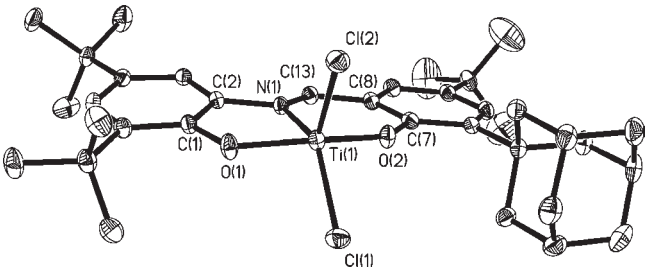

Figure 1. Structure of complex **2** (thermal ellipsoids are drawn at the 30% probability level). Hydrogen atoms and uncoordinated solvent are omitted for clarity. The selected bond lengths (Å) and angles (deg): Ti−O(1) 1.848(3), Ti−O(2) 1.832(3), Ti−N(1) 2.157(3), Ti−Cl(1) 2.2338(1), Ti−Cl(2) 2.2357(1), O(1)−Ti−O(2) 153.75(1), O(2)−Ti−N(1) 80.09(1), O(1)−Ti−N(1) 94.97(1), O(2)−Ti−Cl(1) 94.68(9), O(2)−Ti−Cl(1) 94.68(9), N(1)−Ti−Cl(1) 136.20(9), O(2)−Ti−Cl(2) 100.07(1), O(1)−Ti−Cl(2) 99.43(1), N(1)−Ti−Cl(2) 113.70(9), Cl(1)−Ti−Cl(2) 110.04(5).

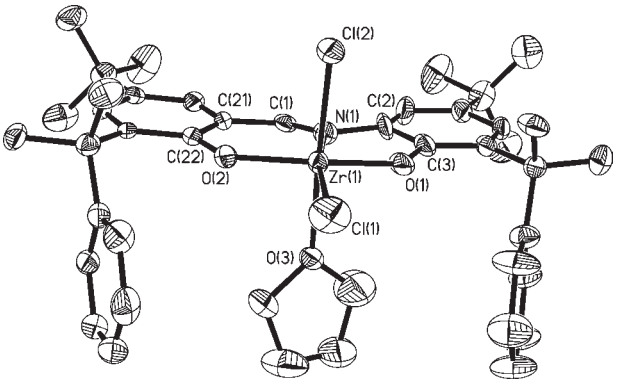

Figure 2. Structure of complex **8** (thermal ellipsoids are drawn at the 30% probability level). Hydrogen atoms and uncoordinated solvent are omitted for clarity. The selected bond lengths (Å) and angles (deg): Zr−O(1) 1.960(4), Zr−O(2) 1.980(4), Zr−O(3) 2.229(4), Zr−N(1) 2.297(1), Zr−Cl(1) 2.406(2), Zr−Cl(2) 2.425(2), O(1)−Zr−O(2) 149.19(2), O(1)−Zr−O(3) 83.77(2), O(2)−Zr−O(3) 86.65(2), O(1)−Zr−N(1) 64.1(3), O(2)−Zr−N(1) 85.9(3), N(3)−Zr−N(1) 84.6(3), O(1)−Zr−Cl(1) 105.08(2), O(2)−Zr−Cl(1) 103.61(1), O(3)−Zr−Cl(1) 87.23(1), N(1)−Zr−Cl(1) 167.1(3), O(1)−Zr−Cl(2) 93.18(1), O(2)−Zr−Cl(2) 95.36(2), O(3)−Zr−Cl(2) 176.67(1), N(1)−Zr−Cl(2) 92.9(3), Cl(1)−Zr−Cl(2) 94.85(8).

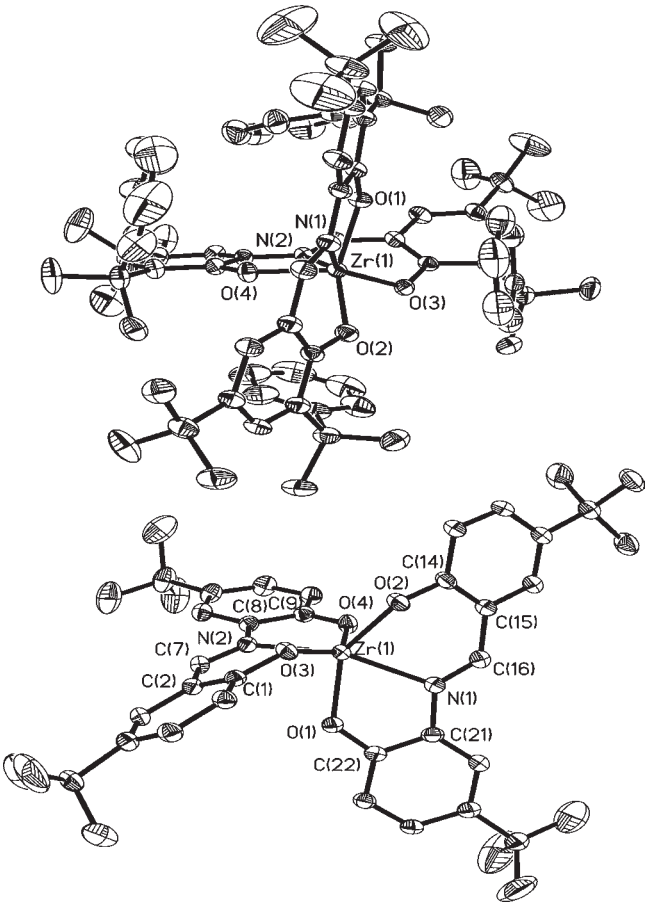

Figure 3. Structure of complex **11** (Hydrogen atoms and uncoordinated solvent are omitted for clarity; in the bottom view, the CMe_2Ph groups are also omitted; thermal ellipsoids are drawn at the 30% probability level). Hydrogen atoms and uncoordinated solvent are omitted for clarity. The selected bond lengths (Å) and angles (deg): Zr−O(1) 2.020(2), Zr−O(2) 2.011(2), Zr−O(3) 2.014(2), Zr−O(4) 2.021(2), Zr−N(1) 2.327(3), Zr−N(2) 2.316(3), O(4)−Zr−O(3) 141.27(1), O(4)−Zr−O(1) 106.72(1), O(3)−Zr−O(1) 93.66(9), O(4)−Zr−O(2) 93.97(1), O(3)−Zr−O(2) 90.19(1), O(1)−Zr−O(2) 140.54(1), O(4)−Zr−N(2) 71.71(1), O(3)−Zr−N(2) 76.84(1), O(1)−Zr−N(2) 87.39(1), O(2)−Zr−N(2) 131.52(1), O(4)−Zr−N(1) 84.85(1), O(3)−Zr−N(1) 133.47(1), O(1)−Zr−N(1) 71.34(1), O(2)−Zr−N(1) 77.69(1), N(2)−Zr−N(1) 142.38(1).

RESULTS AND DISCUSSION

Syntheses and Characterizations of the Titanium and Zirconium Complexes. The phenoxy-imine derivatives **L1**H_2−**L5**H_2 were prepared in good yields by condensation reactions of the corresponding salicyaldehyde with equivalent *o*-aminophenol in ethanol (Scheme 1). The general synthetic routes of these titanium and zirconium complexes are shown in Scheme 2. The pro-ligands **L1**H_2−**L5**H_2were deprotonated by 2 equiv. of ^{n}BuLi, followed by treating with 1 equiv of $TiCl_4$ in toluene at −78 °C to afford the desired titanium complexes **1**−**5** in good yields. The purification was performed by recrystallization from a mixture of CH_2Cl_2 and *n*-hexane at −30 °C. The attempt to apply this method to the preparation of zirconium congeners proved to be unsuccessful. When **L1** and **L4** were used as ligands, the reactions gave bis(ligand) zirconium complexes **10** and **11**, respectively. After further screening experiments, we found a way to synthesize mono(ligand) complexes **7**−**9** by the reaction of lithium salts of **L2**, **L4**, and **L5** with 1 equiv of $ZrCl_4$ in tetrahydrofuran (THF) at −78 °C. However, the reaction of lithium salt of $\mathbf{L_1}$ with $ZrCl_4$ gave bis(ligand) zirconium complex **10**. When $\mathbf{L_3}$ was used, the reaction did not lead to the desired complex and gave a precipitate that would not dissolve in ordinary organic solvents. For a comparative purpose, the THF-solvated complex **6** was prepared by the addition of THF to titanium complex **5** or by the reaction of $TiCl_4$ with 1 equiv of ligand **L5** in THF (Scheme 2). The ^{1}H NMR spectra of pentacoordinate titanium complexes **1**−**5** revealed the CH=N protons, which were shifted downfield approximately 0.08−0.20 ppm relative to free ligands. However, the CH=N protons in six-coordinate titanium complex **6** and zirconium complexes **7**−**9** were shifted upfield approximately 0.10−0.34 ppm relative to free ligand. These results indicate the obvious coordination of the imino nitrogen atom to the metal center.

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The solid-state structures of **2**, **8**, and **11** were determined by single-crystal X-ray diffraction (Figures 1, 2, and 3). The crystallographic data including the collection and refinement parameters was summarized in Table 1. In complex **2**, one crystallographically independent Ti atom adopts a five-coordinate, distorted square-pyramidal geometry. The Ti−O bond lengths 1.848(3) and 1.832(3) Å are close to those observed in the previously reported bis(phenoxy-imine) complex Ti{3-$SiMe_3$-2-(O)C_6H_3CH=N(C_6F_5)}$_2Cl_2$ (1.860 Å, 1.854 Å),[3b] but much longer than those observed in related mono(phenoxy-imine) complexes Ti{3-Bu^t-2-(O)C_6H_3CH=N(2,6-$R_2C_6H_3$)}Cl_3(THF) (1.791 Å) and Ti[2-(4,6-$^tBu_2$-2 -(2-OC_6H_4)N=CH-C_6H_2O]$_2Cl_4$ (1.799 Å).[19] The Ti−N bond length of 2.157(3) Å and Ti−Cl bond lengths of 2.2338(12) Å, 2.2357(1) Å are comparable to those observed in some phenoxy-imine titanium complexes.[3,19] The O−Ti−O bond angle of 153.75(1)° is close to that in complex Ti[2-(4,6-$^tBu_2$-2-(2-OC_6H_4)N=CHC_6H_2O]$_2Cl_4$ (151.93(7)°).[14a] In complexes **8** and **11**, unique Zr atoms adopt a six-coordinate octahedron distorted structure. The pseudo-octahedral zirconium center in **8** is chelated by **L4** in a tridentate meridional fashion, with two cis-chloride atoms and a THF group completing the coordination sphere. The Zr−O, Zr−N, and Zr−Cl bond lengths are close to those observed in the previously reported phenoxy-imine zirconium complexes.[8b] The O−Zr−O bond angle of 149.19(1)° is smaller than that of 158.96(1)° in pyridine-bis(phenolate) zirconium complex.[15a] In complex **11**, the zirconium center is chelated by two **L4** ligands in a mer mode. Most Zr−O, Zr−N, and Zr−Cl bond lengths are approximate to those in **8**. The O−Zr−O bond angles are 140.54(1)° and 141.27(1)°, significantly smaller than that of 153.75(1)° in **8**.

Table 1. Crystal Data and Structural Refinement Details for Complexes 2, 8, and 11

	2	8	11
mol formula	$C_{35}H_{47}Cl_2NO_2Ti$	$C_{43}H_{53}Cl_2NO_3Zr$	$C_{78}H_{90}N_2O_4Zr$
mol wt	632.54	793.98	1210.74
cryst system	monoclinic	monoclinic	triclinic
space group	$P2_1/c$	$P2_1/c$	$P\bar{1}$
a/ Å	14.5814(9)	12.140(6)	14.8459(9)
b/ Å	11.9435(7)	28.562(14)	16.3255(11)
c/ Å	20.4118(12)	15.205(5)	18.7348(14)
α/deg	90	90	87.078(5)
β/deg	104.5360(10)	126.83(3)	70.917(4)
γ/deg	90	90	63.353(4)
V/ Å^3	3441.0(4)	4220(3)	3810.7(4)
Z	4	4	2
abs coeff/mm^{-1}	0.434	0.424	0.189
R_{int}	0.0411	0.0889	0.0430
R_1 ($I > 2\delta$)	0.0625	0.0605	0.0590
wR_2 ($I > 2\delta$)	0.1677	0.1144	0.1683
GOF	1.028	1.000	1.054

Ethylene Polymerization. Upon activation of methylaluminoxane (MAO), these complexes were used as catalysts for ethylene polymerization. The results are summarized in Table 2. Titanium complexes **1**−**6** showed low to moderate activities. It was found that the yield increased with time only within 30 min, and beyond the period no obvious increase in polymer yield was observed, indicating a short lifetime of the active species.[20] R_1 and R_2 groups on the [O$^-$NO$^-$] ligand have an important influence on the catalytic activity. The activity increases remarkably with the increase in the steric hindrance of R_1 and R_2 groups. Complex **5** with bulky R_1 and R_2 groups shows the highest catalytic activity under the same conditions. This result may be

Table 2. Typical Results of Ethylene Polymerization Using Pro-Catalysts 1−9[a]

run	pro-catalyst (μmol)	MAO (equiv)	T (°C)	t (h)	yield (g)	TON[b]	M_n[c] × 10^{-4}	M_w/M_n[c]	T_m[d] (°C)
1	1(10)	1000	20	0.5	0.05	180			
2	2(10)	1000	20	0.5	0.07	250			
3	3(10)	1000	20	0.5	0.10	350			
4	4(10)	1000	20	0.5	0.70	2500	21.9	2.0	137.2
5	5(10)	1000	20	0.5	0.82	2900	22.0	1.8	136.7
6	6(10)	1000	20	0.5	0.78	2800	19.0	2.1	136.6
7	7(0.2)	1000	20	1	0.32	57100	9.9	2.8	136.4
8	8(0.2)	1000	20	1	1.35	241000	11.5	1.9	137.1
9	9(0.2)	500	20	1	0.95	170000	12.2	1.8	138.2
10	9(0.2)	1000	20	1	1.46	261000	10.6	1.9	138.6
11	9(0.2)	2000	20	1	1.01	180000	9.8	1.8	137.9
12	9(0.2)	1000	20	2	3.01	538000	10.0	2.1	138.1
13	9(0.2)	1000	20	4	5.65	1009000	9.5	2.5	138.1
14	9(0.2)	1000	20	6	8.65	1545000	10.2	2.9	138.3
15	9(0.2)	1000	20	10	10.9	1946000	7.8	3.1	138.8
16	9(0.2)	1000	80	1	1.32	236000	2.3	7.2	137.6
17	9(0.2)	1000	80	2	2.12	379000	2.0	7.4	137.3
18	9(0.2)	1000	80	3	2.22	396000	1.7	9.9	137.2
19[e]	9(0.2)	1000	20	2	0.52	93000	9.4	1.9	137.6
20[f]	9(0.2)	1000	20	3	1.50	268000	19.1	2.8	137.0
21[f]	9(0.2)	2000	20	3	1.02	182000	24.9	2.7	137.2

[a] Polymerization conditions: solvent 100 mL of toluene, temperature 20 °C, ethylene pressure 5 bar. [b] mol C_2H_4 (mol M)$^{-1}$. [c] Determined by GPC vs polystyrene standards. [d] Determined by DSC at a heating rate of 10 °C min^{-1}. [e] Ethylene pressure =2 bar. [f] Dry MAO.

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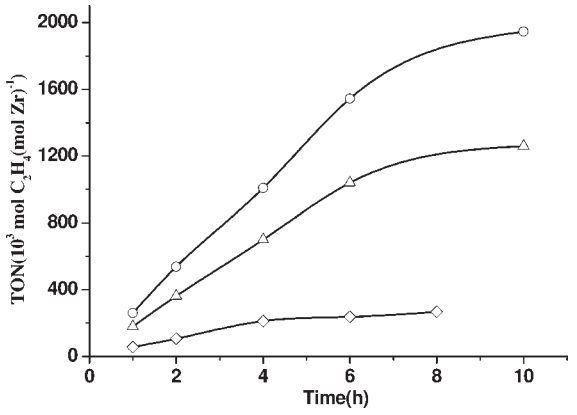

Figure 4. Lifetime plot of ethylene polymerization for complexes **7** (M), **8** (8) and **9** (−) at 20 °C. Reaction conditions: zirconium complex 0.2 μmol, MAO 0.2 mmol, ethylene 5 bar, toluene 100 mL.

attributed to the fact that bulky R_1 and R_2 on the ortho-position of the oxygen atom in the $[O^-NO^-]$ ligand could prevent the coordination of the oxygen atom to a MAO or other titanium complex, and therefore keep the active catalyst molecule from inactivation.[21] THF-solvated complex **6** was synthesized. However, no observable change in catalytic activity was observed.

Upon activation with MAO, the zirconium complexes were found to be more efficient catalyst than the corresponding titanium analogues. At 20 °C, zirconium complex **9** displayed the highest activity with a turnover frequency (TOF) up to 2.61×10^5 mol C_2H_4 (mol Zr)$^{-1}$ h^{-1} for ethylene polymerization. Notably, these complexes are remarkably long-lived (Figure 4). For the most active pro-catalyst **9**, the TON increases linearly with time in the range of 1 to 6 h. The TON at 10 h is less than the extrapolated value (1.95×10^6 vs 2.61×10^6). It should be ascribed to the limited ethylene uptake in the reaction mixture, because the reactor was completely filled with polyethylene after 10 h. On the basis of these observations, conservatively the catalyst half-life must be greater than 16 h. Even at 80 °C, complex **9** activated by MAO forms a catalyst system with a long lifetime ($t_{1/2} > 2$ h) and displays high activity, which is comparable with that at room temperature (Table 2, runs 10, 16−18). Complexes **7** and **8** are also long lifetime pro-catalysts for ethylene polymerization in the presence of 1000 equiv of MAO as activator. The lifetime of catalytic species generated from **7** and **8** are $t_{1/2} > 6$ h and $t_{1/2} > 14$ h, respectively. Also, the resultant polymers at 20 °C exhibits a narrow polydispersity index (PDI) of 1.8−3.1, indicating a single-site catalytic species is in favor of ethylene polymerization (PDI values above 2 were observed in cases with high TON. As mentioned above, under these conditions the reactor is filled with polyethylene and limited mass transfer effects likely result in an increase of the PDI value above 2).[22] The influences of Al/Zr molar ratio, reaction temperature, and ethylene pressure were also studied with complex **9** as pro-catalyst. An obvious increase in polyethylene yield was observed, when the Al/Zr molar ratio increased from 500 to 1000, its productivity of ethylene polymerization greatly enhanced (Table 2, runs 9 and 10). However, further increase of the Al/Zr molar ratio to 2000 resulted in a reduced activity (Table 2, run 11). The increase of the Al/Zr molar ratio has a negative effect on polymer molecular weights. Interesting, when dry MAO (both toluene and $AlMe_3$ were removed) was used as cocatalyst, the resultant polymer has a significantly high molecular weight ($M_n = 24.9 \times 10^4$ g mol^{-1}). An increase in reaction temperature from 20 to 80 °C resulted in the

Table 3. Results of 1-Hexene Polymerization Using Pro-Catalysts 1−9[a]

run	procatalyst	Al:M	yield (g)	TON[b]	M_n[c]	M_w/M_n[c]	[vinylene]/[vinylidene][d]
1	1	1000	0.11	131	496	1.16	86:14
2	2	1000	0.21	250	510	1.18	92:8
3	3	1000	0.21	250	541	1.17	92:8
4	4	1000	0.30	357	533	1.21	94:6
5	5	1000	0.38	452	610	1.15	>99:1
6	6	1000	0.36	429	565	1.22	>99:1
7	7	500	1.96	2333	702	1.24	70:30
8	7	1000	2.51	2988	701	1.27	74:26
9	7	2000	2.02	2405	752	1.22	76:24
10	8	1000	1.65	1964	532	1.12	79:21
11	9	1000	0.35	417	595	1.13	>99:1

[a] Polymerization conditions: cat. = 0.01 mmol total volume 10 mL; 1-hexene (5 g, 6 mmol); reaction temperature 20 °C. reaction time = 24 h. [b] (mol of 1-hexene converted) (mol of M)$^{-1}$ h^{-1}. [c] Determined by GPC in THF vs polystyrene standards. [d] Ratio of the signals intensity $(R_1)CH{=}CH(R_2)$:$(R_3)(R_4)C{=}CH_2$ in oligomer, determined by ^{1}H NMR spectroscopy in $CDCl_3$.

M_n decreasing from 10.0×10^4 to 2.0×10^4 g/mol, indicating that the chain transfer easily occurs at enhanced temperatures (Table 2, runs 12 and 17). And the PDIs of the resulting polymers produced by complex **9** dramatically broaden with the increase of reaction temperature. A decrease of ethylene pressure did not result in a significant decrease of polyethylene molecular weight. ^{13}C NMR analysis indicates that the resultant polymers are linear and have no branches. The melting transition temperature (Tm) of these polymers is in the range of 136.4−138.8 °C. Complexes **10** and **11** are stable to both water and air, and did not show any activity for ethylene polymerization. Similarly, increasing the steric hindrance of R_1 and R_2 groups is beneficial to improving activity of the corresponding titanium catalysts.

1-Hexene Polymerization. In α-olefin oligomerization, regioselectivity is a crucial factor that influence the composition of the resultant oligomers. For example, dimerization of an α-olefin by a metal hydride catalyst would give rise to ten constitutional isomers, if 1,2-insertion, 2,1-insertion, and β-H elimination are combined. Extensive research efforts have been devoted to developing new catalyst systems that can achieve better control regioselectivity in α-olefin oligomerization. However, only very limited catalyst systems with high regioselectivity of α-olefin insertion have been reported.[23]

Inspired by the success of complexes **1**−**9** in catalyzing ethylene homopolymerization, we also explored the homopolymerization of 1-hexene. The results are summarized in Table 3. Upon activation with MAO, complexes **1**−**9** show moderate catalytic activity for 1-hexene polymerization, producing poly (1-hexene) with low molecular weight (496−752) and narrow polydispersity (M_w/M_n = 1.12−1.27). The degree of polymerization is between 5 and 12. The oligomers produced by the zirconium complex **9** (Table 3, run 11) show olefin ^{1}H NMR resonances at δ = 5.34 ppm, in agreement with the presence of vinylene groups [(E)- and (Z)-$R_1CH{=}CHR_2$], whereas no signals for vinylidene end groups ($R_3R_4C{=}CH_2$) (expected around 4.6 ppm) were observed (Figure 5). In the ^{13}C NMR spectra of the oligomers, the signals around 130 ppm were assigned to the vinylene group [(E)- and (Z)-$R_1CH{=}CHR_2$],

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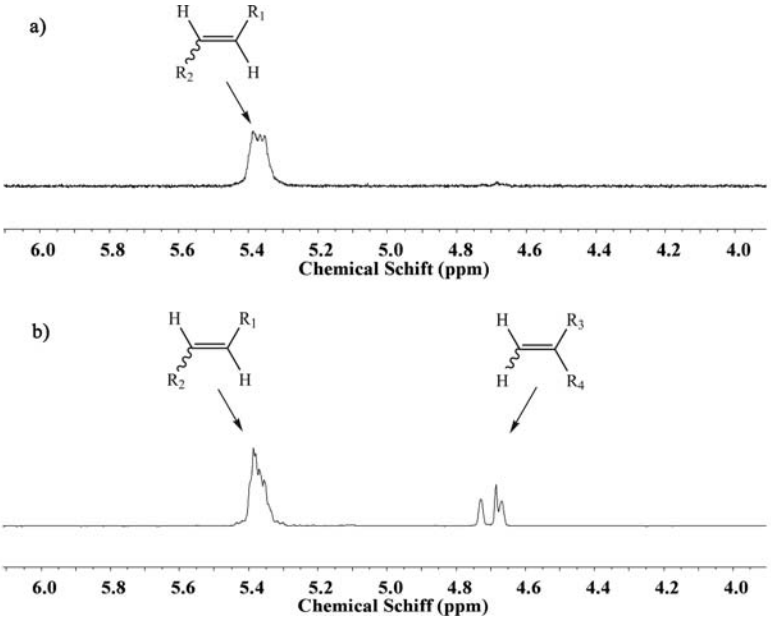

Figure 5. ^{1}H NMR spectrum of the end groups for oligo(1-hexene)s produced by (a) the zirconium catalyst **9**/MAO (Table 3, run 11) and (b) the zirconium catalyst **7**/MAO (Table 3, run 7).

and no signals for vinylidene end groups ($R_3R_4C{=}CH_2$), expected around 150 and 110 ppm, were observed. This indicates that the oligo(1-hexene)s are formed by β-H elimination from a 2,1-enchained zirconium alkyl and that the 2,1-regioselectivity is close to 100%. Remarkably, the nature of the end groups in the resulting oligomers is highly dependent on the substituents in the ortho-position of the oxygen atom in the ligand. With the increase of the steric hindrance of the substituents, the 2,1-regioselectivity was improved significantly. For example, using complex 1 as pro-catalyst, with R_1 = $CPhMe_2$, R_2 = ^{t}Bu, the resultant polymer has 2,1-regioselectivity of 76%, while nearly 100% 2,1-regioselectivity was found in the catalyst system of complex **9** with R_1 = $Si^{t}BuMe_2$, R_2 = $CPhMe_2$. Also, the 2,1-regioselectivity of titanium complexes was greatly enhanced from 86% to 99% via increasing steric hindrance of the substituents from R_1 = R_2 = ^{t}Bu to R_1 = $^{t}BuSiMe_2$, R_2 = $CPhMe_2$. The resultant oligo(1-hexene)s produced by these catalysts are atactic according to the ^{13}C NMR spectrum.

CONCLUSIONS

In summary, we have developed highly active ethylene polymerization and regioselective 1-hexene oligomerization catalysts with tridentate [ONO] ligands. In the presence of methylaluminoxane (MAO), these complexes show good activities in catalyzing ethylene polymerization in comparison with their titanium analogues, and afford high molecular weight polymers with unimodal molecular weight distributions. The catalytic activity can be tuned by changing the R group on the ortho-position of the oxygen atom in the $[O^{-}NO^{-}]$ ligand. The highest TOF of 2.61×10^{5} h^{-1} and half-life of 16 h were observed in the catalyst system regarding complex **9**. Upon activation with MAO, these complexes proved to be active in catalyzing 1-hexene oligomerization with excellent regioselectivity. The 2,1-regioselectivity can be tuned by altering the substitute groups on [ONO] ligands, and the highest 2,1-regioselectivity is up to 99%. These novel complexes represent a remarkable contribution to the limited list of nonmetallocene type group 4 catalysts for ethylene and α-olefin polymerization.

EXPERIMENTAL SECTION

All manipulations involving air- and/or water-sensitive compounds were carried out in standard glovebox or under dry nitrogen using standard Schlenk techniques. Solvents were dried from the appropriate drying agent, distilled, degassed, and stored over 4 Á sieves. Polymerization grade ethylene was further purified by passage through columns of 3 Á molecular sieves and MnO. Methylaluminoxane (MAO), ^{n}BuLi, *n*-hexane, $ZrCl_4$, and $TiCl_4$ were purchased from Aldrich. ^{1}H and ^{13}C NMR spectra were recorded on Varian INOVA-400 MHz type (^{1}H, 400 MHz) (^{13}C, 100 MHz) spectrometer. ^{1}H and ^{13}C NMR chemical shifts were referred to the solvent signal. Mass spectra were measured on a Micromass Q-TOF mass spectrometer instrument using electrospray ionization (ESI). Thermo-gravimetric analyses of all resulted polymers were measured on Mettler-Toledo TGA/SDTA851e. Elemental analyses were performed on a Vario EL microanalyzer. The molecular weight and polydispersity index (PDI) of the polyethylene samples were measured on a PL-GPC 220 type high-temperature chromatograph at 150 °C with 1,2,4-trichlorobenzene as the solvent at a flow rate of 1.0 mL/min. The molecular weight and PDI of the poly(1-hexene) samples were measured on a GPC Agilent 1260 at 40 °C with THF as the solvent at a flow rate of 1.0 mL/min.

[4,6-$^{t}Bu_2$-2-CH=N(4,6-$^{t}Bu_2$-2-OHC_6H_2)C_6H_2OH] (L1H_2). Under nitrogen, to a solution of 3,5-di-*tert*-butylsalicylaldehyde (2.34 g, 10 mmol) and 2-amino-3,5-di-*tert*-butylphenol (2.21 g, 10 mmol) in ethanol were added two drops of acetic acid at room temperature. After refluxing with stirring for 24 h, the resulting mixture was cooled to room temperature to afford a yellow solid. The solid was recrystallized from ethanol to give yellow crystals as the desired product ligand **L1H_2**, yield 3.77 g (86%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 12.64 (s, 1H), 8.68 (s, 1H), 7.47 (d, J = 2.4 Hz, 1H), 7.27 (d, J = 2.4 Hz, 1H), 7.25 (d, J = 3.2 Hz, 1H), 7.00 (d, J = 2.0 Hz, 1H), 6.11 (s,1H), 1.47 (s, 9H), 1.45 (s, 9H), 1.35 (s, 9H), 1.34 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.8, 157.6, 146.1, 142.4, 141.2, 137.1, 135.7, 135.6, 128.5, 127.2, 122.9, 118.7, 112.7, 35.2, 35.1, 34.6, 34.3, 31.7, 31.5, 29.6, 29.5. HRMS (m/z) Calcd. for

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[$L1H_2$+Na^+]: 460.3191, found: 460.3180. Anal. Calcd. for $C_{29}H_{43}NO_2$ (%): C 79.59; H 9.90; N 3.20. Found: C 79.28; H 9.61; N 3.34.

[4-^{t}Bu-6-Ad-2-CH=N(4,6-^{t}Bu$_2$-2-OHC$_6$H$_2$)C$_6$H$_2$OH] ($L2H_2$). The ligand $L2H_2$ was prepared as a similar procedure of $L1H_2$. ^{1}H NMR (400 MHz, $CDCl_3$) δ 12.14 (s, 1H), 8.62 (s, 1H), 7.64 (d, J = 2.4 Hz, 1H), 7.33 (d, J = 2.4 Hz, 1H), 7.20−7.32 (m, 5H), 7.15 (d, J = 2.4 Hz, 1H), 6.91 (d, J = 2.0 Hz, 1H), 5.95 (s,1H), 1.77 (s, 6H), 1.39 (s, 18H), 1.31 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.4, 157.0, 150.5, 146.1, 142.4, 141.2, 136.6, 135.8, 135.6, 128.9, 128.8, 127.7, 125.7, 125.4, 122.9, 119.0, 112.8, 42.4, 35.1, 34.7, 34.4, 31.8, 31.7, 31.6, 29.6. HRMS (m/z) Calcd. for [$L2H_2$+Na^+]: 538.3661, found: 538.3654. Anal. Calcd. for $C_{35}H_{49}NO_2$ (%): C 81.50; H 9.58; N 2.72. Found: C 81.13; H 9.78; N 2.91.

[4-^{t}Bu-6-CMe$_2$Ph-2-CH=N(4,6-^{t}Bu$_2$-2-OHC$_6$H$_2$)C$_6$H$_2$OH] ($L3H_2$). The ligand $L3H_2$ was prepared as a similar procedure of $L1H_2$. ^{1}H NMR (400 MHz, $CDCl_3$) δ 12.68 (s, 1H), 8.68 (s, 1H), 7.42 (d, J = 2.4 Hz, 1H), 6.99 (d, J = 2.0 Hz, 1H), 6.10 (s, 1H), 2.20 (s, 6H), 2.11 (s, 3H), 1.81 (s, 6H), 1.45 (s, 9H), 1.35 (s, 9H), 1.34 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.9, 157.9, 146.1, 142.3, 141.3, 137.4, 135.7, 135.6, 128.5, 127.1, 122.9, 118.7, 112.6, 40.3, 37.4, 37.2, 35.1, 34.6, 34.3, 31.7, 31.5. HRMS (m/z) Calcd. for [$L3H_2$+Na^+]: 522.3348, found: 522.3356. Anal. Calcd. for $C_{34}H_{45}NO_2$ (%): C 81.72; H 9.08; N 2.80. Found: C 81.23; H 8.88; N 3.01.

[4-^{t}Bu-6-CMe$_2$Ph-2-CH=N(4-^{t}Bu-6-CMe$_2$Ph-2-OHC$_6$H$_2$)C$_6$H$_2$OH] ($L4H_2$). The ligand $L4H_2$ was prepared as a similar procedure of L_1H_2. ^{1}H NMR (400 MHz, $CDCl_3$) δ 12.17 (s, 1H), 8.58 (s, 1H), 7.58 (d, J = 2.4 Hz, 1H), 7.38 (d, J = 2.0 Hz, 1H), 7.11−7.28 (m, 11H), 6.96 (s, 1H), 5.46 (s, 1H), 1.72 (s, 6H), 1.69 (s, 6H), 1.36 (s, 18H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.4, 157.1, 150.6, 145.5, 142.6, 141.0, 136.6, 136.1, 135.3, 128.8, 128.2, 128.0, 127.6, 125.9, 125.8, 125.7, 125.4, 123.0, 118.9, 113.8, 42.4, 34.8, 34.4, 31.9, 31.7, 29.7, 29.6. HRMS (m/z) Calcd. for [$L4H_2$+Na^+]: 584.3504, found: 584.3488. Anal. Calcd. for $C_{39}H_{47}NO_2$ (%): C 83.38; H 8.43; N 2.49. Found: C 83.78; H 8.18; N 2.70.

[4-^{t}Bu-6-SiMe$_2$Ph-2-CH=N(4-^{t}Bu-6-CMe$_2$Ph-2-OHC$_6$H$_2$)-C$_6$H$_2$OH] ($L5H_2$). The ligand $L5H_2$ was prepared as a similar procedure of $L1H_2$. ^{1}H NMR (400 MHz, $CDCl_3$) δ 12.13 (s, 1H), 8.63 (s, 1H), 7.51 (s, J = 2.4 Hz, 1H), 7.43 (d, J = 2.4 Hz, 1H), 7.36 (d, J = 2.4 Hz, 1H), 7.17−7.30 (m, 5H), 7.05 (d, J = 2.0 Hz, 1H), 5.62 (s, 1H), 1.75 (s, 6H), 1.39 (s, 9H), 1.32 (s, 9H), 0.88 (s, 9H), 0.31 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.6, 163.5, 150.6, 145.7, 142.8, 141.2, 138.3, 136.3, 135.3, 130.6, 128.3, 125.9, 125.7, 125.0, 123.1, 117.8, 113.8, 42.5, 34.8, 34.2, 31.9, 31.6, 29.8, 27.2, 17.8, −4.6. HRMS (m/z) Calcd. for [$L5H_2$+Na^+]: 580.3587, found: 580.3594. Anal. Calcd. for $C_{36}H_{51}NO_2Si$ (%): C 77.50; H 9.21; N 2.51. Found: C 77.85; H 8.97; N 2.70.

[4,6-^{t}Bu$_2$-2-CH=N(4,6-^{t}Bu$_2$-2-OC$_6$H$_2$)C$_6$H$_2$O]TiCl$_2$ (1). A solution of n-BuLi (6.5 mL, 1.6 M solution in n-hexane, 10.4 mmol) was added dropwise to a stirred solution of ligand $L1H_2$ (2.19 g, 5 mmol) in toluene (20 mL) at −78 °C. The solution was allowed to warm to room temperature and stirred for 2 h, and then was added dropwise to a solution of $TiCl_4$ (0.99 g, 5.21 mmol) in toluene (20 mL). After the resulting mixture was allowed to warm to room temperature and stirred for 24 h, a red solution was obtained. The solvents were removed under vacuum, and the residue was extracted with CH_2Cl_2 (5 mL) and filtered. The filtrate was concentrated to 2 mL and mixed with n-hexane (20 mL). Cooling to room temperature afforded red crystals of complex **1** (2.33 g, 4.20 mmol, 84%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.87 (s, 1H), 7.70 (d, J = 2.4 Hz, 1H), 7.43 (d, J = 2.0 Hz, 1H), 7.22 (d, J = 1.6 Hz, 1H), 7.18 (d, J = 1.2 Hz 1H), 1.54 (s, 9H), 1.46 (s, 9H), 1.38 (s, 9H), 1.35 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.8, 158.2, 155.9, 146.0, 145.3, 141.6, 137.7, 135.3, 133.7, 129.0, 125.2, 123.7, 109.3, 35.4, 35.1, 35.0, 34.9, 31.8, 31.4, 29.9, 29.6. HRMS (m/z) Calcd. for [$C_{29}H_{41}NO_2Cl_2Ti$]$^+$: 553.1994, found: 553.1984. Anal. Calcd. for $C_{29}H_{41}NO_2Cl_2Ti$ (%): C 62.82; H 7.45; N 2.53. Found: C 62.52; H 7.64; N 2.41.

[4-^{t}Bu-6-Ad-2-CH=N(4,6-^{t}Bu$_2$-2-OC$_6$H$_2$)C$_6$H$_2$O]TiCl$_2$ (2). Complex **2** was synthesized in the same way as described above for the synthesis of complex **1** with ligand $L2H_2$ (2.50 g, 5 mmol) as starting material. Pure complex **2** (2.19 g, 3.55 mmol, 71%) was obtained as red crystals. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.72 (s, 1H), 7.73 (d, J = 2.4 Hz, 1H), 7.41 (d, J = 2.4 Hz, 1H), 7.30−7.38 (m, 5H), 7.23 (d, J = 2.4 Hz, 1H), 7.03 (d, J = 2.0 Hz, 1H), 1.76 (s, 6H), 1.41 (s, 9H), 1.35 (s, 9H), 1.33 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.4, 157.6, 156.4, 150.4, 142.7, 142.4, 138.0, 137.7, 137.0, 131.6, 130.0, 129.8, 128.0, 126.5, 125.9, 124.8, 122.9, 108.9, 42.2, 34.7, 34.4, 34.1, 31.8, 31.6. 31.5, 29.8. HRMS (m/z) Calcd. for [$C_{35}H_{47}NO_2Cl_2Ti$]$^+$: 631.2463, found: 631.2471. Anal. Calcd. for $C_{35}H_{47}NO_2Cl_2Ti$ (%): C 66.46; H 7.49; N 2.21. Found: C 66.12; H 7.74; N 2.31.

[4-^{t}Bu-6-CMe$_2$Ph-2-CH=N(4,6-^{t}Bu$_2$-2-OC$_6$H$_2$)C$_6$H$_2$O]TiCl$_2$ (3). Complex **3** was synthesized in the same way as described above for the synthesis of complex **1** with ligand $L3H_2$ (2.58 g, 5 mmol) as starting material. Pure complex **3** (2.06 g, 3.25 mmol, 65%) was obtained as red crystals. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.88 (s, 1H), 7.63 (d, J = 2.0 Hz, 1H), 7.42 (d, J = 2.0 Hz, 1H), 7.22 (s, 1H), 7.19 (d, 1H), 2.24 (s, 6H), 2.17 (s, 3H), 1.91 (d, J = 12 Hz, 3H), 1.80 (d, J = 12 Hz, 3H), 1.44 (s, 9H), 1.38 (s, 9H), 1.38 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.9, 158.7, 157.9, 146.0, 145.0, 141.2, 137.9, 135.1, 133.5, 128.6, 125.0, 123.6, 109.1, 40.6, 37.5, 36.9, 34.9, 34.8, 34.7, 31.6, 31.3, 29.4, 29.0. HRMS (m/z) Calcd. for [$C_{34}H_{43}NO_2Cl_2Ti$]$^+$: 615.2150, found: 615.2158. Anal. Calcd. for $C_{34}H_{43}NO_2Cl_2Ti$ (%): C 66.24; H 7.03; N 2.27. Found: C 66.92; H 7.31; N 2.41.

[4-^{t}Bu-6-CMe$_2$Ph-2-CH=N(4-^{t}Bu-6-CMe$_2$Ph-2-OC$_6$H$_2$)-C$_6$H$_2$O]TiCl$_2$ (4). Complex **4** was synthesized in the same way as described above for the synthesis of complex **1** with ligand $L4H_2$ (2.81 g, 5 mmol) as starting material. Pure complex **4** (2.48 g, 3.65 mmol, 73%) was obtained as red crystals. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.72 (s, 1H), 7.77 (d, J = 2.0 Hz, 1H), 7.41 (d, J = 2.0 Hz, 1H), 7.14−7.32 (m, 12H), 1.82 (s, 6H), 1.78 (s, 6H), 1.39 (s, 9H), 1.33 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.1, 157.4, 148.9, 145.6, 145.0, 140.8, 140.6, 137.5, 135.1, 133.2, 129.0, 128.3, 128.1, 126.6, 126.1, 125.8, 125.6, 125.4, 123.7, 117.8, 109.5, 42.5, 42.1, 35.0, 34.8, 31.7, 31.4, 29.4, 28.7. HRMS (m/z) Calcd. for [$C_{39}H_{45}NO_2Cl_2Ti$]$^+$: 677.2307, found: 677.2317. Anal. Calcd. for $C_{39}H_{45}NO_2Cl_2Ti$ (%): C 69.03; H 6.68; N 2.06. Found: C 69.44; H 6.43; N 2.21.

[4-^{t}Bu-6-SiMe$_2$^{t}Bu-2-CH=N(4-^{t}Bu-6-CMe$_2$Ph-2-OC$_6$H$_2$)-C$_6$H$_2$O]TiCl$_2$ (5). Complex **5** was synthesized in the same way as described above for the synthesis of complex **1** with ligand $L5H_2$ (2.79 g, 5 mmol) as starting material. Pure complex **5** (2.19 g, 3.25 mmol, 65%) was obtained as red crystals. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.71 (s, 1H), 7.72 (s, 1H), 7.47 (s, 1H), 7.18−7.38 (m, 7H), 1.76 (s, 6H), 1.36 (s, 9H), 1.35 (s, 9H), 0.92 (s, 9H), 0.43 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.8, 158.2, 156.6, 150.2, 145.1, 142.6, 140.6, 139.8, 135.3, 132.3, 128.0, 126.9, 125.5, 124.9, 124.7, 122.7, 109.7, 41.9, 35.1, 34.4, 32.1, 31.8, 31.3, 28.5, 26.9, 17.7, −4.7. HRMS (m/z) Calcd. for [$C_{36}H_{49}NO_2Cl_2SiTi$]$^+$: 673.2389, found: 673.2395. Anal. Calcd. for $C_{36}H_{49}NO_2Cl_2SiTi$ (%): C 64.09; H 7.32; N 2.08. Found: C 64.43; H 7.12; N 2.21.

[4-^{t}Bu-6-SiMe$_2$^{t}Bu-2-CH=N(4-^{t}Bu-6-CMe$_2$Ph-2-OC$_6$H$_2$)-C$_6$H$_2$O]TiCl$_2$·THF (6). A solution of complex **5** (1.10 g, 1.62 mmol) was added dropwise to a stirred THF (10 mL) solvent at −78 °C. The solution was allowed to warm to room temperature and stirred for 24 h. The solvents were removed under vacuum, and the residue was extracted with CH_2Cl_2 (5 mL) and filtered. The filtrate was concentrated to 2 mL and mixed with hexane (20 mL). Cooling to room temperature afforded red crystals of complex **6** (1.15 g, 1.54 mmol, 95%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.29 (s, 1H), 7.56 (d, J = 2.4 Hz, 1H), 7.23−7.37 (m, 6H), 7.08 (t, J = 7.2 Hz,

1H), 6.98 (d, J = 1.6 Hz, 1H), 3.51 (br, 4H), 1.70 (s, 6H), 1.66 (br, 4H), 1.36 (s, 9H), 1.30 (s, 9H), 0.93 (s, 9H), 0.35 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.3, 158.7, 154.9, 149.9, 143.7, 143.6, 142.1, 139.3, 135.3, 132.4, 128.4, 127.1, 125.1, 125.0, 124.7, 123.1, 109.3, 71.5, 41.8, 34.6, 33.9, 31.4, 30.9, 28.7, 27.1, 24.9, −4.4. Anal. Calcd. for $C_{40}H_{57}NO_3SiCl_2Ti$ (%): C 64.34; H 7.69; N 1.88. Found: C 64.41; H 7.74; N 1.83.

[4-^{t}Bu-6-CMe$_2$Ph-2-CH=N(4,6-^{t}Bu$_2$-2-OC$_6$H$_2$)C$_6$H$_2$O]ZrCl$_2$·THF (7). A solution of *n*-BuLi (3.2 mL, 1.6 M solution in *n*-hexane, 5.12 mmol) was added dropwise to a stirred solution of ligand **L3H$_2$** (1.25 g, 2.50 mmol) in THF (10 mL) at −78 °C. The solution was allowed to warm to room temperature and stirred for 2 h, and then was added dropwise to a solution of $ZrCl_4$ (0.61 g, 2.63 mmol) in THF (20 mL). After the resulting mixture was allowed to warm to 60 °C and stirred for 24 h, an orange solution was obtained. The solvents were removed under vacuum, and the residue was extracted with CH_2Cl_2 (5 mL) and filtered. The filtrate was concentrated to 4 mL and mixed with hexane (20 mL). Cooling to room temperature afforded orange crystals of complex **7** (0.75 g, 1.03 mmol, 41%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.51 (s, 1H), 7.78 (s, 1H), 7.07−7.35 (m, 8H), 3.50 (br, 1H), 1.66 (s, 6H), 1.40 (s, 9H), 1.35 (s, 9H), 1.30 (s, 9H), 0.87 (t, J = 7.6 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.2, 157.2, 156.3, 150.3, 142.7, 142.4, 138.0, 137.7, 137.0, 131.6, 129.9, 129.8, 128.0, 126.5, 125.9, 124.8, 122.9, 108.8, 71.7, 42.1, 34.9, 34.7, 34.4, 31.5, 31.4, 29.4, 25.3, 22.7. Anal. Calcd. for $C_{38}H_{51}NO_3Cl_2Zr$ (%): C 62.36; H 7.02; N 1.91. Found: C 61.79; H 6.83; N 2.01.

[4-^{t}Bu-6-CMe$_2$Ph-2-CH=N(4-^{t}Bu-6-CMe$_2$Ph-2-OC$_6$H$_2$)C$_6$H$_2$O]-ZrCl$_2$·THF (8). Complex **8** was synthesized in the same way as described above for the synthesis of complex **7** with ligand **L4H$_2$** (1.41 g, 2.50 mmol) as starting material. Pure complex **8** (0.90 g, 1.13 mmol, 45%) was obtained as orange crystals. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.46 (s, 1H), 7.77 (s, 1H), 7.38 (s, 1H), 7.01−7.30 (m, 7H), 3.54 (br, 4H), 1.92 (s, 6H), 1.86 (s, 6H), 1.39 (s, 9H), 1.37 (s, 9H), 0.89 (t, J = 6.8 Hz, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.5, 157.2, 149.1, 145.8, 145.0, 140.7, 140.6, 137.4, 135.4, 133.2, 129.1, 128.5, 128.3, 126.7, 126.1, 125.8, 125.5, 125.3, 123.7, 117.8, 109.3, 72.7, 42.5, 42.1, 35.0, 34.8, 31.7, 31.4, 25.6, 25.4, 22.7. Anal. Calcd. for $C_{43}H_{53}NO_3Cl_2Zr$ (%): C 65.04; H 6.73; N 1.76. Found: C 65.12; H 6.81; N 1.79.

[4-^{t}Bu-6-SiMe$_2$^{t}Bu-2-CH=N(4-^{t}Bu-6-CMe$_2$Ph-2-OC$_6$H$_2$)-C$_6$H$_2$O]ZrCl$_2$·THF (9). Complex **9** was synthesized in the same way as described above for the synthesis of complex **7** with ligand **L5H$_2$** (1.40 g, 2.50 mmol) as starting material. Pure complex **9** (0.79 g, 1.00 mmol, 40%) was obtained as orange crystals. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.53 (s, 1H), 7.60 (s, 1H), 7.41 (s, 1H), 7.17−7.34 (m, 6H), 7.05 (t, J = 7.2 Hz, 1H), 3.43 (br, 4H), 1.62 (s, 6H), 1.39 (s, 6H), 1.32 (s, 9H), 0.93 (s, 6H), 0.88 (t, J = 7.2 Hz, 4H), 0.35 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.2, 158.3, 156.0, 150.5, 142.9, 142.3, 142.0, 137.7, 136.9, 133.0, 127.6, 126.7, 126.3, 124.8, 124.7, 121.6, 109.2, 72.5, 41.8, 34.8, 34.1, 31.7, 31.3, 27.0, 25.2, 22.7, 17.5, −4.4. Anal. Calcd. for $C_{40}H_{57}SiNO_3Cl_2Zr$ (%): C 60.81; H 7.27; N 1.77. Found: C 60.70; H 6.21; N 1.70.

[4,6-^{t}Bu$_2$-2-CH=N(4,6-^{t}Bu$_2$-2-OC$_6$H$_2$)C$_6$H$_2$O]$_2$Zr (10). Complex **10** was synthesized in 30% yield in the way as described above for the syntheses of complex **7**, or in 35% yield by using similar procedure for the preparation of complex **1**. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.87 (s, 1H), 7.43 (s, 1H), 7.33 (s, 1H), 7.29 (s, 1H), 7.17 (s, 1H), 1.38 (s, 9H), 1.33 (s, 6H), 1.25 (s, 9H), 1.13 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.8, 158.7, 158.1, 140.7, 140.3, 138.3, 138.0, 137.3, 130.6, 128.7, 123.7, 121.7, 108.9, 34.9, 34.8, 34.7, 34.5, 31.8, 31.5, 29.7, 29.6. Anal. Calcd. for $C_{58}H_{82}N_2O_4Zr$ (%): C 72.38; H 8.59; N 2.91. Found: C 72.49; H 8.51; N 2.87.

[4-^{t}Bu-6-CMe$_2$Ph-2-CH=N(4-^{t}Bu-6-CMe$_2$Ph-2-OC$_6$H$_2$)-C$_6$H$_2$O]$_2$Zr (11). Complex **11** was synthesized in the same way as described above for the synthesis of complex **1** with ligand **L4H$_2$** (1.41 g, 2.50 mmol) as starting material. Pure complex **11** (0.45 g, 30%) was obtained as orange crystals. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.45 (s, 2H), 7.55 (s, 2H), 7.44 (s, 2H), 7.02−7.37 (m, 24H), 1.56 (s, 12H), 1.53 (s, 12H), 1.39 (s, 18H), 1.37 (s, 18H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.3, 157.5, 149.3, 145.9, 145.0, 140.6, 140.5, 137.5, 135.4, 133.5, 129.0, 128.7, 128.5, 126.9, 126.5, 125.7, 125.5, 125.4, 123.7, 117.9, 109.5, 42.2, 42.3, 35.1, 34.7, 31.6, 31.2, 25.7, 25.4. Anal. Calcd. for $C_{78}H_{90}N_2O_4Zr$ (%): C 77.37; H 7.49; N 2.31. Found: C 77.28; H 7.41; N 2.34.

Ethylene Polymerizations. A dry 250 mL steel autoclave with a magnetic stirrer was charged with 100 mL of toluene, and saturated with ethylene (1.0 bar) at 20 °C. The polymerization reaction was started by injection of a mixture of MAO and a catalyst in toluene. The vessel was repressurized to needed pressure with ethylene immediately, and the pressure was kept by continuously feeding of ethylene. After the specified time period, the polymerization was quenched by injecting acidified methanol [HCl (3M)/methanol = 1:1], and the polymer was collected by filtration, washed with water, methanol, and dried at 60 °C in vacuo to a constant weight.

1-Hexene Polymerizations. A dry 25 mL flask with a magnetic stirrer was charged with 3 g of *n*-hexene at 20 °C. The polymerization reaction was started by injection of a mixture of MAO and a catalyst in toluene. After the specified time period, the polymerization was quenched by injecting acidified methanol [HCl (3M)/methanol = 1:1], Oligo (1-hexene)s were purified by passing their hexane solution through a pipet containig silica gel.

Crystal Structure Determination. Single crystals of complexes **2**, **8**, and **11** for X-ray structural analysis were obtained from a solution of CH_2Cl_2/*n*-hexane. Diffraction data were collected at 293 K on a Bruker SMART-CCD diffractometer using graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). The structures were solved by direct methods[24] and refined by full-matrix least-squares on F^2. All non-hydrogen atoms were refined anisotropically, and the hydrogen atoms were included in idealized position. All calculations were performed using the SHELXTL[25] crystallographic software packages. Details of the crystal data, data collections, and structure refinements are summarized in Table 1.

CCDC-816107 (for **2**), -816109 (for **8**), and -816108 (for **11**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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