Synthesis and Characterization of Titanium(IV) Complexes Bearing Monoanionic [O⁻NX] (X = O, S, Se) Tridentate Ligands and Their Behaviors in Ethylene Homo- and Copolymerizaton with 1-Hexene

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A series of novel titanium(IV) complexes bearing monoanionic [O⁻NX] (X = O, S, Se) ligands is designed by sidearm approach. These complexes were synthesized, characterized, and employed as catalysts in ethylene homo- and copolymerization. X-ray diffraction studies on these new compounds reveal a distorted octahedral coordination of the central metal with the three chlorine ligands in a *mer* disposition. In the presence of modified methylaluminoxane (MMAO), they exhibit moderate to high activity and afford highly linear polyethylene. Variation of the sidearm, including different heteroatom and substituents, proves to modulate both the catalytic activity and the molecular weight of the resulting polyethylene. The complexes also show excellent capability in copolymerization of ethylene with 1-hexene.

Introduction

During the last two decades, single-site catalytic systems based on the metallocene complexes of group IV metals have been extensively studied.[1] Recently, there has been a growing interest in developing new nonmetallocene catalysts, and in expanding beyond the first half of the transition metal series and various ligand backbones,[2−4] as well as allowing access to previously inaccessible polymers.[4] Of the successful nonmetallocene catalysts developed,[2−4] the metal complexes possessing phenoxyimine ligands are one of the promising examples.[5] Nickel complexes bearing salicylaldiminato ligands exhibited good tolerance to functional group and even remained active for olefin polymerization in the presence of polar or protonic solvents.[6,7] Fujita's group and Coates' group described a family of highly active group IV catalysts **I** bearing bis(salicylaldiminato) ligands[8−13] (Scheme 1). They found that titanium complexes **I** were excellent precatalysts for living ethylene polymerization,[9,10] living propylene polymerization with excellent stereoselectivity,[11] and living copolymerization of ethylene with α-olefins.[12a] The synthesis of functional and block copolymers of propylene can also be realized using such catalytic systems.[13] Gibson et al. reported that salicylaldiminato ligands could also be employed to stabilize Cr(III) catalysts.[14]

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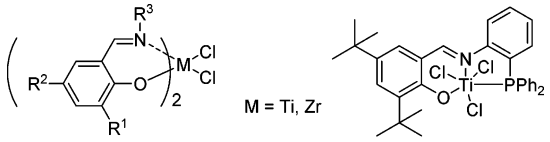
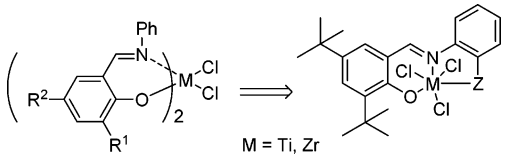
Scheme 1



I **II**

Scheme 2



I **III**

Sidearm approach has proven to be an efficient strategy for the design of organometallic catalysts in organic synthesis. Recently, Kol et al. showed that group IV complexes bearing bis(phenolate) [O⁻NO⁻] and [O⁻NNO⁻] type ligands are good olefin polymerization catalysts, in particular for the polymerization of 1-hexene.[15−20] They found that the pendant amino group of the ligand influenced strongly the activity in polymerization of 1-hexene.[16] Gibson et al. reported that the activities of Cr(III) catalysts, containing salicylaldininato ligands with pendant donors, were higher than those of the corresponding catalysts without sidearm donors.[14] Nickel complexes bearing salicylaldiminato ligands with a carbene as a pendant donor have also been reported.[21] In a previous study on ylide chemistry and asymmetric catalysis, we also found strong sidearm effects on selectivity and catalytic activity in some reactions.[22] Recently, we reported that catalysts bearing a [O⁻NP] ligand (**II**) (Scheme 1) were robust and highly active for ethylene homopolymerization and copolymerization with 1-hexene and with norbornene.[23] We also communicated that [O⁻NS] titanium complexes[24] were good catalysts for olefin polymerization.[25] To further understand the sidearm effects of the extra donor and the structure−reactivity relationship of the catalysts, we herein report the synthesis and characterization of a series of titanium complexes bearing phenoxyimines with O- (**5a**−**5d**), S- (**5e**−**5l**), or Se-donors (**5m**) as sidearms, as well as the behaviors of such complexes in ethylene polymerization and copolymerization with 1-hexene.

Results and Discussion

1. Design and Synthesis of Ligands and Complexes. As described by Fujita[8] and Coates,[11a] bis(salicylaldiminato) titanium complexes **I** showed high performance in ethylene polymerization. We proposed that the introduction of a sidearm group Z containing a donor atom would lead to the formation of mono(salicylaldiminato) titanium complexes **III**, as shown in Scheme 2. Complexes **III** are open for the coordination and insertion of α-olefin, beneficial to ethylene copolymerization with an α-olefin or a bulky olefin. Therefore, different sidearms (O, S, Se) with various electronic and sterically hindered substituents were selected for study.

Ligand Synthesis. The synthetic route for the ligands is shown in Scheme 3. Treatment of phenols **2a**−**2d**, benzenethiols **2e**−**2l**, and benzeneselenol **2m** with 1 equiv of KOH and 1-chloro-2-nitrobenzene at 90 °C for 5 h afforded nitrobenzene derivatives **3a**−**3m**. Nitrobenzenes **3a**−**3m** were reduced by Zn/HOAc, and products **4a**−**4m** were collected, which could be used directly for the next step without further purification. Condensation of salicylal **1a** or **1b**[8b,26] with anilines **4** afforded tridentate ligands **L1**−**L14** in 60−90% yields. The procedure for preparation of imines **L1**−**L14** is very simple and environmental friendly: a mixture of the aniline and aldehyde **1a** or **1b** was refluxed for several hours and cooled to room temperature after the reaction was complete, and the solid was collected as the pure imines. In addition, the mother liquor could be recycled.

Synthesis of Complexes. The ligands were deprotonated by 1.0 equiv of KH, followed by treating with 1.0 equiv of $TiCl_4$ in toluene at room temperature, to afford the desired titanium complexes **5a**−**5n** in good to high yields. The purification of the complexes was performed by recrystallization from toluene upon cooling to −30 °C except for complex **5n**, which was recrystallized from a mixture of dichloromethane and hexane. It is worthy to note that only the monoligated complexes were isolated even if 1.0 equiv of excess ligand was added in the reaction.

2. Characterization of Complexes. Complexes **5a**−**5n** were characterized by NMR, IR, and elemental analysis. Crystals of **5a**, **5e**, **5g**, and **5i** suitable for X-ray structure determination were developed from toluene, and a crystal of **5n** was obtained from dichloromethane/hexane solution. As shown in Figures 1−5, complexes **5a**, **5e**, **5g**, **5i**, and **5n** feature a distorted octahedral coordination of the titanium with the three chlorine ligands in a *mer* disposition, which is a good orientation for olefin insertion and thus favorable for polymerization. The selected bond lengths and angles are listed in Table 1. As shown in Figure 1, the bond angle sum of Ti−O1−C22 (125.2°), Ti−O1−C5 (117.4°), and C5−O1−C22 (117.0°) in **5a** is nearly 360°. The torsion angle of Ti−O1−C22−C27 is 89.7°, and C22,

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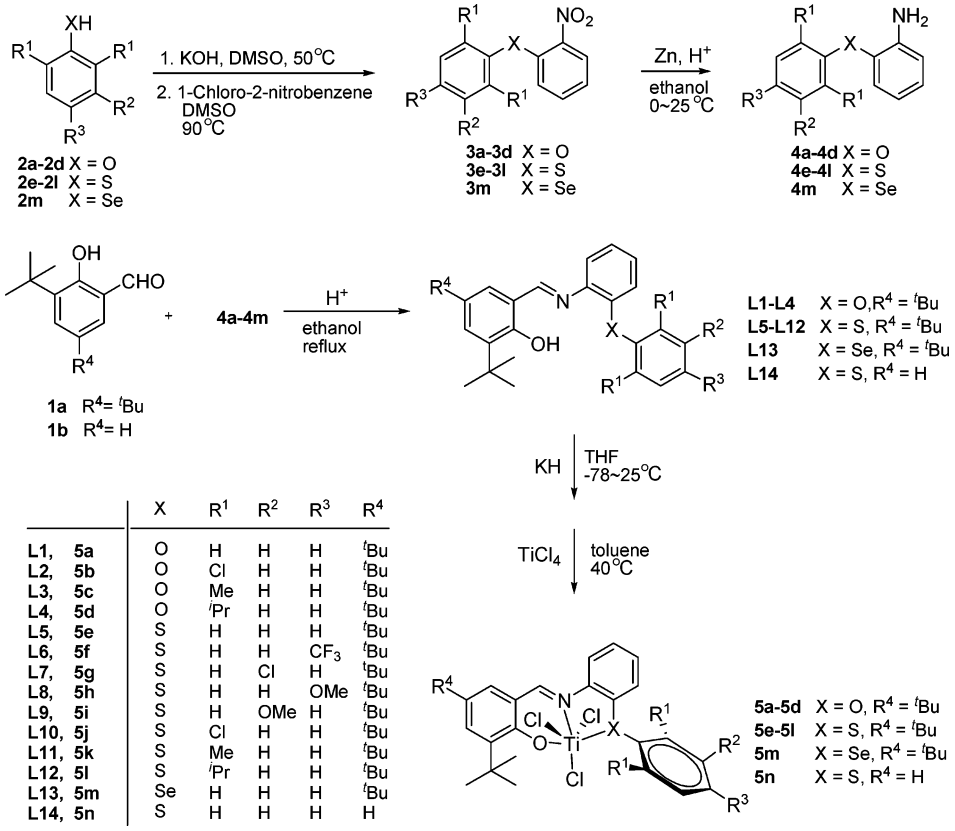
Scheme 3



	X	R^1	R^2	R^3	R^4
L1, 5a	O	H	H	H	^{t}Bu
L2, 5b	O	Cl	H	H	^{t}Bu
L3, 5c	O	Me	H	H	^{t}Bu
L4, 5d	O	^{i}Pr	H	H	^{t}Bu
L5, 5e	S	H	H	H	^{t}Bu
L6, 5f	S	H	H	CF_3	^{t}Bu
L7, 5g	S	H	Cl	H	^{t}Bu
L8, 5h	S	H	H	OMe	^{t}Bu
L9, 5i	S	H	OMe	H	^{t}Bu
L10, 5j	S	Cl	H	H	^{t}Bu
L11, 5k	S	Me	H	H	^{t}Bu
L12, 5l	S	^{i}Pr	H	H	^{t}Bu
L13, 5m	Se	H	H	H	^{t}Bu
L14, 5n	S	H	H	H	H

Ti, C5, and O1 are coplanar. These facts revealed that O1 atom is sp^2 hybridization and the phenyl group is nearly perpendicular to the N1−Ti−O1 plane in **5a**. The molecular structures of sulfur-containing complexes **5e**, **5g**, **5i**, and **5n** (Figures 2−4) are similar, but they are different from that of the oxygen-containing complex **5a**. For example, the bond angles of Ti−S−C22, Ti−S−C1, and C1−S−C22 in **5e** are 115.4°, 98.9°, and 103.3°, respectively, and the sum is 317.8°, suggesting that the S atom in **5e** is sp^3-hybridized. As a result, the phenyl group in **5e** deviated from the [O⁻NS] plane. The Ti−Cl bond lengths in complexes **5e**, **5g**, **5i**, and **5n** are shorter than those of the corresponding Ti−Cl bond in **5a**, suggesting that the electron donation is reduced by using sulfur ligands instead of oxygen

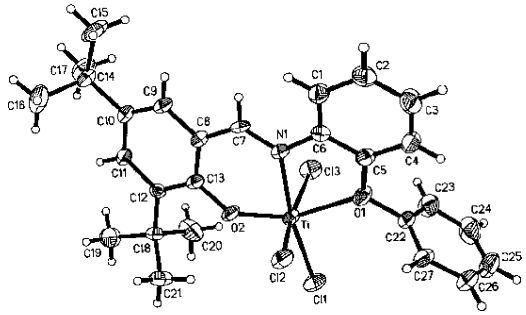


Figure 1. Molecular structure of complex **5a**.

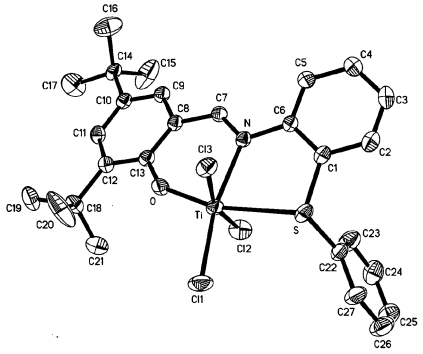


Figure 2. Molecular structure of complex **5e**.

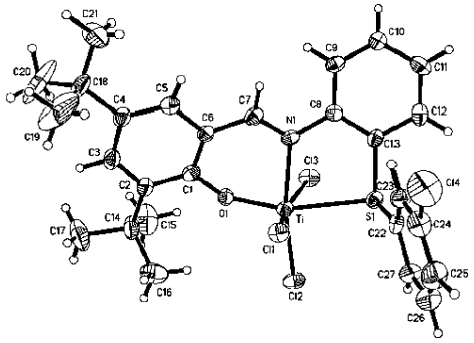


Figure 3. Molecular structure of complex **5g**.

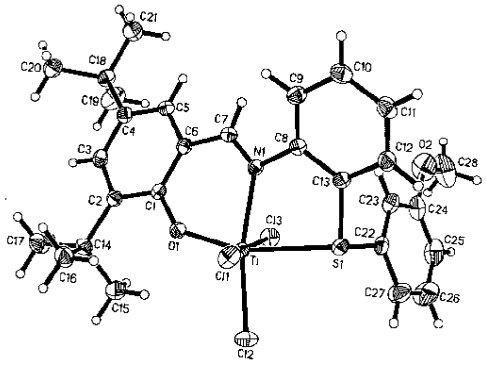


Figure 4. Molecular structure of complex **5i**.

Table 1. Selected Bond Lengths (Å) and Angles (deg) of Complexes 5a, 5e, 5g, 5i, and 5n

	5a	5e	5g	5i	5n
Ti−O(2)	1.806(4)				
Ti−O(1)	2.249(5)	1.7910(19)	1.791(4)	1.8030(18)	1.798(8)
Ti−N(1)	2.219(5)	2.198(2)	2.181(5)	2.164(2)	2.177(8)
Ti−S(1)		2.5908	2.622(2)	2.6044(9)	2.591(3)
Ti−Cl(1)	2.296(2)	2.2509(10)	2.2889(19)	2.3088(9)	2.334(4)
Ti−Cl(2)	2.385(2)	2.2887(10)	2.273(2)	2.2901(9)	2.256(4)
Ti−Cl(3)	2.348(2)	2.3430(10)	2.321(2)	2.2952(9)	2.285(4)
O(1)−Ti−N(1)	72.83(17)	86.44(8)	84.49(18)	84.40(8)	85.9(3)
O(1)−Ti−Cl(1)	97.21(12)	106.21(7)	92.03(14)	98.43(7)	96.3(3)
N(1)−Ti−Cl(1)	169.85(15)	167.35(7)	85.70(13)	86.75(6)	84.5(3)
O(1)−Ti−Cl(2)	83.88(14)	92.76(7)	105.98(14)	108.12(7)	106.5(2)
N(1)−Ti−Cl(2)	83.91(14)	83.81(7)	169.52(15)	167.47(6)	167.5(3)
Cl(1)−Ti−Cl(2)	93.26(8)	95.79(4)	94.36(8)	91.82(3)	95.0(2)
O(1)−Ti−Cl(3)	83.40(14)	96.48(7)	100.40(14)	91.73(7)	94.0(3)
N(1)−Ti−Cl(3)	86.33(14)	83.01(6)	84.32(13)	86.39(6)	83.7(3)
Cl(1)−Ti−Cl(3)	94.58(8)	94.84(4)	163.22(8)	167.12(4)	163.8(1)
Cl(2)−Ti−Cl(3)	165.80(9)	163.38(4)	93.02(7)	92.52(3)	94.00(2)
O(2)−Ti−N(1)	85.69(18)				
O(2)−Ti−O(1)	158.32(17)				
O(2)−Ti−Cl(1)	104.35(15)				
O(2)−Ti−Cl(3)	92.56(16)				
O(2)−Ti−Cl(2)	96.95(16)				
O(1)−Ti−S(1)		164.04(7)	161.51(14)	161.15(7)	163.9(2)
N(1)−Ti−S(1)		77.79(6)	77.02(14)	76.77(6)	78.3(2)
Cl(1)−Ti−S(1)		89.55(4)	86.31(6)	79.94(3)	79.38(1)
Cl(2)−Ti−S(1)		87.99(4)	92.51(7)	90.72(3)	89.4(1)
Cl(3)−Ti−S(1)		79.36(3)	78.32(7)	87.88(3)	87.3(1)

ligands. These results showed that the sidearm could readily modulate the spatial and the electronic properties of the active site for polymerization and thus tune the activity of catalyst as well as the capability for copolymerization as shown later.

3. Ethylene Homopolymerization. The performance of complexes **5a**−**5n** on ethylene polymerization is summarized in Table 2. These complexes showed moderate to high activity for ethylene polymerization in the presence of MMAO (modified methylaluminoxane), depending on the pendant groups. The results indicated that both the property of the donor atom and the substituents on the sidearm significantly affected their behaviors in ethylene polymerization.

(i) Effects of Sidearms. As shown in Table 2, the donor atoms affect the catalytic behavior significantly in ethylene polymerization, in both activity and molecular weight of polyethylene. For example, complexes **5a**−**5d**, with a pendant group containing an oxygen donor, gave only moderate activity (entries 1, 4−7). However, complexes **5e**−**5m**, with a pendant group containing sulfur and selenium donors, respectively, showed much higher activity than the corresponding O-sidearmed complexes under the same polymerization conditions (entries 2−3, 8, and 13−15). In addition, the molecular weight (M_w) of the polyethylene obtained by complexes **5a**, **5e**, and **5m** significantly increased in the order of donor atom: O < S < Se. These results suggested that both the steric hindrance and electronic effects were probably the factors that influenced the behaviors of the complexes in ethylene polymerization. As shown in Figures 1−5, the molecular structures of S-containing complexes **5e**, **5g**, **5i**, and **5n** are very different from that of O-sidearmed complex **5a**. The deviation of the aryl group in the sidearms of compounds **5e**, **5g**, **5i**, and **5n** resulted in less steric hindrance than complex **5a** (Figures 1−5), beneficial to chain growth and reduction of chain transfer in ethylene polymerization and thus increased the activities of catalysts and the molecular weights of polymers. These steric effects were also consistent with the following experimental results: increasing the steric hindrance by replacing H at the *ortho* position of the phenyl group in the sidearm with Cl, Me, or *i*-Pr decreased the catalytic activity greatly and increased the molecular weights in the order R^1 = H, Cl, Me, ^{i}Pr (entries 4−8 and 13−15). Strong electronic effects of substitutes on the sidearmed aryl group were not observed. For example, the complexes both with an electron-deficient group (**5f**, **5g**) and with an electron-rich group (**5h**, **5i**) on the sidearm showed high and similar activity for ethylene polymerization (entries 9−12). During the polymerization, we observed that the color of **5e** and **5m** in toluene solution changed from red to green (Ti(III)),[27] while the color of solution **5a** changed from red to yellow[28] upon activation with MMAO under the same conditions. These results suggested that different active species might be formed in the olefin polymerization using O-sidearmed and S-sidearmed complexes as precatalysts. This is also a possible reason for the different olefin polymerization behaviors of the complexes with O- and S-pendant groups. A clear mechanism awaits further investigation.

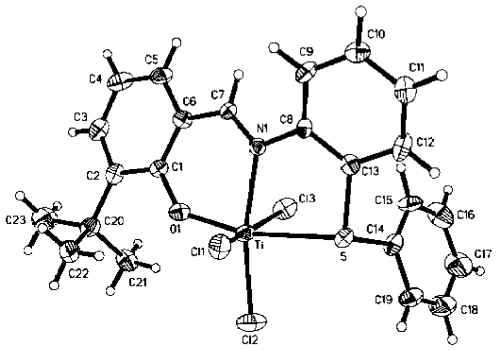


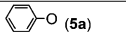
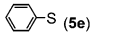
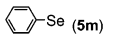
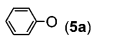
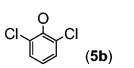
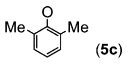
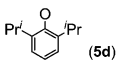
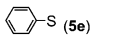
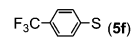
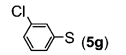
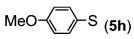
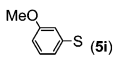
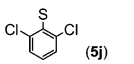
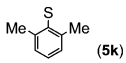
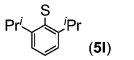
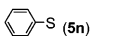
Figure 5. Molecular structure of complex **5n**.

Noticeably, complex **5n** showed much lower activity than **5e**, probably due to its poor solubility in toluene. In addition, molecular weight distribution of the polyethylene obtained by complexes **5e**−**5l** containing sulfur donors ranged from 1.7 to

(27) Eisch, J. J.; Pombrik, S. I.; Zheng, G. X. *Organometallics* **1993**, *12*, 3856−3863.

(28) Mahanthappa, M. K.; Cole, A. P.; Waymouth, R. M. *Organometallics* **2004**, *23*, 836−845.

Table 2. Results of the Ethylene Polymerization Assays[a]

entry	side-arm (complex)	time (min.)	yield (g)	activity [b]	M_n [c]	M_w [c]	M_w/M_n
1	 (5a)	5	0.026	0.032	0.434	1.47	3.39
2	 (5e)	5	1.164	3.98	1.07	2.96	2.75
3	 (5m)	5	0.642	2.38	1.67	5.01	3.00
4[d]	 (5a)	15	0.045	0.020	0.614	2.50	4.07
5[d]	 (5b)	15	0.077	0.023	1.03	3.96	3.84
6[d]	 (5c)	15	0.008	0.002	1.78	4.89	3.31
7[d]	 (5d)	15	0.014	0.003	0.777	11.5	14.9
8	 (5e)	15	1.560	1.73	2.08	5.02	2.04
9	 (5f)	15	0.920	1.17	3.73	7.32	1.95
10	 (5g)	15	0.610	0.74	4.15	12.7	3.07
11	 (5h)	15	1.053	1.26	2.59	5.55	2.14
12	 (5i)	15	0.847	1.02	1.78	4.45	2.49
13	 (5j)	15	0.953	1.22	4.39	7.65	1.74
14	 (5k)	15	0.171	0.20	10.1	18.4	1.87
15	 (5l)	15	0.048	0.06	9.29	25.2	2.71
16	 (5n)	15	0.290	0.13	2.02	4.20	2.10

[a] Polymerization conditions: 3.5 μmol of catalyst in 50 mL of toluene; [Al]/[Ti] = 500; ethylene pressure, 0.1 MPa at 50 °C (oil bath temperature). [b] 10^6 g PE mol^{-1} Ti^{-1} h^{-1} atm^{-1}. [c] Determined by GPC; $\times 10^{-4}$. [d] 10 μmol of catalyst was used.

Table 3. Effects of Ethylene Polymerization Conditions[a]

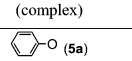
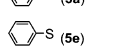
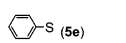
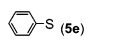
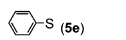
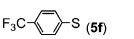
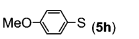
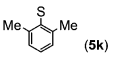
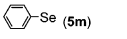
entry	T (°C)[b]	[Al]/[Ti]	yield (g)	activity [c]	M_n[d]	M_w[d]	M_w/M_n[d]
1	50	100	0.550	1.88	2.25	4.02	1.78
2	50	500	1.097	3.73	0.992	2.34	2.36
3	50	1000	1.149	3.93	0.859	2.03	2.36
4	50	1500	1.182	4.04	0.699	1.80	2.58
5	50	2000	1.042	3.56	0.541	1.32	2.44
6	−5	500	0.526	1.80	32.2	59.8	1.86
7	30	500	1.072	3.67	1.61	4.27	2.66
8	80	500	0.420	1.44	0.552	1.36	2.47

[a] Polymerization conditions: 3.5 umol of catalyst **5e** in 50 mL of toluene; ethylene pressure, 0.1 MPa; reaction time, 5 min. [b] Temperature of the bath. [c] 10^6 g PE mol^{-1} Ti^{-1} h^{-1} atm^{-1}. [d] Determined by GPC, $\times 10^{-4}$.

3.1, indicating that they were single-site catalysts. Compound **5d** gave a broad molecular weight distribution, and the reason is unclear.

(ii) Effects of Polymerization Conditions. It was found that the cocatalyst/catalyst molar ratio (Al/Ti ratio) did not influence strongly the catalytic activity of complex **5e**, unlike in other single-site catalysts.[1−4] As shown in Table 3, the activity of complex **5e** was 4.04×10^6 g PE mol^{-1} Ti^{-1} h^{-1} atm^{-1} at the Al/Ti ratio of 1500 (entry 4). The activity decreased slightly (3.73×10^6 g PE mol^{-1} Ti^{-1} h^{-1} atm^{-1}, entry 2) when the Al/Ti ratio was reduced to 500. Even when an extremely low amount of MMAO (Al/Ti ratio = 100) was used, compound **5e** still showed high activity (1.88×10^6 g PE mol^{-1} Ti^{-1} h^{-1} atm^{-1}, entry 1). The molecular weight of the polyethylene proved to be sensitive to the Al/Ti ratio and increased with the decrease of the Al/Ti ratio (entries 1−5), suggesting that there existed chain transfers to aluminum compounds in the olefin polymerization.

Table 4. Results of Ethylene Copolymerization with 1-Hexene Assays[a]

entry	side- arm (complex)	1-hexene (mL)	T[b] (°C)	yield (g)	activity[c]	M_n[d]	M_w[d]	M_w/M_n[d]	H[e] (mol%)
1	 (5a)	5	25	0.062	0.23	9.18	22.9	2.50	14.1
2[f]	 (5e)	1	25	0.575	6.56	5.37	11.5	2.14	14.5
3	 (5e)	1	10	0.757	8.64	11.2	23.7	2.11	8.10
4	 (5e)	5	25	0.680	3.87	6.16	14.6	2.36	30.0
5	 (5e)	10	25	0.534	3.05	4.92	18.4	3.75	29.2
6	 (5f)	5	25	0.684	4.38	5.99	19.6	3.26	28.2
7	 (5h)	5	25	0.627	3.70	7.08	17.4	2.46	25.9
8	 (5k)	5	25	trace	-	-	-	-	-
9	 (5m)	5	25	0.742	6.11	2.85	10.6	3.71	14.6

[a] Polymerization conditions: 7 μmol of catalyst in 50 mL of toluene; MMAO/Ti = 500; ethylene pressure, 0.1 MPa; reaction time, 15 min. [b] Temperature of the bath. [c] 10^5 g polymer mol^{-1} Ti^{-1} h^{-1} atm^{-1}. [d] Determined by GPC, $\times 10^{-4}$. [e] 1-Hexene incoporation in copolymer, determined by ^{13}C NMR. [f] 3.5 μmol of catalyst; toluene, 50 mL.

The effect of the polymerization temperature on the behavior of catalyst **5e** was also studied. Similar to the titanium complex bearing the [N⁻OP] ligand,[23] complex **5e** proved thermally stable from −5 to 80 °C (entries 2, 6−8). The maximum activity of complex **5e** was achieved at 30−50 °C (entries 2, 7), and the catalytic activity was maintained at a high level even when the temperature was lowered to −5 °C (entry 6) or elevated to 80 °C (entry 8). GPC studies of the polyethylene showed that the M_w of the polymer was temperature-dependent. With the increase of the temperature, the M_w of the polymer decreased sharply from 59.8×10^4 g/mol at −5 °C to 1.36×10^4 g/mol at 80 °C, indicating that the high polymerization temperature promoted the chain transfer reaction. In our screened conditions, the highest molecular weight was obtained at −5 °C (entry 6).

The melting point (T_m) of the polymers obtained by complex **5e** is higher than 133 °C, which is the classical T_m for HDPE (high-density polyethylene). This was in full accordance with the ^{13}C NMR studies of the polyethylene, which showed no branches on the polymer backbone.

4. Ethylene Copolymerization with 1-Hexene. The performance of titanium complexes **5** for copolymerization of ethylene with 1-hexene is summarized in Table 4. Both the donor atoms and substituents on the pendant group influenced the copolymerization activity as well as the molar percentage of the comonomer incorporation. The titanium complexes **5e** and **5m** with S and Se in the sidearm Z, respectively, were highly active for copolymerization (entries 4 and 9). However, complex **5a**, with an O-donor as the sidearm, gave only low activity (entry 1). As shown in Table 4, the molecular weight of the copolymer decreased in the order of donor atom O > S > Se. Compound **5e** proved more favorable for the insertion of 1-hexene than **5a** and **5m**. For example, the molar percentage of 1-hexene incorporation in the copolymer obtained by both **5a** and **5m** was much lower than that obtained by **5e** (entries 1 and 9 vs entry 4). Substituent R^1 on the sidearm also influenced strongly the catalytic behavior of the complexes. For instance, compound

5k, bearing methyl groups at the *ortho* positions, was almost inactive for copolymerization, which was in sharp contrast to the high activities of complexes **5e**, **5f**, and **5h** (entries 4, 6−8). Compounds **5f**, **5h**, and **5e** gave similar catalytic activities and molecular weights of polymer as well as 1-hexene incorporations (entries 4, 6, 7), indicating that the electronic properties of R^3 hardly affected the copolymerization behaviors.

The catalytic behaviors of these complexes for copolymerization also depended on the polymerization conditions. As shown in Table 4, lowering the temperature increased the M_w of copolymer but decreased the 1-hexene incorporations (entries 2, 3), probably because the ethylene solubility increased in toluene at low temperature. The increased feed of 1-hexene significantly improved the incorporation but slightly decreased the copolymerization activity (entries 2, 4). Thus, the molar percentage of 1-hexene incorporation could be tuned by employing catalysts with different pendant Z groups as well as the change of polymerization conditions.

Conclusion

In summary, phenoxyimine ligands with pendant donor groups and their monoligand titanium complexes have been synthesized and characterized. The pendant group proved to strongly influence the structure of the corresponding titanium complexes as well as their behaviors in olefin polymerization. Combined with MMAO, these complexes have exhibited moderate to high activity for ethylene polymerization and afforded highly linear polyethylene, even at extremely low Al/Ti ratio and high temperature. In addition, they have also shown excellent capability for ethylene copolymerization with 1-hexene. Investigation of ethylene copolymerization with long chain α-olefin and bulky olefins promoted by these complexes is in progress.

Experimental Section

All manipulations of air- and/or moisture-sensitive compounds were performed under argon atmosphere using standard Schlenk techniques. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Varian XL-300 MHz spectrometer with TMS as the internal standard. Mass spectra were obtained using a HP5959A spectrometer. IR spectra were recorded using a Nicolet AV-360 spectrometer. Elemental analysis was performed by the Analytical Laboratory of Shanghai Institute of Organic Chemistry (CAS). M_n, M_w, and M_w/M_n values of polymers were determined using a Waters Alliance GPC 2000 series at 150 °C (using polystyrene calibration, 1,2,4-trichlorobenzene as the solvent at a flow rate of 1.0 mL/min). ^{13}C NMR data for polymers were obtained using *o*-dichlorobenzene-d_4 as the solvent at 110 °C. Toluene, THF, and hexane were distilled over sodium/benzophenone ketyl prior to use. Dichloromethane was distilled over CaH_2. Compounds **1a**, **1b**, **2a**−**2m**, **3a**−**3m**, and **4a**−**4m** were prepared according to the known procedure.[29] Modified methylaluminoxane (MMAO) was purchased from Akzo Chemical as a 1.6 M toluene solution. Polymerization-grade ethylene was purified by passing through Et_3Al before use.

[*N*-(3,5-Di-*tert*-butylsalicylidene)-2-phenoxylanilinato]Ti(IV)-Cl$_3$ (5a). To a stirred suspension of KH (0.050 g, 1.25 mmol) in THF (10 mL) at −78 °C was added dropwise a solution of **L1** (0.501 g, 1.25 mmol) in THF (30 mL) in 10 min. The resulting mixture was allowed to warm to room temperature and stirred for 2 h. The solvent was removed under reduced pressure, and the residue was dissolved in toluene (80 mL). To this yellow, clear solution was added a solution of titanium tetrachlorides (0.285 g, 1.5 mmol) in toluene (20 mL) dropwise over a period of 20 min at room temperature. The resulting mixture was stirred overnight and filtered, and the solid was washed with CH_2Cl_2 (30 mL × 3). The combined organic filtrates were concentrated under reduced pressure to ca. 30 mL and then were cooled to −30 °C overnight. The reddish crystal was collected and dried in vacuo to give complex **5a.** Yield: 0.402 g (57%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.80 (s, 1H, CH═N), 7.78 (dd, J = 1.2, 7.5 Hz, 2H, Ar−H), 7.68 (d, J = 2.1 Hz, 1H, Ar−H), 7.64−7.46 (m, 4H, Ar−H), 7.26−7.17 (m, 3H, Ar−H), 6.61 (dd, J = 2.1, 7.8 Hz, 1H, Ar−H), 1.54 (s, 9H, *t*-Bu), 1.33 (s, 9H, *t*-Bu). ^{13}C NMR (75 MHz, $CDCl_3$): δ 160.7, 158.2, 154.2, 153.3, 148.4, 136.4, 133.4, 132.7, 130.9, 130.6, 130.4, 128.9, 128.4, 128.2, 127.3, 125.2, 125.1, 123.8, 116.7, 115.2, 35.4, 34.8, 31.1, 29.8. IR (KBr) ν: 1591, 1491, 1457, 1360, 1173, 1022, 885. Anal. Calcd for $C_{27}H_{30}NO_2Cl_3Ti$: C, 58.64; H, 5.45; N, 2.52. Found: C, 60.03; H, 5.76; N, 2.09.

[*N*-(3,5-Di-*tert*-butylsalicylidene)-2-(2,6-dichlorophenoxyl)-anilinato]Ti(IV)Cl$_3$ (5b). The same procedure as that for the preparation of **5a** was used. KH (0.069 g, 1.7 mmol), **L2** (0.800 g, 1.7 mmol), and $TiCl_4$ (0.323 g, 1.7 mmol) were used. Yield: 0.636 g (61%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.84 (s, 1H, CH═N), 7.73 (d, J = 1.8 Hz, 1H, Ar−H); 7.58−7.45 (m, 4H, Ar−H), 7.31−7.19 (m, 3H, Ar−H); 6.66 (d, J = 7.5 Hz, 1H, Ar−H), 1.54 (s, 9H, *t*-Bu), 1.36 (s, 9H, *t*-Bu).^{13}C NMR (75 MHz, $CDCl_3$): δ 162.0, 150.4, 148.0, 146.6, 137.8, 136.6, 136.3, 132.6, 130.7, 130.5, 129.9, 128.9, 128.6, 128.2, 126.7, 125.2, 125.0, 114.4, 109.7, 35.4, 34.7, 31.1, 29.7. IR (KBr) ν: 1594, 1558, 1548, 1489, 1453, 1427, 1224, 1026, 885, 861, 774, 744. Anal. Calcd for $C_{27}H_{28}Cl_5NO_2Ti$: C, 52.00; H, 4.53; N, 2.25. Found: C, 51.76; H, 4.77; N, 1.77.

[*N*-(3,5-Di-*tert*-butylsalicylidene)-2-(2,6-dimethylphenoxyl)-anilinato]Ti(IV)Cl$_3$ (5c). The same procedure as that for the preparation of **5a** was used. KH (0.28 g, 7 mmol), **L3** (3.0 g, 7 mmol), and $TiCl_4$ (1.77 g, 7 mmol) were used. Yield: 2.10 g (49%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.79 (s, 1H, CH═N), 7.72 (d, J = 2.4 Hz, 1H, Ar−H), 7.53 (d, J = 1.8 Hz, 2H, Ar−H); 7.24−7.16 (m, 5H, Ar−H), 6.60 (d, J = 6.3 Hz, 1H, Ar−H), 2.51 (s, 6H, Ar−CH_3), 1.53 (s, 9H, *t*-Bu), 1.36 (s, 9H, *t*-Bu). ^{13}C NMR (75 MHz, $CDCl_3$): δ 164.2, 158.6, 151.5, 150.7, 140.2, 137.1, 137.0, 131.4, 128.9, 127.8, 127.2, 126.6, 125.1, 121.7, 120.8, 118.5, 113.7, 35.1, 34.2, 31.5, 29.4, 16.4. IR (KBr) ν: 2961, 1605, 1586, 1557, 1545, 1494, 1461, 1376, 1245, 988, 867, 750. Anal. Calcd for $C_{29}H_{34}Cl_3NO_2Ti$: C, 59.74; H, 5.83; N, 2.40. Found: C, 58.40; H, 6.10; N, 2.06.

[*N*-(3,5-Di-*tert*-butylsalicylidene)-2-(2,6-di-isoproylphenoxyl)-anilinato]Ti(IV)Cl$_3$ (5d). The same procedure as that for the preparation of **5a** was used. KH (0.80 g, 2 mmol), **L4** (0.960 g, 2 mmol), and $TiCl_4$ (0.38 g, 2 mmol) were used. Yield: 0.932 g (71%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.79 (s, 1H, CH═N), 7.72 (d, J = 2.4 Hz, 1H, Ar−H), 7.57−7.54 (m, 2H Ar−H), 7.38−7.19 (m, 5H, Ar−H), 6.61 (dd, J = 1.5, 7.8 Hz, 1H, Ar−H), 3.81 (hapta, 2H, J = 6.6 Hz, $CH(CH_3)_2$), 1.53 (s, 9H, *t*-Bu), 1.36 (s, 9H, *t*-Bu), 1.33 (d, J = 7.2 Hz, 6H, $CH(CH_3)_2$), 0.95 (d, J = 6.6 Hz, 6H, $CH(CH_3)_2$). ^{13}C NMR (75 MHz, $CDCl_3$): δ 162.3, 153.5, 149.9, 148.0, 142.8, 136.3, 134.6, 132.8, 130.7, 130.0, 129.0, 128.6, 128.2, 127.2, 126.1, 125.2, 124.6, 116.5, 35.5, 34.8, 31.2, 29.8, 27.3, 24.9, 23.9. IR (KBr) ν: 1598, 1560, 1549, 1462, 1434, 1362, 1271, 1253, 1179, 875, 837, 728. Anal. Calcd for $C_{33}H_{42}Cl_3NO_2Ti$: C, 62.03; H, 6.62; N, 2.19. Found: C, 61.64; H, 6.77; N, 1.79.

[*N*-(3,5-Di-*tert*-butylsalicylidene)-2-phenysulfanylanilinato]-Ti(IV)Cl$_3$ (5e). The same procedure as that for the preparation of **5a** was used. KH (0.160 g, 4 mmol), **L5** (1.670 g), and $TiCl_4$ (0.800 g, 4.2 mmol) were used. Yield: 1.81 g (77%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.87 (s, 1H, CH═N); 7.74 (d, J = 1.5 Hz, 1H, Ar−H); 7.73−7.19 (m, 10H, Ar−H), 1.51 (s, 9H, *t*-Bu); 1.36 (s, 9H, *t*-Bu).

(29) Moors, G. G. I.; Harrington, J. K. *J. Med. Chem.* **1975**, *18*, 386−391.

^{13}C NMR (75 MHz, $CDCl_3$): δ 163.9 (CH═N), 151.6, 147.4, 136.3, 135.6, 135.0, 133.2, 132.2, 131.1, 130.4, 129.1, 129.0, 128.9, 128.8, 127.3, 125.4, 119.7, 35.4, 34.7, 31.2, 29.7. IR (KBr) ν: 1581, 1479, 1442, 1236, 1202, 1175, 865. Anal. Calcd for $C_{27}H_{30}NOSCl_3Ti$: C, 56.81; H, 5.30; N, 2.45. Found: C, 57.67; H, 5.73; N, 2.05.

[*N*-(3,5-Di-*tert*-butylsalicylidene)-2-(4-trifluoromethylphenylsulfanyl)anilinato]Ti(IV)Cl$_3$ (5f). The same procedure as that for the preparation of **5a** was used. KH (0.040 g, 1 mmol), **L6** (0.485 g, 1 mmol), and $TiCl_4$ (0.23 g, 1.2 mmol) were used. Yield: 0.510 g (78%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.90 (s, 1H, CH═N); 7.77 (d, J = 2.1 Hz, 1H, Ar−H), 7.69−7.54 (m, 6H, Ar−H), 7.40 (d, J = 5.1 Hz, 2H, Ar−H), 7.23 (m, 1H, Ar−H), 1.52 (s, 9H, *t*-Bu); 1.34 (s, 9H, *t*-Bu). ^{19}F NMR (282.3 MHz, $CDCl_3$): δ 63.2. IR (KBr) ν: 1607, 1556, 1327, 1246, 1169, 1062, 1012, 876. Anal. Calcd for $C_{28}H_{29}NOF_3SCl_3Ti$: C, 52.64; H, 4.58; N, 2.19. Found: C, 52.95; H, 4.96; N, 1.90.

[*N*-(3,5-Di-*tert*-butylsalicylidene)-2-(3-chlorophenysulfanyl)anilinato]Ti(IV)Cl$_3$ (5g). The same procedure as that for the preparation of **5a** was used. KH (0.140 g, 3.5 mmol), **L7** (1.581 g, 3.5 mmol), and $TiCl_4$ (0.67 g, 3.5 mmol) were used. Yield: 1.60 g (76%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.89 (s, 1H, CH═N); 7.75−7.53 (m, 6H, Ar−H), 7.29−7.15 (m, 4H, Ar−H), 1.52 (s, 9H, *t*-Bu); 1.37 (s, 9H, *t*-Bu). ^{13}C NMR (75 MHz, $CDCl_3$): δ 164.1 (CH═N), 151.7, 147.6, 136.7, 136.3, 135.9, 135.0, 133.4, 132.6, 131.3, 130.6, 130.2, 129.1, 129.0, 128.2, 128.1, 127.3,127.2, 124.3, 119.9, 35.4, 34.8, 31.2, 29.7. IR (KBr) ν: 1585, 1542, 1473, 1364, 1245, 1184, 870. Anal. Calcd for $C_{27}H_{29}NOSCl_4Ti$: C, 53.58; H, 4.83; N, 2.33. Found: C, 54.36; H, 5.22; N, 2.11.

[*N*-(3,5-Di-*tert*-butylsalicylidene)-2-(4-methoxylphenysulfanyl)anilinato]Ti(IV)Cl$_3$ (5h). The same procedure as that for the preparation of **5a** was used. KH (0.140 g, 3.5 mmol), **L8** (1.56 g, 3.5 mmol), and $TiCl_4$ (0.67 g, 3.5 mmol) were used. Yield: 1.53 g (71%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.90 (s, 1H, CH═N); 7.74 (s, 1H, Ar−H), 7.60−7.54 (m, 4H, Ar−H), 7.46−7.33 (m, 3H, Ar−H), 6.88(d, J = 5.7 Hz, 2H, Ar−H), 3.79 (s, 3H, OCH_3); 1.52 (s, 9H, *t*-Bu); 1.36 (s, 9H, *t*-Bu). ^{13}C NMR (75 MHz, $CDCl_3$): δ 163.9 (CH═N), 161.3, 160.4, 151.1, 147.4, 136.4, 134.7, 133.1, 131.7, 131.3, 131.1, 130.3, 127.3, 125.4, 119.5, 114.7, 55.4, 35.4, 34.8, 31.2, 29.7. IR (KBr) ν: 1614, 1593, 1494, 1463, 1388, 1250, 1180, 1026, 878. Anal. Calcd for $C_{28}H_{29}NO_2S\ Cl_3Ti$: C, 55.95; H, 5.33; N, 2.33. Found: C, 56.45; H, 5.41; N, 2.24.

[*N*-(3,5-Di-*tert*-butylsalicylidene)-2-(3-methoxylphenysulfanyl)anilinato]Ti(IV)Cl$_3$ (5i). The same procedure as that for the preparation of **5a** was used. KH (1.56 g, 3.5 mmol), **L9** (1.56 g, 3.5 mmol), and $TiCl_4$ (0.67 g, 3.5 mmol) were used. Yield: 1.78 g (85%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.85 (s, 1H, CH═N); 7.73 (s, 1H, Ar−H), 7.64−7.54 (m, 5H, Ar−H), 7.26−7.22 (m, 1H, Ar−H), 6.90−6.83 (m, 3H, Ar−H), 3.73 (s, 3H, OCH_3); 1.52 (s, 9H, *t*-Bu); 1.35 (s, 9H, *t*-Bu). ^{13}C NMR (75 MHz, $CDCl_3$): δ 163.9 (CH═N), 161.5, 159.7, 151.5, 147.4, 136.1, 136.0, 135.7, 133.1, 132.3, 131.3, 130.3, 129.9, 127.3, 125.4, 121.2, 119.7, 114.6, 55.4, 35.3, 34.7, 31.2, 29.7. IR (KBr) ν: 1591, 1541, 1476, 1362, 1286, 1246, 1185, 1043, 858. Anal. Calcd for $C_{28}H_{29}NO_2SCl_3Ti$: C, 55.95; H, 5.33; N, 2.33. Found: C, 56.52; H, 5.44; N, 2.24.

[*N*-(3,5-Di-*tert*-butylsalicylidene)-2-(2,6-dichlorophenysulfanyl)anilinato]Ti(IV)Cl$_3$ (5j). The same procedure as that for the preparation of **5a** was used. KH (0.075 g, 1.9 mmol), **L10** (0.911 g, 1.9 mmol), and $TiCl_4$ (0.38 g, 2 mmol) were used. Yield: 0.887 g (73%). ^{1}H NMR (300 MHz, CD_2Cl_2): δ 8.85 (s, 1H, CH═N); 7.83 (d, J = 2.4 Hz, 1H, Ar−H), 7.66−7.27 (m, 8H, Ar−H), 1.54 (s, 9H, *t*-Bu); 1.40 (s, 9H, *t*-Bu). ^{13}C NMR (75 MHz, $CDCl_3$): δ 163.9 (CH═N), 158.3, 145.9, 141.9, 140.5, 137.0, 131.4, 130.6, 128.9, 128.3, 127.0, 126.9, 126.4, 126.0, 124.3, 118.3, 118.1, 35.1, 34.1, 31.4, 29.4. IR (KBr) ν: 1645, 1597, 1540, 1473, 1423, 1270, 1183, 852. Anal. Calcd for $C_{27}H_{28}NOSCl_5Ti$: C, 52.80; H, 4.47; N, 2.24. Found: C, 52.26; H, 4.93; N, 1.70.

[*N*-(3,5-Di-*tert*-butylsalicylidene)-2-(2,6-dimethylphenysulfanyl)anilinato] Ti(IV)Cl$_3$ (5k). The same procedure as that for the preparation of **5a** was used. KH (0.065 g, 1.6 mmol), **L11** (0.72 3 g, 1.6 mmol), and $TiCl_4$ (0.31 g, 1.6 mmol) were used. Yield: 0.62 g (64%). ^{1}H NMR (300 MHz, CD_2Cl_2): δ 8.91 (s, 1H, CH═N); 7.83 (d, J = 2.4 Hz, 1H, Ar−H), 7.68−7.44 (m, 4H, Ar−H), 7.26−7.09 (m, 4H, Ar−H), 2.29 (s, 6H, CH_3); 1.53 (s, 9H, *t*-Bu); 1.41 (s, 9H, *t*-Bu). ^{13}C NMR (75 MHz, CD_2Cl_2): δ 163.8 (CH═N), 161.4, 154.3, 154.1, 150.4, 137.7, 136.6, 135.0, 134.6, 132.9, 132.8, 132.1, 129.8, 129.1, 127.1, 119.4, 116.9, 37.2, 36.6, 32.7, 31.4, 20.6. IR (KBr) ν: 1582, 1536, 1472, 1374, 1276, 1246, 1179, 872. Anal. Calcd for $C_{29}H_{34}NOSCl_3Ti$: C, 58.14; H, 5.68; N, 2.33. Found: C, 57.84; H, 5.43; N, 2.09.

[*N*-(3,5-Di-*tert*-butylsalicylidene)-2-(2,6-di-isopropylphenysulfanyl)anilinato]Ti(IV)Cl$_3$ (5l). The same procedure as that for the preparation of **5a** was used. KH (0.161 g, 4 mmol), **L12** (2.00 g, 4 mmol), and $TiCl_4$ (0.76 g, 4 mmol) were used. Yield: 1.83 g (70%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.54 (s, 1H, CH═N); 7.74 (d, J = 1.8 Hz, 1H, Ar−H), 7.70 (d, J = 7.5 Hz, 1H, Ar−H), 7.49−7.03 (m, 6H, Ar−H), 6.47 (d, J = 8.1 Hz, 1H, Ar−H)), 3.57 (hapta, 2H, J = 6.9 Hz, $CH(CH_3)_2$); 1.62 (s, 9H, *t*-Bu); 1.35 (s, 9H, *t*-Bu); 1.15 (d, J = 14.7 Hz, 12H, $CH(CH_3)_2$). ^{13}C NMR (75 MHz, $CDCl_3$): δ 170.4 (CH═N), 160.3, 154.0, 147.2, 137.5, 132.2, 130.7, 130.1, 129.0, 128.2, 127.6, 126.8, 126.5, 125.9, 125.5, 125.2, 124.4, 35.4, 34.7, 31.9, 31.2, 29.8, 25.4, 24.1. IR (KBr) ν: 1598, 1560, 1549, 1462, 1362, 1271, 1179, 1002, 875. Anal. Calcd for $C_{33}H_{42}NOSCl_3Ti$: C, 60.51; H, 6.46; N, 2.14. Found: C, 59.38; H, 7.04; N, 1.58.

[*N*-(3,5-Di-*tert*-butylsalicylidene)-2-phenylselanylanilinato]-Ti(IV)Cl$_3$ (5m). The same procedure as that for the preparation of **5a** was used. KH (0.100 g, 2.5 mmol), **L13** (1.15 g, 2.5 mmol), and $TiCl_4$ (0.475 g, 2.5 mmol) were used. Yield: 1.01 g (65%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.79 (s, 1H, CH═N); 7.74−7.26 (m, 11H, Ar−H), 1.51 (s, 9H, *t*-Bu); 1.35 (s, 9H, *t*-Bu). ^{13}C NMR (75 MHz, CD_2Cl_3): δ 167.2 (CH═N), 163.0, 155.1, 149.6, 138.4, 137.8, 135.0, 134.9, 134.0, 133.1, 132.2, 132.0, 131.3, 130.9, 129.4, 126.1, 122.8, 37.1. 36.6, 32.8, 31.3. IR (KBr) ν: 1645, 1606, 1557, 1472, 1249, 853. Anal. Calcd for $C_{27}H_{30}NOSeCl_3Ti$: C, 52.50; H, 4.90; N, 2.27. Found: C, 53.21; H, 5.37; N, 2.01.

[*N*-(3-*tert*-Butylsalicylidene)-2-phenylsulfanylanilinato]Ti(IV)-Cl$_3$ (5n). The same procedure as that for the preparation of **5a** was used. KH (0.100 g, 3 mmol), **L14** (1.083 g, 3 mmol), and $TiCl_4$ (0.57 g, 3 mmol) were used. Yield: 1.1 g (71%). ^{1}H NMR (300 MHz, CD_2Cl_2): δ 8.91 (s, 1H, CH═N); 7.76−7.64 (m, 6H, Ar−H), 7.40−7.24 (m, 6H, Ar−H), 1.50 (s, 9H, *t*-Bu). ^{13}C NMR (75 MHz, CD_2Cl_2): δ 165.7 (CH═N), 164.9, 153.5, 138.6, 137.5, 137.4, 137.0, 136.6, 134.3, 132.6, 130.9, 130.8, 129.5, 127.1, 126.6, 121.7, 37.0, 31.2. IR (KBr) ν: 1582, 1545, 1468, 1376, 1254. Anal. Calcd for $C_{23}H_{22}NOSCl_3Ti$: C, 53.67; H, 4.31; N, 2.72. Found: C, 54.19; H, 4.37; N, 2.37.

Polymerization Procedure. To a 100 mL flame-dried flask was added 50 mL of freshly distilled toluene (and the required amount of 1-hexene in the case of copolymerization) at the desired polymerization temperature. After 10 min, MMAO was added. The resulting mixture was stirred for a further 5 min, and the precursor catalyst solution in toluene was injected via a syringe. The polymerization was carried out for the desired time and then quenched with concentrated HCl in ethanol (100 mL, HCl/ethanol, 1:20, v/v). The precipitated polymer was collected, washed with ethanol, and then dried overnight in a vacuum oven at 50 °C.

X-ray Structure Determination. Data collections for complexes **5a**, **5e**, **5g**, **5i**, and **5n** were performed at 20 °C on a Bruker SMART diffractometer with graphite-monochromated Mo Kα

Table 5. Crystallographic Data and Refinement for Complexes 5a, 5e, 5g, 5i, and 5n

	5a	**5e**	**5g**	**5i**	**5n**
empirical formula	$C_{37.50}H_{42}NO_2Cl_3Ti$	$C_{27}H_{30}NOSCl_3Ti$	$C_{28}H_{30}NOC_{l7}STi$	$C_{29}H_{33}NO_2C_{l6}STi$	$C_{23}H_{22}NOSCl_3Ti$
fw	692.97	570.83	724.64	720.2	514.73
temperature (K)	293(2)	293(2)	293(2)	293(2)	293(2)
λ(Mo Kα) (Å)	0.71073	0.71073	0.71073	0.71073	0.71073
cryst syst	triclinic	monoclinic	monoclinic	monoclinic	monoclinic
space group	$P\bar{1}$	$P2(1)/c$	$P2(1)/n$	$P2(1)/c$	$P2(1)$
a (Å)	11.748(7)	12.663(2)	12.846(5)	14.8394(12)	8.758(4)
b (Å)	13.365(8)	17.026(3)	14.395(5)	13.6848(11)	11.801(6)
c (Å)	13.646(8)	13.131(2)	19.068(6)	17.5778(14)	11.899(6)
α (deg)	91.911(10)	90	90	90	90
β (deg)	91.691(10)	98.186(3).	102.623(8)	111.990(2)	105.016(8)
γ (deg)	112.739(10)	90	90	90	90
V (Å^3)	1973(2)	2802.4(7)	3441(2)	3309.9(5)	1187.8(10)
Z	2	4	4	4	2
D_{calcd} (g/cm^3)	1.167	1.353	1.399	1.445	1.439
absorp coeff (mm^{-1})	0.450	0.686	0.875	0.834	0.801
F(000)	726	1184	1480	1480	528
cryst size (mm)	0.680 × 0.521 × 0.505	0.945 × 0.459 × 0.176	0.283 × 0.207 × 0.125	0.345 × 0.3175 × 0.127	0.499 × 0.424 × 0.287
$2\theta_{max}$ (deg)	50	56.6	54	54	55.9
no. of reflens collected	9333	16 260	19 948	19232	2539
no. of indep reflens	6746 (R_{int} = 0.1545)	6408 (R_{int} = 0.1188)	6408 (R_{int} = 0.1417)	6408 (R_{int} = 0.0662)	2227 (R_{int} = 0.0978)
goodness-of-fit on F^2	1.057	0.904	0.748	0.938	1.023
final R indexes [$I > 2\sigma(I)$]	0.0959	0.0530	0.0688	0.0493	0.0763

radiation (λ = 0.71073 Å). The SADABS absorption correction was applied. The structures were solved by direct methods and refined on F^2 by full-matix least-squares techniques with anisotropic thermal parameters for non-hydrogen atoms. Hydrogen atoms were placed at the calculated positions and were included in the structure calculation without further refinement of the parameters. All calculations were carried out using the SHELXS-97 program. Crystal data and processing parameters for complexes **5a**, **5e**, **5g**, **5i**, and **5n** are summarized in Table 5.

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Supporting Information Available: X-ray crystallographic data of **5a**, **5e**, **5g**, **5i**, and **5n**; synthesis of ligands **L1**−**L14**; ^{1}H and ^{13}C NMR spectra of complexes **5a**−**5n**. These materials are available free of charge via the Internet at http://pubs.acs.org.

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