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Synthesis and Characterization of Novel Tridentate [NOP] Titanium Complexes and Their Application to Copolymerization and Polymerization of Ethylene

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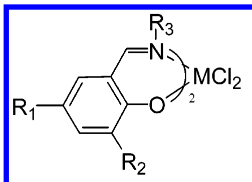
Novel titanium complexes containing monoanionic [NOP] ligands based on a phenoxy−imine ligand and their derivatives were synthesized and characterized. Their performance as ethylene polymerization and copolymerization catalysts were studied. Upon treatment with MMAO, the [NOP]$TiCl_3$ complexes were robust and highly active for the polymerization of ethylene, even at very low cocatalyst/catalyst ratios. These catalysts also have good copolymerization capabilities.

Introduction

Study of the polymerization of olefins by soluble, well-defined transition-metal complexes is an ever-growing area.[1] Recently much attention has been paid to the non-metallocene catalysts, which include early-,[2] middle-,[3] and late-transition-metal[4] and lanthanide[5] species incorporating non-cyclopentadiene-based ligands. For non-metallocene systems with group IV metals, complexes derived from chelating diamido ligands[2a,c] were reported to be good polymerization catalysts. Very recently, Kol et al.[2e,f] reported [ONO] and [ONNO] ligand systems and found that their [ONNO] zirconium complexes were highly active in the polymerization of 1-hexene. Fujita et al.[2g−q] developed an FI catalyst family based on bis(salicylaldiminato) ligands (Chart 1). They and Coates et al.[2g−m] reported independently that these complexes were excellent precatalysts for olefin polymerization, including living olefin polymerization and highly syndiospecific polymerization of propylene. Coates et al. proposed a mechanistic model for stereocontrolled propene polymerization.[2m−p] This catalyst was also proved to be a good promoter for the synthesis of functional propylene copolymers and block copolymers.[2q] We noticed that most of the non-metallocene group 4 precatalysts described above were dihalide (or dialkyl or monohalide monoalkyl) complexes. In comparison, only a few of the trihalide (or trialkyl) non-metallocene precursors were found to be active for olefin polymerization.[6] One of the reasons is probably that the space of the central metal in the trichloride complex is more

Chart 1. FI Catalyst Family



R_1=H, Me, *t*-Bu
R_2=Me, *i*-Pr, *t*-Bu, cumyl et al
R_3=Ph, C_6F_5, cyclohexyl, Ph with different substituents

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† Hu and Sun have made the same contribution to this paper.

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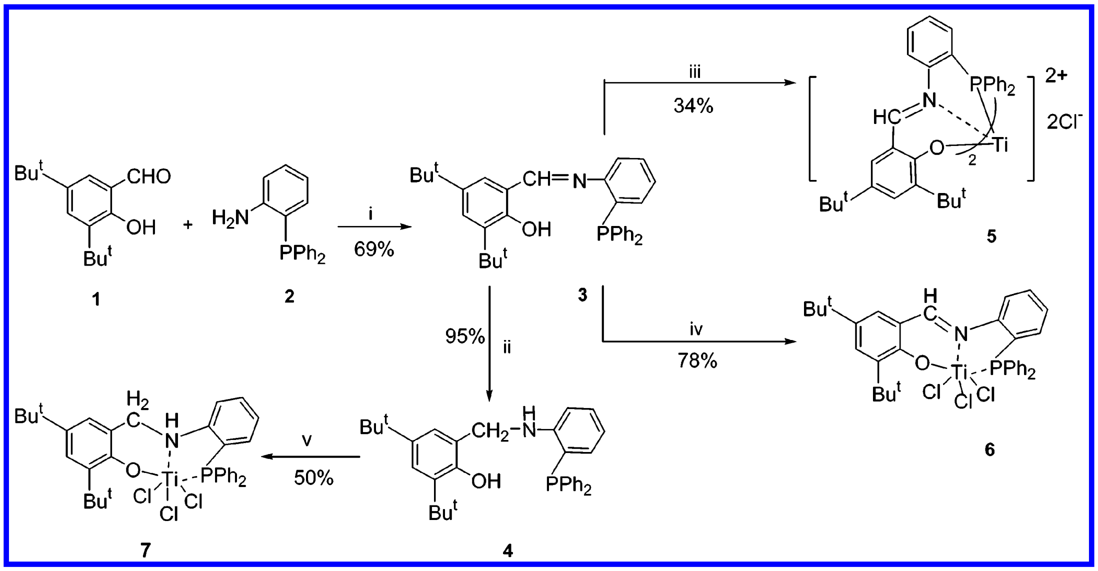
Scheme 1[a]



[a] Reagents and conditions: (i) EtOH, AcOH, reflux; (ii) $LiAlH_4$, 0 °C; (iii) (1) NaH, −78 °C, THF, (2) 0.5 equiv of $TiCl_4$, toluene; (iv) (1) KH, −78 °C, THF, (2) 1.2 equiv of $TiCl_4$, toluene; (v) (1) NaH, −78 °C, THF, (2) 2.5 equiv of $TiCl_4$.

open than in the similar dichloride species because the chlorine atom is small, influencing the chain-transfer process of polymerization. Considering the different electronic properties and spaces of the reactive sites between trichloride and dichloride complexes, we designed several trichloride complexes based on the monoanion ligand **3**, in which we installed an intramolecular coordinating P donor as a bulky side arm on the phenoxy−imine O−N system (Scheme 1) and found that they are highly active for olefin polymerization. In this paper, we wish to report the synthesis and structural characterization of these complexes and their performance in the polymerization and copolymerization of olefins in detail.

Results and Discussion

Ligand and Complex Synthesis. The synthesis of complexes **5**−**7** is outlined in Scheme 1. The phenoxy−imine ligand **3**, bearing a diphenylphosphorus group, was readily synthesized from 3,5-di-*tert*-butylsalicyaldehyde (**1**) in 69% yield by the Schiff base condensation of aldehyde **1** with *o*-(diphenylphosphino)aniline (**2**), which was prepared by the known procedure.[7] After deprotonation by alkali-metal hydride at −78 °C in THF, imine **3** could react with $TiCl_4$ to give the desired trichloride complex **6** in 78% yield in the presence of a slight excess of $TiCl_4$ ($TiCl_4$/**3** = 1.2/1.0 (mol/mol)). Interestingly, we tried to synthesize compound **5**, a bis(ligand) complex, by using Fujita's procedure but failed.[2p] It was found that this compound could be prepared in 34% yield by using the procedure for the preparation of complex **6**, except the mole ratio of $TiCl_4$/**3** was changed to 0.5. The complex **7** shown in Scheme 1 was prepared from compound **4** in 50% yield, using the same procedure as that producing complex **6** but with NaH instead of KH. Ligand **4** was obtained easily in 95% yield from imine **3** by reduction. The three complexes **5**−**7** were all purified easily by recrystallization from toluene.

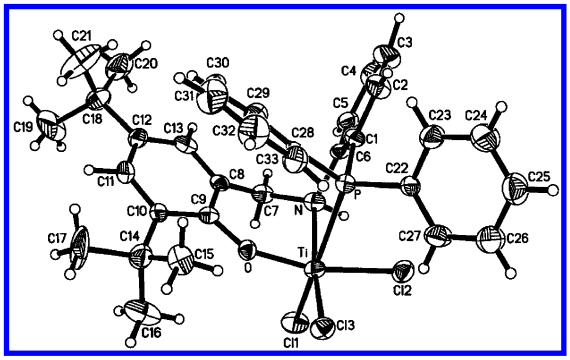


Figure 1. Molecular structure of **7** (toluene solvent molecules present in the unit cell are omitted). Selected bond lengths (Å) and angles (deg): Ti−O = 1.772(4), Ti−P = 2.6484(19), Ti−N = 2.269(5), Ti−Cl(1) = 2.2938(18), Ti−Cl(2) = 2.343(2), Ti−Cl(3) = 2.2463(19), C(7)−N = 1.506(9); N−Ti−P = 75.68(15), N−Ti−Cl(1) = 89.11(15), Cl(3)−Ti−P = 91.62, O−Ti−Cl(2) = 164.57(14), Cl(1)−Ti−Cl(3) = 103.46(7), Cl(1)−Ti−Cl(2) = 90.39, Cl(2)−Ti−Cl(3) = 95.89(8).

Characterization of Complexes 5−7 and Single-Crystal X-ray Structure Analysis of Complex 7. All the compounds were well characterized by $^{1}H\{^{13}C\}$ NMR, ^{31}P NMR, FT-IR, elemental analysis, and mass analysis. A single crystal of the complex **7** suitable for X-ray diffraction study was grown from toluene. As expected, the molecular structure of compound **7** is shown in Figure 1 as a titanium trichloride complex with only one phenoxy−amine ligand featuring a phosphorus group. The geometry at the titanium center could be described as a slightly distorted octahedral structure in which the five atoms, i.e. Ti, Cl(1), Cl(3), N, and P, are coplanar to within 0.09 Å. Also, O and Cl(2) are in a trans configuration. The bond length Ti−P is 2.6484(19) Å, which is longer than what would be expected from the covalent radii (r_{cov}(Ti) = 1.32 Å,

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Table 1. Results of Ethylene Polymerization by Complexes 5−7 with MMAO[a]

entry	procat.[b]	amt of cocat (equiv)	T (°C)	time (min)	yield (g)	activity[c]	M_w[d]	M_w/M_n
1	**5** (3.6)	1000	50	60	trace	nd[e]	nd	nd
2	**6** (2)	1500	50	30	1.41	14.1	20.8	2.35
3	**6** (2)	500	50	30	1.23	12.3	23.6	2.08
4	**6** (2)	100	50	30	0.94	9.4	29.4	2.17
5	**6** (2)	50	50	30	0.25	2.5	48.0	2.39
6	**6** (2)	500	30	30	0.72	7.2	72.2	1.53
7	**6** (2)	500	−30	30	0.42	4.2	20.3.	1.91
8	**6** (2)	500	0	30	0.74	7.4	53.5	1.81
9	**6** (2)	500	60	30	1.13	11.3	14.0	2.06
10	**6** (2)	500	70	30	0.54	5.4	14.2	2.11
11	**6** (2)	500	100	30	0.52	5.2	7.3	2.43
12[f]	**6** (23.2)	500	50	60	32.5	1.4	170[g]	nd
13	**7** (2)	500	50	5[h]	0.69	41.4	22.5	3.33
14	**7** (2)	100	50	5	0.40	24.0	26.1	2.20
15	**7** (2)	50	50	5	0.33	19.8	20.4	2.29
16	**7** (0.5)	1000	50	5	0.45	108.0	26.2	1.95
17	**7** (2)	1000	100	5	0.36	21.6	7.7	1.54
18[f]	**7** (19.6)	500	50	60	36.07	18.4	16.0	2.86

[a] General polymerization conditions: total volume 20 mL, $P_{\mathrm{ethylene}} = 1$ atm, toluene, MMAO-4 from Akzo-Nobel as cocatalyst. [b] The amount of catalyst (in μmol) is given in parentheses. [c] In units of 10^5 g of PE/((mol of cat.) h atm). [d] 10^4 by GPC relative to polystyrene standard. [e] nd = not determined. [f] 7 atm of ethylene pressure in 2 L autoclave; total volume 515 mL and MAO as the cocatalyst. [g] Measured in Decalin at 135 °C using an Ubbelohde viscometer. [h] Stirring stopped at this time due to polymer precipitation.

r_{cov}(P) = 1.06 Å),[8] suggesting that the interaction between Ti−P is somewhat weak, probably due to the steric crowding of the bulky ligands around the P atom. In this trichloride complex, the three chlorine atoms were located cis to one another, which is favorable for polymerization.

^{31}P NMR gave a single peak for all the ligands and complexes, indicating that they are pure compounds. ^{31}P NMR signals for these compounds ranged from −20 to 40 ppm. In the case of ligand **4**, the chemical shift in ^{31}P NMR is −19.54 ppm, while the value for complex **7** shifted to 4.63 ppm, suggesting that the coordination of the phosphorus atom to the metal center resulted in its ^{31}P NMR resonance moving downfield. As the ^{31}P NMR resonance of ligand **3** is −13.63 ppm whereas the value for complex **5** is 39.69 ppm, we proposed that the diphenylphosphine group of complex **5** coordinated to titanium as shown in Scheme 1. This might explain its lower activity for ethylene polymerization compared with those of complexes **6** and **7** (entry 1 vs entries 2−12 & entries 13−18 in Table 1).

Ethylene Polymerization. The active catalysts were generated in situ in toluene by addition of modified methylaluminoxane (MMAO-4 purchased from Akzo-Nobel) to the precursors in toluene. The polymerization results are collected in Table 1. As shown in Table 1, the Ti complex **5** with a bis(phenoxy−imine) ligand was less effective toward ethylene polymerization. Gratifyingly, the titanium catalysts **6** and **7** with a mono-(phenoxy−imine) ligand for ethylene polymerization were highly active (entry 1 vs entries 2−18 in Table 1), with an activity comparable to that of an early-transition-metal metallocene. Most worthy of note is the fact that the activity of compound **6** (or **7**)/MMAO did not change very much when the cocatalyst/catalyst ratio decreased from 1500 to 50 (entries 2−5 for complex **6**/MMAO and entries 13−15 for complex **7**/MMAO), suggesting that its activity could be maintained at a high level even at very low Al/catalyst ratios. For example, when the cocatalyst is as low as 50 equiv relative to complex **6**, the activity is still higher than 5×10^5 g of PE/((mol of cat.) h atm). This character distinguished it from most of the existing catalysts. As presented in Table 1, the temperature tolerances of both complexes **6** and **7** for performing polymerizations were rather good (entries 3, 6−11, 13, and 17). Under our optimized conditions, although good activities of compound **6** were achieved from −30 to 100 °C (entries 3 and 6−11), the best results were obtained by performing polymerization at 50 °C (entry 3). Noticeably, the activity of **6** at −30 °C was competitive with that at 100 °C (entries 7 and 11), indicating the robustness of the catalysts, and the [NOP] ligand could stabilize catalytic Ti species even at high temperature. Polymer analysis showed that the molecular weight of polyethylene was pressure-dependent. As shown in entries 3 and 12 in Table 1, the molecular weight increased from 22×10^4 (M_w) under atmospheric pressure to 170×10^4 (M_v) under 7 atm of ethylene at 50 °C. The increase in polymer molecular mass when the ratio of cocatalyst/catalyst decreased could be easily explained in terms of a corresponding decrease in chain transfer. Also, the molecular weight changed with the polymerization temperature and it reached to its highest level at 30 °C, which could be tentatively traced to the balance between chain transfer and chain propagation caused by the different temperature. ^{1}H and ^{13}C NMR analysis (spectra given in the Supporting Information) of the polyethylene produced revealed that the polymer is highly linear polyethylene with no detectable branches. This result was also consistent with the analysis of differential scanning calorimetry (T_m values 131−141 °C). The molecular weight distribution of the polyethylene determined by GPC was between 1.54 and 3.33, similar to those of PE produced by single-site catalysts.[9]

Ethylene Copolymerization. Both complexes **6** and **7** were good catalysts, not only for polymerization of ethylene but also for copolymerization of ethylene with other olefins. As shown in Table 2, titanium trichlorides **6** and **7** also exhibited high catalytic activity for the copolymerization of ethylene with 1-hexene (entries 1−4 and 10) and norbornene (entries 5−9). Moreover, the molar percentage of the comonomer incorporation could be tuned by initial comonomer concentration. For example, the molar percentage of the hexane incorporation increased from 5% to 41% while the hexene concentration was enhanced from 0.27 to 5.33 M (entries 1−4). Also, the molar percentage of the norbornene incorporation increased from 4.1% to 35.3% while the norbornene concentration was enhanced from 0.22 to 3.74 M (entries 5−8). This splendid copolymerization capability may be

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Table 2. Copolymerization of Ethylene with 6/MMAO and 7/MMAO[a]

entry	comonomer[b] (amt (M))	procat. (amt (μmol))	amt of cocat. (equiv)	time (min)	yield (g)	activity[c]	incorporation[d] (mol %)	M_w[e]	M_w/M_n
1	hex (0.27)	**6** (9.27)	266	10	1.48	9.58	5.1	3.0	2.66
2	hex (1.06)	**6** (9.27)	266	10	2.11	13.6	15.2	2.2	2.42
3	hex (2.12)	**6** (9.27)	266	10	2.73	17.7	21.0	4.8	1.26
4	hex (5.33)	**6** (9.27)	266	10	2.90	18.7	41.1	6.2	2.87
5	NBE (0.22)	**6** (9.27)	500	30	1.81	3.90	4.1	21.0	2.96
6	NBE (0.75)	**6** (9.27)	500	30	1.48	3.2	13.6	20.7	2.35
7	NBE (1.87)	**6** (9.27)	500	30	1.10	2.4	22.9	22.9	2.28
8	NBE (3.74)	**6** (9.27)	500	30	0.65	1.4	35.3	15.0	3.25
9	NBE (1.68)	**7** (12.3)	500	10	0.72	3.5	21.1	12.5	1.53
10	hex (2.05)	**7** (9.24)	250	17	1.51	5.8	15.8	7.0	2.19

[a] General polymerization conditions: cocat. MMAO-4, 50 °C, 1 atm of ethylene, total volume (E/hexane) 15 mL. [b] Comonomer in feed, hex.: hexane, NBE: norbornene. [c] In units of 10^5 g of PE/((mol of cat.) h atm). [d] Hexene incorporation by ^{1}H NMR and norbornene incorporation by ^{13}C NMR. [e] 10^4 determined by GPC versus polystyrene standard.

attributed to the decreased steric hindrance around the active site with only one chelating ligand.

Conclusions

In summary, several novel titanium(IV) complexes based on a phenoxy–imine ligand with a phosphorus donor were synthesized and characterized. By introduction of such a side arm, titanium(IV) complexes with a chelating mono(ligand) could be formed in which the steric hindrance around the active site is less than that of the corresponding complex with bis(ligands) coordinated. In the presence of MMAO, the trichloride complexes described above are robust and highly active for the polymerization of ethylene to highly linear polyolefin. Also, complex **6** could even keep its high activity at very low cocatalyst/catalyst ratios (50/1 (mol/mol)). Moreover, these catalysts show good copolymerization capability of ethylene with 1-hexene and norbornene, which may be attributed to the open active site.

Experimental Section

General Considerations. All manipulations of air- and/or water-sensitive compounds were carried out under dry argon using standard Schlenk techniques. NMR spectra were recorded on a Varian Mercury 300 or Bruker AM300 instrument at 300 MHz (^{1}H), 121.5 MHz (^{31}P), or 75.5 MHz (^{13}C). Chemical shifts for ^{1}H NMR and ^{13}C NMR were referenced to residual nondeuterated solvent shifts. ^{31}P NMR chemical shifts are given in ppm relative to an 85% H_3PO_4 external reference. The NMR spectra of all the compounds and complexes were recorded at ambient temperature unless otherwise stated.

The polymer samples for NMR were prepared by dissolving the polymer into 1,2-dichlorobenzene in a 5 mm o.d. tube at 120∼135 °C. Mass spectra were obtained using the direct insertion probe method on a HP5989A instrument operating at 70 eV. Element analysis was performed on a Vario EL III instrument. IR analysis was detected with a Perkin-Elmer 983 instrument.

Molecular weights (M_w and M_n) and polydispersities were determined with a Waters high-temperature GPC 2000 at 150 °C using polystyrene calibration. 1,2,4-Trichlorobenzene was employed as a solvent. Transition melting temperatures of the polymers were determined by DSC with a Perkin-Elmer Pyris 1 differential scanning calorimeter, measured upon reheating the polymer sample to 200 °C at a heating rate of 10 °C/min. X-ray crystallographic data were collected using a Bruker AXS D8 X-ray diffractometer.

Materials. Toluene, hexane, hexene, diethyl ether, and tetrahydrofuran were distilled over sodium benzophenone ketyl under nitrogen. Methylene chloride was distilled over P_2O_5 and CaH_2 under nitrogen. Titanium tetrachloride was distilled prior to use. Ethylene was purified before use. Modified methylaluminoxane was purchased from Akzo Nobel with 7 wt % Al in toluene and MAO from Akzo Nobel with 15% Al in toluene. Deuterated solvents were dried using standard procedures and stored in the glovebox. Compound **1** was prepared as described in the literature.[10] Other chemicals were commercially available and used without further purification.

Synthesis of Ligand 3. To a solution of 3,5-di-*tert*-butylsalicyaldehyde (8.2 g, 34.4 mmol) and (*o*-aminophenyl)diphenylphosphine (9.6 g, 34.6 mmol) in ethanol (50 mL) were added a few 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/ether to give pale yellow crystals as the desired product **3**; yield 11.8 g (69%). ^{1}H NMR ($CDCl_3$): δ 1.30 (s, 9H, $-C(CH_3)_3$), 1.43 (s, 9H, $-C(CH_3)_3$), 7.41–6.85 (m, 16H, Ar *H*), 8.42 (s, 1H, C*H*=N). ^{13}C NMR ($CDCl_3$): δ 29.31, 31.42, 34.03, 35.00, 117.47, 117.49, 118.08, 126.45, 126.80, 127.94, 128.32, 128.42, 128.66, 129.80, 132.88, 133.05, 133.22, 134.11, 134.38, 136.00, 136.13, 136.80, 140.03, 151.48, 151.73, 158.11, 163.35, 163.38. ^{31}P NMR ($CDCl_3$): δ −13.63 (s). Anal. Calcd for $C_{33}H_{36}NOP$: C, 80.30; H, 7.35; N, 2.84. Found: C, 80.39; H, 7.59; N, 2.77. EI–MS (*m*/*z* (%)): 493 (100) [M$^+$]. IR (KBr): $\nu_{C=N}$ 1615 cm^{-1}.

Synthesis of Ligand 4. To a suspension of $LiAlH_4$ (0.3 g, 8.0 mmol) in ether (5 mL) was slowly added a solution of ligand **3** (0.98 g, 2.0 mmol) in ethyl ether (5 mL). After the mixture was stirred for 2 h at room temperature, water (5 mL) and H_2SO_4 (20%; 6 mL) aqueous were added sequentially at 0 °C. The organic phase was separated and washed with water (5 mL × 3). The aqueous phase was extracted with ether (5 mL × 3). The combined organic layers were dried with anhydrous Na_2SO_4. The solvent was removed under vacuum, and the residue was purified by column chromatography on silica gel using petroleum/EtOAc (30:1) as eluent to give the white product **4**; yield 0.94 g (95%). ^{1}H NMR ($CDCl_3$): δ 1.22 (s, 18H, $-C(CH_3)_3$), 4.22 (d, $J = 4.8$ Hz, 2H, CH_2NH), 4.72 (q, $J = 5.7$ Hz, 1H, N*H*), 6.75–7.56 (m, 16H, Ar *H*). ^{13}C NMR ($CDCl_3$): δ 29.59, 31.65, 34.16, 34.83, 49.06, 49.08, 113.55, 120.56, 122.13, 123.47, 123.62, 123.85, 123.87, 123.99, 128.68, 128.77, 129.05, 130.46, 133.58, 133.70, 133.73, 133.84, 134.43, 134.52, 136.37, 141.26, 149.64, 149.88, 153.19. ^{31}P NMR ($CDCl_3$): δ −19.54 (s). Anal. Calcd for $C_{33}H_{38}NOP$: C, 79.97; H, 7.73; N, 2.83. Found: C, 79.83; H, 7.40; N, 2.76. EI–MS (*m*/*z* (%)): 277 (100), 495 (12.86) [M$^+$]. IR (KBr): ν_{N-H} 3285 cm^{-1}.

Synthesis of Complex 5. To a slurry of NaH (48 mg, 2.0 mmol) in THF (5 mL) at −78 °C was added a solution of ligand **3** (986 mg, 2.0 mmol) in 20 mL of THF. The resulting solution was warmed to room temperature and stirred for 1 h. Then a solution of $TiCl_4$ (0.11 mL, 1.0 mmol) in 20 mL of toluene was

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(10) Larrow, J. F.; Jacobsen, E. N.; Gao, Y.; Hong, Y.; Nie, X.; Zepp, C. M. *J. Org. Chem.* **1994**, *59*, 1939.

added dropwise over a 3 h period at −78 °C. The solution was warmed to room temperature and stirred for 3 h. The solvent was removed under vacuum to give the crude product. This crude product was dissolved in anhydrous CH_2Cl_2 (80 mL). The resulting mixture was stirred for 15 min and then filtered. The organic filtrate was concentrated under vacuum and hexane (2 mL) was added to give the yellow product. The pure product **5** was obtained by recrystallization from toluene; yield 754 mg (34%). ^{1}H NMR ($CDCl_3$): δ 1.04 (s, 9H, $-C(CH_3)_3$), 1.16 (s, 9H, $C(CH_3)_3$), 7.62−7.02 (m, Ar *H*), 8.18 (m, 2H, C*H*=N, Ar *H*). ^{13}C NMR ($CDCl_3$): δ 29.69, 31.19, 34.63, 35.25, 119.91, 125.24, 127.06, 128.17, 128.41, 128.53, 128.98, 129.21, 130.68, 131.45, 132.61, 133.40, 134.12, 134.26, 135.21, 137.32, 146.29, 153.04, 158.38, 161.76, 162.14, 165.24. ^{31}P NMR ($CDCl_3$): δ 39.69 (s). Anal. Calcd for $C_{66}H_{70}Cl_2N_2O_2P_2Ti$: C, 71.80; H, 6.39; N, 2.54. Found: C, 71.50; H, 6.73; N, 2.38. EI−MS (*m*/*z* (%)): 493 (100) $[M - TiCl_2 - C_{33}H_{36}NOP]^+$. IR (KBr): $\nu_{C=N}$ 1607 cm^{-1}.

Synthesis of Complex 6. To a slurry of KH (60 mg, 1.50 mmol) in THF (10 mL) was added a solution of ligand **3** (740 mg, 1.50 mmol) in THF (10 mL) at 0 °C. The resulting suspension was warmed to room temperature and stirred for 1 h. After the solvent was removed under vacuum, 30 mL of toluene was added to the residue, followed by a solution of $TiCl_4$ (0.20 mL, 1.80 mmol) in toluene (10 mL). After the mixture was stirred for a further 3 h, the solvent was removed under vacuum, anhydrous CH_2Cl_2 (20 mL) was added to the residue, and the mixture was stirred for 15 min and then filtered. The organic filtrate was concentrated, and then hexane (2 mL) was added to precipitate the brown-red product; the pure product **6** was obtained by recrystallization from toluene. Yield: 760 mg (78%). ^{1}H NMR ($CDCl_3$): δ 1.33 (s, 9H, $-C(CH_3)_3$), 1.51 (s, 9H, $-C(CH_3)_3$), 7.76−7.26 (m, 16H, Ar *H*), 8.74 (s, 1H, C*H*=N). ^{13}C NMR ($CDCl_3$): δ 29.72, 31.21, 34.64, 35.28, 119.91, 120.01, 125.25, 125.74, 126.19, 127.09, 128.18, 128.41, 128.54, 128.99, 129.18, 129.24, 130.66, 131.01, 131.50, 132.61, 133.38, 134.15, 134.28, 135.32, 136.33, 146.28, 155.89, 156.18, 160.42, 160.49, 165.22. ^{31}P NMR ($CDCl_3$): δ 18.93. Anal. Calcd for $C_{33}H_{35}Cl_3NOPTi$: C, 61.28; H, 5.45; N, 2.17. Found: C, 60.36; H, 6.01; N, 2.01. EI−MS (*m*/*z* (%)): 591 (100), 610 (25.27) $[M - Cl]^+$, 612 (17.92), 614 (3.00), 492 (19.82) $[M - TiCl_3]^+$. IR (KBr): $\nu_{C=N}$ 1593 cm^{-1}.

Synthesis of Complex 7. To a slurry of NaH (9.2 mg, 0.4 mmol) in 10 mL of THF at 0 °C was added a solution of ligand **4** (200 mg, 0.4 mmol) in THF (5 mL). The resulting suspension was warmed to room temperature and stirred for 1 h. Then the solvent was removed under vacuum. A 40 mL portion of toluene was added to the residue, and then a solution of $TiCl_4$ (0.11 mL, 1.0 mmol) in toluene (10 mL) was added. After it was stirred for 3 h, the mixture was filtered and the organic filtrate was concentrated under vacuum to give a red-brown solid (crude product). The pure product **7** was obtained by recrystallization from toluene. Yield: 130 mg (50%). ^{1}H NMR ($CDCl_3$): δ 1.23 (s, 9H, $-C(CH_3)_3$), 1.27 (s, 9H, $-C(CH_3)_3$), 3.9 (dd, J = 13.5, 6 Hz, 1H, CH_2), 4.7 (d, J = 13.5 Hz, 1H, CH_2), 7.9−6.7 (m, Ar *H*), 8.3 (br s, 1H, N*H*). ^{31}P NMR ($CDCl_3$): δ 4.63. Anal. Calcd for $C_{33}H_{37}Cl_3NOPTi$: C, 61.09; H, 5.75; N, 2.16. Found: C, 61.16; H, 5.79; N, 1.85. EI−MS (*m*/*z* (%)): 576 (100), 612 (7.62) $[M - Cl]^+$, 614 (4.54), 616 (0.84). IR (KBr): ν_{N-H} 3167 cm^{-1}.

General Procedure of Ethylene Polymerization under Atmospheric Pressure. A solution of complex in toluene was added to a flame-dried Schlenk flask with toluene saturated by ethylene. The MMAO solution was injected into the flask via syringe with stirring. The reaction was quenched after a period of time, and the polymer was precipitated in acidic ethanol, filtered, washed with ethanol, and dried at 50 °C under vacuum to constant weight.

General Procedure of Ethylene Polymerization under 7 atm. A 2 L autoclave equipped with a magnetic stirring bar was first purged by N_2 overnight and then charged with the desired amount of MAO and toluene (500 mL) under nitrogen. The solution was saturated under 7 atm of ethylene. A solution of catalyst in toluene (15 mL) was added to the reactor under a pressure somewhat higher than atmospheric pressure at 50 °C. The pressure of the reactor was raised to 7 atm and maintained until the reactor was vented. The polymer was precipitated in acidic ethanol, filtered, washed with ethanol, and then dried at 50 °C under vacuum to constant weight.

General Procedure of Ethylene Copolymerization under Atmospheric Pressure. A flame-dried Schlenk flask was charged with the desired amounts of toluene, comonomer, and MMAO. The solution was saturated by ethylene. A solution of catalyst in toluene was injected into the reactor via syringe to initiate the polymerization. After the desired period of time, the reactor was vented. The polymer was precipitated in acidic ethanol, filtered, washed with ethanol, and then dried at 50 °C under vacuum to constant weight.

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Supporting Information Available: Figures giving NMR spectra of the polymers and tables giving X-ray data for **7**. This material is available free of charge via the Internet at http://pubs.acs.org.

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