

Synthesis and Characterization of Tridentate [O⁻N(H)X] Titanium Complexes and Their Applications in Olefin Polymerization

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ABSTRACT: A series of [O⁻N(H)X]TiCl₃ complexes derived from (arylamino)methylene phenol are prepared. The molecular structures of the complexes are characterized by ¹H NMR, ¹³C NMR, and X-ray analysis. Upon activation with modified methylaluminoxane (MMAO), the titanium complexes display high thermal stability and single-site like ethylene (co)polymerization behavior at the temperatures of up to 150 °C. 1-Octene and 1-octadecene prove suitable to be incorporated into polyethylene

backbone at 110 °C and the highest activity of 1.89×10^6 g/mol (Ti)·h·atm can be achieved. The pendant group X has great influence on the catalytic behaviors of the complexes, and PPh₂ proves to be the optimal group. © 2013 Wiley Periodicals, Inc. *J. Polym. Sci., Part A: Polym. Chem.* **2013**, *51*, 2495–2503

KEYWORDS: catalyst; copolymerization; high temperature; polyolefins; titanium complexes

INTRODUCTION Thermal stability of catalysts for olefin is extremely important for their application in industry.¹ So far, several metallocene catalysts such as CGC-type complexes and Ph₂C(Cp)(Flu)ZrCl₂/(Me₂PhNH·(B(C₆F₅)₄)-(^tBu₃Al)) were disclosed to be able to produce polyolefins in high activities at temperatures above 100 °C.² Although non-metallocene complexes^{3–11} such as Ni(II)- and Pd(II)-based diimine complexes,⁴ salicylaldiminato complexes,⁵ Fe(II) and Co(II) based pyridine diimine complexes,⁶ phenoxy titanium half-sandwich complexes,⁷ amine bis(phenolate) metals complexes,⁸ and bis(β-enaminoketonato)metal complexes⁹ prove superior in catalyzing the olefins polymerizations, only a few catalysts was highly thermally stable and active when the polymerization was run at temperatures higher than 100 °C.¹⁰ We have developed a serial of [O⁻NX]TiCl₃ (X = O, S, P, Se) complexes based on either salicylaldiminato or β-carbonyleamine, which are highly active for the ethylene polymerization and copolymerization at 80 and 100 °C respectively in the presence of MMAO.¹² In view of unstability of the imine ligand skeleton under the polymerization conditions, very recently,¹³ we further designed and synthesized [O⁻N(H)X]TiCl₃ (X = S, P) titanium complexes. In the presence of MMAO, [O⁻N(H)X]TiCl₃ complexes show good thermal stability and are highly active in catalyzing the ethylene polymerization even at 150 °C. Both 1-octene and 1-octadecene could be copolymerized with ethylene smoothly. 5.9 mol%

incorporation ratio of 1-octene with an activity of 7.4×10^5 g/mol(Ti)·h·atm could be achieved at 110 °C when **4a**/MMAO was used. In this article, we wish to report the results in details.

EXPERIMENTAL

General Informations

All air and moisture sensitive operations were carried out under nitrogen atmosphere using Schlenk techniques. ¹H NMR, ¹³C NMR, and ³¹P NMR spectra were recorded on Varian Mercury 300 Spectrometer or Varian 400 MR spectrometer. Mass spectra were carried out with a HP5989A spectrometer. Elemental analyses were performed by the Analytical Laboratory of Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences. Number-average molecular weight (M_n), weight average molecular weight (M_w), and molecular weight dispersity (M_w/M_n) values of polymers were determined at 150 °C by a Polymer Laboratories-Gel Permeation Chromatograph (PL-GPC 220) using 1,2,4-trichlorobenzene as the mobile phase with a flow rate of 1.0 mL/min. Polystyrene standards were used for calibrations. LS type columns of PLgel 10 μm MIXED-B and MIXED-D were used in series. Polymerization was carried out in stainless-steel autoclave (Parr Instrument Company, 452HC). ¹H NMR and ¹³C NMR data of polymer recorded on Varian 400 MR spectrometer at 110 °C using *o*-dichlorobenzene-d₄ as the

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solvent. The melting temperature (T_m) was measured by differential scanning calorimetry DSC (Q200, TA) at a heating rate of $10\text{ }^\circ\text{C min}^{-1}$ from -80 to $200\text{ }^\circ\text{C}$. X-ray were collected at 293 K on a Bruker SMART 1000 CCD diffractometer using Mo K ($\lambda = 0.71073\text{ \AA}$) radiation. An empirical absorption was applied using the SADABS program. All molecular structures were solved by direct methods and subsequent Fourier difference techniques and refined anisotropically for all nonhydrogen atoms by full-matrix least-squares calculations on F2 using the SHELXTL program package. All hydrogen atoms were geometrically fixed using the riding Model. Toluene, hexane, dichloromethane (CH_2Cl_2) and other solvents were purified by MB SPS-800 system (column MB-KOL MT2- $150\text{ }^\circ\text{C}$). Trimethylbenzene was purchased from Sinopharm and distilled with sodium before use. Norbornene (NBE) was purchased from Alfa Aesar and distilled over sodium before use. MMAO (MMAO-3A, heptane solution) was purchased from Akozo Nobel. Ethylene ($>99.95\%$) was further purified ($\text{O}_2 < 1\text{ ppm}$, $\text{H}_2\text{O} < 1\text{ ppm}$) before use by PEN molecular sieves from Dalian Samat Chemicals. The comonomers were purchased from Alfa Aesar (purity $> 98\%$), distilled with sodium before use. **3a** was synthesized according to literature.^{12(a)} The supplementary material available via the Internet at <http://www.interscience.wiley.com/jpages/0887-624X/suppmat>.

Synthesis of 2,4-Bis(*t*-butyl)-6-(2-(diphenylphosphinyl)phenyl)aminomethyl phenol (**3b**)

To a solution of 2,4-bis(*tert*-butyl)-6-(2-(diphenylphosphino)phenyl)aminomethyl phenol (0.36 g, 0.73 mmol) in tetrahydrofuran (THF) was added hydrogen peroxide (0.03 g, 0.88 mmol) at $0\text{ }^\circ\text{C}$. After 0.5 h, the reaction mixture was extracted with diethyl ether. The organic layer was washed with water and dried over sodium sulfate. White solids were obtained by concentration of the solution. Yield: 0.37 g (100 %).

$^1\text{H NMR}$ (300 MHz, CDCl_3 , δ): δ 7.66–7.57 (m, 5H), 7.50–7.36 (m, 4H), 7.18 (s, 1H), 7.11 (s, 1H), 6.98–6.95 (s, 1H), 6.88–6.76 (m, 3H), 5.30 (brs, 1H, NH), 4.31 (d, $J = 4.5\text{ Hz}$, 2H, CH_2), 1.28 (s, 9H, $\text{C}(\text{CH}_3)_3$), 1.26 (s, 9H, $\text{C}(\text{CH}_3)_3$). $^{31}\text{P NMR}$ (121 MHz, CDCl_3 , δ): δ 36.5. $^{13}\text{C NMR}$ (75 MHz, CDCl_3 , δ): δ 152.9, 152.2(2), 152.2(0), 141.4, 136.2, 133.7(4), 133.7(2), 133.3, 133.2, 132.2(1), 132.2(0), 132.0, 131.9, 130.6, 128.8, 128.6, 123.8, 123.3, 122.2, 118.4, 118.3, 117.2, 115.8, 114.0, 113.9, 47.9, 34.7, 34.1, 31.6, 29.6. IR (KBr, cm^{-1}): $\nu = 3541$ (w), 3052 (s), 2919 (s), 2851 (s), 1586 (m), 1496 (m), 1431 (s), 1260 (m), 1161 (s), 1088 (m), 1026 (s), 741 (s), 694 (s). MS (ESI, m/z): 512 $[\text{M}+\text{H}]^+$. HRMS (ESI, m/z): $[\text{M}+\text{H}]^+$: calcd for $\text{C}_{33}\text{H}_{39}\text{NO}_2\text{P}+1$: 512.2719 $[\text{M}+\text{H}]^+$; found: 512.2713.

Synthesis of 2-Phenyl-6-(2-(diphenylphosphino)phenylaminomethyl)-phenol (**3e**)

To a solution of 2-hydroxy-(1,1'-biphenyl)-3-carbaldehyde (0.59 g, 3.0 mmol) and 2-(diphenylphosphino)aniline (0.83 g, 3.0 mmol) in ethanol was added a drop of acetic acid, the resulting mixture was refluxed for 8 h. The solid was collected and dissolved in THF. To the resulting solution was

added lithium aluminum hydride (0.09 g, 2.27 mmol). After refluxing for 2 h, the reaction mixture was quenched by water, washed with 20% aqueous NaOH. The organic layer was separated and concentrated. The product was afforded by concentration of solution. Yield: 1.04 g (76 %)

$^1\text{H NMR}$ (300 MHz, CDCl_3 , δ): δ 7.66–7.60 (m, 2H), 7.54–7.38 (m, 8H), 7.26–6.95 (m, 8H), 6.90–6.54 (m, 4H), 5.05 (brs, 1H, NH), 4.33 (d, $J = 5.4\text{ Hz}$, 2H, $-\text{CH}_2$). $^{31}\text{P NMR}$ (121 MHz, CDCl_3 , δ): δ -20.1 . $^{13}\text{C NMR}$ (75 MHz, CDCl_3 , δ): δ 152.5, 150.2, 150.0, 139.4, 137.6, 134.9, 134.8, 134.0, 133.8, 133.5, 132.3, 132.0, 131.9, 131.8, 130.9, 130.5, 129.6, 129.2, 128.9, 128.8, 128.6 (5), 128.6 (0), 128.3, 127.9, 127.1, 124.9, 124.1, 122.2, 122.1, 119.9, 119.5, 112.8, 46.9 IR (KBr, cm^{-1}): $\nu = 3674$ (w), 2988 (s), 2901 (s), 2536 (s), 1585 (m), 1431 (m), 1529 (m), 1067 (m), 741 (s), 693 (s). MS (ESI, m/z): 460 $[\text{M}+\text{H}]^+$. HRMS (ESI, m/z): $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{31}\text{H}_{27}\text{NOP}+1$: 460.1814 $[\text{M}+\text{H}]^+$, found: 460.1825.

Synthesis of 2,4-Di-*tert*-butyl-6-(1-(2-(diphenylphosphino)phenylamino)-2,2-dimethylpropyl)phenol (**3f**)

To a solution of 1-[3,5-bis(1,1-dimethylethyl)-2-hydroxyphenyl]-2,2-dimethyl-1-propanone (1.0 g, 3.44 mmol), 2-(diphenylphosphino)aniline (1.15 g, 4.13 mmol) and Et_3N (5 mL) in dichloromethane (5 mL) was added TiCl_4 (0.41 g, 2.0 mmol) at $0\text{ }^\circ\text{C}$. After stirring for 2 h at $0\text{ }^\circ\text{C}$, the reaction mixture was quenched with water. The resulting solid was collected and washed with dichloromethane. After purification by flash column chromatography (base Al_2O_3 , petroether as eluant), the obtained yellow solid was reduced by lithium aluminum hydride (0.03 g, 0.89 mmol) in THF under refluxing for 2 h. The reaction mixture was quenched by water, washed with 20% aqueous NaOH. The organic layer was separated and concentrated. The pure product was precipitated by concentration of solution. Yield: 0.36 g (73 %).

$^1\text{H NMR}$ (300 MHz, CDCl_3 , δ): δ 8.93 (s, 1H, -OH), 7.40–7.31 (m, 10H), 7.16–7.06 (m, 2H), 6.91–6.86 (m, 1H), 6.76–6.66 (m, 3H), 5.41 (d, $J = 8.4\text{ Hz}$, 1H, -NH), 3.91 (s, 1H, $-\text{CH}_2$), 1.31 (s, 9H, $-\text{C}(\text{CH}_3)_3$), 1.28 (s, 9H, $-\text{C}(\text{CH}_3)_3$), 0.92 (s, 9H, $-\text{C}(\text{CH}_3)_3$). $^{31}\text{P NMR}$ (121 MHz, CDCl_3 , δ): δ -20.8 . $^{13}\text{C NMR}$ (75.5 MHz, δ): δ 154.0, 150.1, 149.8, 139.5, 135.9, 135.0, 134.9, 134.3, 134.2, 134.1, 134.0, 133.9, 133.7, 130.5, 129.2(5), 129.2(0), 128.9, 128.8, 128.7, 125.5, 123.5, 123.4, 122.2, 121.6, 120.2, 114.1, 72.0, 36.9, 34.8, 34.0, 31.7, 29.5, 27.4. IR (KBr, cm^{-1}): $\nu = 3358$ (w), 2958 (s), 2926 (s), 2873 (s), 1720 (s), 1587 (m), 1469 (m), 1223 (m), 1049 (s), 880 (s), 742 (m), 692 (s). MS (ESI, m/z): 552 $[\text{M}+\text{H}]^+$. HRMS (ESI, m/z): $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{37}\text{H}_{47}\text{NOP}+1$: 552.3375 $[\text{M}+\text{H}]^+$, found: 552.3390.

Synthesis of Complex 4 (**4c** as an Example)

To a solution of **3c** (0.40 g, 1 mmol) in toluene (5 mL) was added TiCl_4 (0.21 g, 1.1 mmol) in toluene (5 mL) at room temperature. The resulting mixture was stirred for 24 h at room temperature and then heated to $50\text{ }^\circ\text{C}$ for further 2 h. After filtration, the solvent was removed under reduced pressure to afford red powder, which was recrystallized in toluene/hexane (v/v: 10/1) to give complex **4c**.

4b 0.29 g (88 % yield). ^1H NMR (300 MHz, CDCl_3 , δ): δ 8.09–8.02 (m, 2H), 7.93–7.86 (m, 2H), 7.76–7.68 (m, 4H), 7.56–7.51 (m, 4H), 7.37 (s, 1H), 7.19–7.04 (m, 3H), 5.50 (brs, 1H), 5.12 (brs, 1H), 4.14 (d, $J = 14.7$ Hz, 1H), 1.61 (s, 9H, $-\text{C}(\text{CH}_3)_3$), 1.35 (s, 9H, $-\text{C}(\text{CH}_3)_3$). ^{31}P NMR (121 MHz, CDCl_3): δ 40.8. ^{13}C NMR (75 MHz, CDCl_3 , δ): δ 162.8, 152.9, 146.9, 134.7, 134.6, 134.4, 133.6, 133.5, 133.5, 133.4, 133.2, 129.7, 129.5, 129.3, 128.2, 127.3, 127.1, 125.8, 125.5, 124.3, 123.9, 119.8, 118.9, 118.4, 117.5, 50.8, 35.5, 34.8, 31.6, 30.5. IR (KBr, cm^{-1}): $\nu = 3259$ (s), 3055 (m), 2955 (s), 2864 (s), 1596 (m), 1451 (m), 1236 (s), 1172 (m), 1060 (m), 913 (s), 751 (s). Anal. Calcd for $\text{C}_{33}\text{H}_{37}\text{Cl}_3\text{NO}_2\text{PTi}$: C, 59.62; H, 5.61; N, 2.11; found: C, 59.90; H, 5.24; N, 1.78.

4c 0.51 g (89 % yield). ^1H NMR (300 MHz, CDCl_3 , δ): δ 7.66–7.61 (m, 3H), 7.54 (t, $J = 7.5$ Hz, 2H), 7.46–7.44 (m, 1H), 7.36–7.35 (m, 2H), 7.19–7.17 (m, 2H), 6.68 (dd, $J = 3.9$ Hz, 5.7 Hz, 1H), 5.68 (brs, 1H), 4.94–4.72 (m, 2H), 1.55 (s, 9H, $-\text{C}(\text{CH}_3)_3$), 1.33 (s, 9H, $-\text{C}(\text{CH}_3)_3$). ^{13}C NMR (75 MHz, CDCl_3 , δ): δ 161.6, 154.9, 154.4, 148.0, 137.8, 135.9, 130.7, 130.3, 129.4, 129.0, 128.5, 128.2, 125.3, 124.8(2), 124.8(0), 124.3, 123.7, 115.4, 54.6, 35.5, 34.8, 31.4, 30.2. IR (KBr, cm^{-1}): $\nu = 3158$ (m), 2960 (s), 2868 (s), 1589 (s), 1489 (s), 1236 (m), 1172 (m), 861 (s), 754 (m), 691 (s). Anal. Calcd for $\text{C}_{27}\text{H}_{32}\text{Cl}_3\text{NO}_2\text{Ti}$: C, 58.24; H, 5.79; N, 2.52; found: C, 58.68; H, 6.07; N, 2.11.

4d 1.04 g (92% yield). ^1H NMR (300 MHz, CDCl_3 , δ): δ 7.75–7.72 (m, 1H), 7.56 (t, $J = 7.5$ Hz, 1H), 7.42–7.29 (m, 3H), 7.24–7.16 (m, 4H), 7.11–7.09 (m, 1H), 6.82 (s, 1H), 6.30–6.65 (brs, 1H), 5.10 (brs, 1H), 4.32 (brs 1H), 1.40 (s, 9H, $-\text{C}(\text{CH}_3)_3$), 1.22 (s, 9H, $-\text{C}(\text{CH}_3)_3$). ^{13}C NMR (75 MHz, CDCl_3 , δ): δ 160.2, 147.2, 137.8, 136.1, 133.3, 131.4, 130.1, 130.0, 129.4, 129.3, 129.0, 128.9, 128.5, 128.2, 127.1, 125.3, 125.0, 124.3, 58.0, 35.1, 34.6, 31.3, 29.8. IR (KBr, cm^{-1}): $\nu = 3122$ (w), 2957 (m), 2868 (s), 1582 (m), 1479 (s), 1441 (s), 1238 (s), 1127 (m), 887 (s), 750 (m). Anal. Calcd for $\text{C}_{27}\text{H}_{32}\text{Cl}_3\text{NO}_2\text{Ti} \cdot 1.5\text{C}_6\text{H}_5\text{CH}_3$: C, 63.08; H, 6.63; N, 1.96; found: C, 62.53; H, 6.36; N, 1.72.

4e 0.55 g (90 % yield). ^1H NMR (300 MHz, CDCl_3 , δ): δ 7.79–7.32 (m, 13H), 7.19–7.18 (m, 3H), 6.84–6.81 (m, 6H), 6.46 (brs, 1H), 5.55–5.46 (m, 1H), 4.41–4.32 (m, 1H). ^{31}P NMR (121 MHz, CDCl_3): δ 17.6. ^{13}C NMR (75 MHz, CDCl_3 , δ): δ 159.2, 151.7, 149.1, 138.0, 137.8, 136.6, 136.3, 135.6, 134.4, 134.3, 133.7, 132.2, 132.1, 131.8, 131.0, 130.6, 130.1, 130.0, 129.9, 129.6, 129.4, 129.0, 128.7, 128.6, 128.5, 128.4, 128.2, 127.9, 127.6, 127.5, 127.1, 126.8, 126.6, 126.4, 125.3, 123.5, 57.8. IR (KBr, cm^{-1}): $\nu = 3352$ (w), 3159 (s), 3056 (s), 1586 (m), 1481 (m), 1436 (m), 1229 (m), 1122(m), 911 (s), 785 (s), 639 (s). Anal. Calcd for $\text{C}_{31}\text{H}_{25}\text{Cl}_3\text{NOPTi}$: C, 60.77; H, 4.11; N, 2.29; found: C, 59.95; H, 4.11; N, 2.55.

4f 0.57 g (81% yield). ^1H NMR (300 MHz, CDCl_3 , δ): δ 7.85 (t, $J = 8.7$ Hz, 2H), 7.70–7.31 (m, 7H), 7.19–7.12 (m, 1H), 6.98 (t, $J = 6.9$ Hz, 2H), 6.86–6.80 (m, 1H), 6.45(4)–6.45(0) (m, 1H), 5.97–5.96 (m, 1H), 4.08 (s, 1H), 1.32 (s, 9H, $-\text{C}(\text{CH}_3)_3$), 1.19 (s, 9H, $-\text{C}(\text{CH}_3)_3$), 1.13 (s, 9H, $-\text{C}(\text{CH}_3)_3$). ^{31}P NMR (121 MHz, CDCl_3 , δ): δ 12.8. ^{13}C NMR

(75 MHz, CDCl_3 , δ): δ 159.5, 157.6, 157.3, 144.9, 135.6, 135.5, 135.0, 133.6, 133.0, 132.9, 130.9, 130.8, 130.5, 130.3, 129.9, 129.4, 129.0, 128.6, 128.5, 128.3, 128.2, 128.0, 126.6, 125.3, 123.4, 82.3, 37.5, 35.0, 34.3, 31.5, 30.5, 28.6. IR (KBr, cm^{-1}): $\nu = 3254$ (s), 3057 (s), 2959 (s), 2906 (s), 2868 (s), 1589 (m), 1480 (s), 1436 (s), 1363 (m), 1261 (m), 1089 (m), 1027 (m), 968 (m), 871 (m), 768 (m). Anal. calcd for $\text{C}_{37}\text{H}_{45}\text{Cl}_3\text{NOPTi}$: C, 63.04; H, 6.43; N, 1.99; Found: C, 63.78; H 6.78; N, 1.75.

General Procedure for Ethylene Polymerization

A 300 mL dried stainless-steel autoclave was charged with solvent (50 mL) and stirred for 30 min (IKA RCT stirrer; stirring rate of 500 rpm) at the desired temperature. Desired amount of MMAO (1.88 M in heptane) was added and the solution was stirred for 5 min. Then, catalyst (5 μmol , 1 $\mu\text{mol mL}^{-1}$ in toluene) was added and followed by the feeding of ethylene to the desired pressure. By the time to end the polymerization, the autoclave was vented and the reaction mixture was poured into acidified ethanol (200 mL, 10% HCl) and stirred for 12 h. The polymer was filtered, collected, washed with ethanol, and dried to constant weight under vacuum at 70 $^\circ\text{C}$.

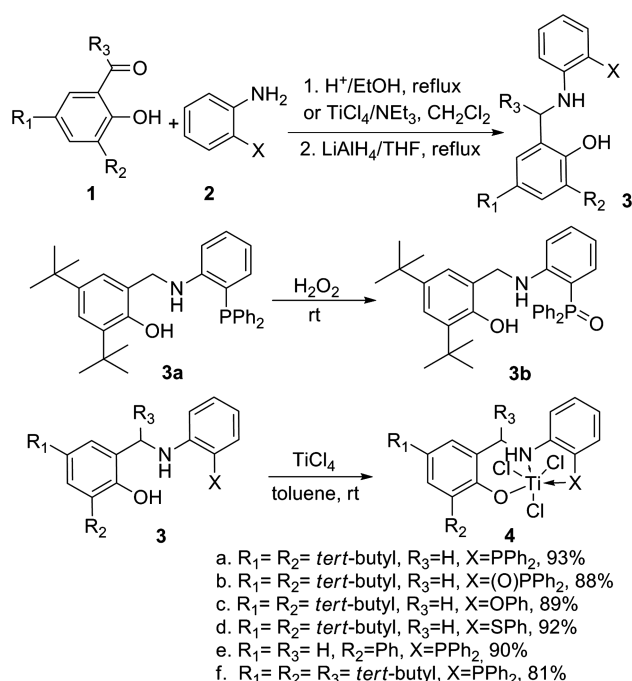
General Procedure for Ethylene Copolymerization

A 300 mL dry stainless-steel autoclave was charged with solvent and kept at the desired temperature for 30 min. The comonomer and desired amount of MMAO (1.88 M in heptane) was added and the solution was stirred for 5 min. Adding catalyst (5 μmol , 1 $\mu\text{mol mL}^{-1}$ in toluene) to the reaction system and the autoclave was fed with ethylene to the desired pressure. The polymerization was quenched by acidified ethanol (200 mL, 10% HCl). The polymer was filtered, collected, washed with ethanol and dried to constant weight under vacuum at 70 $^\circ\text{C}$.

RESULTS AND DISCUSSION

Synthesis and Characterization of Ligands and Titanium Complexes

(Arylamino)methylene phenol was synthesized from the corresponding salicylaldehydes and aniline. As shown in Scheme 1, the condensation reaction between salicylaldehyde and substituted aniline in the presence of either catalytic amount of acid or TiCl_4 generated imine compounds smoothly. Without separation and further purification, the *in situ* formed imine compounds could be reduced into ligands **3** readily in 73% to quantitative yields. **3b** was obtained quantitatively by oxidation of **3a**. Without the pretreatment **3** with base, the reaction between **3** and excess of TiCl_4 in toluene at room temperature gave complexes **4** as red solids in 81–93% yields. All compounds were well characterized by ^1H NMR, ^{13}C NMR and elemental analysis. ^1H NMR of the complexes **4** show that the chemical shift of $\text{CH}_2\text{-N}$ move toward downfield relative to the corresponding ligands, indicating the coordination effect of nitrogen to the metal. The ^{13}C NMR signal of C-N in **4f** at 80 ppm, relative to those in complex **4b-e** (around 50 ppm), suggesting an apparent fragment distortion induced by steric R^3 group. For



SCHEME 1 Synthesis of ligands and complexes.

complexes **4e** and **4f**, ^{31}P NMR signals shift downfield from around -20 ppm to 17.6 and 12.8 ppm separately, demonstrating that phosphorus is probably coordinated to the metal. The ^{31}P NMR signals of **3b** and **4b** appeared at 36.5 and 40.8 ppm, respectively.

Molecular structures of **4** (Figs. 1–4) were further determined by X-ray diffraction (Table 1). As shown in Figure 1

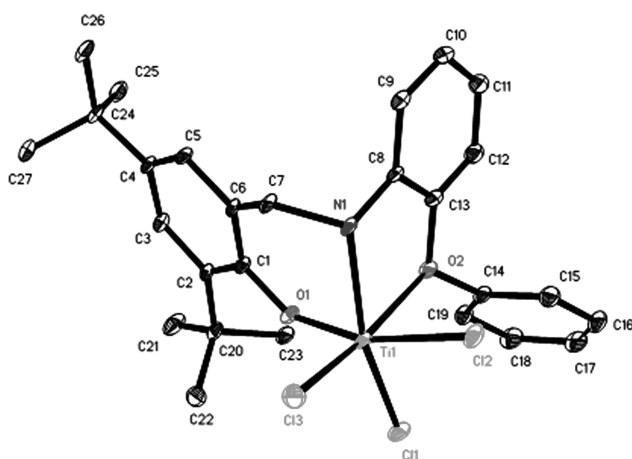


FIGURE 1 The molecular structure of **4c**. Selected bond lengths (Å) and angles(deg). Ti(1)–O(1), 1.809(3); Ti(1)–N(1), 2.225(3); Ti(1)–O(2), 2.304(3); Ti(1)–Cl(1), 2.2612(13); Ti(1)–Cl(2), 2.3813(13); Ti(1)–Cl(3), 2.2610(12); O(1)–C(1), 1.373(4); C(6)–C(7), 1.491(6); C(7)–N(1), 1.520(4); N(1)–C(8), 1.469(5); O(1)–Ti(1)–N(1), 83.31(12); O(1)–Ti(1)–Cl(3), 96.90(9); N(1)–Ti(1)–Cl(3), 96.60(9); O(1)–Ti(1)–Cl(1), 97.89(10); N(1)–Ti(1)–Cl(1), 163.19(9); Cl(3)–Ti(1)–Cl(1), 102.56(5); O(1)–Ti(1)–O(2), 86.57(11); N(1)–Ti(1)–O(2), 74.67(11).

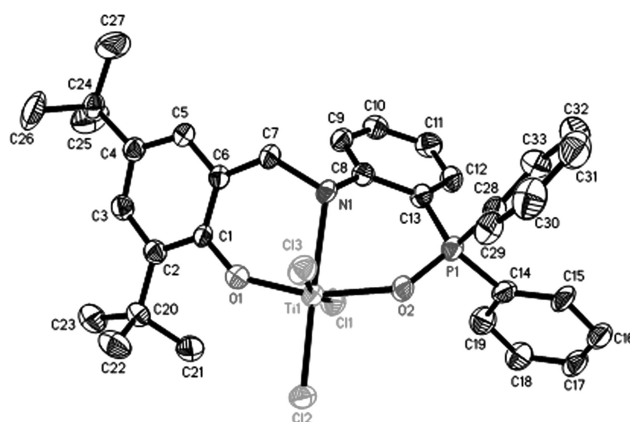


FIGURE 2 The molecular structure of **4b**. Selected bond lengths (Å) and angles(deg) Ti(1)–O(1), 1.772(5); Ti(1)–N(1), 2.326(6); Ti(1)–O(2), 1.993(3); Ti(1)–Cl(1), 2.326(3); Ti(1)–Cl(2), 2.249(2); Ti(1)–Cl(3), 2.362(3); O(1)–C(1), 1.359(8); C(6)–C(7), 1.497(10); C(7)–N(1), 1.491(9); N(1)–C(8), 1.442(9); O(1)–Ti(1)–N(1), 83.5(2); O(1)–Ti(1)–Cl(3), 94.19(18); N(1)–Ti(1)–Cl(3), 81.35(18); O(1)–Ti(1)–Cl(1), 90.09(18); N(1)–Ti(1)–Cl(1), 89.28(17); Cl(3)–Ti(1)–Cl(1), 169.17(10); O(1)–Ti(1)–O(2), 161.8(2); N(1)–Ti(1)–O(2), 78.6(2).

for example, the geometry around the titanium of **4c** adopts a distorted octahedron geometry and O(1)–O(2)–Cl(2)–Cl(3) are nearly coplanar. Titanium deviates from the plane 0.2380 (0.0012) Å. Three chlorine atoms are in a *mer* position: Cl(3)–Ti(1)–Cl(1) angle is 102.56(5)°, Cl(2)–Ti(1)–Cl(1) and Cl(2)–Ti(1)–Cl(3) are 95.00(5)° and 91.30(5)°, indicating that three chlorines are located in a *cis* position to each other, which is beneficial to the insertion of olefins. The

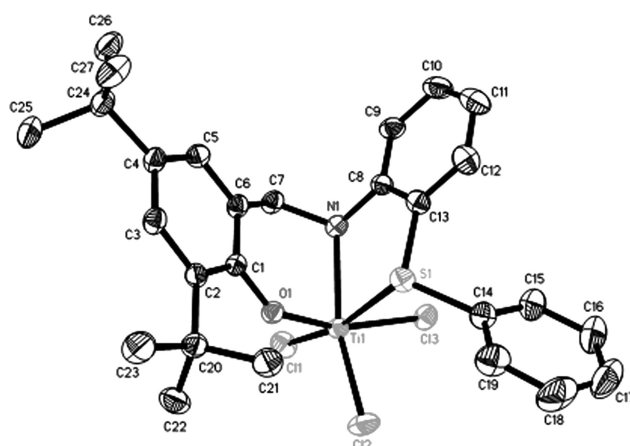


FIGURE 3 The molecular structure of **4d**. Selected bond lengths (Å) and angles(deg) Ti(1)–O(1), 1.791(2); Ti(1)–N(1), 2.249(3); Ti(1)–S(1), 2.6215(3); Ti(1)–Cl(1), 2.2599(12); Ti(1)–Cl(2), 2.2439(13); Ti(1)–Cl(3), 2.3569(11); O(1)–C(1), 1.365(4); C(6)–C(7), 1.508(5); C(7)–N(1), 1.499(5); N(1)–C(8), 1.461(5); O(1)–Ti(1)–N(1), 83.51(11); O(1)–Ti(1)–Cl(3), 162.61(9); N(1)–Ti(1)–Cl(3), 80.94(8); O(1)–Ti(1)–Cl(1), 96.41(9); N(1)–Ti(1)–Cl(1), 93.04(9); Cl(3)–Ti(1)–Cl(1), 92.14(4); O(1)–Ti(1)–S(1), 80.03(8); N(1)–Ti(1)–O(2), 74.94(8).

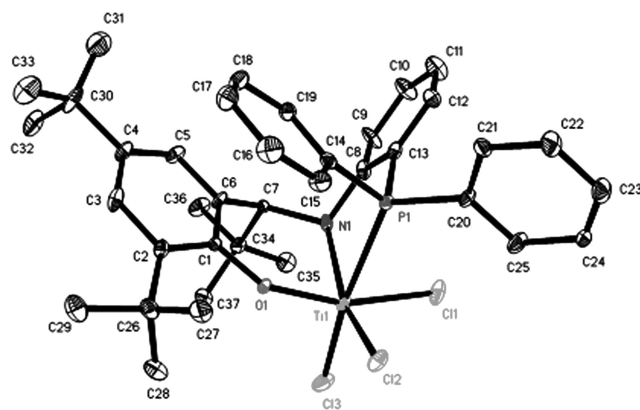


FIGURE 4 The molecular structure of **4f**. Selected bond lengths (Å) and angles(deg) Ti(1)—O(1), 1.777(4); Ti(1)—N(1), 2.295(5); Ti(1)—P(1), 2.624(2); Ti(1)—Cl(1), 2.355(2); Ti(1)—Cl(2), 2.2581(19); Ti(1)—Cl(3), 2.3569(11); O(1)—C(1), 1.374(6); C(6)—C(7), 1.518(7); C(7)—N(1), 1.525(6); N(1)—C(8), 1.460(7); O(1)—Ti(1)—N(1), 80.80(16); O(1)—Ti(1)—Cl(3), 97.57(13); N(1)—Ti(1)—Cl(3), 101.66(13); O(1)—Ti(1)—Cl(1), 158.24(14); N(1)—Ti(1)—Cl(1), 77.50(12); Cl(3)—Ti(1)—Cl(1), 88.32(7); O(1)—Ti(1)—P(1), 90.89(13); N(1)—Ti(1)—P(1), 74.79(12).

sum of angles around N1 (C7—N1—Ti1, C8—N1—Ti1, and C7—N1—C8) is 339.9°, which means that the nitrogen is sp^3 hybridization. The bond length of Ti(1)—N(1) is longer than that of the corresponding phenoxyl-imine complex (2.225(3) Å vs. 2.152(4) Å).^{12(c)} The bond length of Ti1—O2 (2.304(3) Å) is slightly longer than the sum of the covalent radii of titanium and oxygen ($r_{cov(Ti)} = 1.60$ Å, $r_{cov(O)} = 0.66$ Å),¹⁴ suggesting a weak interaction existed between titanium and pendant ether group.

TABLE 2 Crystal Data Comparisons of **4b**, **4c**, **4d**, and **4f**

Bond angle (°)	4b	4c	4d	4f
C7—N1—C8	116.9(6)	113.2(3)	113.3(3)	110.0(4)
O1—Ti—X	161.8(2)	86.57(11)	80.03(8)	90.89(13)

4b, **4d**, and **4f** showed similar molecular structures to that of **4c**. The geometry around titanium is distorted octahedron and three chlorines locate in a *mer* position. The sums of angles around N1 are smaller than 350°, indicating that N1 adopts a sp^3 hybridization. When a ^tBu group was introduced on C7 (**4f**), N(1), P(1), Cl(2), and Cl(3) are coplanar and the centre titanium deviates from the plane 0.1154 (0.0016) Å. The bond angle of C7—N1—C8 is 110(4)°, while that of complex **4a** is 117°. ^{12(a)} In the case of PPh₂=O was introduced as a pendant group, the oxygen coordinated with titanium to form two six-membered rings. The bond length of Ti—O(2) is shorter than that in **4c** (1.993(3) versus 2.304(3) Å). Regardless of the different substitution on the fragment of the ligand, similar bond angle of C7—N1—C8 was observed for the four molecules. However, bond angle of O1—Ti—X (X = O, S, P) differs considerably from each other (Table 2).

Ethylene Polymerization

Upon activation by MMAO, **4a–f** were evaluated at high temperature (110–150 °C) for ethylene polymerization (Table 3). High activity and high molecular weight were observed when the polymerization was preceded under 1 atm ethylene pressure. The catalysts structure, Al/Ti ratio, reaction temperature, and ethylene pressure influenced both the activities and the molecular weight of the resulting

TABLE 1 Crystal Data and Details of Data Collection for **4b**, **4c**, **4d**, and **4f**

	4b	4c	4d	4f
Formula	C ₃₃ H ₃₇ Cl ₃ NO ₂ PTi	C ₃₄ H ₄₀ Cl ₃ NO ₂ Ti	C _{37.5} H _{43.5} Cl ₃ NOSTi	C _{40.5} H ₄₈ Cl ₃ NOPTi
<i>F_w</i> (g/mol)	664.86	648.92	710.54	750.02
Crystalsyst	Monoclinic	Triclinic	Triclinic	Monoclinic
Space group	P2(1)/c	P-1	P-1	C2/c
<i>a</i> , Å	11.360(3)	10.365(3)	10.4147(10)	41.287(16)
<i>b</i> , Å	13.042(4)	14.244(3)	14.2401(14)	10.704(4)
<i>c</i> , Å	21.950(6)	14.322(6)	14.3818(14)	18.274(7)
<i>V</i> , Å ³	3252.1(15)	1791.2(3)	1827.3(11)	7836(5)
<i>Z</i>	4	2	2	8
D _{calc} , Mg/m ³	1.358	1.203	1.291	1.271
2θ range, deg	1.82 to 25.50	1.61 to 25.05	1.66 to 26.00	1.97 to 25.05
<i>F</i> (1000)	1384	680	745	3152
Reflections collected/unique	15465/6030 [<i>R</i> (int) = 0.1286]	11082/6219 [<i>R</i> (int) = 0.0506]	10031/7052 [<i>R</i> (int) = 0.0239]	24963/6935 [<i>R</i> (int) = 0.1209]
Data/restraints/parameters	6030/0/381	6219/0/370	7052/4/398	6935/84/481
Goodness of fit	0.939	0.977	1.027	1.027
<i>R</i> ¹ (<i>I</i> > 2σ(<i>I</i>))	0.0792	0.0797	0.0588	0.0757
w <i>R</i> ² (<i>I</i> > 2σ(<i>I</i>))	0.2798	0.2142	0.1732	0.2279

TABLE 3 Polymerization of ethylene under high temperature^a

Entry	Cat.	Al/Ti	T_p (°C)	Time (min)	Solvent	Yield (g)	Activity ^b	$M_w^{c,d}$	M_w/M_n^c
1	4a	200	110	2	Toluene	0.22	1.32	9.3	2.3
2	4a	500	110	2	Toluene	0.90	5.40	12.6	2.8
3	4a	1000	110	2	Toluene	0.77	4.61	10.4	2.4
4	4a	2000	110	2	Toluene	0.62	3.73	3.6	2.3
5	4a	500	110	2	Trimethylbenzene	0.73	4.39	2.5	2.7
6	4a	500	130	2	Trimethylbenzene	0.56	3.37	1.7	2.2
7	4a	500	150	2	Trimethylbenzene	–	–	–	–
8 ^e	4a	500	150	2	Trimethylbenzene	0.45	0.54	15.9	2.3
9	4b	500	110	2	Toluene	0.22	1.32	10.4	2.4
10 ^e	4c	500	110	2	Toluene	–	–	–	–
11 ^e	4d	500	110	2	Toluene	0.19	0.22	18.5	3.8
12	4e	500	110	2	Toluene	0.16	0.96	9.8	2.3
13	4f	500	110	2	Toluene	0.72	4.32	3.8	2.0
14	4a	500	30	2	Toluene	0.18	1.08	24.3	1.8
15	4a	500	50	2	Toluene	0.45	2.70	19.3	1.8
16	4a	500	70	2	Toluene	0.81	4.86	18.0	1.9
17	4a	500	90	2	Toluene	1.13	6.78	15.8	2.6
18	4a	500	110	5	Toluene	2.05	4.92	13.7	2.9
19	4a	500	110	15	Toluene	2.86	2.29	15.1	2.9
20	4a	500	110	30	Toluene	3.16	1.26	18.2	3.1

^a Solvent, 50 mL; cat., 5 μ mol; 1 atm ethylene.^b 10^6 g/mol·h·atm.^c Determined by GPC.^d 10^4 g/mol.^e 5 atm ethylene.

polyethylene. When the ethylene polymerization was catalyzed by **4a** at 110 °C and 200 Al/Ti ratio, an activity of 1.32×10^6 g/mol(Ti)·h·atm was obtained. Increasing the molar ratio of Al/Ti to 500 resulted in the activity increasing (5.40×10^6 g/mol(Ti)·h·atm, entry 1 vs. 2). However, no apparent elevation could be observed when the ratio was further improved (entries 2–4). Trimethylbenzene was also a suitable solvent (entry 5). The polymerization carried out at 130 °C in trimethylbenzene under 1 atm ethylene pressure generated PE in a high activity of 3.37×10^6 g/mol(Ti)·h·atm. Though no polymer could be separated when the polymerization was proceeded under 1 atm ethylene pressure at 150 °C (entry 7), an activity of 0.54×10^6 g/mol(Ti)·h·atm was achieved at 150 °C under 5 atm pressure (entry 8).

The structures of the complexes have great impact on the activity. **4c** was totally inactive to the polymerization at 110 °C even under 5 atm pressures. Replacing the pendant group from OPh group with SPh (**4d**) generated a moderate activity (entry 11). As X-ray analysis revealed that O2 atom in **4c** is sp^2 hybridization and the S atom in **4d** is sp^3 hybridization, a synergistic effect between the steric hindrance and electronic properties of the metal center was probably the reason for different behavior of polymerization. **4b**, in which O=PPh₂ group coordinates with titanium by oxygen atom, gave a clearly higher activity (1.32×10^6 g/mol(Ti)·h·atm) than that of **4c**, indicating that the hindrance around

titanium is a more important factor than electronic property to influence the catalytic behavior of the complexes. When two ^tBu groups at R¹ and R² positions were replaced by H and phenyl groups separately (**4b**), a reduced activity of 0.96×10^6 g/mol(Ti)·h·atm was produced (entry 12). Introducing a *tert*-butyl group on (Ar)-C7-N1 fragment (**4f**) results in the structure of complex deviates greatly in comparison with that of **4a**,^{10(a)} however, it catalyzed ethylene polymerization quite smoothly to give PE in an activity of 4.32×10^6 g/mol(Ti)·h·atm at 110 °C and 500 Al/Ti ratio.

The thermal stability of the catalysts could be established by comparing the polymerization results under different temperatures. As shown in Table 3, the activity of **4a**/MMAO was dependent on the polymerization temperature. For example, the temperature rise led to enhancement first and then decrease of activity. The highest activity of 6.78×10^6 g/mol(Ti)·h·atm was at 90 °C (entries 14–18 vs. 2). Further increasing the temperature to 110 °C reduced the activity slightly (entry 2 vs. 18). When the polymerization time was prolonged to 5 min., a high activity of 4.9×10^6 g/mol(Ti)·h·atm could be achieved. Though the polymerization mixture became more and more viscous, satisfied activities were still achieved even if the polymerization was carried out for 30 min. at 110 °C (entries 18–20 vs. 2). These results suggested that the catalytic species is quite stable over 100 °C.

TABLE 4 Copolymerization of Ethylene/1-Olefins and Ethylene/NBE with **4a** at 50 °C^a

Entry ^a	Comonomer (mmol)	Time (min)	Yield (g)	Activity ^b	Incorporation (mol %) ^c	M_w^d (10 ⁴ g/mol)	M_w/M_n^d
1	Hexene(10)	5	0.43	1.04	0.8	21.7	2.5
2	Hexene(20)	5	0.50	1.21	1.8	22.8	2.4
3	Hexene(40)	5	0.21	0.52	1.8	20.6	2.6
4	Hexene(80)	5	0.32	0.77	2.1	19.2	2.6
5	Octene (20)	15	3.26	2.61	2.7	11.2	2.1
6	Dodecene(40)	15	0.80	0.64	5.9	10.2	2.2
7	Dodecene(80)	15	1.26	1.01	11.7	11.0	2.0
8	NBE(10)	15	0.24	0.19	4.1	14.0	2.3
9	NBE(20)	15	0.18	0.14	7.5	10.2	2.9

^a Conditions: 50 °C; 1 atm of ethylene; toluene, 50 mL; Al/Ti = 500; catalyst **4a**, 5 μmol.

^b 10⁶ g/mol·h·atm.

^c Determined by ¹³C NMR.

^d Determined by GPC.

We have tried the synthesis of complex with X as CH₂Ph. The treatment of TiCl₄ either with equivalent ligand (X = CH₂Ph) or with equivalent potassium (or lithium) salt of the ligand (X = CH₂Ph) gave a mixture. Attempts to purify it failed. This is totally different from the examples that containing coordination group as a sidearm. In the presence of MMAO, no polymer was generated when the resulted mixture was used to catalyze the ethylene polymerization at 110 °C.

Whatever catalyst, narrow molecular weight distributions (M_w/M_n) of the produced PE featured character of single-site catalyst. The M_w of the resulting polymers decreased with the increase of polymerization temperature; and, with the prolonging polymerization time from 2 to 30 min, the molecular weight distribution (M_w/M_n) of the produced PE changed slightly. A sharp decrease on molecular weight of the resulted PE from 10.4×10^4 g/mol to 3.6×10^4 g/mol was observed in the case of improving Al/Ti ratio from 500 to 2000, indicating that chain transfer to aluminum was a main way of chain termination. ¹³C NMR analysis exhibited the polymers are linear. The highest M_w was obtained when -SPh was introduced as a sidearm group (entry 11). In the case of **4f**, M_w was only 3.8×10^4 g/mol.

Ethylene Copolymerization with α -Olefins

The copolymerization of ethylene and different comonomers was screened using **4** activated with MMAO under different conditions. As shown in Table 4, **4a** was first selected to catalyze both the ethylene/ α -olefins and ethylene/NBE copolymerizations at 50 °C. In the presence of MMAO, **4a** showed high activity for the copolymerization and the incorporation ratio could be improved by controlling the loading of comonomer. For example, the incorporation ratio rise from 0.8 to 2.1 mol % when 80 mmol instead of 20 mmol 1-hexene was added (entries 1–4). 1-Octene and 1-dedocene also worked efficiently, and the copolymer was obtained in an activity of 1.0×10^6 g/mol(Ti)·h·atm with 11.7 mol % incorporation ratio when 80 mmol 1-dedocene and ethylene gas was

treated at 50 °C and 500 Al/Ti ratio. NBE is also a good comonomer and the incorporation ratio also could be improved by controlling the loading of comonomer. When 20 mmol NBE was used as a comonomer in the presence of **4a**/MMAO, 7.5 mol % incorporation ratio was achieved (entry 9).

Tables 5 and 6 summarized the results of the ethylene/ α -olefins copolymerization at 110 °C in the presence of **4**/MMAO. The influences of the monomer feed on the activity and incorporation ratio were first screened in toluene under 1 atm ethylene pressure. As shown in Table 5, the copolymerization proceeded well and the highest activity of 1.52×10^6 g/mol(Ti)·h·atm was achieved when 20 mmol 1-octene and ethylene were copolymerized by **4a**/MMAO. Compared with that at 50 °C (2.61×10^6 g/mol(Ti)·h·atm, entry 5, Table 4), the activity of the copolymerization of ethylene/octene decreased slightly at 110 °C (entry 2, Table 5). In both cases, narrow molecular weight distributions were observed but molecular weight of the produced copolymer reduced from 11.2×10^4 g/mol to 5.4×10^4 g/mol when changing the temperature from 50 to 110 °C. The initial concentration of the comonomer is proportional to the incorporation rate. Consequently, improved incorporation ratio of 1-octene could be achieved by increasing the initial amount of octene. The activity was slightly reduced while increasing the co-monomer concentration, as reported for other systems.¹⁵ As a result, when 40 mmol 1-octene was added, the copolymer (T_m 101.1 °C) was generated in an activity of 0.99×10^6 g/mol(Ti)·h·atm and 3.4 mol % incorporation ratio (entry 3). The highest incorporation ratio of 5.9 mol % with an activity of 0.74×10^6 g/mol(Ti)·h·atm was obtained in the case of 80 mmol octene being used. Under this condition, the T_m of the resulting copolymer decreased to 87.8 °C, probably due to decrease in crystallinity of copolymer with the incorporation of comonomer (entry 4).

The structure of the complexes also obviously influenced the copolymerization. **4d** gave low activity even under 5 atm

TABLE 5 Copolymerization of Ethylene and 1-Octene Under High Temperature^a

Entry	Cat.	Octene (mmol)	Yield (g)	Activity ^b	Incorp. ratio ^c	M_w^d (10^4 g/mol)	M_w/M_n^d	T_m (°C) ^e
1	4a	10	1.51	1.21	1.1	7.9	2.2	116.0
2	4a	20	1.90	1.52	1.3	5.4	2.3	111.9
3	4a	40	1.24	0.99	3.4	7.4	2.3	101.1
4	4a	80	0.93	0.74	5.9	5.1	2.2	87.7
5	4b	20	0.35	0.28	0.8	7.7	2.6	117.6
6 ^f	4d	20	0.30	0.05	2.0	3.9	3.9	117.8
7	4e	20	0.28	0.22	1.5	5.7	2.3	118.2
8	4f	20	1.52	1.22	1.0	7.0	2.4	117.2

^a Toluene, 50 mL; cat. 5 μ mol; Al/Ti = 500; 1 atm ethylene; 15 min; 110 °C.^b 10^6 g/mol·h·atm.^c Determined by ¹³C NMR.^d Determined by GPC.^e Determined by DSC.^f Ethylene pressure: 5 atm.

ethylene atmosphere, and 2.0 mol % incorporation ratio was obtained. Either **4b** or **4e** gave lower activities than that of **4a**. Similar to the polymerization of ethylene, the introduction of ^tBu at C7 position has little impact on the activity as well as incorporation (entry 8).

1-Octadecene is also a suitable comonomer at 110 °C. For example, both **4a** and **4f** could copolymerize ethylene and 1-octadecene in an activity above 1.0×10^6 g/mol(Ti)·h·atm with moderate incorporation ratio (entries 1 and 5). Although similar incorporation ratios of the resulting copolymers could be obtained when complexes **4b–e** were applied as catalysts for the copolymerization, low to moderate copolymerization activities were observed in the cases (entries 2–4).

CONCLUSIONS

A series of titanium complexes bearing phenoxy-amine were prepared and characterized. In the presence of MMAO, these titanium complexes displayed unusual thermal stability and single-site ethylene (co)polymerization behavior under the temperatures of up to 150 °C. The highest activity of ethylene polymerization was achieved as 5.40×10^6 g/mol(Ti)·h·atm at 110 °C. The characters are

presumably deduced from both the stability of the ligands and their strong coordination to titanium. α -Olefins, such as 1-octene and 1-octadecene, were proved suitable comonomer to be incorporated into polyethylene in the presence of the new complexes at 110 °C. The highest activity of the ethylene/1-octadecene copolymerization was 1.89×10^6 g/mol(Ti)·h·atm at 110 °C. Increasing the molar ratio of comonomer led to improved incorporation ratio; and correspondingly, T_m of the produced polymer could be reduced to 87.7 °C. The pendant group X has great influence on tailoring the structure of polymers and PPh₂ tested to be the best choice. Decreasing the steric hindrance deteriorated the activity. These results and the easy modification feature of the complexes are helpful in developing efficient catalysts used in solution polymerization.

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TABLE 6 Copolymerization of Ethylene and 1-Octadecene Under High Temperature^a

Entry	Cat.	Yield (g)	Activity ^b	Incorp. ratio ^c	M_w^d (10^4 g/mol)	M_w/M_n^d	T_m (°C) ^e
1	4a	2.36	1.89	1.2	8.3	2.6	116.4
2	4b	0.43	0.34	0.7	9.7	2.5	117.4
3 ^f	4d	0.37	0.06	1.3	8.5	2.9	118.8
4	4e	0.31	0.25	1.1	13.5	2.3	109.3
5	4f	1.65	1.32	1.7	7.5	2.7	115.8

^a Toluene, 50 mL; cat., 5 μ mol; comonomer, 20 mmol; 1 atm ethylene pressure, 15 min, 110 °C.^b 10^6 g/mol·h·atm.^c Determined by ¹³C NMR.^d Determined by GPC.^e Determined by DSC.^f Ethylene pressure: 5 atm.

REFERENCES AND NOTES

- 1 (a) B. T. Huang, W. Chen, *Metalocene Catalysts and Their Olefin Polymers*; Chemical Engineering Press: Beijing, **2000**; (b) O. B. de Oliveira, S. T. Brandao, A. J. D. de Freitas, da E. P. Silva, S. M. P. Meneghetti, M. R. Meneghetti, *Polym. Int.* **2008**, *57*, 1012–1016; (c) C. S. Popeney, A. L. Rheingold, Z. Guan, *Organometallics* **2009**, *28*, 4452–4463.
- 2 (a) A. Yano, M. Sone, S. Yamada, S. Hasegawa, M. Sato, A. Akimoto, *J. Mol. Catal. A: Chem.* **2000**, *156*, 133–141; (b) S. Hasegawa, M. Sone, M. Tanabiki, M. Sato, A. Yano, *J. Polym. Sci. Part A: Polym. Chem.* **2000**, *38*, 4641–4648; (c) A. S. Ionkin, W. J. Marshall, D. J. Adelman, B. B. Fones, B. M. Fish, M. F. Schifffauer, *Organometallics* **2006**, *25*, 2978–2992; (d) K.-S. Son, F. Jöge, R. M. Waymouth, *Macromolecules* **2008**, *41*, 9663–9668; (e) T.-J. Kim, S.-K. Kim, J. S. Hahn, M.-A. Ok, J. H. Song, D.-H. Shin, J. Ko, M. Cheong, J. Kim, H. Won, M. Mitoraj, M. Srebro, A. Michalak, S. O. Kang, *Macromolecules* **2009**, *42*, 6932–6943.
- 3 (a) G. J. P. Britovsek, V. C. Gibson, D. F. Wass, *Angew. Chem. Int. Ed. Engl.* **1999**, *38*, 428–447; (b) S. D. Ittel, L. K. Johnson, M. Brookhart, *Chem. Rev.* **2000**, *100*, 1169–1203; (c) S. Mecking, *Angew. Chem. Int. Ed. Engl.* **2001**, *40*, 534–540; (d) V. C. Gibson, S. K. Spitzmesser, *Chem. Rev.* **2003**, *103*, 283–315; (e) H. Makio, T. Fujita, *Acc. Chem. Res.* **2009**, *42*, 1532–1544; (f) B. M. Boardman, G. C. Bazan, *Acc. Chem. Res.* **2009**, *42*, 1597–1606; (g) A. Nakamura, S. Ito, K. Nozaki, *Chem. Rev.* **2009**, *109*, 5215–5244; (h) S. Budagumpi, K.-H. Kim, I. Kim, *Coord. Chem. Rev.* **2011**, *255*, 2785–2809; (i) J.-Q. Wu, Y.-S. Li, *Coord. Chem. Rev.* **2011**, *255*, 2303–2314; (j) N. Nakata, T. Toda, A. Ishii, *Polym. Chem.* **2011**, *2*, 1597–1610; (k) C. Redshaw, Y. Tang, *Chem. Soc. Rev.* **2012**, *41*, 4484–4510.
- 4 Selected examples, see: (a) L. K. Johnson, C. M. Killian, M. Brookhart, *J. Am. Chem. Soc.* **1995**, *117*, 6414–6415; (b) D. H. Camacho, E. V. Salo, J. W. Ziller, and Z. Guan, *Angew. Chem. Int. Ed. Engl.* **2004**, *43*, 1821–1825; (c) G. Noël, J. C. Röder, S. Dechert, H. Pritzkow, L. Bolk, S. Mecking, F. Meyer, *Adv. Synth. Catal.* **2006**, *348*, 887–897; (d) C. S. Popeney, C. M. Levins, Z. Guan, *Organometallics* **2011**, *30*, 2432–2452.
- 5 Selected examples, see: (a) T. R. Younkin, E. F. Connor, J. I. Henderson, S. K. Friedrich, R. H. Grubbs, D. A. Bansleben, *Science* **2000**, *287*, 460–462; (b) J. Saito, M. Mitani, J. Mohri, Y. Yoshida, S. Mastui, S. Ishii, S. Kojoh, N. Kashiwa, T. Fujita, *Angew. Chem. Int. Ed. Engl.* **2001**, *40*, 2918–2920; (c) J. Tian, P. D. Hustad, G. W. Coate, *J. Am. Chem. Soc.* **2001**, *123*, 5134–5135; (d) S. Matsui, M. Mitani, J. Saito, Y. Tohi, H. Makio, N. Matsukawa, Y. Takagi, K. Tsuru, M. Nitabaru, T. Nakano, H. Tanaka, N. Kashiwa, T. Fujita, *J. Am. Chem. Soc.* **2001**, *123*, 6847–6856; (e) M. Mitani, J. Mohri, Y. Yoshida, J. Saito, S. Ishii, K. Tsuru, S. Matsui, R. Furuyama, T. Nakano, H. Tanaka, S. Kojoh, T. Mastui, N. Kashiwa, T. Fujita, *J. Am. Chem. Soc.* **2002**, *124*, 3327–3336; (f) M. Mitani, R. Furuyama, J. Mohri, J. Saito, S. Ishii, H. Terao, N. Kashiwa, T. Fujita, *J. Am. Chem. Soc.* **2002**, *124*, 7888–7889; (g) J.-Q. Wu, L. Pan, S.-R. Liu, L.-P. He, Y.-S. Li, *J. Polym. Sci. Part A: Polym. Chem.* **2009**, *47*, 3573–3582; (h) Y. Patil, A. M. Raspolli Galletti, G. Silly, B. Ameduri, *J. Fluorine Chem.* **2011**, *132*, 1207–1212; (i) N. A. Kolhatkar, A. M. Monfette, S. Lin, M. J. Miri, *J. Polym. Sci. Part A: Polym. Chem.* **2012**, *50*, 986–995.
- 6 Selected examples, see: (a) B. L. Small, M. Brookhart, A. M. A. Bennett, *J. Am. Chem. Soc.* **1998**, *120*, 4049–4050; (b) G. J. P. Britovsek, V. C. Gibson, B. S. Kimberley, P. J. Maddox, S. J. McTavish, G. A. Solan, A. J. P. White, D. Williams, *J. Chem. Commun.* **1998**, 849–850; (c) C. Görl, T. Englmann, H. G. Alt, *Appl. Catal. A Gen.* **2011**, *403*, 25–35.
- 7 Selected examples, see: (a) Q. Wu, Y. Lu, *J. Polym. Sci. Part A: Polym. Chem.* **2002**, *40*, 1421–1425; (b) W. Wang, M. Fujiki, K. Nomura, *J. Am. Chem. Soc.* **2005**, *127*, 4582–4583; (c) H. Zhang, K. Nomura, *J. Am. Chem. Soc.* **2005**, *127*, 9364–9365; (d) K. Nomura, K. Itagaki, M. Fujiki, *Macromolecules* **2005**, *38*, 2053–2055; (e) K. Nomura, W. Wang, M. Fujiki, J. Liu, *Chem. Commun.* **2006**, 2659–2661; (f) M. Srebro, Ł. Piekos, T.-J. Kim, M. Cheong, M.-A. Ok, S. O. Kang, A. Michalak, *Organometallics* **2010**, *29*, 5341–5352; (g) K. Nomura, N. Suzuki, D.-H. Kim, H. J. Kim, *Macromol. React. Eng.* **2012**, *6*, 351–356.
- 8 Selected examples, see: (a) S. Fokken, T. P. Spaniol, J. Okuda, F. G. Sernetz, R. Mülhaupt, *Organometallics* **1997**, *16*, 4240–4242; (b) F. G. Sernetz, R. Mülhaupt, S. Fokken, J. Okuda, *Macromolecules* **1997**, *30*, 1562–1569; (c) E. Y. Tshuva, I. Goldberg, M. Kol, H. Weitman, Z. Goldschmidt, *Chem. Commun.* **2000**, 379–380; (d) E. Y. Tshuva, I. Goldberg, M. Kol, *J. Am. Chem. Soc.* **2000**, *122*, 10706–10707; (e) E. Y. Tshuva, I. Goldberg, M. Kol, Z. Goldschmidt, *Organometallics* **2001**, *20*, 3017–3028; (f) E. Y. Tshuva, I. Goldberg, M. Kol, Z. Goldschmidt, *Chem. Commun.* **2001**, 2120–2121; (g) E. Y. Tshuva, S. Groysman, I. Goldberg, M. Kol, Z. Goldschmidt, *Organometallics* **2002**, *21*, 662–670.
- 9 Selected examples, see: (a) X.-F. Li, Y.-G. Li, Y.-S. Li, Y.-X. Chen, N.-H. Hu, *Organometallics* **2005**, *24*, 2502–2510; (b) L.-M. Tang, Y.-Q. Duan, L. Pan, Y.-S. Li, *J. Polym. Sci. Part A: Polym. Chem.* **2005**, *43*, 1681–1689; (c) L. Pan, W.-P. Ye, J.-Y. Liu, M. Hong, Y.-S. Li, *Macromolecules* **2008**, *41*, 2981–2983; (d) Y.-Y. Long, Y.-X. Wang, J.-Y. Liu, Y.-S. Li, *J. Polym. Sci. Part A: Polym. Chem.* **2012**, *50*, 638–648.
- 10 (a) X. Li, Z. Hou, *Macromolecules* **2010**, *43*, 8904–8909; (b) K. A. Frazier, R. D. Froese, Y. He, J. Klosin, C. N. Theriault, P. C. Vosejka, Z. Zhou, *Organometallics* **2011**, *30*, 3318–3329; (c) F. Marchetti, G. Pampaloni, Y. Patil, A. M. Raspolli Galletti, F. Renili, S. Zacchini, *Organometallics* **2011**, *30*, 1682–1688; (d) F. Guo, M. Nishiura, H. Koshino, Z. Hou, *Macromolecules* **2011**, *44*, 6335–6344; (e) L. Pan, K. Zhang, M. Nishiura, Z. Hou, *Angew. Chem. Int. Ed. Engl.* **2011**, *50*, 12012–12015; (f) A.-Q. Jia, J.-Q. Wang, P. Hu, G.-X. Jin, *Dalton Trans.* **2011**, *40*, 7730–7736; (g) P. Hu, J.-Q. Wang, F. Wang, G.-X. Jin, *Chem. Eur. J.* **2011**, *17*, 8576–8583; (h) P. Hu, Y.-L. Qiao, J.-Q. Wang, G.-X. Jin, *Organometallics* **2012**, *31*, 3241–3247.
- 11 (a) R. Eaves, S. Parkin, F. T. Ladipo, *Inorg. Chem.* **2007**, *46*, 9495–9502; (b) S. Zhang, W.-H. Sun, T. Xiao, X. Hao, *Organometallics* **2010**, *29*, 1168–1173; (c) P. P. Fontaine, J. Klosin, N. T. McDougal, *Organometallics* **2012**, *31*, 6244–6251.
- 12 (a) W.-Q. Hu, X.-L. Sun, C. Wang, Y. Tang, L.-P. Shi, W. Xia, J. Sun, H.-L. Dai, X.-X. Li, X.-L. Yao, X.-R. Wang, *Organometallics* **2004**, *23*, 1684–1688; (b) C. Wang, X.-L. Sun, Y.-H. Guo, Y. Gao, B. Liu, Z. Ma, W. Xia, L.-P. Shi, Y. Tang, *Macromol. Rapid Commun.* **2005**, *26*, 1609–1614; (c) C. Wang, Z. Ma, X.-L. Sun, Y. Gao, Y.-H. Guo, Y. Tang, L.-P. Shi, *Organometallics* **2006**, *25*, 3259–3266; (d) M.-L. Gao, C. Wang, X.-L. Sun, C.-T. Qian, Z. Ma, S.-Z. Bu, Y. Tang, Z. Xie, *Macromol. Rapid Commun.* **2007**, *28*, 1511–1516; (e) X.-H. Yang, C.-R. Liu, C. Wang, X.-L. Sun, Y.-H. Guo, X.-K. Wang, Z. Wang, Z. Xie, Y. Tang, *Angew. Chem. Int. Ed. Engl.* **2009**, *48*, 8009–8102.
- 13 S. Matsui, M. Mitani, J. Saito, Y. Tohi, H. Makio, N. Matsukawa, Y. Takagi, K. Tsuru, M. Nitabaru, T. Nakano, H. Tanaka, N. Kashiwa, T. Fujita, *J. Am. Chem. Soc.* **2001**, *123*, 6847–6856.
- 14 B. Cordero, V. Gómez, A. E. Platero-Prats, M. Revés, J. Echeverría, E. Cremades, F. Barragán, S. Alvarez, *Dalton Trans.* **2008**, 2832–2838.
- 15 (a) J. C. W. Chien, T. Nozaki, *J. Polym. Sci. Part A: Polym. Chem.* **1993**, *31*, 227–237; (b) P. Kumkaew, L. Wu, P. Prasertthadam, S. E. Wanke, *Polymer* **2003**, *44*, 4791–4803; (c) K. Heiland, W. Kaminsky, *Makromol. Chem.* **1992**, *193*, 601–610.