

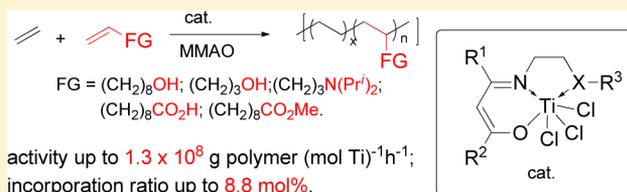
Copolymerization of Ethylene with Functionalized Olefins by [ONX] Titanium Complexes

Zhou Chen, Jun-Fang Li, Wen-Jie Tao, Xiu-Li Sun,* Xiao-Hong Yang, and Yong Tang*

State Key Laboratory of Organometallic Chemistry, Shanghai Institute of Organic Chemistry, CAS, Shanghai, P. R. China

Supporting Information

ABSTRACT: A series of titanium complexes bearing [ONX] tridentate ligands have been synthesized and characterized. The complexes containing sulfur or phosphine donors showed high activity in the copolymerization of ethylene with 9-decen-1-ol (up to 1.3×10^8 g polymer (mol Ti) $^{-1}$ h $^{-1}$) with an incorporation ratio of up to 8.8 mol %. Moreover, they have also shown excellent capability for copolymerization of ethylene with AlBu $_3$ (or *tert*-butylchlorodimethylsilane) pretreated 4-penten-1-ol, ω -alkenoic acid, and ω -alkenoic ester, as well as unprotected tertiary amine.



INTRODUCTION

Functionalized polyolefins possess, to a large extent, the original properties of the polyolefins as well as some unique properties such as permeability, affinity for dyes, and compatibility with more polar polymers. The synthesis of polyolefins bearing functional groups along the chain backbone has been attracting interest in past decades.^{1,2} The copolymerization of ethylene with polar alkenes provides an easy and low-cost access to functionalized polyethylenes. Of the methods documented, two strategies, including the use of late transition metal catalysts and early transition metal catalysts by masking the functional group of polar alkenes with Lewis acids such as triethylaluminum, have been reported. Although many catalysts have been developed, only a few catalysts exhibit high activity to afford polymers with good contents of polar comonomers.^{1,3–7} For instance, α -diimine palladium complexes could copolymerize ethylene with polar monomers, such as acrylates, methyl vinyl ketones, and silyl vinyl ethers to yield highly branched copolymers.³ Nickel complexes bearing salicylaldiminato ligands exhibited good tolerance to functional group and promoted the copolymerization of ethylene with 5-norbornene-1-ol with comonomer incorporation up to 22 wt %.⁴ Neutral palladium phosphine–sulfonate complexes⁵ prove to be remarkably efficient for the copolymerization of olefins with polar acrylate and its derivatives, producing highly linear copolymers with in-chain polar monomer incorporation. Although early transition metal catalysts are known for their intolerance to polar group due to their high oxophilicity,⁶ by protecting the functional group with trialkylaluminum or in the presence of a large amount of excess cocatalysts, zirconocene/methylaluminoxane (MAO) catalysts offer a good way to copolymerize ethylene and propylene with monomers containing functional groups.⁷ For example, Aaltonen^{7b} et al. reported ethylene and propylene were copolymerized with 10-undecen-1-ol using stereorigid zirconocene catalysts with an activity of up to 6.7×10^6 g polymer (mol Zr) $^{-1}$ h $^{-1}$ and 3.1 wt % (0.5

mol %) incorporation ratio at an Al/Zr molar ratio of 12600. Compared with the late-transition metal and zirconium catalysts, the titanium catalysts proved to be poor for the copolymerization of ethylene and polar alkenes. Marques^{7f} et al. reported [Cp*Si(Me) $_2$ N-*t*-Bu]TiCl $_2$ (CGC) could copolymerize ethylene with 5-hexen-1-ol with an activity of up to 5.1×10^5 g polymer (mol Ti) $^{-1}$ h $^{-1}$ and exhibited a high sensitivity toward the polar group. Recently, Fujita et al. reported that titanium complexes bearing bis(phenoxyimine) ligands were active catalysts for the copolymerization of ethylene with acetyl-protected hex-5-en-1-ol with an activity of up to 5.15×10^5 g polymer (mol Ti) $^{-1}$ h $^{-1}$ and 0.74 mol % incorporation ratio. Even in the presence of an excess amount of hex-5-enyl acetate to DMAO, these complexes can produce copolymers with an activity of 1.5×10^4 g polymer (mol Ti) $^{-1}$ h $^{-1}$ and 3.20 mol % comonomer content.⁸ Li and co-workers have documented that bis(β -enaminoketonato)titanium catalysts copolymerized ethylene with trialkylaluminum protected 5-norbornene-2-methanol in an activity of up to 2.5×10^6 g polymer (mol Ti) $^{-1}$ h $^{-1}$ and 5.3 mol % incorporation ratio.⁹ Very recently, we have reported titanium complexes bearing tridentate ligands were robust and highly active in the polymerization of ethylene,¹⁰ and copolymerization of ethylene with α -olefin, ω -alkenol, or ω -alkenoic acid.^{10,11} To further understand the structure–reactivity relationship of the catalysts, we synthesized and characterized a series of titanium complexes bearing [ONX] tridentate ligands. Investigation on the behaviors of these complexes in copolymerization of ethylene with ω -alkenol, ω -alkenoic acid, ω -alkenoic ester, and ω -alkenyltertiary amine unveiled the highest activity of 1.3×10^8 g copolymer (mol Ti) $^{-1}$ h $^{-1}$ could be achieved. In this paper, we wish to report the results in detail.

Received: February 6, 2013

Revised: March 15, 2013

Published: March 27, 2013

Table 1. Synthesis of Ligands and Complexes

	X	R ¹	R ²	R ³	yield (%) ^a
3a, 4a	S	C ₆ H ₅	C ₆ H ₅	CH ₃	90
3b, 4b	O	C ₆ H ₅	C ₆ H ₅	CH ₃	76
3c, 4c	P	C ₆ H ₅	C ₆ H ₅	(Ph) ₂	76
3d, 4d	N	C ₆ H ₅	C ₆ H ₅	(CH ₂) ₄	84
3e, 4e	S	C ₆ H ₅	C ₆ H ₅	<i>n</i> -Pr	98
3f, 4f	S	C ₆ H ₅	C ₆ H ₅	<i>i</i> -Pr	60
3g, 4g	S	C ₆ H ₅	C ₆ H ₅	C ₆ H ₅	77
3h, 4h	S	C ₆ H ₅	C ₆ H ₅	Cyclohexyl	82
3i, 4i	S	<i>p</i> -CH ₃ C ₆ H ₄	<i>p</i> -CH ₃ C ₆ H ₄	<i>n</i> -Pr	92
3j, 4j	S	<i>p</i> -CF ₃ C ₆ H ₄	C ₆ H ₅	<i>n</i> -Pr	92
3k, 4k	S	C ₆ H ₅	<i>p</i> -CF ₃ C ₆ H ₄	<i>n</i> -Pr	91
3l, 4l	S	CF ₃	C ₆ H ₅	CH ₃	86
3m, 4m	S	CH ₃	C ₆ H ₅	<i>n</i> -Pr	86

^aIsolated yield of 4.

EXPERIMENTAL SECTION

General Methods. All air or moisture sensitive manipulations were carried out under nitrogen atmosphere using Schlenk techniques or in a glovebox. ¹H NMR, ¹³C NMR spectra were recorded on Varian Mercury 300 spectrometer or Varian 400 NMR spectrometer. Mass spectra were carried out with a HPS989A spectrometer. Elemental analysis was performed by the Analytical Laboratory, Shanghai Institute of Organic Chemistry. *M_n*, *M_w*, and *M_w*/*M_n* values of polymers were determined with Agilent Technologies PL-GPC 220 High Temperature Chromatography at 150 °C (polystyrene calibration, 1,2,4-trichlorobenzene as a solvent at a flow rate of 1.0 mL·min⁻¹). ¹H and ¹³C NMR data of polymers were obtained using *o*-dichlorobenzene-*d*₄ as a solvent at 110 °C. X-ray crystallographic data was collected using a Bruker AXSD8 X-ray diffractometer. Toluene, hexane, dichloromethane (DCM) and tetrahydrofuran (THF) were purified by MB SPS-800 system. Modified methylaluminoxane (MMAO-3A) was purchased from Akzo Chemical as a 1.88 M heptane solution. The catalyst, *rac*-ethenebis(indenyl)zirconium dichloride (*rac*-Et[Ind]₂ZrCl₂ (**4n**)) was purchased as powder from Alfa-Aesar. Polymerization-grade ethylene was purified before use. Complexes **4a**, **4e**, **4f**, **4g**, **4i**, **4j** and **4m** were synthesized as described previously.¹¹ The new complexes were prepared as follows:

General Procedure for the Synthesis of Titanium Complexes 4. [3-((2-Methoxyethyl)imino)-1,3-diphenylprop-1-en-1-olate]TiCl₃ (**4b**). To a suspension of potassium hydride (KH) (0.2 g, 5.3 mmol) in dry THF (30 mL) was added a solution of **3b** (1.0 g, 3.6 mmol) in THF (10 mL) at -78 °C. The resulting suspension was warmed to room temperature and stirred for 3 h. The solvent was removed under reduced pressure and the residue was dissolved in dry DCM (20 mL). It was then added dropwise into a solution of TiCl₄ (1.0 g, 5.3 mmol) in DCM (30 mL) at -78 °C. The solution was allowed to warm to room temperature and stirred for 18 h. The solid was filtered off and washed with DCM (10 mL). The solvent was removed under reduced pressure and the residue was dissolved in a mixed solvent of dry toluene (20 mL) and THF (10 mL), and then kept at -30 °C overnight. The resulting reddish crystals were collected and dried under reduced pressure to give complex **4b**: 1.2 g (76%). ¹H NMR (300 MHz, CDCl₃): δ 7.86–7.83 (m, 2H, Ar-H), 7.54–7.31 (m, 8H, Ar-H), 6.42 (s, 1H, =CH), 4.40 (s, 3H, OCH₃), 4.14 (t, 2H, J = 5.4 Hz, OCH₂), 3.93 (t, 2H, J = 5.4 Hz, NCH₂). ¹³C NMR (100 MHz, CDCl₃): δ 170.6, 170.1, 136.3, 132.2, 131.7, 130.3, 129.3, 129.0, 127.2, 126.1, 109.5, 76.0, 68.1, 53.7. Anal. Calcd for C₁₈H₁₈Cl₃NO₂Ti (432.99): C, 49.75; H, 4.17; N, 3.22. Found: C, 49.98; H, 4.44; N, 2.87.

[3-((2-(Diphenylphosphino)ethyl)imino)-1,3-diphenylprop-1-en-1-olate]TiCl₃ (**4c**). A procedure similar to that described for **4a** was followed to yield **4c**: 0.7 g (76%). ¹H NMR (300 MHz, CDCl₃): δ 7.88–7.81 (m, 6H, Ar-H), 7.52–7.29 (m, 14H, Ar-H), 6.35 (s, 1H, =CH), 4.19–4.07 (m, 2H, NCH₂), 2.75–2.68 (m, 2H, PCH₂). ¹³C NMR (75 MHz, CDCl₃): δ 170.6, 168.9, 138.3, 132.8, 132.7, 1332.5, 132.3, 132.1, 131.9, 131.6, 130.6, 129.5, 129.4, 129.2, 128.8, 128.7, 128.2, 127.5, 127.2, 125.8, 125.6, 109.0, 54.9 (d, J = 9.0 Hz), 24.8 (d, J = 22.1 Hz). ³¹P NMR (121.4 MHz, CDCl₃): δ 17.16. Anal. Calcd for C₂₉H₂₅Cl₃NOPTi (587.02): C, 59.16; H, 4.28; N, 2.38. Found: C, 58.97; H, 4.27; N, 2.30.

[1,3-Diphenyl-3-((2-(pyrrolidin-1-yl)ethyl)imino)prop-1-en-1-olate]TiCl₃ (**4d**). A procedure similar to that described for **4b** was followed to yield **4d**: 1.2 g (84%). ¹H NMR (300 MHz, CDCl₃): δ 7.81 (d, 2H, J = 7.5 Hz, Ar-H), 7.51–7.33 (m, 8H, Ar-H), 6.32 (s, 1H, =CH), 4.23–4.17 (m, 2H, N(CH₂CH₂)₂), 3.80 (t, 2H, J = 5.1 Hz, NCH₂), 3.58–3.52 (m, 2H, N(CH₂CH₂)₂), 2.97 (t, 2H, J = 5.1 Hz, NCH₂), 2.14–2.10 (m, 2H, N(CH₂CH₂)₂), 1.93–1.90 (m, 2H, N(CH₂CH₂)₂). ¹³C NMR (75 MHz, CDCl₃): δ 170.2, 169.6, 136.8, 132.5, 131.9, 129.9, 129.2, 128.8, 127.1, 126.1, 108.9, 63.0, 57.1, 54.9, 22.1. Anal. Calcd for C₂₁H₂₃Cl₃N₂O₂Ti (472.04): C, 53.25; H, 4.89; N, 5.91. Found: C, 53.30; H, 5.14; N, 5.74.

[3-((2-(Cyclohexylthio)ethyl)imino)-1,3-diphenylprop-1-en-1-olate]TiCl₃ (**4h**). A procedure similar to that described for **4b** was followed to yield **4h** (1.1 g, 82%). ¹H NMR (300 MHz, CDCl₃): δ 7.83 (d, 2H, J = 6.6 Hz, Ar-H), 7.52–7.29 (m, 8H, Ar-H), 6.40 (s, 1H, =CH), 4.04 (brs, 2H, NCH₂), 3.55–3.48 (m, 1H, SCH), 3.10 (brs, 1H, SCH₂), 2.92 (brs, 1H, SCH₂), 2.77 (brs, 1H, Cy-H), 2.02–1.37 (m, 9 H, Cy-H). ¹³C NMR (75 MHz, CDCl₃): δ 170.6, 169.6, 137.6, 132.1, 132.0, 129.8, 129.3, 128.9, 127.2, 125.8, 109.5, 79.0, 57.5, 49.9, 33.4, 25.6(2), 25.5(6). Anal. Calcd for C₂₃H₂₆Cl₃NOSTi (517.03): C, 53.25; H, 5.05; N, 2.70. Found: C, 52.89; H, 4.96; N, 2.53.

[3-Phenyl-3-((2-(propylthio)ethyl)imino)-1-(4-(trifluoromethyl)phenyl)prop-1-en-1-olate]TiCl₃ (**4k**). To a stirred solution of TiCl₄ (1.5 g, 8.0 mmol) in dry toluene (50 mL) at -78 °C was added dropwise a solution of **3k** (2.0 g, 6.1 mmol) in dry toluene (10 mL) over 20 min. The solution was allowed to warm to room temperature and stirred for 16 h. The solvent was removed under reduced pressure and the residue was dissolved in dry toluene (100 mL). The solution was concentrated under reduced pressure to about 20 mL and kept at -30 °C overnight. Dark red crystals were collected and dried under reduced pressure to yield complex **4k** (0.61 g, 91%). ¹H NMR (300 MHz, CDCl₃): δ 7.93 (d, 2H, J = 8.1 Hz, Ar-H), 7.67 (d, 2H, J = 8.4 Hz, Ar-H), 7.54–7.52 (m, 3H, Ar-H), 7.32–7.30 (m, 2H, Ar-H),

6.43 (s, 1H, =CH), 4.20–4.03 (m, 2H, NCH₂), 3.49–3.40 (m, 1H, SCH₂), 3.26–3.19 (m, 1H, SCH₂), 3.01–2.92 (m, 1H, SCH₂), 2.77–2.73 (m, 1H, SCH₂), 2.00–1.87 (m, 2H, CH₂CH₂CH₃), 1.14 (t, 3H, J = 7.2 Hz, CH₂CH₂CH₃). ¹³C NMR (100 MHz, CDCl₃): δ 170.6, 167.6, 137.3, 135.6, 133.1 (q, J = 32.7 Hz), 130.0, 129.5, 127.4, 125.9 (q, J = 3.3 Hz), 123.6 (q, J = 270.6 Hz), 57.4, 41.7, 36.4, 21.8, 13.5. ¹⁹F NMR (376 MHz, CDCl₃): δ –63.03. Anal. Calcd for C₂₁H₂₁Cl₃F₃NOSTi (544.98): C, 46.14; H, 3.87; N, 2.56. Found: C, 45.92; H, 4.22; N, 2.42.

[4,4,4-Trifluoro-3-((2-(methylthio)ethyl)imino)-1-phenylbut-1-en-1-olate]TiCl₃ (**4h**). A procedure similar to that described for **4b** was followed to yield **4h** (1.3 g, 86%). ¹H NMR (300 MHz, CDCl₃): δ 7.91 (d, 2H, J = 7.8 Hz, Ar–H), 7.61–7.47 (m, 3H, Ar–H), 6.76 (s, 1H, =CH), 4.44 (brs, 2H, NCH₂), 3.45–3.36 (m, 1H, SCH₂), 2.93–2.86 (m, 1H, SCH₂), 2.83 (s, 3H, SCH₃). ¹³C NMR (75 MHz, CDCl₃): δ 175.1, 156.4 (q, J = 28.9 Hz), 133.2, 131.8, 129.2, 127.6, 118.7 (q, J = 285.3 Hz), 100.8 (q, J = 4.5 Hz), 55.6, 38.2, 22.8. ¹⁹F NMR (282 MHz, CDCl₃): δ –63.33. Anal. Calcd for C₁₃H₁₃Cl₃F₃NOSTi (440.92): C, 35.28; H, 2.96; N, 3.17. Found: C, 35.26; H, 3.09; N, 3.08.

General Procedure for Pretreating Comonomers with AlBu₃. To a solution of comonomer (0.1 mol) in toluene (30 mL) was added AlBu₃ (0.12 mol for ω-alkenol, 0.22 mol for ω-alkenoic acid and ester) at –20 °C. The resulting mixture was allowed to warm to room temperature and the solution was stirred for 24 h. Toluene was added until the total volume of the solution was 100 mL for further use.

General Procedure of Copolymerization of Ethylene and Polar Monomers. A desired amount of toluene was transferred into a flask and saturated with ethylene at polymerization temperature. Modified-methylaluminoxane (MMAO) and comonomer were syringed into the flask in sequence, and the mixture was stirred for 10 min. The polymerization was started by adding a solution of **4** in DCM. After the desired time, the copolymerization was quenched with acidified ethanol and poured into a large amount of acidified ethanol (300 mL, 10% HCl (v/v) in ethanol). The precipitated copolymer was collected, washed with ethanol, and then dried at 60 °C under reduced pressure until a constant weight.

RESULTS AND DISCUSSION

Synthesis and Characterization of Complexes **4**.

Complexes **4a–4m** were prepared in moderate to good yields by treatment of TiCl₄ and ligands or the corresponding deprotonated ligands as shown in Table 1. They were fully characterized by ¹H, ¹³C, ¹⁹F, and ³¹P NMR spectra and elemental analysis. Crystal of **4h** suitable for X-ray structure determination was developed from toluene. As shown in Figure 1, complex **4h** features a distorted octahedral coordination of the titanium with three chlorine ligands in a *mer* position. The bond angle sum of C(5)–S–C(6) (103.5°), C(5)–S–Ti (96.8°), and C(6)–S–Ti (113.6°) is 313.9°, suggesting that the S atom in **4h** is sp³-hybridized. The dihedral angle between phenyl group (R²) on enolate moiety and the C1–C2–C3–N1–Ti1–O1 ring is 17.68°, while that between phenyl group (R¹) on imine and the C1–C2–C3–N1–Ti1–O1 ring is 71.70°.

Ethylene Copolymerization with 9-Decen-1-ol. Using 9-decen-1-ol as a model monomer, the performances of the titanium complexes **4** were explored initially. The results indicated that the polymerization conditions significantly affected the copolymerization. In addition, the performance of complexes **4a–4m** on the copolymerization showed that both the property of the coordination atom X and the substituent of the β-carbonylenamine affected their behaviors in the copolymerization.

(1). **Optimization of Copolymerization Conditions.** We first protected the hydroxyl group with 1.2 equiv of AlBu₃ and examined the copolymerization by using the titanium complex

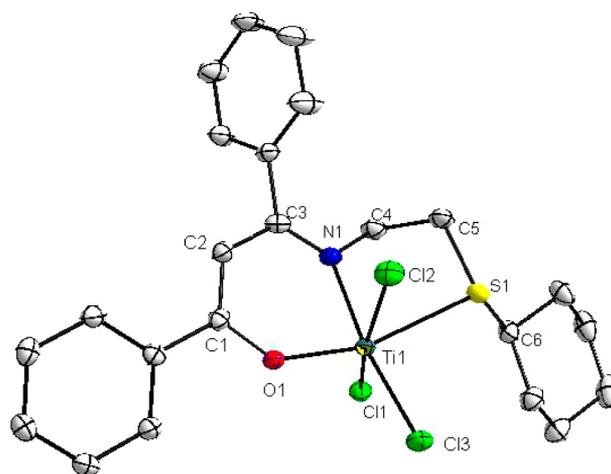


Figure 1. Molecular Structure of Complex **4h** (H atoms are omitted for clarity). Selected bond lengths(Å) and angles (deg): Ti(1)–O(1) = 1.836(1), Ti(1)–N(1) = 2.153(1), Ti(1)–Cl(3) = 2.277(1), Ti(1)–Cl(1) = 2.285(1), Ti(1)–Cl(2) = 2.327(1), Ti(1)–S(1) = 2.617(1); O(1)–Ti(1)–N(1) = 84.36(5), O(1)–Ti(1)–Cl(3) = 103.38(4), N(1)–Ti(1)–Cl(3) = 171.58(4), O(1)–Ti(1)–Cl(1) = 96.98(4), N(1)–Ti(1)–Cl(1) = 87.64(4), Cl(3)–Ti(1)–Cl(1) = 94.582(19), O(1)–Ti(1)–Cl(2) = 94.57(4), N(1)–Ti(1)–Cl(2) = 82.96(4), Cl(3)–Ti(1)–Cl(2) = 93.024(19), Cl(1)–Ti(1)–Cl(2) = 164.31(2), O(1)–Ti(1)–S(1) = 162.82(4), N(1)–Ti(1)–S(1) = 79.20(4), Cl(3)–Ti(1)–S(1) = 92.773(17), Cl(1)–Ti(1)–S(1) = 87.363(17), Cl(2)–Ti(1)–S(1) = 78.57(16).

4a/MMAO as a catalyst. Some representative results are summarized in Table 2. Significant influences of copolymeriza-

Table 2. Effects of Copolymerization Conditions.^a

entry	T (°C)	Al/Ti	W (g)	M _w ^{b,c}	PDI ^b	activity ^d	incorp ^e (mol %)
1	0	1000	0.2125	23.8	3.0	0.7	5.8
2	25	1000	0.4604	7.7	2.8	1.5	8.2
3	40	1000	0.4746	5.6	1.6	1.5	8.8
4	60	1000	0.2209	2.9	3.5	0.7	8.5
5	40	200	0.1949	13.1	3.4	0.6	5.8
6	40	500	0.4612	6.8	2.6	1.5	6.7
7	40	2000	0.3130	4.1	2.7	1.0	8.8
8 ^f	40	1000	0.9612	6.0	2.8	3.3	6.4

^aConditions: toluene (50 mL), 9-decen-1-ol (10 mmol) pretreated with AlBu₃ (12 mmol), 5 min, 3.5 μmol of catalyst. ^bDetermined by GPC. ^c10⁴ g/mol. ^d10⁶ g/mol-h. ^eDetermined by ¹H NMR. ^fDecen-1-ol (5 mmol) pretreated with AlBu₃ (6 mmol).

tion conditions on the activity of polymerization and incorporation ratio of 9-decen-1-ol were observed. Raising the temperature from 0 to 25 °C increased the activity to 1.5 × 10⁶ g polymer (mol Ti)⁻¹ h⁻¹ and the incorporation ratio of 9-decen-1-ol was improved to 8.2 mol % from 5.8 mol %. The comonomer incorporation ratio of the copolymer was increased to 8.8 mol % at 40 °C while the catalytic activity was similar to that at 25 °C (entry 2 vs 3, Table 2). The increase of insertion ratio is probably due to the reduction of ethylene concentration in solvent at relatively high temperature. Further elevating the temperature to 60 °C resulted in a decrease of activity and the incorporation ratio was no longer increased. GPC studies of the copolymer 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 23.8 × 10⁴ g/mol at 0

Table 3. Effects of the Side Arm^a

entry	side arm (catalyst)	W (g)	$M_w^{b,c}$	PDI ^b	activity ^d	incorp ^e (mol %)
1	SCH ₃ (4a)	0.4746	5.6	1.6	1.5	8.8
2	OCH ₃ (4b)	0.0828	17.7	3.2	0.3	6.2
3	PPh ₂ (4c)	0.6430	2.9	1.5	2.1	4.1
4	N(CH ₂) ₄ (4d)	—	—	—	—	—

^aConditions: toluene (50 mL), 9-decen-1-ol (10 mmol) pretreated with AlBu₃ (12 mmol), 5 min, 3.5 μmol of catalyst, 40 °C. ^bDetermined by GPC. ^c10⁴ g/mol. ^d10⁶ g/mol·h. ^eDetermined by ¹H NMR.

Table 4. Effects of Complexes Structure on the Copolymerization^a

4a-4h

4i

4j R¹ = *p*-MeC₆H₄
4k R¹ = *p*-CF₃C₆H₄
4l R¹ = Ph
4m R¹ = Ph

entry	catalyst (μmol)	R	W (g)	$M_w^{b,c}$	PDI ^b	activity ^d	incorp ^e (mol %/wt %)
1	4a (3.5)	Me	0.9612	6.0	2.8	3.3	6.4/27.5
2	4e (3.5)	ⁿ Pr	1.2709	2.5	3.4	4.4	4.8/22.1
3	4f (3.5)	ⁱ Pr	1.2886	6.5	3.0	4.4	3.6/17.0
4	4g (3.5)	Ph	0.3980	5.6	2.9	1.4	4.1/19.2
5	4h (3.5)	Cy	1.5437	5.6	2.4	5.2	3.5/17.0
6	4i (3.5)	<i>p</i> -MeC ₆ H ₄	1.6332	1.9	2.9	5.6	4.8/23.3
7	4j (3.5)	<i>p</i> -CF ₃ C ₆ H ₄	1.5032	2.6	2.6	5.1	4.1/19.7
8	4k (3.5)	Ph	0.9604	7.0	2.5	3.3	2.7/13.2
9	4l (3.5)	—	0.5770	6.5	2.5	2.0	2.3/11.7
10	4m (3.5)	Me	0.7006	1.4	3.1	2.4	3.5/16.9
12	4n(Zr) (3.5)	—	0.2967	14.3	4.4	1.0	2.2/11.2
13 ^f	4n(Zr) (0.1)	—	0.0470	11.4	1.8	14	1.4/7.4
14 ^f	4i (0.1)	<i>p</i> -MeC ₆ H ₄	0.4245	7.8	2.3	130	3.3/16.0
15 ^g	4i (0.1)	<i>p</i> -MeC ₆ H ₄	1.1933	5.3	3.8	24	2.4/12.0
16 ^h	4i (0.1)	<i>p</i> -MeC ₆ H ₄	1.5981	5.5	3.8	16	2.2/11.1

^aConditions: toluene (50 mL), 9-decen-1-ol (5 mmol) pretreated with AlBu₃ (6 mmol), 5 min, 3.5 μmol of catalyst, 3.5 mmol of MMAO, and 40 °C. ^bDetermined by GPC. ^c10⁴ g/mol. ^d10⁶ g/mol·h. ^eDetermined by ¹H NMR. ^f2 min. ^g30 min. ^h60 min.

°C to 2.9×10^4 g/mol at 60 °C, indicating that the high polymerization temperature promoted the chain transfer reaction more than chain propagation. Decreasing the Al/Ti molar ratio from 1000 to 500, the comonomer incorporation ratio slightly decreased to 6.7 mol % and the catalytic activity was still maintained (entry 6, Table 2). Complex **4a** showed good activity (0.6×10^6 g polymer (mol Ti)⁻¹ h⁻¹) with an incorporation ratio of 5.8 mol % even when a low amount of MMAO (Al/Ti ratio = 200) was used (entry 5, Table 2). When the Al/Ti ratio arrived at 2000, the catalytic activity slightly decreased and the incorporation ratio of 9-decen-1-ol did not change (entry 7, Table 2). Reducing the initial concentration of 9-decen-1-ol resulted in the improvement of activity and decrease of the comonomer incorporation ratio (entry 3 vs 8, Table 2).

(2). *Effects of the Side Arm.* As shown in Table 3, the donor atoms in the side arm affect the catalytic behavior significantly in the copolymerization of ethylene with AlBu₃-protected 9-decen-1-ol, in terms of activity and comonomer incorporation ratio. Complex **4b**, with a pendant -OMe group, gave only moderate activity (0.3×10^6 g polymer (mol Ti)⁻¹ h⁻¹) in a good incorporation ratio (6.2 mol %) of comonomer (entry 2, Table 3). And, complex **4d**, bearing N(CH₂)₄ group, did not produce any polymers under the same polymerization conditions. While the complexes **4a** and **4c**, with a pendant group containing sulfur and phosphine donors respectively, showed much higher activity than the corresponding **4b** and **4d**

under the same conditions. These results are similar to our previous report on the copolymerization of ethylene with α -olefin.¹² Compared with **4c**, **4a** gave the polymer with high molecular weight and high incorporation ratio, probably resulting from the steric hindrance as well as the electronic properties of the pendant group.

(3). *Substituent Effects.* The substituent effects of titanium complexes **4** on the copolymerization of ethylene and AlBu₃-protected 9-decen-1-ol are summarized in Table 4. The substituent on the pendant group and aryl group influenced the copolymerization activity as well as the incorporation ratio of 9-decen-1-ol. As shown in Table 4, the activity of complex **4a** was 3.3×10^6 g polymer (mol Ti)⁻¹ h⁻¹ with a high incorporation ratio (6.7 mol %). Compared with **4a**, **4e** with a *n*-propyl thioether group gave a lower incorporation ratio of 9-decen-1-ol (4.8 mol %) and a slightly higher activity (4.4×10^6 g polymer (mol Ti)⁻¹ h⁻¹) (entry 1 vs 2). Complex **4f** with an isopropyl thioether group has a much lower incorporation ratio (3.6 mol %) and similar activity as complex **4e**, suggesting that increasing the steric hindrance on sulfur donor decreased the incorporation ratio of comonomer. Noticeably, complex **4g** with a phenyl thioether group showed lower activity (1.4×10^6 g polymer (mol Ti)⁻¹ h⁻¹) than **4a** (entry 4). Complex **4h** with a cyclohexylthioether group exhibited a slightly higher activity (5.2×10^6 g polymer (mol Ti)⁻¹ h⁻¹) than **4f** and the comonomer incorporation ratio of the polymers obtained with the two catalysts **4h** and **4f** are almost the same (entry 3 vs 5).

Table 5. Ethylene Copolymerization with Other Comonomers^a

entry	FG (mmol)	Al/Ti	W (g)	$M_w^{b,c}$	PDI ^b	activity ^d	incorp ^e /mol %
1 ^f	(CH ₂) ₉ OH (5)	1000	0.8277	4.7	4.8	2.8	1.4
2	(CH ₂) ₈ OTBS (5)	1000	0.4414	n.d. ⁱ	n.d. ⁱ	1.5	2.9
3	(CH ₂) ₈ OTBS (5)	3000	1.2251	8.9	2.6	4.2	5.6
4	(CH ₂) ₃ OTBS (5)	3000	0.2689	8.9	2.5	0.9	1.8
5	(CH ₂) ₃ NPr ₂ (5)	3000	0.8263	n.d. ⁱ	n.d. ⁱ	2.8	1.9
6 ^g	(CH ₂) ₈ COOH (5)	1000	1.6605	0.3	2.0	5.7	2.5
7 ^{g,h}	(CH ₂) ₈ COOMe (5)	1000	0.2020	2.9	2.4	0.4	1.3

^aConditions: toluene (50 mL), 5 min, 3.5 μ mol of **4a**, and 40 °C. ^bDetermined by GPC. ^c 10^4 g/mol. ^d 10^6 g/mol-h. ^eDetermined by ¹H NMR. ^fComonomer was pretreated with AlBu₃ (6 mmol). ^gComonomer was pretreated with AlBu₃ (11 mmol). ^h10 min. ⁱNot detected.

Electronic effects of substitute R¹ on enolate moiety in ligand **4** could be observed. Compared with **4e**, **4i** that bears electron-donating group at the *para*-position of the phenyl group (R¹ = 4-MeC₆H₅), displayed higher activity (5.6×10^6 g polymer (mol Ti)⁻¹ h⁻¹), while the introduction of electron-withdrawing group (R¹ = 4-CF₃C₆H₅, **4k**) led to a reduced activity (3.3×10^6 g polymer (mol Ti)⁻¹ h⁻¹) (entry 6, 8 vs 2). The electronic effects of substitutes on imine site are very weak. For example, the activity of **4j** with a 4-trifluoromethylphenyl substituent on imine was similar to that of complex **4e** (entry 2 vs 7). Replacing the 4-MeC₆H₅ group of **4j** with either Me or CF₃ (**4l** and **4m**) reduced slightly the activities. Compared with the electronic properties, the steric hindrance has more impact on the activity and monomer content. The molecular weight distribution is in the range of 2.3–3.4, similar to those of polyethylene produced by a single-site catalyst. As a control, *rac*-ethenebis(indenyl)zirconium dichloride **4n** proceeded the copolymerization with an activity of 1.0×10^6 g polymer (mol Zr)⁻¹ h⁻¹ and 2.2 mol % incorporation ratio under these conditions. Further studies showed that lowering the loading of the precatalyst **4i** increased the activity to 1.3×10^6 g polymer (mol Ti)⁻¹ h⁻¹ with an incorporation ratio of 3.3 mol % (entry 14). In comparison, the Zr-complex **4n** showed nearly one order lower activity (1.4×10^7 g polymer (mol Ti)⁻¹ h⁻¹) in combined with MMAO under these conditions (entry 13). Noticeably, high activities (1.6×10^7 g polymer (mol Ti)⁻¹ h⁻¹) could be maintained even when the polymerization time was prolonged to 60 min. (entry 16). In this case, the insertion ratio of monomer decreased slightly and the molecular weight distribution widened slightly (entry 14 vs 16).

Ethylene Copolymerization with Other Comonomers.

The copolymerization of ethylene with other polar vinyl comonomers were investigated by using **4a**/MMAO. Some representative results are summarized in Table 5. Compared with 9-decen-1-ol, 4-penten-1-ol is also a suitable comonomer giving good activity while the incorporation ratio was much lower (1.4 mol %) (entry 1). The copolymerization of ethylene and *tert*-butyldimethylsilyl (TBS)-protected 9-decen-1-ol proceeded very well. As shown in Table 5, complex **4a** afforded functionalized PE with high activity (1.5×10^6 g polymer (mol Ti)⁻¹ h⁻¹) and good incorporation ratio (2.9 mol %) even in the presence of an excess amount of the *tert*-butyl(dec-9-enoxy)dimethylsilane relative to MMAO (entry 2). However, as the Al/Ti ratio was increased to 3000, the catalytic activity and the incorporation ratio of comonomer were both improved (entry 3). The copolymerization of ethylene with TBS-protected 4-penten-1-ol also produced copolymer with good activity and good incorporation ratio (entry 4). Noticeably, even without pretreating the comonomer with ^tBu₃Al, the copolymerization of ethylene with N, N-diisopropylpent-4-en-

1-amine proceeded very well with a good activity (2.8×10^6 g polymer (mol Ti)⁻¹ h⁻¹) and good incorporation ratio (1.9 mol %) (entry 5). Moreover, comonomers containing various carbonyl groups were tested in copolymerization. The activity (5.7×10^6 g polymer (mol Ti)⁻¹ h⁻¹) of 10-undecenoic acid on the polymerization was similar to that of the corresponding alcohol with good incorporation ratio (2.5 mol %); however, the copolymerization of ethylene with methyl undec-10-enoate showed one order lower activity (0.4×10^6 g polymer (mol Ti)⁻¹ h⁻¹) and lower incorporation ratio (1.3 mol %) (entry 6 vs 7). In addition, molecular weight distribution of most copolymers ranged from 2.0 to 2.6 except that of the copolymer containing 4-penten-1-ol, which has a broad molecular weight distribution, and the reason is unclear.

CONCLUSION

In summary, a series of titanium complexes bearing [ONX] tridentate ligands has been synthesized and characterized. The complexes with a pendant group containing sulfur and phosphine donors, respectively, showed high activity in the copolymerization even at low Al/Ti ratios. The electronic properties and steric hindrance of the pendant group proved to strongly influence the copolymerization. The highest activity of the copolymerization of ethylene with 9-decen-1-ol reached 1.3×10^8 g polymer (mol Ti)⁻¹ h⁻¹ with the incorporation ratio of 3.3 mol %. In addition, they have also shown excellent capability to catalyze the copolymerization of ethylene with 4-penten-1-ol, 5-*N,N*-diisopropylamino-1-pentene, undec-10-enoic acid, and methyl undec-10-enoate. These observations will be helpful for the design of early transition metal catalyst for the copolymerization of ethylene with polar olefins.

ASSOCIATED CONTENT

Supporting Information

General experimental procedures, synthesis of the ligands **3a–3m** and complexes **4a**, **4e**, **4f**, **4g**, **4i**, **4j**, and **4m**, NMR spectra of complexes **4a–4m**, and NMR spectra of copolymers; X-ray crystallographic data of **4h**. These materials are available free of charge via the Internet at <http://pubs.acs.org>.

AUTHOR INFORMATION

Corresponding Author

*E-mail: (X.-L.S.) xlsun@sioc.ac.cn; (Y.T.) tangy@sioc.ac.cn.

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

We are grateful for the financial support from the Natural Sciences Foundation of China (No. 21121062, and 21174159),

the Major State Basic Research Development Program (Grant No. 2009CB825300) and the Chinese Academy of Sciences.

REFERENCES

(1) Selected reviews on functional olefins: (a) Boffa, L. S.; Novak, B. M. *Chem. Rev.* **2000**, *100*, 1479. (b) Coates, G. W. *Chem. Rev.* **2000**, *100*, 1223. (c) Chung, T. C. *Prog. Polym. Sci.* **2002**, *27*, 39. (d) Yanjarappa, M. J.; Sivaram, S. *Prog. Polym. Sci.* **2002**, *27*, 1347. (e) Boen, N. K.; Hillmyer, M. A. *Chem. Soc. Rev.* **2005**, *34*, 267. (f) Dong, J.-Y.; Hu, Y. *Coord. Chem. Rev.* **2006**, *250*, 47. (g) Chen, E. Y.-X. *Chem. Rev.* **2009**, *109*, 5157. (h) Nakamura, A.; Ito, S.; Nozaki, K. *Chem. Rev.* **2009**, *109*, 5215. (i) Boardman, B. M.; Bazan, G. C. *Acc. Chem. Res.* **2009**, *42*, 1597. (j) Redshaw, C.; Tang, Y. *Chem. Soc. Rev.* **2012**, *41*, 4484.

(2) (a) Kondo, Y.; Garcia-Cuadrado, D.; Hartwig, J. H.; Boen, N. K.; Wagner, N. L.; Hillmyer, M. A. *J. Am. Chem. Soc.* **2002**, *124*, 1164. (b) Bae, C.; Hartwig, J. F.; Harris, N. K.; Swiek, K. A.; Long, R. O.; Anderson, K. S.; Hillmyer, M. A. *J. Am. Chem. Soc.* **2005**, *127*, 767. (c) Bae, C.; Hartwig, J. F.; Chung, H.; Harris, N. K.; Swiek, K. A.; Hillmyer, M. A. *Angew. Chem., Int. Ed.* **2005**, *44*, 6410.

(3) (a) Johnson, L. K.; Mecking, S.; Brookhart, M. *J. Am. Chem. Soc.* **1996**, *118*, 267. (c) Mecking, S.; Johnson, L. K.; Wang, L.; Brookhart, M. *J. Am. Chem. Soc.* **1998**, *120*, 888. (c) Chen, G.; Ma, X. S.; Guan, Z. *J. Am. Chem. Soc.* **2003**, *125*, 6697. (d) Camacho, D. H.; Salo, E. V.; Ziller, J. W.; Guan, Z. *Angew. Chem., Int. Ed.* **2004**, *43*, 1821. (f) Luo, S.; Jordan, R. F. *J. Am. Chem. Soc.* **2006**, *128*, 12072.

(4) (a) Wang, C. M.; Friedrich, S.; Younkin, T. R.; Li, R. T.; Grubbs, R. H.; Bansleben, D. A.; Day, M. W. *Organometallics* **1998**, *17*, 3149. (b) Younkin, T. R.; Connor, E. F.; Henderson, J. I.; Friedrich, S. K.; Grubbs, R. H.; Bansleben, D. A. *Science* **2000**, *287*, 460.

(5) (a) Drent, E.; van Dijk, R.; van Ginkel, R.; van Oort, B.; Pugh, R. I. *Chem. Commun.* **2002**, 744. (b) Luo, S.; Vela, J.; Lief, G. R.; Jordan, R. F. *J. Am. Chem. Soc.* **2007**, *129*, 8946. (c) Kochi, T.; Noda, S.; Yoshimura, K.; Nakamura, A.; Nozaki, K. *J. Am. Chem. Soc.* **2007**, *129*, 8948. (d) Weng, W.; Shen, Z.; Jordan, R. F. *J. Am. Chem. Soc.* **2007**, *129*, 15450. (e) Guironner, D.; Roesle, P.; Rünzi, T.; Göttker-Schnetmann, I.; Mecking, S. *J. Am. Chem. Soc.* **2009**, *131*, 422. (f) Ito, S.; Munakata, K.; Nakamura, A.; Nozaki, K. *J. Am. Chem. Soc.* **2009**, *131*, 14606. (g) Rünzi, T.; Fröhlich, D.; Mecking, S. *J. Am. Chem. Soc.* **2010**, *132*, 17690. (h) Shen, Z.; Jordan, R. F. *Macromolecules* **2010**, *43*, 8706. (i) Ito, S.; Kanazawa, M.; Munakata, K.; Kuroda, J.-i.; Okumura, Y.; Nozaki, K. *J. Am. Chem. Soc.* **2011**, *133*, 1232. (j) Daigle, J.-C.; Piche, L.; Claverie, J. P. *Macromolecules* **2011**, *44*, 1760. (k) Carrow, B. P.; Nozaki, K. *J. Am. Chem. Soc.* **2012**, *134*, 8802.

(6) (a) Giannini, U.; Brückner, G.; Pellino, E.; Cassata, A. *Polym. Lett.* **1967**, *5*, 527. (b) Giannini, U.; Brückner, G.; Pellino, E.; Cassata, A. *J. Polym. Sci.: Part C* **1968**, *22*, 157.

(7) (a) Kesti, M. R.; Coates, G. W.; Waymouth, R. M. *J. Am. Chem. Soc.* **1992**, *114*, 9679. (b) Aaltonen, P.; Fink, G.; Löfgren, B.; Seppälä, J. *Macromolecules* **1996**, *29*, 5255. (c) Stehling, U. M.; Stein, K. M.; Kesti, M. R.; Waymouth, R. M. *Macromolecules* **1998**, *31*, 2019. (d) Hakala, K.; Löfgren, B.; Helaja, T. *Eur. Polym. J.* **1998**, *34*, 1093. (e) Stehling, U. M.; Stein, K. M.; Fischer, D.; Waymouth, R. M. *Macromolecules* **1999**, *32*, 14. (f) Marques, M. M.; Correia, S. G.; Ascenso, J. R.; Ribeiro, A. F. G.; Gomes, P. T.; Dias, A. R.; Foster, P.; Rausch, M. D.; Chien, J. C. W. *J. Polym. Sci. Part A* **1999**, *37*, 2457. (g) Hagihara, H.; Murata, M.; Uozumi, T. *Macromol. Rapid Commun.* **2001**, *22*, 353. (h) Imuta, J.-I.; Kashiwa, N.; Toda, Y. *J. Am. Chem. Soc.* **2002**, *124*, 1176. (i) Expósito, M. T.; Vega, J. E.; Ramos, J.; Osio-Barcina, J.; García-Martínez, A.; Martín, C.; Martínez-Salazar, J. *J. Appl. Polym. Sci.* **2008**, *109*, 1529. (j) Zhao, P.; Shpasser, D.; Eisen, M. S. *J. Polym. Sci., Part A: Polym. Chem.* **2012**, *50*, 523.

(8) Terao, H.; Ishii, S.; Mitani, M.; Tanaka, H.; Fujita, T. *J. Am. Chem. Soc.* **2008**, *130*, 17636.

(9) (a) Hong, M.; Wang, Y.-X.; Mu, H.-L.; Li, Y.-S. *Organometallics* **2011**, *31*, 4678. (b) Hong, M.; Liu, J.-Y.; Li, B.-X.; Li, Y.-S. *Macromolecules* **2011**, *44*, 5659. (c) Hong, M.; Li, Y.; Li, B.; Li, Y.-S. *Macromol. Rapid Commun.* **2012**, *33*, 998.

(10) Yang, X.-H.; Wang, Z.; Sun, X.-L.; Tang, Y. *Dalton Trans.* **2009**, 8945.

(11) Yang, X.-H.; Liu, C.-R.; Wang, C.; Sun, X.-L.; Guo, Y.-H.; Wang, X.-K.; Wang, Z.; Xie, Z.; Tang, Y. *Angew. Chem., Int. Ed.* **2009**, 8099.

(12) Wang, C.; Ma, Z.; Sun, X.-L.; Gao, Y.; Guo, Y.-H.; Tang, Y.; Shi, L.-P. *Organometallics* **2006**, *25*, 3259.