Synthesis, Characterization, and Ethylene (Co)Polymerization Behavior of Trichlorotitanium 2-(1-(Arylimino)propyl)quinolin-8-olates

WEI HUANG,¹ WENJUAN ZHANG,¹ SHAOFENG LIU,¹ TONGLING LIANG,¹ WEN-HUA SUN^{1,2}

¹Key Laboratory of Engineering Plastics and Beijing National Laboratory for Molecular Science, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100190, China

²State Key Laboratory for Oxo Synthesis and Selective Oxidation, Lanzhou Institute of Chemical Physics, Chinese Academy of Sciences, Lanzhou 730000, China

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ABSTRACT: A series of trichlorotitanium complexes containing 2-(1-(arylimino)propyl)quinolin-8-olates was synthesized by stoichiometric reaction of titanium tetrachloride with the corresponding potassium 2-(1-(arylimino)propyl)quinolin-8-olates and was fully characterized by elemental analysis, nuclear magnetic resonance spectroscopy, and by single-crystal X-ray diffraction study of representative complexes. All titanium complexes, when activated with methylaluminoxane, exhibited high catalytic activity toward ethylene polymerization [up to 1.15×10^6 g mol⁻¹(Ti) h⁻¹] and ethylene/ α -olefin copolymeriza-

tion [up to 1.54×10^6 g mol⁻¹ (Ti) h⁻¹]. The incorporation of comonomer was confirmed to amount up to 2.82 mol % of 1-hexene or 1.94 mol % of 1-octene, respectively. © 2011 Wiley Periodicals, Inc. J Polym Sci Part A: Polym Chem 49: 1887–1894, 2011

KEYWORDS: addition polymerization; 2-(1-(arylimino)propyl)quinolin-8-olates; copolymerization; ethylene homopolymerization; metal-organic catalysts/organometallic catalysts; polyethylene (PE); trichlorotitanium pro-catalyst

INTRODUCTION Metallocene pro-catalysts have gained much attention in practical olefin polymerization because these catalysts allow the production of fine-designed polyolefins with controllable molecular weight and dispersity, with specific tactility, and also with good α -olefins comonomer inclusion.¹ As a consequence, half-metallocene pro-catalysts have been developed to investigate their catalytic behavior in ethylene polymerization and copolymerization,² with a view to the ease of fine-tuning the half-metallocene catalysts through variation of the anionic derivatives.³ Recently, normal titanium complexes ligated by amidinate,⁴ amide,⁵ and alkoxy⁶ have been explored extensively in olefin (co)polymerization, and the well-known representatives are bis(imino phenolato)titanium (FI catalysts) and bis(iminopyrrolido)titanium (PI catalysts) pro-catalysts.⁷ Using arylonates bearing bridged N-donors as multidentate ligands, the bis-ligated metal complexes were commonly obtained;⁸ however, the trichlorometallic complexes (LMCl₃) were difficult to access and rarely investigated.9 Our trials with multidentate ligands of quinolinolate derivatives illustrated that their transition metal complexes showed good catalytic activities in ethylene (co)polymerization,^{3(d),10} whereas their aluminum complexes exhibited high efficiency for the ring-opening polymerization of ε -caprolactone.¹¹

In this study, we report on the synthesis and characterization of a series of trichlorotitanium 2-(1-(arylimino)propyl)- quinolin-8-olate complexes. On treatment with methylaluminoxane (MAO), all of these titanium pro-catalysts showed high activities toward ethylene polymerization and copolymerization. The influences of reaction parameters on their catalytic performance have been investigated in detail.

EXPERIMENTAL

General Considerations

All manipulations of air and/or moisture-sensitive compounds were carried out under nitrogen atmosphere in a glove box or using standard Schlenk techniques. MAO (1.46 M in toluene) was purchased from Albemarle. Potassium hydride (KH), purchased from Beijing Reagent Chemicals, was washed with *n*-hexane to remove mineral oil before use. Toluene, n-hexane, and n-heptane were refluxed in the presence of sodium and benzophenone and distilled under nitrogen atmosphere. Dichloromethane (CH₂Cl₂), 1-hexene, and 1octene were dried over calcium hydride and distilled under nitrogen atmosphere. FTIR spectra were recorded on a Perkin Elmer FTIR 2000 spectrometer using KBr disc in the range of 4000–400 cm⁻¹. Elemental analysis was performed on a Flash EA 1112 microanalyzer. ¹H NMR and ¹³C NMR spectra were recorded on a Bruker DMX 400 MHz instrument at ambient temperature using tetramethylsilane (TMS) as an internal standard at 25 $\,^\circ\text{C.}$ ^{13}C NMR spectra of the polymers were recorded on a Bruker DMX-300 MHz

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instrument at 110 °C in deuterated 1,2-dichlorobenzene with TMS as an internal standard. Differential scanning calorimetry (DSC) trace and melting points of polyethylene were obtained from the second scanning run on a Perkin-Elmer DSC-7 at a heating rate of 10 °C min⁻¹. Molecular weights and polydispersity indices of (co)polyethylenes were determined by the gel permeation chromatography (GPC) method using a PL-GPC 220 instrument at 135 °C in 1,2,4-trichlorobenzene with polystyrene as the standard.

Synthesis of 2-(1-(Arylimino)propyl)quinolin-8-ol Derivatives (L1–L6)

2-(1-(2,6-Dimethylphenylimino)propyl)quinolin-8-ol (L1), 2-(1-(2,6-diethylphenyl-imino)propyl)quinolin-8-ol (L2), 2-(1-(2,6-diisopropylphenylimino)propyl)quinolin-8-ol (L3), and 2-(1-(2,6-dichlorophenylimino)propyl)quinolin-8-ol (L6) were prepared according to the literature.¹¹ Using the same procedure, the two new compounds L4 and L5 were synthesized.

2-(1-(Mesitylimino)propyl)quinoline-8-ol (L4)

The mixture of 0.402 g (2.0 mmol) 1-(8-hydroxyquinoline-2-yl)propan-1-one, 0.324 g (2.4 mmol) 2,4,6-trimethylaniline, and a catalytic amount of *p*-toluenesulfonic acid (0.10 g) in 20 mL toluene was refluxed for 24 h. After toluene evaporation, 2-(1-(mesitylimino)propyl)quinoline-8-ol (**L4**) was purified on column chromatography (silica gel, petroleum ether/ ethyl acetate = 20:1) and was obtained as a yellow green solid in 0.271 g (42.6%).

¹H NMR (CDCl₃, 400 MHz, ppm): δ 8.50 (d, J = 8.5 Hz, 1H, quino-*H*), 8.26 (d, J = 8.2 Hz, 1H, quino-*H*), 8.15 (s, 1H, O*H*), 7.51 (t, J = 7.4 Hz, 1H, quino-*H*), 7.40 (d, J = 7.6 Hz, 1H, quino-*H*), 7.23 (d, J = 7.1 Hz, 1H, quino-*H*), 6.91 (s, 2H, Ar-*H*), 2.81–2.77 (m, 2H, N=CCH₂CH₃), 2.31 (s, 3H, Ar-CH₃), 2.04 (s, 6H, Ar-CH₃), 1.08 (t, J = 7.3 Hz, 3H, N=CCH₂CH₃). ¹³C NMR (CDCl₃, 100 MHz, ppm): δ 171.3 (CH=N), 155.2, 153.4, 152.5, 146.0, 136.7, 132.5, 129.1, 128.8, 128.7, 125.1, 120.5, 118.0, 110.4, 23.1, 20.1, 18.2, 11.7. IR (KBr, cm⁻¹): 3415 (O—H) (w), 3004 (m), 1634 (CH=N) (m), 1526 (s), 1443 (m), 1256 (m), 1210 (m), 1041 (m), 1027 (s), 852 (m), 797 (m), 768 (w), 710 (m), 520 (w). mp: 82 °C. Anal. Calcd for C_{21H22}N₂O: C, 79.21; H, 6.96; N, 8.80. Found: C, 79.23; H, 7.04; N, 8.76.

2-(1-(2,6-Diethyl-4-methylphenylimino)propyl) quinoline-8-ol (L5)

Using the same procedure, 2-(1-(2,6-diethyl-4-methylphenylimino)propyl)quinolin-8-ol (**L5**) was isolated as an orange yellow solid in 43.2% yield (0.298 g).

¹H NMR (CDCl₃, 400 MHz, ppm): δ 8.47 (d, J = 8.6 Hz, 1H, quino-*H*), 8.24 (d, J = 8.3 Hz, 1H, quino-*H*), 8.16 (s, 1H, O*H*), 7.50 (t, J = 7.9 Hz, 1H, quino-*H*), 7.39 (d, J = 8.2 Hz, 1H, quino-*H*), 7.23 (d, J = 7.8 Hz, 1H, quino-*H*), 6.94 (s, 2H, Ar-*H*), 2.83–2.77 (m, 2H, N=CCH₂CH₃), 2.45–2.37 (m, 2H, Ar-CH₂CH₃), 2.32–2.26 (m, 2H, Ar-CH₂CH₃), 2.34 (s, 3H, Ar-CH₃), 1.17 (t, J = 7.5 Hz, 6H, Ar-CH₂CH₃), 1.07 (t, J = 7.4 Hz, 3H, N=CCH₂CH₃). ¹³C NMR (CDCl₃, 100 MHz, ppm): δ 170.7 (CH=N), 153.5, 152.5, 145.0, 137.1, 136.7, 132.6, 130.8, 129.0, 128.8, 126.7, 120.5, 118.0, 110.4, 24.7, 23.3, 21.4, 13.7, 11.6. IR (KBr, cm⁻¹): 3440 (O—H) (m), 3042 (m), 2964 (m), 2917

(w), 2845 (m), 1635 (CH=N) (s), 1575 (m), 1511 (s), 1421 (s), 1355 (m), 1300 (m), 1246 (m), 1190 (m), 1162 (s), 1076 (m), 934 (s), 852 (s), 799 (m), 752 (w), 721 (m), 665 (w), 592 (w). mp: 118 °C. Anal. Calcd for $C_{23}H_{26}N_2O$: C, 79.73; H, 7.56; N, 8.09. Found: C, 78.99; H, 7.66; N, 7.96.

Synthesis of Trichlorotitanium 2-(1-(Arylimino)propyl)quinolin-8-olates (C1–C6) *Trichlorotitanium 2-(1-(2,6-Dimethylphenylimino)* propyl)quinolin-8-olate (C1)

To a solution of 0.304 g (1.00 mmol) 2-(1-(2,6-dimethylphenylimino)-propyl)quinolin-8-ol in 30 mL toluene, 0.040 g (1.00 mmol) KH was added at -78 °C. The mixture was stirred for 4 h. After addition of 0.334 g (1.00 mmol) TiCl₄·(THF)₂ at -78 °C, the mixture was slowly warmed up to room temperature and stirred for 6 h. After solvent evaporation, the residue was extracted with CH₂Cl₂ (3 × 20 mL), and the filtrate was combined and concentrated into about 20 mL. The concentrated solution was covered with *n*-heptane and kept for 3 days to obtain brown crystals of trichlorotitanium 2-(1-(2,6-dimethylphenylimino)propyl)quinolin-8-olate (**C1**) in 0.280 g (61.3%).

¹H NMR (CDCl₃, 400 MHz, ppm): 8.69 (d, J = 8.1 Hz, 1H, quino-*H*), 8.00 (d, J = 8.6 Hz, 1H, quino-*H*), 7.89 (t, J = 8.4 Hz, 1H, quino-*H*), 7.72 (d, J = 8.4 Hz, 1H, quino-*H*), 7.25 (d, J = 8.1 Hz, 1H, quino-*H*), 7.15 (d, J = 8.0 Hz, 2H, Ar-*H*), 7.04 (t, J = 7.8 Hz, 1H, Ar-*H*), 2.92–2.86 (m, J = 7.9 Hz, 2H, N=CCH₂CH₃), 2.54 (s, 6H, Ar-CH₃), 1.26 (t, J = 7.3 Hz, 3H, N=CCH₂CH₃). ¹³C NMR (CDCl₃, 100 MHz, ppm): δ 179.3 (CH=N), 163.4, 145.0, 141.3, 133.7, 131.3, 129.8, 129.5, 129.2, 128.8, 128.4, 125.5, 120.6, 111.8, 25.2, 21.3, 19.5, 11.9. Anal. Calcd for C₂₀H₁₉Cl₃N₂OTi: C, 52.49; H, 4.19; N, 6.12. Found: C, 52.38; H, 4.11; N, 6.33.

Trichlorotitanium 2-(1-(2,6-Diethylphenylimino) propyl)quinolin-8-olate (C2)

Using the same procedure as for the synthesis of **C1**, **C2** was prepared by using **L2** instead of **L1** as brown crystals in 1.22 g (86.5%).

¹H NMR (CDCl₃, 400 MHz, ppm): δ 8.69 (d, J = 8.3 Hz, 1H, quino-*H*), 8.06 (d, J = 8.3 Hz, 1H, quino-*H*), 7.91 (t, J = 8.0 Hz, 1H, quino-*H*), 7.71 (d, J = 8.2 Hz, 1H, quino-*H*), 7.25 (d, J = 8.1 Hz, 1H, quino-*H*), 7.12 (d, J = 7.3 Hz, 2H, Ar-*H*), 7.04 (t, J = 7.8 Hz, 1H, Ar-*H*), 3.14–3.08 (m, 2H, N=CCH₂CH₃), 2.88–2.86 (m, 2H, Ar-CH₂CH₃), 2.67–2.61 (m, 2H, Ar-CH₂CH₃), 1.36 (t, J = 7.5 Hz, 6H, Ar-CH₂CH₃), 1.29 (t, J = 7.2 Hz, 3H, N=CCH₂CH₃). ¹³C NMR (CDCl₃, 100 MHz, ppm): δ 178.5 (CH=N), 154.2, 153.6, 141.4, 138.9, 137.7, 131.3, 129.6, 129.3, 128.9, 124.2, 121.8, 118.8, 111.2, 24.9, 23.7, 13.9, 11.6. Anal. Calcd for C₂₂H₂₃Cl₃N₂OTi: C, 54.41; H, 4.77; N, 5.77. Found: C, 54.18; H, 4.82; N, 6.13.

Trichlorotitanium 2-(1-(2,6-Diisopropylphenylimino) propyl)quinolin-8-olate (C3)

Using the same procedure as for the synthesis of **C1**, **C3** was formed as brown solid in 1.62 g (89.6%).

¹H NMR (CDCl₃, 400 MHz, ppm): δ 8.58 (d, J = 8.6 Hz, 1H, quino-*H*), 8.00 (d, J = 8.6 Hz, 1H, quino-*H*), 7.93 (t, J = 8.4

Hz, 1H, quino-*H*), 7.53 (d, J = 8.0 Hz, 1H, quino-*H*), 7.19 (t, J = 7.2 Hz, 1H, quino-*H*), 7.01 (d, J = 7.7 Hz, 2H, Ar-*H*), 6.95 (t, J = 7.8 Hz, 1H, Ar-*H*), 3.39–3.33 (m, 2H, Ar-*CH*(CH₃)₂), 2.91–2.86 (m, 2H, N=CCH₂CH₃), 1.30 (d, J = 6.5 Hz, 6H, Ar-CH(CH₃)₂), 1.26 (d, J = 7.5 Hz, 6H, Ar-CH(CH₃)₂), 1.21 (t, J = 6.8 Hz, 3H, N=CCH₂CH₃). ¹³C NMR (CDCl₃, 100 MHz, ppm): δ 178.9 (CH=N), 164.1, 143.9, 141.6, 139.6, 130.4, 129.2, 128.4, 128.2, 125.4, 124.6, 120.6, 117.2, 112.4, 29.8, 28.6, 25.4, 24.0, 21.6, 12.3. Anal. Calcd for C₂₄H₂₇Cl₃N₂OTi: C, 56.11; H, 5.30; N, 5.45. Found: C, 56.04; H, 5.54; N, 5.23.

Trichlorotitanium 2-(1-(Mesitylimino)propyl)quinolin-8-olate (C4)

Using the same procedure as for the synthesis of **C1**, **C4** was isolated as a brown solid in 1.37 g (63.7%).

¹H NMR (CDCl₃, 400 MHz, ppm): δ 8.70 (d, J = 8.5 Hz, 1H, quino-H), 8.07 (d, J = 8.3 Hz, 1H, quino-H), 7.89 (t, J = 8.0 Hz, 1H, quino-H), 7.71 (d, J = 7.5 Hz, 1H, quino-H), 7.27 (d, J = 7.5 Hz, 1H, quino-H), 7.02 (s, 2H, Ar-H), 2.89–2.84 (m, 2H, N=CCH₂CH₃), 2.49 (s, 3H, Ar-CH₃), 2.37 (s, 6H, Ar-CH₃), 1.34 (t, J = 7.8 Hz, 3H, N=CCH₂CH₃). ¹³C NMR (CDCl₃, 100 MHz, ppm): δ 179.3 (CH=N), 155.7, 154.1, 153.2, 146.9, 137.2, 133.6, 129.9, 129.2, 129.2, 125.9, 121.5, 118.7, 111.7, 23.4, 20.6, 18.3, 11.8. Anal. Calcd for C₂₁H₂₁Cl₃N₂OTi: C, 53.48; H, 4.49; N, 5.94. Found: C, 53.62; H, 4.59; N, 5.71.

Trichlorotitanium 2-(1-(2,6-Diethyl-4-methylphenylimino)propyl)quinolin-8-olate (C5)

Using the same procedure as for the synthesis of **C1**, **C5** was observed as a brown solid in 2.05 g (72.2%).

¹H NMR (CDCl₃, 400 MHz, ppm): δ 8.69 (d, J = 8.6 Hz, 1H, quino-*H*), 8.06 (d, J = 8.2 Hz, 1H, quino-*H*), 7.08 (t, J = 7.9 Hz, 1H, quino-*H*), 7.71 (d, J = 8.2 Hz, 1H, quino-*H*), 7.25 (d, J = 8.1 Hz, 1H, quino-*H*), 7.04 (s, 2H, Ar-*H*), 3.14–3.08 (m, 2H, N=CCH₂CH₃), 2.88–2.86 (m, 2H, Ar-CH₂CH₃), 2.67–2.61 (m, 2H, N=CCH₂CH₃), 2.40 (s, 3H, Ar-CH₃), 1.36 (t, J = 7.8 Hz, 3H, N=CCH₂CH₃), 1.29 (t, J = 7.14 Hz, 6H, Ar-CH₂CH₃). ¹³C NMR (CDCl₃, 100 MHz, ppm): δ 178.5 (CH=N), 154.2, 153.5, 147.9, 137.6, 137.1, 131.3, 129.2, 130.7, 126.3, 123.8, 120.9, 118.4, 111.3, 24.4, 23.7, 18.3, 13.7, 11.7. Anal. Calcd for C₂₃H₂₅Cl₃N₂OTi: C, 55.28; H, 5.04; N, 5.61. Found: C, 55.53; H, 4.91; N, 5.46.

Trichlorotitanium 2-(1-(2,6-Dichlorophenylimino)propyl)quinolin-8-olate (C6)

Using the same procedure as for the synthesis of **C1**, **C6** was produced as a brown solid and recrystallized in CH₂Cl₂ laying 1-heptane to form brown crystals in 1.54 g (59.4%). δ 8.71 (d, J = 8.5 Hz, 1H, quino-H), 8.12 (d, J = 8.2 Hz, 1H, quino-H), 7.91 (t, J = 7.8 Hz, 1H, quino-H), 7.72 (d, J = 7.4 Hz, 1H, quino-H), 7.02 (d, J = 7.4 Hz, 1H, quino-H), 7.02 (d, J = 7.5 Hz, 2H, Ar-H), 6.98 (t, J = 7.4 Hz, 1H, Ar-H), 3.01–2.96 (m, 2H, N=CCH₂CH₃), 1.46 (t, J = 7.6 Hz, 3H, N=CCH₂CH₃). ¹³C NMR (CDCl₃, 100 MHz, ppm): δ 179.7 (CH=N), 154.3, 153.7, 150.1, 138.9, 137.1, 132.7, 131.7, 128.8, 128.1, 127.7, 123.5, 121.8, 113.4, 21.7, 11.6. Anal. Calcd for C₁₈H₁₃Cl₅N₂OTi: C, 43.37; H, 2.63; N, 5.62. Found: C, 43.61; H, 2.55; N, 5.58.

X-Ray Structure Determination

Crystals of C1 and C6 suitable for single-crystal X-ray analysis were obtained by overlaying their CH₂Cl₂ solutions with *n*-heptane. Single-crystal X-ray diffraction for C1 and C6 were performed on a Rigaku RAXIS Rapid IP diffractometer with graphite-monochromated Mo K α radiation ($\lambda = 0.71073$ Å) at 173(2) K. Cell parameters are obtained by global refinement of the positions of all collected reflections. Intensities are corrected for Lorentz and polarization effects and empirical absorption. The structures are solved by direct methods and refined by full-matrix least-squares on F2. All nonhydrogen atoms are refined anisotropically. Structure solution and refinement are performed by using the SHELXL-97 package.¹² Crystal data collection and refinement details are given in Table 1. CCDC 801330 (C1) and 801331 (C6) are given in the Supporting Information crystallographic data, which could be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/ data_request/cif.

Procedures for Ethylene Polymerization and Copolymerization

A stainless steel autoclave (0.5 L) equipped with a mechanical stirrer and a temperature controller was heated in vacuum at 80 °C, recharged with ethylene three times, and then cooled to room temperature under ethylene atmosphere. A toluene solution of the titanium pro-catalyst (with comonomer) was transferred into the reactor. After the desired reaction temperature was reached and the required amount of cocatalyst (with 100 mL volume in total) was added, the autoclave was immediately pressurized to 10 atm. The ethylene pressure was kept constant during the reaction through feeding ethylene. After a due time, the feeding ethylene was stopped, and the autoclave was placed in a water-ice bath for 1 h in order to be cooled. The resultant mixture was poured into a 10% HCl-ethanol solution. The solid polymer was collected, washed with water and ethanol several times, and dried under vacuum to constant weight.

RESULTS AND DISCUSSION

Synthesis and Characterization of Trichlorotitanium 2-(1-(Arylimino)propyl)quinolin-8-olates (C1–C6)

We used metal-chloride exchange in our previous syntheses of titanium complexes,¹³ and this approach allowed for the preparation of the complexes **C1-C6** in moderate to good yields (59.4–89.6%) by stoichiometric reaction of TiCl₄·(THF)₂ with the corresponding potassium 2-(1-(arylimino)propyl)quinolin-8-olates in toluene (Scheme 1). The elemental analyses are fully consistent with the molecular formula LTiCl₃.

The peaks of the hydroxyl groups in the free ligands appear at about 8.1 ppm in the ¹H NMR spectra. These peaks disappear during the formation of their titanium complexes as phenols are deprotonated before the formation of Ti-0bonds. The complexation can also be monitored in the ¹³C NMR spectra as the CH=N resonances of the bound ligands appear around 178–180 ppm, and they are shifted downfield by 8–9 ppm when compared with the free ligands.

	C1	C6
Empirical formula	$C_{20}H_{19}CI_3N_2OTi$	$C_{18}H_{13}CI_5N_2OTi$
Formula weight	457.62	498.45
Crystal color	Red	Red
Temperature (K)	173(2)	173(2)
Wavelength (Å)	0.71073	0.71073
Crystal system	Monoclinic	Triclinic
Space group	P2(1)/n	P-1
a (Å)	12.425(3)	8.1176(16)
b (Å)	14.117(3)	10.646(2)
<i>c</i> (Å)	13.289(3)	15.062(3)
α (°)	90	97.25(3)
β (°)	92.64(3)	98.63(3)
γ (°)	90	112.25(3)
Volume (Å ³)	2328.6(8)	1166.9(4)
Ζ	4	2
$D_{\text{calc}} (\text{mg m}^{-3})$	1.305	1.419
μ (mm ⁻¹)	0.723	0.949
<i>F</i> (000)	936	500
Crystal size (mm)	$0.20\times0.10\times0.09$	$0.46 \times 0.21 \times 0.09$
heta range (°)	2.11–27.48	1.40-27.46
Limiting indices	$16 \leq h \leq 16$	$-10 \leq h \leq 10$
	$-18 \leq k \leq 17$	$-13 \leq k \leq 13$
	−16 ≤ <i>l</i> ≤ 17	−19 ≤ <i>l</i> ≤ 19
Number of reflections collected	18,698	14,288
Number of unique reflections	5337	5319
R _{int}	0.0689	0.0434
Completeness to θ (%)	99.8 ($ heta =$ 27.48)	99.3(θ = 27.46)
Goodness-of-fit on F^2	1.157	1.086
Final <i>R</i> indices [$l > 2\sigma$ (<i>I</i>)]	R1 = 0.0750	R1 = 0.0520
	wR2 = 0.2091	wR2 = 0.1376
R indices (all data)	R1 = 0.0989	R1 = 0.0627
	wR2 = 0.2118	wR2=0.1453
Largest diff peak, hole (<i>e</i> Å ⁻³)	0.368, -0.479	0.42, -0.421

TABLE 1 Crystallographic Data and Refinement Details for Compl	exes C1 and C6
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SCHEME 1 Synthesis of titanium complexes **C1–C6**.



FIGURE 1 Molecular structure of C1 (ellipsoids enclose 30% electronic density; H atoms are omitted for clarity).

To clarify the absolute molecular structure, two representative complexes **C1** and **C6** were measured by the single-crystal X-ray diffraction. The molecular structures are illustrated in Figures 1 and 2, and the selected bond lengths and bond angles are tabulated in Table 2.

The structural features of complexes C1 and C6 are rather similar, and therefore, the structure of complex C1 is discussed. Figure 1 shows that titanium is coordinated by one tridentate ligand and three chlorine atoms, adopting a distorted octahedral geometry with O1, N1, N2, and Cl1 in the base plane and two more chlorines (Cl2 and Cl3) located in trans-apical positions and enclosing an Cl(3)-Ti(1)-Cl(2) angle of 171.54(6)°. The 2-(1-(2,6-dimethylphenylimino)propyl)quinolin-8-olate is located around the titanium center in a meridianal manner (N^N^O). The phenyl ring of the Schiff base moiety is twisted out of the coordination plane with the dihedral angle of 73.1°. The similar conformational phenomenon was observed in the aluminum analogs.¹¹ The angles \angle (N1-Ti1-N2) and \angle (O1-Ti1-N1) are 70.49° and 77.62°, respectively, and their sum of 148.1° is identical to the angle (01-Ti1-N2). The bond distances Ti-Cl (2.2763-2.3550 Å) are similar to those in the reported titanium complexes.^{9(c)} The Ti-N bonds (Ti1-N1: 2.108(4) Å, Ti1-N2: 2.283(4) Å) are also in the common range with slight difference due to the nature of ligands.

Catalytic Behavior for Ethylene Polymerization

The pro-catalyst C3 was used in the selection of a suitable cocatalyst. Although the combination with alkylaluminum



FIGURE 2 Molecular structure of C6 (ellipsoids enclose 30% electronic density; H atoms are omitted for clarity).

TABLE 2 Selected	Bond	Lengths	(Å)	and	Bond	Angles	(°)
for C1 and C6							

	C1	C6
Bond lengths (Å)		
Ti(1)—O(1)	1.868(3)	1.871(2)
Ti(1)—N(1)	2.108(4)	2.117(2)
Ti(1)—N(2)	2.283(4)	2.265(3)
Ti(1)—CI(1)	2.2763(15)	2.2736(10)
Ti(1)—CI(2)	2.2922(14)	2.3098(11)
Ti(1)—CI(3)	2.3550(16)	2.3157(11)
Bond angles (°)		
O(1)—Ti(1)—N(1)	77.62(14)	77.24(10)
O(1)—Ti(1)—N(2)	148.06(14)	147.09(9)
N(1)—Ti(1)—N(2)	70.49(14)	69.88(9)
O(1)—Ti(1)—Cl(1)	106.89(11)	107.19(7)
N(1)—Ti(1)—Cl(1)	173.23(11)	175.00(7)
N(2)—Ti(1)—Cl(1)	105.03(11)	105.72(7)
O(1)—Ti(1)—Cl(2)	92.81(11)	93.49(8)
N(1)—Ti(1)—Cl(2)	90.52(11)	89.02(7)
N(2)—Ti(1)—CI(2)	85.98(11)	84.69(7)
CI(1)—Ti(1)—CI(2)	94.26(6)	92.98(4)
O(1)—Ti(1)—Cl(3)	89.75(11)	90.41(8)
N(1)—Ti(1)—CI(3)	82.15(11)	82.90(7)
N(2)—Ti(1)—CI(3)	87.59(11)	87.05(7)
CI(1)—Ti(1)—CI(3)	92.71(6)	94.63(4)
CI(2)—Ti(1)—CI(3)	171.54(6)	170.03(4)

cocatalysts such as AlMe₃, AlEt₃, EtAlCl₂, and Et₂AlCl failed, pro-catalyst C3 showed good activity in ethylene polymerization with MAO and MAO. With the molar Al/Ti ratio of 1500 at 20 °C within 30 min, we measured activities of 2.80 imes 10^5 g mol⁻¹(Ti) h⁻¹ for MAO and of 2.19 \times 10⁵ g mol⁻¹(Ti) h^{-1} for MMAO, and detailed investigations were conducted using MAO as cocatalyst (entries 1-8, Table 3). By variation of the molar Al/Ti ratio at 20 °C, the maximal activity of 1.06×10^6 g mol⁻¹(Ti) h⁻¹ was achieved at the Al/Ti ratio of 5000, and an optimum ratio of Al/Ti for titanium catalytic systems was often observed.¹⁴ The catalytic activities were slightly affected by the reaction temperature, and the optimum value of 1.16 \times 10⁶ g mol⁻¹(Ti) h⁻¹ was realized at 60 °C (entries 3 and 6-8, Table 3), a value which agrees closely with traditional FI catalysts.15 Increasing temperatures led to a decrease of molecular weights from 389 kg mol^{-1} at 40 °C to 266 kg mol^{-1} at 80 °C. This temperature dependence is in line with the expected increase of chain transfers and terminations at elevated temperatures. The DSC analysis corroborated that the polyethylenes with the melting points from 131.3 °C to 138.7 °C are high-density polyethylenes.

The performances of the other pro-catalysts were extensively studied with the reaction conditions that involve an Al/Ti ratio of 5000 at 60 $^{\circ}$ C within 30 min (entries 9–13, Table 3).

TABLE 3 Ethyler	ne Polymerization	Results by	C1-C6/MAO S	Systems ^a
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Entry	Complexes	Al/Ti	<i>T</i> (°C)	Polymer (g)	Activity [10 ⁵ g mol ⁻¹ (Ti) h ⁻¹]	<i>M</i> _w ^b (10 ⁵ g mol ^{−1})	$M_{\rm w}/M_{\rm n}^{\rm b}$	7 _m ° (°C)
1	C3	3,000	20	1.27	5.10	3.85	12.4	138.7
2	C3	4,000	20	1.40	5.60	3.72	13.2	138.4
3	C3	5,000	20	2.66	10.6	3.69	15.9	138.0
4	C3	6,000	20	1.92	7.70	3.63	26.9	137.7
5	C3	7,000	20	1.40	5.60	3.56	32.4	135.3
6	C3	5,000	40	2.74	11.0	3.39	16.9	133.3
7	C3	5,000	60	2.88	11.5	3.17	17.7	132.0
8	C3	5,000	80	1.24	5.00	2.66	20.8	131.7
9	C1	5,000	60	0.540	2.20	3.38	10.2	132.0
10	C2	5,000	60	0.830	4.20	3.32	12.1	132.7
11	C4	5,000	60	1.24	5.00	2.47	16.2	131.3
12	C5	5,000	60	1.84	7.40	1.88	13.4	132.7
13	C6	5,000	60	1.88	7.60	2.62	15.1	132.7

 $^{\rm a}$ Conditions: 5 μmol Ti, total volume 100 mL toluene, 30 min, 10 atm ethylene.

The catalytic activities follow the order C3 (*i*Pr) > C2 (Et) > C1 (Me) (entries 3, 9, and 10, Table 3), and hence, the bulkier substituent on the ortho-position of the aryl group appears to enhance the active species and to result in a higher activity.^{7(b)} The solubilities of the complexes (C1-C3) follow the order of C3 (*i*Pr) > C2 (Et) > C1 (Me) and might well affect that observed catalytic activities. Solubility effects on the activities of pro-catalysts are also reflected by the results obtained with ligands with an additional *para*-methyl in pro-catalysts C4 and C5: C4 (2,4,6-trimethylphenyl) > C1 (2,6-dimethylphenyl) and C5 (2,6-diethyl-4-methylphenyl) > ^b Determined by GPC.

^c Determined by DSC.

C2 (2,6-diethylphenyl). Moreover, electron-donating ligands are expected to be advantageous for the stabilization of electron-deficient titanium complexes and to result in better activities, $^{7(b),16}$ and this expectation is borne out by the general observations of the title titanium pro-catalysts. In comparison to the catalytic systems of CpTiCl₃/MAO,^{3(e)} the pro-catalysts described here exhibit higher activity in ethylene polymerization. This result suggests that the bulky multidentate ligands stabilize the active species better than the Cp group.

The wide molecular distributions of the polyethylenes suggest that the catalytic systems comprise many different

TABLE 4	Copoly	vmerization	of Eth	vlene with	1-Olefin	by C1–C6 /	MAO ^a
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Entry	Complex	Monomer	Polymer (g)	Activity [10 ⁵ g mol ⁻¹ (Ti) h ⁻¹]	<i>M</i> _w ^b (10 ⁵ g mol ^{−1})	$M_{\rm w}/M_{\rm n}^{\rm b}$	T _m ^c (°C)
1	C3	$0.05M C_{6}^{=}$	0.280	11.2	3.34	19.0	133.7
2	C3	$0.1M C_{6}^{=}$	0.272	10.9	4.22	14.2	130.3
3	C3	$0.3M C_{6}^{=}$	0.104	4.16	2.39	10.4	127.0
4	C1	$0.1M \ C_{6}^{=}$	0.162	6.48	2.21	19.4	130.7
5	C2	$0.1M C_{6}^{=}$	0.223	8.92	6.09	15.8	130.4
6	C4	$0.1M C_{6}^{=}$	0.391	15.6	2.69	13.2	128.0
7	C5	$0.1M C_{6}^{=}$	0.254	11.6	2.37	11.6	129.3
8	C6	$0.1M C_{6}^{=}$	0.242	9.53	5.07	12.1	124.7
9	C1	0.1M C ₈	0.074	2.89	5.77	23.6	131.7
10	C2	$0.1M C_8^{=}$	0.096	3.84	2.45	21.4	130.7
11	C3	0.1M C ₈	0.122	4.88	2.26	21.2	129.3
12	C4	$0.1M C_8^{=}$	0.144	5.76	2.69	18.9	130.0
13	C5	0.1M C ₈ ⁼	0.074	2.96	2.10	16.5	130.0
14	C6	$0.1M C_8^{=}$	0.052	2.08	2.64	15.5	130.7

 a Condition: 1 μmol complex, Al/Ti = 5000, toluene (total volume 100 mL), 15 min, 60 °C, 10 atm.

^b Determined by GPC.

^c Determined by DSC.

active species. We envision that the presence of three chlorides adopting *mer*-coordination in the pro-catalysts allow for the formations of a variety of active species by abstraction of varying numbers of chlorine ligands and their replacement with MAO species.

Ethylene/1-Hexene and Ethylene/ 1-Octene Copolymerization

The trichlorotitanium pro-catalysts provide more space around the active center, and one is naturally led to consider whether this might be beneficial for the fabrication of branched polyethylene. Therefore, we explored the copolymerization of ethylene with α -olefins with the current catalytic systems. The optimum reaction condition with an Al/Ti ratio of 5000 at 60 °C within 30 min was used in exploring the suitable concentration of 1-hexene $(C_6^{=})$ using C3 (entries 1–3, Table 4). We observed a decrease in the catalytic activities as the comonomer concentration increased, and this phenomenon is commonly observed with half-titanocene imino-indolate and halftitanocene amidate.^{3(b,c)} By balancing the incorporation of comonomer and catalytic performance, the concentration of comonomer was fixed as 0.1 M for both 1-hexene ($C_6^{=}$) and 1octene ($C_8^{=}$) at initial toluene solution. All pro-catalysts C1-C6 showed high catalytic activities toward the copolymerization of ethylene with either 1-hexene or 1-octene (Table 4).

The data in Table 4 show that the pro-catalysts exhibit better activities with 1-hexene than with 1-octene. With reference to the data in Table 3, a positive "comonomer effect" occurs in the copolymerization of ethylene with 1-hexene (Table 4), whereas a negative comonomer effect was observed in the copolymerization of ethylene with 1-octene (Table 4). Therefore, the title pro-catalysts are promising for applications in the copolymerization of ethylene with 1-hexene.

The DSC analysis showed lower melting points for all copolymers, and this result is indicative of effective incorporation of α -olefins. The GPC data showed slightly lower molecular weights and wider molecular distributions of the obtained



FIGURE 3 ¹³C NMR spectrum of ethylene/1-hexene copolymer by the **C4**/MAO system (entry 6 in Table 4).



FIGURE 4 ¹³C NMR spectrum of ethylene/1-octene copolymer by the **C4**/MAO system (entry 12 in Table 4).

copolymers when compared with the polyethylenes produced by homopolymerization of ethylene. To clarify the incorporation of α -olefins, ¹³C NMR measurement was used to check the representative copolymers by **C4**/MAO system. The ¹³C NMR spectrum of the ethylene/1-hexene copolymer (entry 6, Table 4) is shown in Figure 3. The spectrum shows the typical characteristics of linear low-density polyethylene¹⁷ and indicated the incorporation of 2.82 mol % of 1-hexene. The monomer sequence distributions determined by the ¹³C NMR spectrum showed that the obtained poly(ethylene-1-hexene) contained isolated 1-hexene units (HHH), (EEE)_m, EHE, EHH, HEH, HEEH, EEEH, EEHE + EEHH, and so forth.¹⁸

In addition, the 13 C NMR spectrum (Fig. 4) of ethylene/1octene copolymer (entry 12, Table 4) indicates a 1.94 mol % incorporation of 1-octene in the resulting polymer.

CONCLUSIONS

trichlorotitanium 2-(1-(arylimino)propyl)quinolin-8-The olates (C1-C6) were designed, synthesized, and fully characterized. All titanium pro-catalysts demonstrated high activities toward ethylene polymerization and copolymerization. The mer-coordination of three chlorides provides more space around active center, leads to the formation of a variety of active species, and results in the production of polymers with wide molecular weight distributions. The positive comonomer effect was observed in the copolymerization with 1hexene, whereas a negative comonomer effect was found in the copolymerization of ethylene with 1-octene. The catalytic activities toward ethylene polymerization varied in the order **C3** $(R^1 = {}^iPr, R^2 = H) >$ **C6** $(R^1 = Cl, R^2 = H) >$ **C5** $(R^1 =$ Et, $R^2 = Me$) > C4 ($R^1 = R^2 = Me$) > C2 ($R^1 = Et$, $R^2 = H$) > C1 ($R^1 = Me$, $R^2 = H$). This ordering indicates that the catalytic activity of the electron-deficient titanium pro-catalysts is enhanced by bulky, electron-donating alkyl substituents. Considerable incorporation of comonomers was

achieved with 2.82 mol % of 1-hexene or 1.94 mol % of 1-octene, respectively.

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