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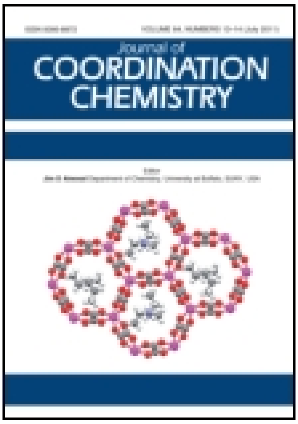

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The synthesis, structure, and ethylene polymerization of dimeric salicylaldiminato titanium complexes

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A series of dimeric titanium complexes bearing salicylaldiminates, [4-R-6-^{t}Bu-2-(CH=N^{n}Bu)$C_6H_2OTiCl_2(\mu\text{-}Cl)]_2$ [R = H (**1**); R = ^{t}Bu (**2**); R = NO_2 (**3**)], have been synthesized in high yield (>90%) by the reaction of corresponding 4-R-6-^{t}Bu-2-(CH=N^{n}Bu)$C_6H_2OSiMe_3$ with $TiCl_4$. The molecular structure of **2** has been confirmed by single-crystal X-ray diffraction analysis. When activated with methylaluminoxane, these complexes exhibit good catalytic activity for ethylene polymerization.

Keywords: Titanium complex; Polymerization; Homogeneous catalysis; Salicylaldiminato ligand

1. Introduction

Polyolefins are the largest volume synthetic materials used in the world and have been applied in almost every aspect of our daily lives. The growing demand for high-performance polyolefin products has inspired extensive research to optimize catalyst performance and polymer properties [1]. Non-metallocene metal catalysts, including group 4 transition metal complexes, chromium complexes, and late transition metal complexes, can produce a variety of high-performance polyolefin products, including isotactic polypropylene [2], syndiotactic polypropylene [3], polynorbornene [4], linear low-density polyethylene [5], isotactic polystyrene [6], and cyclo-olefin copolymer [7]. Consequently, development of non-metallocene metal catalysts is an ever-growing area.

Salicylaldiminate complexes are an important family of non-cyclopentadienyl ligands because of their easy preparation and simple modification. Organometallic complexes containing salicylaldiminates can be used to produce polyolefin products and control polymer properties by modification of the electronic character, geometry, and steric hindrance around the catalytically active metal. Grubbs reported neutral nickel catalysts bearing mono(salicylaldiminato) ligands that showed high activity for ethylene homopolymerization [8]. Gibson studied chromium complexes bearing bis(salicylaldiminato) and mono(salicylaldiminato) ligands for ethylene polymerization [9].

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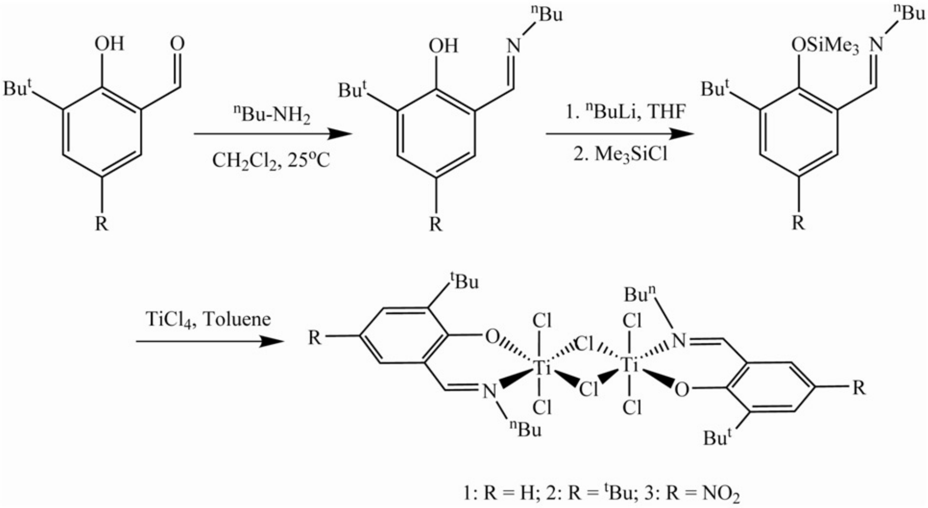

Scheme 1. Preparation of **1**–**3**.

Our group also synthesized a series of chromium catalysts with salicylaldiminato ligands for ethylene polymerization [10].

Bis(salicylaldiminato) group 4 catalysts are among the most successful "non-metallocene" catalysts. Fujita and Coates independently developed these catalysts to produce high-molecular weight polyethylene, isotactic and syndiotactic polypropylene, *etc.* with high catalytic activity or living polymerization [11]. Recently, some mono(salicylaldiminato) ligated group 4 catalysts were prepared and showed good catalytic activity for ethylene polymerization. Most of the salicylaldiminate group 4 precatalysts described above were monomeric; only a few dimeric salicylaldiminate group 4 metal complexes have been described, and their olefin polymerization chemistry has not been reported [12, 13]. The space of the central metal in the dimeric complex is more close than in the monomeric species, influencing the chain-transfer process of polymerization. Considering the different electronic properties and spaces of reactive sites between dimeric and monomeric complexes, we designed several dimeric complexes based on the salicylaldiminate (scheme 1) and found that they are active for olefin polymerization. Here, we report a series of dimeric salicylaldiminate titanium complexes $[4\text{-R-}6\text{-}^t\text{Bu-}2\text{-}(\text{CH}{=}\text{N}^n\text{Bu})\text{C}_6\text{H}_2\text{OTiCl}_2(\mu\text{-Cl})]_2$ [R = H (**1**); R = ^{t}Bu (**2**); R = NO$_2$ (**3**)] having different electronic substituents and explore their catalytic activities for ethylene homopolymerization.

2. Experimental

2.1. *General procedures*

Reactions with organometallic reagents were carried out under nitrogen using standard Schlenk techniques or in an inert-atmosphere glovebox. Solvents were dried with the appropriate drying agent, distilled, degassed, and stored over 4 Å sieves. Polymerization grade ethylene was further purified by passage through columns of 3 Å molecular sieves and MnO. Methylaluminoxane (MAO) and ^{n}BuLi were purchased from Aldrich. Elemental analyses were performed on a Vario EL microanalyzer.

2.2. *Preparation*

2.2.1. 6-^{t}Bu-2-(CH=N^{n}Bu)C_6H_3OH (L_1H). Under nitrogen, activated molecular sieves (4 Å, 1.00 g), dichloromethane (10 cm^3), 3-tertbutylsalicylaldehyde (1.78 g, 10 cm^3) and butylamine (0.73 g, 10 cm^3) were added into a 50 cm^3 Schlenk tube, and the mixture was stirred at room temperature. After stirring for 24 h, the reaction mixture was filtered through a pad of Celite on a medium glass fritted funnel. Then all solvents were removed in vacuo. The residue was purified by column chromatography on silica gel using petroleum ether/ethyl acetate (10 : 1) as the mobile phase to give **L_1H** as a bright yellow oil (2.10 g, 90%). ^{1}H NMR (400 MHz, $CDCl_3$, 25°C): $\delta = 14.20$ (s, 1H), 8.33 (s, 1H), 7.30 (d, $J = 7.6$ Hz, 1H), 7.09 (d, $J = 7.6$ Hz, 1H), 6.79 (t, $J = 7.6$ Hz, 2H), 3.58 (t, $J = 7.6$ Hz, 2H), 1.66–1.71 (m, 2H), 1.44 (s, 9H), 1.38–1.42 (m, 2H), 0.96 (t, $J = 8.0$ Hz, 3 H). ^{13}C NMR (100.5 MHz, $CDCl_3$, 25°C): $\delta = 165.3$, 160.9, 137.6, 129.6, 129.3, 118.9, 117.8, 59.4, 35.0, 33.2, 29.5, 20.5, 14.0. Anal. Calcd for $C_{15}H_{23}NO$ (233.35): C, 77.21; H, 9.93; N, 6.00. Found: C, 77.29; H, 9.87; N, 5.93.

2.2.2. 4,6-^{t}Bu$_2$-2-(CH=N^{n}Bu)C_6H_2OH (L_2H). **L_2H** was prepared in a similar procedure to **L_1H**. ^{1}H NMR (400 MHz, $CDCl_3$, 25°C): $\delta = 13.82$(s, 1H), 8.41 (s, 1H), 7.43 (d, $J = 7.6$ Hz, 1H), 7.25 (d, $J = 7.6$ Hz, 1H), 3.49 (t, $J = 8.0$ Hz, 2 H), 1.65–1.70 (m, 2H), 1.44 (s, 9H), 1.32 (s, 9H), 1.26-1.32 (m, 2H), 0.92 (t, $J = 8.0$ Hz, 3H). ^{13}C NMR (100.5 MHz, $CDCl_3$, 25°C): $\delta = 165.6$, 158.4, 139.9, 136.7, 126.7, 125.8, 118.0, 59.3, 35.1, 34.2, 33.1, 31.6, 29.6, 20.4, 13.9. Anal. Calcd for $C_{19}H_{31}NO$ (289.46): C 78.84; H 10.79; N 4.84. Found: C, 78.79; H, 10.70; N, 4.79.

2.2.3. 4-NO$_2$-6-^{t}Bu-2-(CH=N^{n}Bu)C_6H_2OH (L_3H). **L_3H** was prepared in a similar procedure to **L_1H**. ^{1}H NMR (400 MHz, $CDCl_3$, 25°C): $\delta = 15.52$ (s, 1H), 8.30 (s, 1H), 8.18 (d, $J = 2.8$ Hz, 1H), 8.10 (d, $J = 2.8$ Hz, 1H), 3.65 (t, $J = 7.6$ Hz, 2H), 1.73–1.77 (m, 2H), 1.45–1.49 (m, 2H), 1.43 (s, 9H), 1.32 (s, 9H), 0.99 (t, $J = 8.0$ Hz, 3H). ^{13}C NMR (100.5 MHz, $CDCl_3$, 25°C): $\delta = 171.3$, 164.8, 140.9, 137.4, 127.4, 125.2, 116.0, 56.5, 35.4, 32.5, 29.1, 20.3, 13.8. Anal. Calcd for $C_{15}H_{22}N_2O_3$ (278.35): C, 64.73; H, 7.97; N, 10.06. Found: C, 64.68; H, 7.90; N, 10.11.

2.2.4. 6-^{t}Bu-2-(CH=N^{n}Bu)C_6H_3OTiCl$_2$(μ-Cl)$_2$ (1). Under nitrogen, a solution of 6-^{t}Bu-2-(CH = N^{n}Bu)C_6H_3OLi was prepared at −78°C by addition of ^{n}BuLi (2.55 mmol) to 6-^{t}Bu-2-(CH=N^{n}Bu)C_6H_3OH (0.58 g, 2.50 mmol) in THF (10 cm^3). The solution was allowed to warm to room temperature, stirred for 2 h, and then was added dropwise to $(CH_3)_3SiCl$ (0.23 g, 2.55 mmol) in THF (10 cm^3). The resulting mixture was allowed to warm to room temperature and stirred for 15 h. The solvents were removed under vacuum, and the residue was extracted with toluene (20 cm^3) and filtered. The filtrate was added to a solution of $TiCl_4$ (0.47 g, 2.5 mmol) in toluene

($20\,cm^3$) at 0°C, during which time the color changed from yellow to orange. Cooling to 0°C afforded orange crystals of **1** after several days (0.88 g, 91%). Anal. Calcd for $C_{30}H_{44}N_2O_2Cl_6Ti_2$ (773.13): C, 46.61; H, 5.74; N, 3.62. Found: C, 46.68; H, 5.71; N, 3.57. ^1H NMR (400 MHz, $CDCl_3$, 25°C): $\delta = 8.49$ (s, 1H), 7.43 (d, $J = 7.6$ Hz, 1H), 7.22 (d, $J = 7.6$ Hz, 1H), 6.95 (t, $J = 7.6$ Hz, 2H), 4.05 (t, $J = 7.6$ Hz, 2H), 1.85-1.89 (m, 2H), 1.48 (s, 9H), 1.44-1.47 (m, 2H), 1.03 (t, $J = 8.0$ Hz, 3H). ^{13}C NMR (100.5 MHz, $CDCl_3$, 25°C): $\delta = 165.4$, 163.8, 145.7, 133.5, 129.6, 124.4, 121.5, 60.3, 34.8, 32.9, 29.5, 20.4, 13.9. IR (cm^{-1}): 2959 (s), 2871 (s), 1663 (s), 1609 (m), 1483 (m), 1458 (m), 1437 (m), 1389 (m), 1360 (m), 1308 (m), 1268 (m), 1200 (m), 1145 (m), 1090 (w), 1029 (m), 854 (m), 795 (m), 751 (s), 679 (m), 619 (w).

2.2.5. $4,6\text{-}^tBu_2\text{-}2\text{-}(CH{=}N^nBu)C_6H_2OTiCl_2(\mu\text{-}Cl)_2$ (2). Complex **2** was synthesized in the same way as described for **1** with $4,6\text{-}^tBu_2\text{-}2\text{-}(CH{=}N^nBu)C_6H_2OH$ (0.72 g, 2.50 mmol) as starting material. Pure **2** (1.02 g, 92%) was obtained as orange crystals. Anal. Calcd for $C_{38}H_{60}N_2O_2Cl_6Ti_2$ (885.35): C, 51.55; H, 6.83; N, 3.16. Found: C, 51.60; H, 6.78; N, 3.13. ^1H NMR (400 MHz, $CDCl_3$, 25°C): $\delta = 8.57$ (s, 1H), 7.68 (d, $J = 7.6$ Hz, 1H), 7.44 (d, $J = 7.6$ Hz, 1H), 4.06 (t, $J = 8.0$ Hz, 2H), 1.84–1.89 (m, 2H), 1.52 (s, 9H), 1.42–1.46 (m, 2H), 1.36 (s, 9H), 0.99 (t, 3H). ^{13}C NMR ($CDCl_3$, 100.5 MHz): δ 165.7, 161.3, 148.1, 136.7, 130.9, 128.5, 124.6, 60.2, 35.2, 34.9, 32.5, 31.3, 29.5, 20.4, 13.8. IR (cm^{-1}): 2959 (s), 2871 (s), 1662 (s), 1610 (m), 1479 (m), 1463 (m), 1423 (m), 1393 (m), 1364 (m), 1272 (m), 1230 (m), 1199 (m), 1158 (m), 1050 (w), 853 (m), 758 (m), 640 (w).

2.2.6. $4\text{-}NO_2\text{-}6\text{-}^tBu\text{-}2\text{-}(CH{=}N^nBu)C_6H_2OTiCl_2(\mu\text{-}Cl)_2$ (3). Complex **3** was synthesized in the same way as described for synthesis of **1** with $4\text{-}NO_2\text{-}6\text{-}^tBu\text{-}2\text{-}(CH{=}N^nBu)C_6H_2OH$ (0.70 g, 2.50 mmol) as starting material. Pure **3** (1.02 g, 92%) was obtained as orange crystals. Anal. Calcd for $C_{38}H_{60}N_2O_2Cl_6Ti_2$ (863.12): C, 41.75; H, 4.90; N, 6.49. Found: C, 41.82; H, 4.96; N, 6.41. ^1H NMR (400 MHz, $CDCl_3$, 25 °C): 8.46 (s, 1H), 8.42 (d, $J = 2.8$ Hz, 1H), 8.28 (d, $J = 2.8$ Hz, 1H), 4.20 (t, $J = 7.6$ Hz, 2H), 1.91–1.96 (m, 2H), 1.61–1.65 (m, 2H), 1.51 (s, 9H), 1.36 (s, 9H), 1.06 (t, $J = 8.0$ Hz, 3H). ^{13}C NMR (100.5 MHz, $CDCl_3$, 25 °C): $\delta = 171.5$, 167.8, 149.1, 137.4, 131.7, 127.9, 122.6, 57.4, 35.9, 33.0, 29.0, 20.2, 13.7. IR (cm^{-1}): 2958 (s), 2875 (s), 1667 (s), 1613 (s), 1558 (m), 1529 (m), 1488 (m), 1454 (m), 1386 (w), 1327 (s), 1275 (m), 1219 (m), 1111 (m), 1029 (w), 909 (m), 799 (w), 747 (m), 719 (m), 660 (w).

2.3. *X-ray crystallography*

Single crystals of **2** for X-ray structural analysis were obtained from a solution of $CH_2Cl_2/^n$hexane. Diffraction data were collected at 293 K on a Bruker SMART-CCD diffractometer using graphite-monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å). Details of the crystal data, data collection, and structure refinement are summarized in table 1. The structures were solved by direct methods [14] and refined by full-matrix least-squares on F^2. All non-hydrogen atoms were refined anisotropically and hydrogen atoms were included in idealized positions. All calculations were performed using SHELXTL [15] crystallographic software packages.

Table 1. Crystal data and structural refinement details for **2**.

Molecular formula	$C_{38}H_{60}Cl_6N_2O_2Ti_2$
Molecular weight	885.38
Crystal system	Monoclinic
Space group	$C2/c$
Unit cell dimensions (Å, °)	
a	20.428(10)
b	14.174(7)
c	16.931(8)
α	90.00
β	107.088(18)
γ	90.00
Volume (Å^3), Z	4686(4), 4
Calculated density (g cm^{-3})	1.255
$F(000)$	1856
Absorption coefficient (mm^{-1})	0.714
Collect. range (°)	$3.14 \le \theta \le 25.00$
Independent reflection	4125
R_{int}	0.1045
Data/restraints/parameters	4125/96/264
R_1 ($I > 2\delta$)	0.0663
wR_2 (I > 2δ)	0.1582
Goodness-of-fit on F^2	1.019
Largest difference peak and hole (e Å^{-3})	0.297 and −0.390

2.4. *General procedure of polymerization reactions*

A dry 200 cm^3 steel autoclave was charged with 60 cm^3 of toluene solution of MAO, thermostated at desired temperature and saturated with ethylene (1.0 bar). The system was maintained by continuously stirring for 30 min, and then polymerization was started by injection of a solution of titanium complex (5 µmol) in toluene (1.67 cm^3). The vessel was repressurized with ethylene immediately and the pressure was kept by continuously feeding monomer. After 30 min, the polymerization was quenched by injecting acidified methanol [HCl (3 M)/methanol = 1 : 1]. The mixture was stirred and the polymer was collected by filtration, washed with water, methanol, and dried *in vacuo*.

3. Results and discussion

3.1. *Complex synthesis*

Schiff bases $\mathbf{L_1H}$–$\mathbf{L_3H}$ were synthesized in high yields by condensation of the corresponding salicylaldehyde with the ^{n}BuNH$_2$ in dry methanol. The titanium complexes **1**–**3** were prepared in 90–92% yield by three steps from $\mathbf{L_1H}$–$\mathbf{L_3H}$ as shown in scheme 1. All complexes were characterized by elemental analysis, IR spectra, and NMR spectroscopy. The ^{1}H NMR spectra of **1**–**3** revealed that CH=N protons are shifted upfield approximately 0.16 ppm relative to free ligands. Also, IR spectra of these complexes show imine C=N stretch at 1662–1667 cm^{-1}, red shifted 17 cm^{-1} in comparison with the free ligands, indicating coordination of the imino nitrogen to the metal center. The order of the chemical Schiff of the CH=N protons is **2** > **1** > **3**.

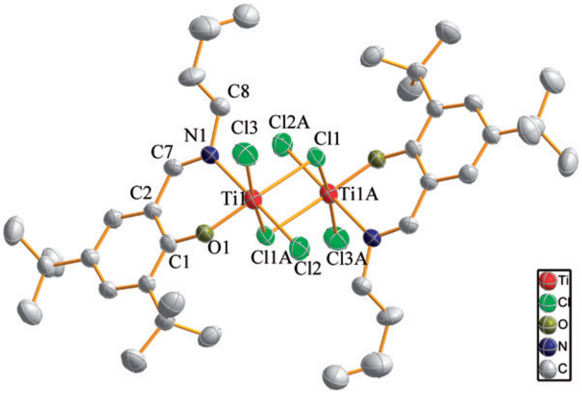

Figure 1. Structure of **2** (thermal ellipsoids are drawn at the 30% probability level). Hydrogen atoms are omitted for clarity.

Table 2. Selected bond lengths (Å) and angles (°) for **2**.

Ti(1)–O(1)	1.778(3)	Ti(1)–N(1)	2.172(4)
Ti(1)–Cl(1)	2.4409(16)	Ti(1)–Cl(1A)	2.5129(18)
Ti(1)–Cl(2)	2.3338(12)	Ti(1)–Cl(3)	2.2355(18)
N(1)–C(1)	1.284(6)	O(1)–Ti(1)–N(1)	83.11(14)
O(1)–Ti(1)–Cl(1)	160.62(12)	O(1)–Ti(1)–Cl(1A)	83.81(11)
O(1)–Ti(1)–Cl(2)	96.55(11)	O(1)–Ti(1)–Cl(3)	88.57(12)
N(1)–Ti(1)–Cl(1)	88.03(11)	N(1)–Ti(1)–Cl(1A)	84.20(11)
N(1)–Ti(1)–Cl(2)	175.57(12)	N(1)–Ti(1)–Cl(3)	88.57(12)

The wavenumber of the imine C=N is **3** > **1** > **2**. These results imply that ligand electronic effect has a significant influence on the chemical Schiff of the CH=N and frequency of the imine C=N stretch.

3.2. *Structure description*

Crystals of **2** suitable for single-crystal X-ray structure diffraction were grown by cooling saturated solution of **2** in mixed CH_2Cl_2/hexane (1 : 10 by volume). The ORTEP of the molecular structure is depicted in figure 1. Selected bond lengths and angles are summarized in table 2. Single-crystal X-ray analysis reveals that **2** is binuclear, with two bridging chlorides. The two titaniums are six-coordinate with octahedral geometry. Each titanium is bonded to four chlorides and the bidentate salicylaldiminate *via* oxygen and nitrogen. The bonding of the salicylaldiminate is common, and the bond lengths are very similar to those observed for $Ti\{3\text{-}Bu^t\text{-}2\text{-}(O)C_6H_3CH{=}NPh\}Cl_3(THF)$ and $[Ti\{3\text{-}Bu^t\text{-}2\text{-}(O)\text{-}C_6H_3CH{=}N\ (2,6\text{-}Pr^i{}_2C_6H_3)\}Cl(\mu\text{-}Cl)_3TiCl_3]$. The terminal Ti–Cl bond lengths ranging from 2.236 to 2.272 Å, and bridging Ti–Cl bond lengths (2.513 Å, 2.4409 Å) are longer than those of known Ti–Cl bond lengths in similar dimeric complexes [12, 13]. Although **1** and **3** were isolated as crystals, their quality was not suitable for single-crystal X-ray structure determination.

Table 3. Results of ethylene polymerization using precatalysts **1–3**[a].

Run	Catalyst	MAO : Catalyst	T (°C)	Yield (g)	Activity[b] $\times 10^{-6}$	M_w[c] $\times 10^4$	M_w/M_n[c]
1	**1**	500	25	0.60	0.72	17.8	1.8
2	**1**	1000	25	0.68	0.82	17.1	1.8
3	**1**	1500	25	0.65	0.78	16.6	1.9
4	**2**	500	25	0.46	0.55	18.2	1.9
5	**2**	1000	25	0.85	1.02	17.6	1.9
6	**2**	1500	25	0.74	0.93	14.2	2.0
7	**2**	1000	40	0.79	0.95	10.3	2.2
8	**2**	1000	60	0.65	0.78	9.6	2.4
9	**3**	500	25	0.38	0.46	14.1	2.1
10	**3**	1000	25	0.44	0.53	13.2	2.0
11	**3**	1500	25	0.40	0.48	13.6	2.1

[a] Polymerization conditions: solvent 60 mL of toluene, catalyst 5 μmol, ethylene pressure 5 bars, time 10 min.
[b] g PE (mol cat.)$^{-1}$ h^{-1}.
[c] Determined by GPC.

3.3. *Ethylene polymerization*

The ethylene polymerizations with **1**–**3** as precatalysts are summarized in table 3. Upon activation with MAO, **1**–**3** show good catalytic activity ($0.46–1.02 \times 10^6$ g PE (mol catalyst)$^{-1}$ h^{-1}) for ethylene polymerization. Catalytic activity increases with increases in MAO/catalyst ratio and reaches the highest catalyst activity at MAO/catalyst of 1000; further increasing the MAO/catalyst ratio results in a decrease in catalytic activities. Molecular weights of the polymer obtained gradually decreased with increasing MAO concentration, indicating that chain transfer to aluminum took place during polymerization. Influence of reaction temperature on ethylene reactivity was studied with the **2**/MAO system. Elevation of the reaction temperature from 25°C to 60°C resulted in a sharp decrease in polymerization activity and increase in molecular weight distribution, indicating that the system was unstable at higher temperature (entries 5, 7, and 8, table 3). The order of catalyst activity for ethylene polymerization under similar conditions (entries 2, 5, and 10, table 3) is $\mathbf{2} > \mathbf{1} > \mathbf{3}$, which implies that the remote electron-donating electronic effect also increased activity for the polymerization. The gel permeation chromatography (GPC) analysis reveals that the polyethylene obtained with **1–3** possesses relatively high molecular weight with unimodal molecular weight distribution ($M_w = 9.6–18.2 \times 10^4$, $M_w/M_n = 1.8–2.4$). A typical GPC diagram is shown in figure 2.

4. Conclusion

Three dimeric titanium complexes bearing salicylaldiminates have been synthesized and structurally characterized. They display good catalytic activity up to 1.02×10^6 g PE (mol catalyst)$^{-1}$ h^{-1} for ethylene polymerization upon treatment with MAO. The catalytic activity of these complexes and the molecular weight of the produced polyethylenes can be tuned by changing the substituents on the aryl ring. These new

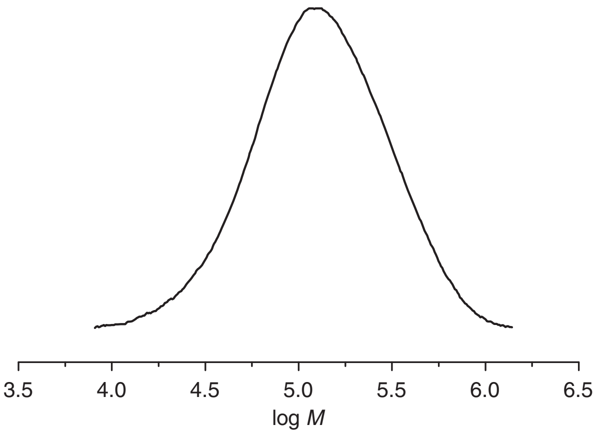

Figure 2. The GPC trace of the polypropylene sample prepared with **2** (run 5 in table 3).

catalysts represent an addition to the limited list of dimeric group 4 ethylene polymerization catalysts [16].

Supplementary material

CCDC 792936 contains the supplementary crystallographic data for **2**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.

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