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Novel titanium complexes bearing two chelating phenoxy-imine ligands and their catalytic performance for ethylene polymerization

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Three substituted salicylaldimine ligands (1a, 2a, 3a) and their titanium complexes bis[*N*-(5-nitrosalicylidene)-2,6-diisopropylanilinato]titanium(IV)dichloride (1), bis[*N*-(5-chlorosalicylidene)-2,6-diisopropylanilinato]titanium(IV)dichloride (2) and bis[*N*-(5-bromosalicylidene)-2,6-diisopropylanilinato]titanium(IV)dichloride (3) were synthesized and characterized by mass spectra, ^{1}H NMR and elemental analyses, as well as complex 1 by X-ray structure analysis. In the presence of methylaluminoxane (MAO), 1, 2 and 3 are efficient catalysts for ethylene polymerization in toluene. Under the conditions of $T = 60\,°C$, $p = 0.2$ MPa, and $n(\text{MAO})/n(\text{cat}) = 1500$, the activities of 1–3 reached $4.55–8.80 \times 10^6$ g of PE (mol of Ti h bar)$^{-1}$, which is much higher than that of the unsubstituted complex bis[*N*-(salicylidene)-2,6-diisopropylanilinato]titanium(IV)dichloride (4). The viscosity-average molecular weight of polyethylene ranged from 24.8×10^4 to 44.9×10^4 g/mol for 1–3 and the molecular weight distribution M_w/M_n from 1.85 to 2.34. The effects of reaction conditions on the polymerization were examined in detail. The increase in ethylene pressure and rise in polymerization temperature are favorable for 1–3/MAO to rise the catalytic activity and the molecular weight of polyethylene.

KEYWORDS: catalysts; ethylene polymerization; salicylaldimine; titanium complexes

INTRODUCTION

In the past decade, there have been many rapid advances in the catalysis of olefin polymerization by non-metallocence complexes, including the early and late transition metals.[1,2] Among them, organometallic complexes containing Schiff bases have been widely used and investigated with a vast array of metals. They are attractive ligands because of their ease of preparation and modification of both steric and/or electronic effects. In 1998, Wang *et al.*[3] reported the synthesis of several Ni(II) monosalicylaldiminato systems which are highly active for the polymerization of ethylene. The effect of various substitutents on the catalytic activity was investigated. Bulky substituents in 3-position of the salicylaldiminato ring were found to enhance the activity of the catalyst as well as an electron-withdrawing group in the 5-position, while a relatively electron-rich group in the 5-position decreases the catalytic activity. In 2002, Carlini *et al.*[4] first reported on the copolymerization of ethylene with methyl methacrylate (MMA) using coordination-type catalysts such as [5-nitro-*N*-(2,6-diisopropylphenyl)salicylaldiminato]nickel(II) and [3,5-dinitro-*N*-(2,6-diisopropylphenyl)salicylaldiminatenickel(II). When activated with MAO, these catalytic systems produce copolymers with a low content of MMA co-units (3–6 mol%) and a high viscosity-average molecular weight M_v of $10–30 \times 10^4$ E/MMA. Based on the concept of ligand-oriented catalyst design research, Fujita *et al.*[5–13] have studied

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well-defined titanium complexes featuring nonsymmetric fluorinated bis(phenoxy-imine) ligands for olefin polymerization catalysts and found that perfluorinated bis(phenoxy-imine) titanium complexes (perfluorinated Ti-FI catalysts[6–8]) can mediate highly controlled, thermally robust living polymerization of both ethylene and propylene. Recently, studies on the fluorinated Ti–FI catalysts have been actively pursued in both academic and industrial research centers. Although most fluorinated FI catalysts display very high polymerization activities under mild conditions, the material of primary amine with F or CF_3 groups is difficult to obtain commericially and the molecular weight distribution (MWD) of the produced polymers is very narrow. We now report on the polymerization of ethylene catalyzed by titanium complexes with an electron-withdrawing group in the 5-position of the non-fluorinated salicylaldiminato ring, producing polymers with different MWDs compared to that catalyzed by fluorinated FI catalysts.

EXPERIMENTAL

All manipulations involving air- or moisture-sensitive procedures were performed under an argon atmosphere with standard Schlenk techniques. All chemical reagents used were of analytical grade and were further purified as given in the literature. Toluene was freshly distilled under argon from purple sodium–benzophenone ketyl solutions. ^1H NMR and ^{13}C NMR spectra were recorded on a Bruker Avance 500 instrument. Electron impact mass spectra (EIMS) were measured on an HP 6890/5973 gas chromatography/mass spectrometry instrument (70 eV and 50–270 °C) and elemental analyses were conducted on a Perkin Elmer 240 elemental analyzer.

MAO (10% w/w toluene solution, Albemarle Co.) was used as received. Chemical pure grade ethylene was purified with a column of MnO and 4 Å molecular sieves.

Synthesis of (2-OH)(5-NO_2) $C_6H_3CH{=}N$-2,6-$C_6H_3{}^iPr_2$ (1a)

5-Nitrosalicylaldehyde (4.17 g, 25 mmol), formic acid (1 ml), and 2,6-diisopropylaniline (4.45 g, 25 mmol) were stirred in ethyl alcohol (50 ml) at 80 °C for 2 h. Upon cooling to 0 °C, a yellow solid precipitated from the reaction mixture. The solid was filtered, washed with cold ethyl alcohol, and then dried in vacuo to afford **1a** as a yellow solid.

Yield: 7.40 g (90.8%). ^1H NMR ($CDCl_3$, δ, ppm): 14.28 (s, 1H, OH), 8.39 (s, 1H, CH=N), 8.35 (d, $J = 2.7$ Hz, 1H, aryl), 8.31 (d, $J = 9.3$ Hz, 1H, aryl), 7.22 (brs, 3H, aryl), 7.15 (d, $J = 9.0$ Hz, 1H, aryl), 2.97 (sept, $J = 6.9$ Hz, 2H, i-C_3H_7), 1.20 (d, $J = 6.9$ Hz, 12H, i-C_3H_7). EIMS (70eV) m/z (%): 326 (83) $[M]^+$, 311 (75) $[M - CH_3]^+$, 269, 252, 188. ELEM. ANAL. Calcd for $C_{19}H_{22}N_2O_3$ (326.40 g/mol): C, 69.92%; H, 6.79%; N, 8.58%. Found: C, 70.00%; H, 6.70%; N, 8.50%.

Synthesis of (2-OH)(5-Cl)$C_6H_3CH{=}N$-2,6-$C_6H_3{}^iPr_2$ (2a)

In analogy to the synthesis of **1a**, 5-chlorsalicylaldehyde (3.91 g, 25 mmol), formic acid (1 ml), 2,6-diisopropylaniline (4.45 g, 25 mmol), and ethanol (50 ml) afforded **2a** as a yellow solid.

Yield: 7.64 g (91.3%). ^1H NMR ($CDCl_3$, δ, ppm): 13.29 (s, 1H, OH), 8.31 (s, 1H, CH=N), 7.49–7.55 (m, 2H, aryl), 7.24 (m, 3H, aryl), 6.71 (d, $J = 8.6$ Hz, 1H, aryl), 3.07 (sept, $J = 6.8$ Hz, 2H, i-C_3H_7), 1.20 (d, $J = 6.8$ Hz, 12H, i-C_3H_7). EIMS (70eV) m/z (%): 315 (90) $[M]^+$, 300 (86) $[M - CH3]^+$, 284, 272, 258, 243, 223, 204, 188. ELEM. ANAL. Calcd. for $C_{19}H_{22}ClNO$ (315.84 g/mol): C, 72.25%; H, 7.02%; N, 4.43%. Found: C, 72.26%; H, 7.30%; N, 4.41%.

Synthesis of (2-OH)(5-Br)$C_6H_3CH{=}N$-2,6-$C_6H_3{}^iPr_2$ (3a)

In analogy to the synthesis of **1a**, 5-bromosalicylaldehyde (5.03 g, 25 mmol), formic acid (1 ml), 2,6-diisopropylaniline (4.45 g, 25 mmol) and ethanol (50 ml) afforded **3a** as a yellow solid.

Yield: 8.35 g (92.5%). ^1H NMR ($CDCl_3$, δ, ppm): 13.25 (s, 1H,OH), 8.27 (s, 1H, CH=N), 7.46–7.59 (m, 2H, aryl), 7.20 (m, 3H, aryl), 6.96 (d, $J = 8.7$ Hz, 1H, aryl), 2.95 (sept, $J = 6.8$ Hz, 2H, i-C_3H_7), 1.19 (d, $J = 6.9$ Hz, 12H, i-C_3H_7). EIMS (70eV) m/z (%): 359 (96) $[M]^+$, 344 (92) $[M - CH_3]^+$, 302, 287, 223, 188. Elem. Anal. calcd for $C_{19}H_{22}BrNO$ (360.29 g/mol): C, 63.34%; H, 6.15%; N, 3.89%. Found: C, 63.27%; H, 6.40%; N, 3.85%.

Synthesis of [2-O-(5-R)$C_6H_3CH{=}N$-2,6-$C_6H_3{}^iPr_2]_2TiCl_2$ (R = NO_2 (1), Cl (2), Br (3))

To a stirred solution of **1a, 2a** or **3a** (10.0 mmol) in dried dichloromethane (40 ml) was added 0.48 g (20.0 mmol) NaH slowly over a 15 min period. The solution was stirred for 2 h at room temperature and then filtered. The resulting filtrate was added dropwise over a 30 min period to a stirred solution of $TiCl_4$ (0.95 g, 5.0 mmol) in dried dichloromethane (60 ml) at −78 °C. The mixture was allowed to warm to room temperature and stirred for another 18 h. The resulting mixture was concentrated in vacuo to give a solid, to which dried dichloromethane (60 ml) was added. After stirring for 30 min, the resulting mixture was filtered and the residue washed with dried dichloromethane. The combined organic filtrates were concentrated *in vacuo* to afford the crude complex which was washed with diethyl ether (10 ml) and hexane (30 ml) and dried *in vacuo.*

1: Reddish brown powder. Yield:2.23 g (58.1%). ^1H NMR ($CDCl_3$, δ, ppm): 8.30–8.37 (m, 2H, CH=N), 6.81–7.31 (m, 12H, aryl), 2.95–3.15 (m, 4H, i-C_3H_7), 1.16 (d, $J = 6.7$ Hz, 24H, i-C_3H_7). EIMS (70eV) m/z (%):770.0($[M]^+$, 10), 767.9, 696.2, 326.2, 296.2, 269.0, 223.0, 174.1, 162.1, 132.0, 91.0. Elem. Anal. calcd for $C_{52}H_{58}Cl_2N_4O_6Ti$ (953.82 g/mol): C, 65.48%; H, 6.13%; N, 5.87%. Found: C, 65.51%; H, 6.09%; N, 5.84%.

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2: Reddish brown powder. Yield: 1.48 g (39.7%). ^{1}H NMR ($CDCl_3$, δ, ppm): 7.64–8.17 (m, 2H, CH=N), 6.99–7.27 (m, 12H, aryl), 2.87–3.18 (m, 4H, *i*-C_3H_7), 1.06 (d, J = 6.7 Hz, 24H, *i*-C_3H_7). Elem. Anal. calcd for $C_{38}H_{42}Cl_4N_2O_2Ti$ (748.46 g/mol): C, 60.98%; H, 5.66%; N, 3.74%. Found: C, 60.73%; H, 5.68%; N, 3.75%.

3: Reddish brown powder. Yield: 1.47 g (35.1%). ^{1}H NMR ($CDCl_3$, δ, ppm): 7.75–8.08 (m, 2H, CH=N), 6.96–7.40 (m, 12H, aryl), 2.88–3.19 (m, 4H, *i*-C_3H_7), 1.09 (d, J = 6.8 Hz, 24H, *i*-C_3H_7). Elem. Anal. calcd for $C_{38}H_{42}Br_2Cl_2N_2O_2Ti$ (837.36 g/mol): C, 54.51%; H, 5.06%; N, 3.35%. Found: C, 54.57%; H, 5.10%; N, 3.36%.

X-ray structure determination of complex 1

The crystal data and details of data collection are given in Table 1. Intensity data were collected at 173 K on a Siemens Smart CCD diffractometer, using graphite monochromated Mo-K$_\alpha$ radiation, ω- and ψ-scan technique, $\lambda = 0.71073$ Å. The structure was solved by direct methods using SHELXS-97[14] and was refined on $F2$ using SHELXL-97.[15] All non-hydrogen atoms were refined anisotropically and the hydrogen atoms were placed in calculated positions and assigned to an isotropic displacement parameter of 0.08 Å^2. SADABS[16] was used to perform area-director scaling. The geometrical aspects of the structures were analyzed using the Diamond program.[17] CCDC-606 375 contains the supplementary crystallographic data. Copies of the data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html or on application to the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44 1223-336-033; email: deposit@ccdc.cam.ac.uk).

Polymerizations

The polymerizations were carried out in a 100 ml steel autoclave equipped with a mechanical stirrer. The container was thoroughly degassed and purged with ethylene for several cycles. The solvent, the mixture of the catalyst, and the MAO solution were added into the prefilled monomer container sequentially, and the system was kept under a certain pressure and temperature. After a given reaction time, the polymerization was quenched by the addition of ethanol containing 10% HCl. The polymerization mixture was poured into a large amount of ethanol containing 10% of HCl. The precipitated polymer was collected by filtration and washed with ethanol for several times and then dried *in vacuo* at 60 °C to a constant weight.

Molecular weight measurements

The intrinsic viscosity [η] of polyethylene in decahydronaphathrene was measured with an Ubbelohde viscometer at 135 ± 0.1 °C. The viscosity-averaged molecular weight (M_η) was calculated according to the equation[18] $[\eta] = 6.67 \times 10^{-4}\ M_\eta^{0.67}$. The weight-average molecular weight (M_v) and the molecular weight distributions of some polymers were determined by gel-permeation chromatography (GPC) on a Waters 150 ALC/GPC system in 1,2,4-trichlorobenzene solution at 135 °C, using polystyrene columns as a standard.

Table 1. Crystal data and structure refinement details for **1**

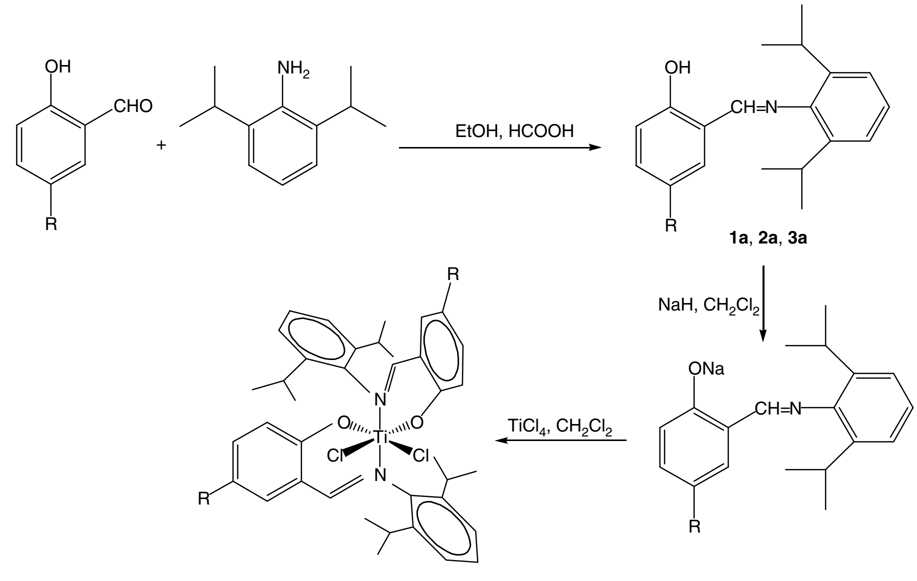
Parameter	Data
Formula	$C_{38}H_{42}Cl_2N_4O_6Ti{\bullet}2C_7H_8$
Formula weight (g/mol)	953.82
Crystal system	monoclinic
Space group	C_c (No. 9)
Unit cell dimensions (Å, deg)	$a = 8.7158(3), \alpha = 90$ $b = 24.7830(8)$, $\beta = 100.274(1)$ $c = 23.4767(7), \gamma = 90$
Volume (Å^3)	49 897.7(3)
Z	4
Calculated density (mg/m^3)	1.270
Absorption coefficient (mm^{-1})	0.331
F(000)	2008
Crystal size (mm^3)	0.36 × 0.32 × 0.18
θ range for data collection (deg)	1.64–27.00
Index ranges	$-11 \leq h \leq 11$ $-31 \leq k \leq 28$ $-27 \leq l \leq 29$
Reflections collected	18 523
Independent reflections	9792 [R(int) = 0.0802]
Maximum and minimum transmission	0.956483 and 0.731838
Data/restraints/parameters	9792/2/596
Goodness-of-fit on F^2	1.023
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0662$ $wR_2 = 0.1818$
R indices (all data)	$R_1 = 0.1132$ $wR_2 = 0.2202$
Largest difference peak and hole (e × Å^{-3})	0.341 and −0.386

Melting points

The melting point temperatures (T_m) of PE were recorded with a Perkin Elmer DSC-7 differential scanning calorimeter from 50 to 200 °C at a heating rate of 10 °C/min.

RESULTS AND DISCUSSION

The salicylaldimine ligands **1a, 2a** and **3a** were easily prepared by simple condensation of the appropriate substituted salicylaldehydes with 2,6-diisopropylaniline in excellent yields. They react with sodium hydride in tetrahydrofuran yielding the corresponding sodium salts, which react with $TiCl_4$ forming the titanium complexes **1, 2** and **3** as reddish brown solids (Scheme 1).



1 ($R = NO_2$), **2** ($R = Cl$), **3** ($R = Br$)

Scheme 1. Synthetic route to titanium complexes **1–3**.

Single crystals of **1**, containg two molecules of toluene per titanium complex, suitable for X-ray diffraction, were obtained by recrystallization from toluene. The molecular structure is shown in Fig. 1. The coordination geometry around the titanium center is distorted tetragonal bipyramidal TiL_2Cl_2 with the nitrogen atoms N(3) and N(1) in the apical positions and the two oxygen atoms O(4) and O(1) as well as the two chlorine atoms Cl(1) and Cl(2) *cis* to each other in equatorial positions. The N(1)–Ti–N(3) angle is slightly reduced to 174.17(19)°, the Ti–Cl, Ti–N and Ti–O bond lengths of 2.29, 2.20/2.23, and 1.86/1.87 Å, respectively, fall in the expected regions.

Polymerization of ethylene with complexes 1,2 and 3

Complexes **1, 2** and **3** have been studied as catalysts in combination with MAO for ethylene polymerization. In order to understand the effects of experimental parameters on the polymerization as well as possible, variations in temperature, monomer pressure and the molar ratio of MAO/Cat were examined in detail.

Table 2 illustrates the influence of the polymerization temperature on activity and polymer molecular weight. Our results show that 60 °C is the optimum polymerization temperature for complexes **1–3** from the aspect of activity of the catalytic system. Temperatures in the range of 25–60 °C are favorable for reaching a high catalytic activity in the range 25–60 °C. However, above 60 °C, the activities of the catalysts become lower with increasing temperature. This may result from the deactivation process due to the poor thermal stability of the cationic active center. Table 2 shows also that the molecular weight of the polymers also depends upon the polymerization temperature. A competition between the termination and propagation steps determines the molecular weight of the polymer. Higher temperatures increase the rate of β-hydride chain transfer which is over the propagation rate and affords a polymer with lower molecular weight.

Table 2. Effect of reaction temperature on ethylene polymerization for complex **1–4–** MAO[a]

Entry	Complex	Temperature (°C)	Yield of PE(g)	Activity [g PE(mmol cat h/bar)]	M_v ($\times 10^{-4}$ g/mol)
1	**3**	25	0.40	180	44.9
2	**3**	50	0.60	274	39.7
3	**3**	60	1.00	455	32.4
4	**3**	75	0.51	233	28.6
5	**2**	25	0.71	324	33.8
6	**2**	50	1.16	525	28.2
7	**2**	60	1.63	732	22.8
8	**2**	75	0.67	306	15.5
9	**1**	25	0.70	318	24.8
10	**1**	50	1.09	494	18.9
11	**1**	60	1.94	880	11.3
12	**1**	75	0.79	357	8.6
13[b]	**4**	60	0.56	13	—

[a] Conditions: pressure, 0.2 MPa; $n_{Al}/n_{Ti} = 1500$; time, 30 min for complexes **1–3** and 1 h for complex **4**; catalyst, 2.2 µmol for complexes **1–3** and 22 µmol for complex **4**; solvent, 30 ml toluene for **1–3** and 300 ml toluene for complex **4** {bis[*N*-(2, 6-diisopropylphenyl)-salicylaldiminato]$TiCl_2$}.[20]

Using the same conditions, the polymerization activities (entries 3, 7, 11, 13) show the following results: (1) the catalytic

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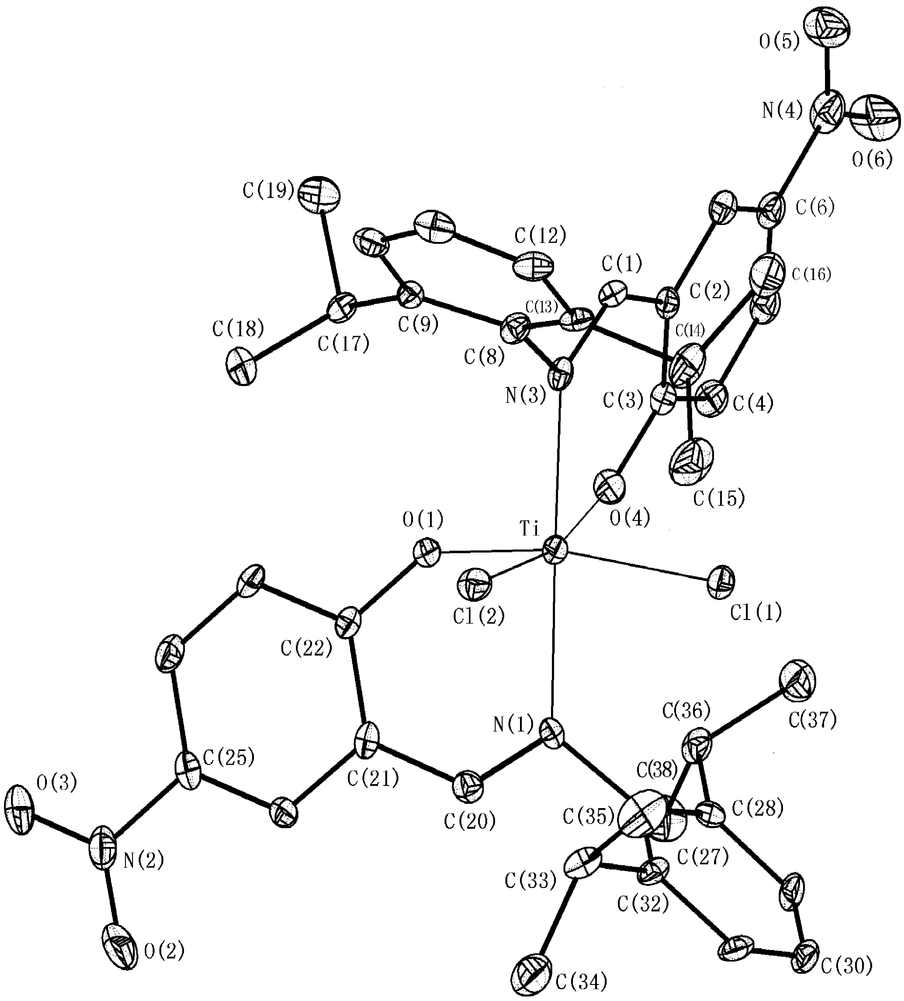

Figure 1. ORTEP[19] diagram of the structure of **1** in the crystal. The hydrogen atoms are omitted. Selected bond lengths (Å) and angles (deg): Ti–O(2) 1.866(4), Ti–O(4) 1.876(5), Ti Cl(1) 2.2943 (19), Ti–Cl(2) 2.2922(19), Ti–N(1) 2.2365(5), Ti–N(3) 2.207(5), Cl(1)–Ti–Cl(2) 96.18(7), N(1)–Ti–O(1) 82.49(18), N(3)–Ti–O(4) 82.08(19), N(1)–Ti–N(3) 174.17(19).

activities of **1–3** are much lower than that of fluorinated FI catalysts, especially perfluorinated FI catalysts, but much higher than that of complex **4**,[20] which has no substituent in the 5-position of the salicylaldiminato ring; and (2) containing the strongest electron-withdrawing group among all three complexes, complex **1** has the highest activity. A possible explanation[3,9] for this increasing activity is the introduction of an electron-withdrawing group such as nitro or halogen, creating a more electrophilic titanium center which causes an increase in metal–carbon reactivity.

The influence of the reaction pressure and the MAO/catalyst molar ratio on ethylene polymerization for complexes **1–3** is shown in Figs 2 and 3, respectively.

Figure 2 shows that with increasing ethylene pressure the coordination and insertion of ethylene becomes more favorable. Both the catalytic activity and the molecular weight of the polymer are significantly promoted under the examined increasing pressure. Figure 3 demonstrates an increasing catalytic activity of the catalysts with increasing MAO/Cat molar ratio up to 2000. A high MAO/Cat molar ratio is necessary for eliminating all kinds of impurities existing in the polymerization medium, generating the active species. The molecular weight of the polymers obtained by catalysts **1–3** decreases significantly with a MAO/Cat molar ratio of up to 1500.

The molecular weight and molecular weight distributions (M_w/M_n) of some polymers are measured by gel permeation

Table 3. Characteristics of PE, resulting from GPC[a] and DSC investigations

Entry	Complex	M_w[b]	M_v[b]	M_n[b]	M_p[b]	PDI	M.P.[c]
1	**3**	48.7	44.6	26.4	36.7	1.85	134
5	**2**	37.2	3.37	17.0	31.7	2.18	133
9	**1**	25.4	23.9	10.8	15.8	2.34	132

[a] Conditions: temperature, 25 °C; pressure, 0.2 MPa; $n_{Al}/n_{Ti} = 1500$; time, 30 min; solvent: toluene (30 ml).
[b] in $\times 10^4$ g/mol.
[c] M.P., melting point determined by DSC.

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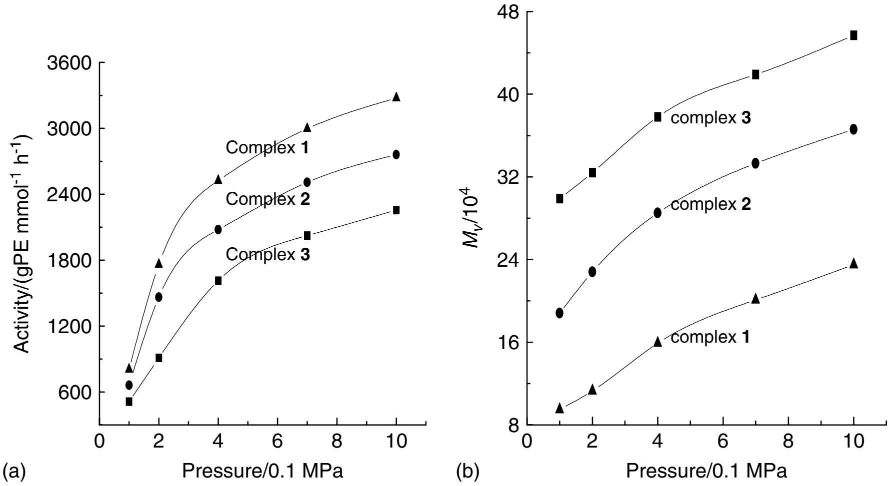

Figure 2. Influence of the polymerization pressure on the activity and M_η (polymerization conditions: 60 °C, 30 min, 2.2 μmol of **1, 2** or **3**, Al/Ti = 1500, 30 ml of toluene).

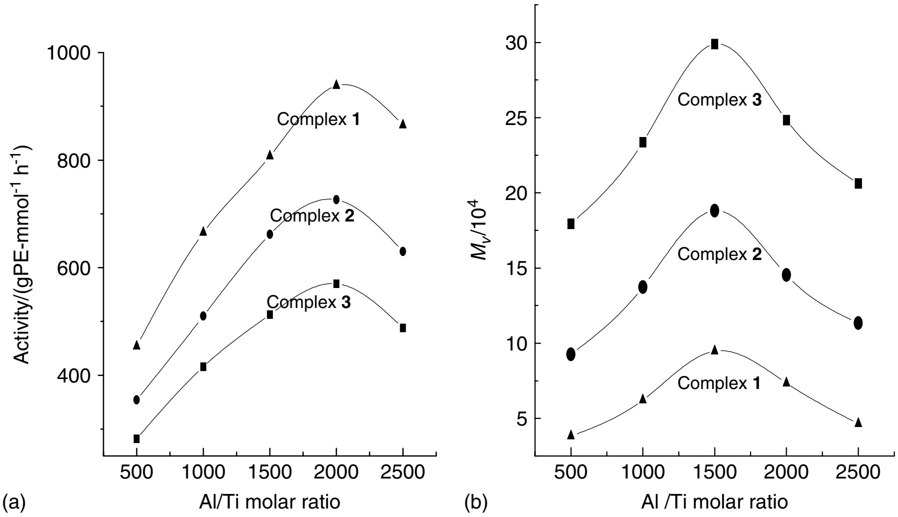

Figure 3. Influence of the MAO/catalyst molar ratio on the activity and M_η (polymerization conditions: 60 °C, 0.1 × 10^5 Pa, 30 min, 2.2 μmol **1, 2** or **3**, 30 ml of toluene).

chromatography (GPC). The results are shown in Table 3 and Fig. 4. All melting points of PE are higher than 132 °C, which indicates that the polyethylene produced by complex **1** is highly linear and highly crystalline.[21]

CONCLUSIONS

The titanium complexes **1, 2** and **3** with an electron-withdrawing group in the 5-position of the non-fluorinated salicylaldiminato ring have been synthesized and the structure of complex **1** was determined by X-ray structure analysis. Complexes **1–3** are active catalysts for ethylene polymerization in the presence of MAO. Although the

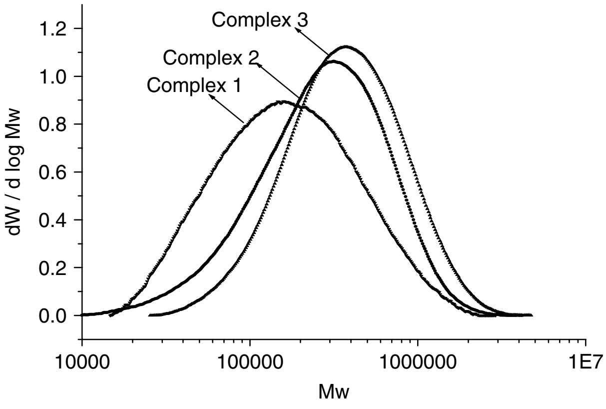

Figure 4. GPC profiles for PE obtained by **1, 2** and **3**.

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catalytic activities of **1–3** are lower than those of fluorinated FI catalysts, they are much higher than that of complex **4** with no substituent in the 5-position of the salicylaldiminato ring. The molecular weight distribution of polyethylene produced by **1–3** is broader (MWD = 1.85–2.34) than that obtained by fluorinated FI catalysts. High melting points indicate a high linearity and high crystallinity of the resulting polyethylene.

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