

Syntheses of Some New Group 4 non-Cp Complexes Bearing Schiff-base, Thiophene Diamide Ligands Respectively and Their Catalytic Activities for α -Olefin Polymerization

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Totally sixteen new titanium and zirconium non-Cp complexes supported by Schiff-base, or thiophene diamide ligands have been synthesized. The complexes are obtained by the reaction of $M(\text{OPr-}i)_4$ ($M=\text{Ti, Zr}$) with the corresponding Schiff-base ligand in 1 : 1 molar ratio in good yield. The thiophene diamide titanium complex has been prepared from trimethylsilyl amine [N,S,N] ligand and TiCl_4 in toluene at 120 °C. All complexes are well characterized by ^1H NMR, IR, MS and elemental analysis. When activated by excess methylaluminoxane (MAO), complexes show moderate catalytic activity for ethylene polymerization, and complex **1f** ($\text{R}^1=\text{CH}_3$, $\text{R}^2=\text{Br}$) exhibits the highest activity for ethylene and styrene polymerization. When the complexes were preactivated by triethylaluminum (TEA), both polymerization activities and syndiotacticity of the polymers were greatly improved.

Keywords titanium or zirconium, non-Cp complex, TEA, polymerization structure

Introduction

Tremendous advances have been witnessed during the last decade in the syntheses and application of Group 4 metal complexes because of the motivity which comes from both academic and industrial field. Among them, studies have been dominated by the complexes supported by bis or mono cyclopentadienyl ligands, such as Cp_2MX_2 or half sandwich amide (CGC) complexes.¹⁻⁶ At that time chemists paid a little attention to the non-cyclopentadienyl complexes, but in recent years, many chemists have changed their views from the Cp field to the non-Cp field.⁷⁻¹¹

The development of Cp complexes is very sophisticated and countless patents have almost involved the whole Cp field.¹²⁻¹⁴ However, another branch of non-Cp complexes can be supported by many kinds of ancillary ligands. The most important finding of non-Cp complexes was reported by McConville *et al.*¹⁵ that propylene-bridged aryl substituted diamido Group 4 complexes promote the living polymerization of α -olefin. And more recently, Fujita and his co-workers¹⁶⁻¹⁹ found that the Group 4 complexes with bidentate salicylaldehyde chelate ligands show extremely high activity in ethylene polymerization.

To our interest, it would be a challenging and promising work in the effort to develop new kinds of non-Cp catalysts of Group 4 metal, and further study their cata-

lytic activities for olefins, such as ethylene, styrene and methyl methacrylate (MMA), and we have synthesized a series of such complexes and studied their catalytic activities. As in the previous communications,^{20,21} we have reported a part of the results, here we present the full details.

Experimental

Chemical reagents and methods

All operations were carried out under a dry argon atmosphere using standard Schlenk techniques. Toluene, diethyl ether, tetrahydrofuran (THF) and hexane were refluxed over sodium/benzophenone ketyl, from which they were distilled prior to use. Polymerization-grade ethylene was purified by Et_3Al before use. Styrene was dried by CaH_2 , then distilled under reduced pressure and stored at -20 °C in darkness. Schiff-base ligands **a—j**,²² $\text{Ti}(\text{OPr-}i)_4$ and $\text{Zr}(\text{OPr-}i)_4 \cdot \text{HOPr-}i$ ²³ 2,5-bis-(dimethylchlorosilyl)thiophene^{24,25} were prepared as described in the literatures. The cocatalyst methylaluminoxane (10%) (MAO) in toluene was purchased from Witco GmbH.

IR spectra were recorded on a Nicolet Magna-IR 550, or a Nicolet 55XC spectrometer as KBr disks. Elemental analyses were carried out on an EA-1106 type analyzer. ^1H NMR, ^{13}C NMR were recorded on a Bruker AM-300 MHz or a Bruker AVANCE-500 MHz

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spectrometer with TMS as internal standard and MS spectra on an HP 5989A instrument.

Synthesis of **1a** ($R^1=H$, $R^2=H$)

To a solution of Schiff-base ligand **a** (1.08 g, 3.4 mmol) in 30 mL of toluene was added dropwise $Ti(OPr-i)_4$ (0.97 g, 3.4 mmol) in 15 mL of toluene at 50 °C within 0.5 h. The mixture was stirred overnight. The solvent was removed *in vacuo* and the residue was recrystallized by toluene. The yellow-green crystal (1.25 g) was obtained in 76% yield. 1H NMR ($CDCl_3$, 300 MHz) δ : 7.26–6.71 (m, 11H), 6.27 (s, 1H), 6.25 (s, 1H), 5.35–5.36 (m, 1H), 4.75–4.77 (m, $J=6.3$ Hz, 2H), 1.17 (d, $J=6.3$ Hz, 12H); IR (KBr) ν : 3050, 3029, 2955, 2924, 2869, 1620, 1598, 1570, 1450, 1430, 1423, 1296, 1190, 1059, 1027, 990, 815 cm^{-1} ; MS (70 eV) m/z (%): 328 ($M^+ - C_6H_5O - OPr-i$, 100). Anal. calcd for $C_{26}H_{28}N_2O_4Ti$: C 65.00, H 5.89, N 5.83; found C 64.92, H 5.82, N 5.41.

Synthesis of **1b** ($R^1=H$, $R^2=OCH_3$)

It was made in the same way as **1a** from ligand **b** and $Ti(OPr-i)_4$. A yellow-green solid was obtained, after recrystallization with toluene, an analytical sample was gained, yield 82%. 1H NMR ($CDCl_3$, 300 MHz) δ : 7.32–6.79 (m, 9H), 6.28 (s, 1H), 6.25 (s, 1H), 5.40 (s, 1H), 4.81–4.83 (m, $J=6.3$ Hz, 2H), 3.83 (s, 6H), 1.22 (d, $J=6.3$ Hz, 12H); IR (KBr) ν : 3028, 2963, 2929, 2859, 1623, 1589, 1548, 1476, 1442, 1378, 1358, 1299, 1160, 1039, 991, 868, 828, 774, 742 cm^{-1} ; MS (70 eV) m/z (%): 540 (M^+ , 2), 108 ($Ti-OPr^+-i+1$, 100). Anal. calcd for $C_{28}H_{32}N_2O_6Ti$: C 62.22, H 5.98, N 5.18; found C 61.59, H 5.69, N 5.36.

Synthesis of **1c** ($R^1=H$, $R^2=Br$)

It was made in the same way as **1a** from ligand **c** and $Ti(OPr-i)_4$. A yellow-green solid was obtained in 75% yield. 1H NMR ($CDCl_3$, 500 MHz) δ : 7.52–6.87 (m, 9H), 6.22 (s, 1H), 6.19 (s, 1H), 5.35–5.36 (m, 1H), 4.84–4.85 (m, $J=6.0$ Hz, 2H), 1.25 (d, $J=6.0$ Hz, 12H); IR (KBr) ν : 3053, 3024, 2965, 2924, 2861, 1614, 1589, 1532, 1461, 1374, 1305, 1190, 1161, 1127, 1075, 990, 866, 849, 821, 795 cm^{-1} ; MS (70 eV) m/z (%): 43 (Pr^+-i , 43). Anal. calcd for $C_{26}H_{26}N_2O_4Br_2Ti$: C 48.93, H 4.11, N 4.39; found C 48.56, H 3.99, N 4.41.

Synthesis of **1d** ($R^1=H$, $R^2=Bu-t$)

Complex **1d** was synthesized by using the same procedure as **1a**. Color, yellowish; yield 77%. 1H NMR ($CDCl_3$, 300 MHz) δ : 7.40–7.00 (m, 9H), 6.21 (s, 1H), 6.18 (s, 1H), 5.15–5.05 (m, 1H), 4.75–4.60 (m, 2H), 1.65–1.15 (m, 30H); IR (KBr) ν : 3061, 3027, 2962, 2930, 2902, 2863, 1618, 1586, 1544, 1478, 1373, 1361, 1306, 1184, 1125, 997, 982, 844, 793, 745 cm^{-1} ; MS (70 eV) m/z (%): 43 (Pr^+-i , 100). Anal. calcd for $C_{34}H_{44}N_2O_4Ti$: C 68.90, H 7.50, N 4.72; found C 68.49, H 7.60, N 5.13.

Synthesis of **1e** ($R^1=CH_3$, $R^2=H$)

Complex **1e** was synthesized by using the same procedure as for **1a**. Color, yellowish; yield 72%. 1H NMR ($CDCl_3$, 300 MHz) δ : 7.28–6.91 (m, 10H), 6.30–6.08 (m, 2H), 5.40–5.21 (m, 1H), 4.77–4.72 (m, 2H), 2.28–2.29 (m, 3H), 1.26–1.03 (m, 12H); IR (KBr) ν : 3049, 3028, 2965, 2925, 2858, 1614, 1546, 1471, 1447, 1384, 1339, 1311, 1162, 1123, 1030, 996, 866, 822, 754 cm^{-1} . Anal. calcd for $C_{27}H_{30}N_2O_4Ti$: C 65.58, H 6.13, N 5.66; found C 65.30, H 6.21, N 5.80.

Synthesis of **1f** ($R^1=CH_3$, $R^2=Br$)

Complex **1f** was synthesized by using the same procedure as **1a**. Color, yellowish; yield 80%. 1H NMR ($CDCl_3$, 300 MHz) δ : 7.60–6.50 (m, 8H), 6.20–6.00 (m, 2H), 5.10–5.00 (m, 1H), 4.80–4.60 (m, 2H), 2.27–2.28 (m, 3H), 1.25–0.95 (m, 12H); IR (KBr) ν : 3023, 3029, 2967, 2926, 2862, 1618, 1577, 1494, 1461, 1374, 1362, 1328, 1304, 1162, 1131, 1110, 985, 866, 823, 778, 722 cm^{-1} ; MS (70 eV) m/z (%): 43 (Pr^+-i , 100). Anal. calcd for $C_{27}H_{28}N_2O_4Br_2Ti$: C 49.72, H 4.33, N 4.29; found C 50.08, H 4.64, N 4.37.

Synthesis of **1g** ($R^1=CH_3$, $R^2=OCH_3$)

Complex **1g** was synthesized by using the same procedure as for **1a**. Color, yellow; yield 82%. 1H NMR ($CDCl_3$, 300 MHz) δ : 7.15–6.60 (m, 8H), 6.18–6.05 (m, 2H), 5.15–5.10 (m, 1H), 4.80–4.60 (m, 2H), 3.79–3.80 (m, 6H), 2.37–2.15 (m, 3H), 1.20–0.98 (m, 12H); IR (KBr) ν : 3052, 3029, 2955, 2925, 2869, 1620, 1580, 1400, 1430, 1423, 1296, 1190, 1058, 1028, 989, 815 cm^{-1} ; MS (70 eV) m/z (%): 91 ($C_6H_5O^+$, 100). Anal. calcd for $C_{29}H_{34}N_2O_6Ti$: C 62.81, H 6.19, N 5.05; found C 62.53, H 6.05, N 5.16.

Synthesis of **1h** ($R^1=H$, $R^2=CH_3$)

Complex **1h** was synthesized by using the same procedure as **1a**. Color, yellow-green; yield 79%. 1H NMR ($CDCl_3$, 500 MHz) δ : 7.26–6.86 (m, 9H), 6.21 (s, 1H), 6.18 (s, 1H), 5.40 (s, 1H), 4.76–4.78 (m, $J=6.1$ Hz, 2H), 2.33 (s, 6H), 1.18 (d, $J=6.1$ Hz, 12H); IR (KBr) ν : 2965, 2922, 2859, 1620, 1588, 1546, 1476, 1378, 1308, 1161, 1129, 991, 966, 828, 775 cm^{-1} ; MS (70 eV) m/z (%): 43 (Pr^+-i , 100). Anal. calcd for $C_{28}H_{32}N_2O_4Ti$: C 66.13, H 6.36, N 5.51; found C 65.88, H 6.25, N 5.80.

Synthesis of **1i** ($R^1=H$, $R^2=Cl$)

Complex **1i** was synthesized by using the same procedure as **1a**. Color, yellow-green; yield 82%. 1H NMR ($CDCl_3$, 500 MHz) δ : 7.27–6.80 (m, 9H), 6.22 (s, 1H), 6.19 (s, 1H), 5.28 (s, 1H), 4.77–4.78 (m, 2H), 1.12–1.18 (m, 12H); IR (KBr) ν : 2967, 2926, 2861, 1620, 1589, 1536, 1376, 1307, 1127, 1001, 964, 806, 805, 734 cm^{-1} ; MS (70 eV) m/z (%): 43 (Pr^+-i , 100). Anal. calcd for $C_{26}H_{26}N_2O_4Cl_2Ti$: C 56.85, H 4.78, N 5.10; found C 56.66, H 4.67, N 5.37.

Synthesis of 1j

To a 100 mL Schlenk bottle, ligand **j** (1.07 g, 5 mmol) and 30 mL of toluene was added. Ti(OPr-*i*)₄ (1.42 g, 5 mmol) in 20 mL of toluene was added dropwise during 0.5 h at room temperature. The mixture was stirred overnight at 80 °C (oil bath). A red solid was formed, and then filtered, the residue was further washed by toluene 30 mL × 2 and dried *in vacuo*, the analytical product (1.08 g) was obtained in 92% yield. ¹H NMR (CDCl₃, 500 MHz) δ: 9.46 (s, 2H), 7.86–6.36 (m, 16H); IR (KBr) ν: 3013, 2922, 2852, 1605, 1583, 1574, 1544, 1478, 1377, 1297, 1280, 1232, 966, 926, 847, 799 cm⁻¹; MS (70 eV) *m/z* (%): 469 (M⁺, 100). Anal. calcd for C₂₆H₁₈N₂O₄Ti: C 66.39, H 3.86, N 5.95; found C 65.70, H 4.02, N 5.82.

Synthesis of 2a (R¹=H, R²=H)

Ligand **a** (0.74 g, 2.3 mmol), 30 mL of toluene were placed into a flask, and then Zr(OPr-*i*)₄•HOPr-*i* (0.88 g, 2.3 mmol) dissolved in 15 mL toluene was added dropwise to it during 0.5 h at 50 °C. The mixture was stirred overnight, then the solvent was removed *in vacuo*, and recrystallized by hot hexane to give a white solid in 26% yield (0.31 g). IR (KBr) ν: 3026, 2963, 2926, 2857, 1610, 1587, 1546, 1470, 1446, 1390, 1209, 1140, 1016, 865 cm⁻¹; MS (70 eV) *m/z* (%): 43 (Pr⁺-*i*, 100), 149 (ZrOPr⁺-*i*, 29). Anal. calcd for C₂₆H₂₈N₂O₄Zr: C 59.62, H 5.40, N 5.35; found C 59.27, H 5.24, N 5.49.

Synthesis of 2b (R¹=H, R²=OCH₃)

By using the same procedure of complex **2a**, ligand **b** (0.83 g, 2.2 mmol) and Zr(OPr-*i*)₄•HOPr-*i* (0.85 g, 2.2 mmol) gave **2b** as a white powder in 25% yield (0.32 g). IR (KBr) ν: 3027, 2961, 2924, 2834, 1622, 1587, 1547, 1478, 1382, 1302, 1269, 1136, 1059, 1038, 954, 826 cm⁻¹; MS (70 eV) *m/z* (%): 43 (Pr⁺-*i*, 93). Anal. calcd for C₂₈H₃₂N₂O₆Zr: C 57.60, H 5.54, N 4.80; found C 57.29, H 5.31, N 5.00.

Synthesis of 2c (R¹=H, R²=Br)

By using the same procedure of complex **2a**, ligand **c** (0.83 g, 1.8 mmol) and Zr(OPr-*i*)₄•HOPr-*i* (0.68 g, 1.8 mmol) gave **2c** as a white powder in 28% yield (0.34 g). IR (KBr) ν: 3029, 2955, 2924, 2869, 1613, 1589, 1570, 1430, 1423, 1409, 1296, 1190, 1059, 1027, 990, 815 cm⁻¹; MS (70 eV) *m/z* (%): 679 (M⁺+1, 9), 43 (Pr⁺-*i*, 78). Anal. calcd for C₂₆H₂₆N₂O₄Br₂Zr: C 45.82, H 3.84, N 4.11; found C 45.36, H 3.54, N 4.30.

Synthesis of 2d (R¹=H, R²=Bu-*t*)

By using the same procedure of complex **2a**, ligand **d** (0.88 g, 2.1 mmol) and Zr(OPr-*i*)₄•HOPr-*i* (0.80 g, 2.1 mmol) gave **2d** as a white powder in 83% yield (1.08 g). IR (KBr) ν: 3029, 2962, 2924, 2857, 1610, 1546, 1471, 1446, 1311, 1003, 963, 916, 865, 845, 822 cm⁻¹; MS (70 eV) *m/z* (%): 43 (Pr⁺-*i*, 100), 149 (ZrOPr⁺-*i*, 25). Anal. calcd for C₃₄H₄₄N₂O₄Zr: C 64.21, H 6.97, N 4.40; found C 64.00, H 6.87, N 4.60.

Synthesis of 2e (R¹=CH₃, R²=H)

By using the same procedure of complex **2a**, ligand **e** (0.65 g, 2.0 mmol) and Zr(OPr-*i*)₄•HOPr-*i* (0.77 g, 2.0 mmol) gave **2e** as a white powder in 25% yield (0.26 g). IR (KBr) ν: 3029, 2960, 2903, 2859, 1617, 1583, 1543, 1479, 1379, 1362, 1310, 1261, 1164, 1142, 1015, 965, 842 cm⁻¹; MS (70 eV) *m/z* (%): 43 (Pr⁺-*i*, 100), 149 (ZrOPr⁺-*i*, 43). Anal. calcd for C₂₇H₃₀N₂O₄Zr: C 60.29, H 5.63, N 5.21; found C 59.75, H 5.30, N 5.43.

Synthesis of 1k

A solution of LiNAr'(SiMe₃) (Ar'=2,6-diisopropylphenyl) (1.33 g, 5.2 mmol) in 50 mL of DME was added slowly to a solution of 2,5-bis(dimethylchlorosilyl)thiophene (0.70 g, 2.6 mmol) in 20 mL of DME at -30 °C. The mixture was allowed to warm to room temperature and stirred overnight. The solvent was removed *in vacuo* and the residue was extracted with hexane 10 mL × 3. The solvent was reduced to 5 mL and stored at -20 °C for 5 h to obtain ligand **k** as a white solid (0.98 g, yield 54%). ¹H NMR (CDCl₃, 500 MHz) δ: 7.51 (s, 2H), 7.28–7.06 (m, 6H), 3.57–3.59 (m, *J*=6.59 Hz, 4H), 1.27 (d, *J*=6.59 Hz, 12H), 1.18 (d, *J*=6.59 Hz, 12H), 0.34 (s, 12H), 0.01 (s, 18H); MS (70 eV) *m/z* (%): 694 (M⁺, 0.2). Anal. calcd for C₃₈H₆₆N₂SSi₄: C 65.63, H 9.59, N 4.03; found C 65.38, H 9.64, N 4.36.

A solution of ligand **k** (0.38 g, 0.54 mmol) in 50 mL of toluene was cooled to 0 °C, to this solution was added slowly 0.52 mL of a toluene solution of TiCl₄ (1.04 mol·L⁻¹, 0.54 mmol) at -78 °C, then it was warmed to room temperature and heated to 120 °C for 12 h. The solution turned to black red, then the solvent was removed *in vacuo*. The residue was washed by hexane 10 mL × 3 and recrystallized by CH₂Cl₂ to afford a red dark solid **1k** (0.17 g) in 46% yield. ¹H NMR (CDCl₃, 500 MHz) δ: 7.25–7.08 (m, 6H), 7.45 (s, 2H), 3.60–6.61 (m, 4H), 1.25–1.27 (m, 12H), 1.18–1.20 (m, 12H), 0.71 (s, 12H); IR (KBr) ν: 2964, 2928, 2870, 2565, 1614, 1516, 1464, 1445, 1414, 1366, 1260, 1088, 1058, 1017, 903, 800, 751 cm⁻¹; MS (70 eV) *m/z* (%): 45 (SiMe⁺+2, 100), 42 (SiN⁺, 26). Anal. calcd for C₃₂H₄₈N₂SSi₂TiCl₂: C 57.55, H 7.26, N 4.19; found C 57.38, H 7.64, N 4.36.

Ethylene polymerization

A 100 mL flask equipped with an ethylene inlet, magnetic stirrer and vacuum line, was filled with various proportions of toluene. MAO was added, and the flask was placed in a bath at the desired polymerization temperature for 10 min. The polymerization reaction was started by adding the catalyst precursor. The polymerization was carried out for 0.5 h and then quenched with 3% HCl in ethanol (100 mL). The precipitated polymer was filtered and then dried overnight in a vacuum oven at 80 °C.

Styrene polymerization

A small ampule bottle was used for polymerization.

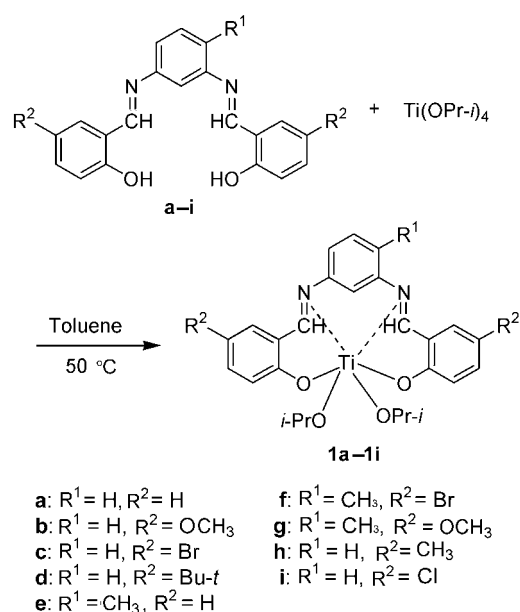
Styrene (2 or 11 mL), various proportions of toluene, MAO, and various proportions of Ti compound (or pre-activated by TEA) in toluene were injected into the bottle in that order under an argon atmosphere. The bottle was put into an oil bath at the desired temperature for the selected time. The polymerization mixture was quenched with 10% HCl in ethanol, filtered, washed, and dried in a vacuum oven at 80 °C for 24 h to a constant weight. The polymer was then extracted with 2-butanone for 2 h to remove any atactic polymer. The syndiotactic polymer was obtained as the amount of polymer insoluble in 2-butanone. Melting points were determined by differential scanning calorimetry (DSC). The thermograms were recorded with a TA Instrument DSC 2910 Modulated DSC Universal V1.10B apparatus.

Results and discussion

Tetradentate Schiff-base titanium complexes

Schiff-base ligands **a—i** were prepared from the reaction of *m*-phenylene diamine and appropriate salicylaldehyde derivatives using a standard condensation protocol.²² Complexes **1a—1i** were readily synthesized in high yields by reaction of Ti(OPr-*i*)₄ with the appropriate ligands **a—i** as follows in Scheme 1.

Scheme 1



The complexes are well characterized by elemental analysis, IR, MS and ¹H NMR spectroscopy. In the IR spectra of complexes, the bands of C=N (about 1600 cm⁻¹ in the ligand) are shifted to higher frequencies around 1620 cm⁻¹ due to the coordination between azomethine nitrogen and the central metal.

We are also surprised by the ¹H NMR spectroscopy of complexes **1a—1i**, just as one typical complex **1i** showed in Figure 1, three hydrogen atoms of complex **1i** are greatly shifted to the high field by δ 1.6 for H_c and

2.5 for H_d compared with those of the ligand. Usually when ligand coordinates to the central metal, the peaks of ¹H NMR will slightly shift to the low field. It can be successfully explained by the π-electron cycle system of aromatic compound, as given in Figure 2, to [18]-annulene, H_f: δ 9.28 and H_g: δ -2.99. The Schiff-base titanium complex **1i** can also be looked as a π-electron cycle system of aromatic compound (Figure 3), H_c and H_d are in the shielding region which leads to the high-field shift of the peaks in the ¹H NMR spectra.

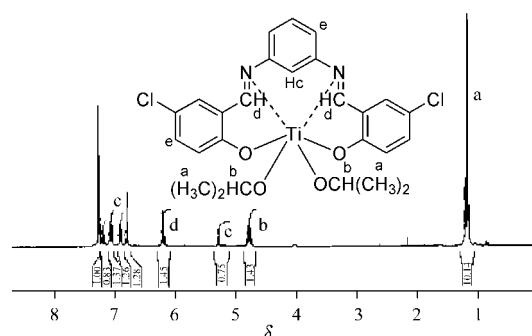


Figure 1 ¹H NMR spectrum of complex **1i**.

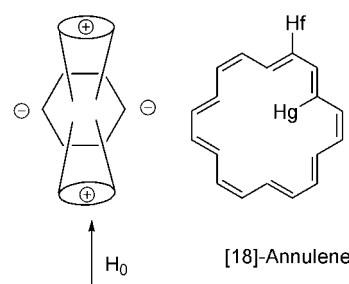


Figure 2 Shielding of [18]-annulene.

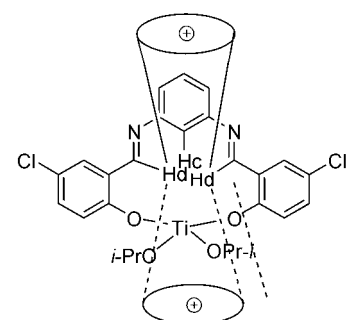
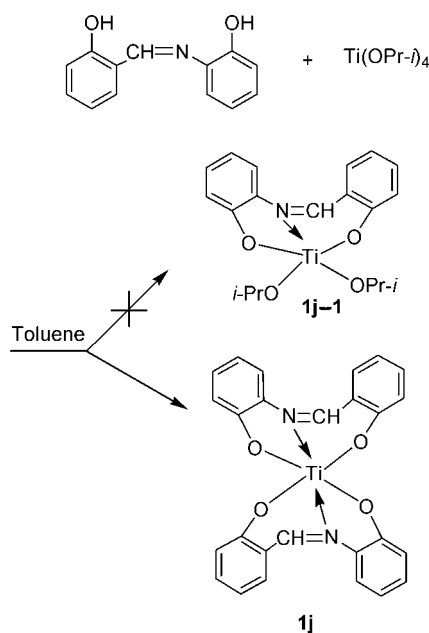


Figure 3 Shielding of complex **1i**.

Tridentate Schiff-base titanium complex

Tridentate Schiff-base ligand **j** was prepared by the similar method of **a—i**, using the condensation reaction. We tried to synthesize the designed complexes **1j—1** by the reaction of Ti(OPr-*i*)₄ with **j** (Scheme 2) which has the structure with only one tridentate Schiff-base ligand, and it is supposed to be a good precursor for olefin polymerization. In fact the spiro complex **1j** was formed as a red powder in extremely high yield 92% (based on ligand **j**) by using the molar ratio of **j** : Ti(OPr-*i*)₄ as 1 : 1.

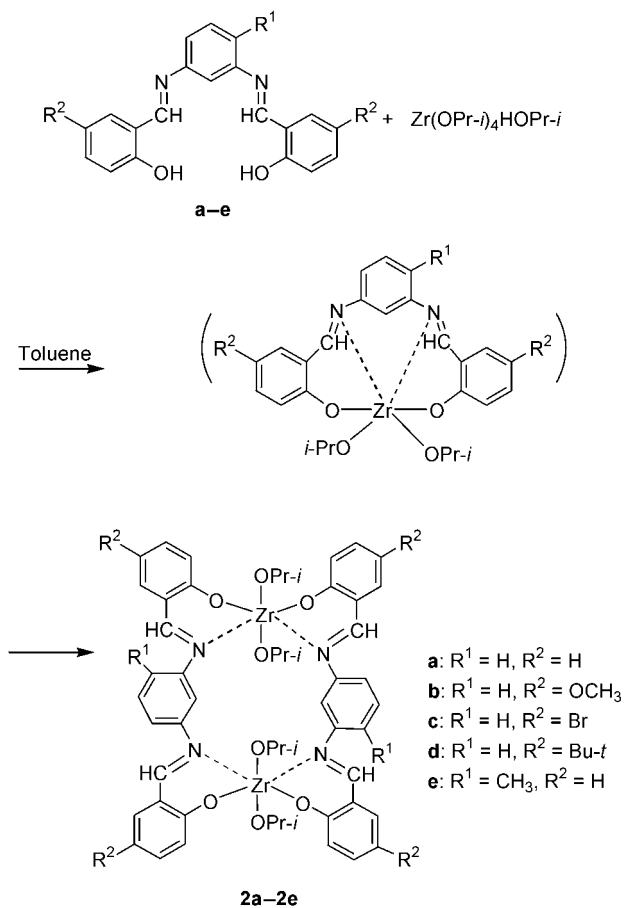
Scheme 2



Tetradentate Schiff-base zirconium complexes

We used the similar procedure of complexes **1a—1i** for complexes **2a—2e** by the reaction of Schiff-base ligand with $Zr(OPr-i)_4 \cdot HOPr-i$ as showed in Scheme 3.

Scheme 3



Complexes **2a—2e** were obtained by the recrystallization from hexane. After recrystallization they are insoluble in organic solvent again, so in fact these complexes were obtained as the structure showed in Scheme 3 according to the literature.²³ All the complexes are well characterized by elemental analysis, IR and MS spectra.

Thiophene diamide titanium complexes

The thiophene diamide ligand **k**^{24,25} was readily synthesized by the reaction of 2,5-bis(dimethylchlorosilyl)-thiophene with $Ar'N(SiMe_3)Li$ ($Ar' = 2,6-i-Pr_2C_6H_3$). The reaction of **k** with $TiCl_4$ in toluene at 120 °C affords the thiophene diamide [N,S,N]₂-titanium complex **1k** in good yield. The product was recrystallized from CH_2Cl_2 . And we suppose that sulfur atom coordinates with the central metal just as the similar kind of pyridine diamide complexes.²⁶

Ethylene polymerization by complexes **1a—1i**, **1k** and **2a—2e**

Ethylene polymerization was performed by using complexes **1a—1i**, **1k** (Scheme 4) in the presence of MAO at the temperature 50 °C. As showed in Table 1, the activity of complexes **1a—1i** was moderate for ethylene polymerization in comparison to that of Cp_2TiCl_2 . Among them, complex **1f** ($R^1 = CH_3, R^2 = Br$) shows the highest activity, almost seven times higher than that of complex **1b** ($R^1 = H, R^2 = OCH_3$). The substituents on ligands affect the catalytic activity of the complexes, the activity of **1b** ($R^1 = H, R^2 = OCH_3$) is the lowest. This can be reasoned by that the oxygen atom (OCH₃ group) in complex might consume some methylaluminoxane (MAO), and lead to the decrease of the concentration of MAO.²⁷

Scheme 4

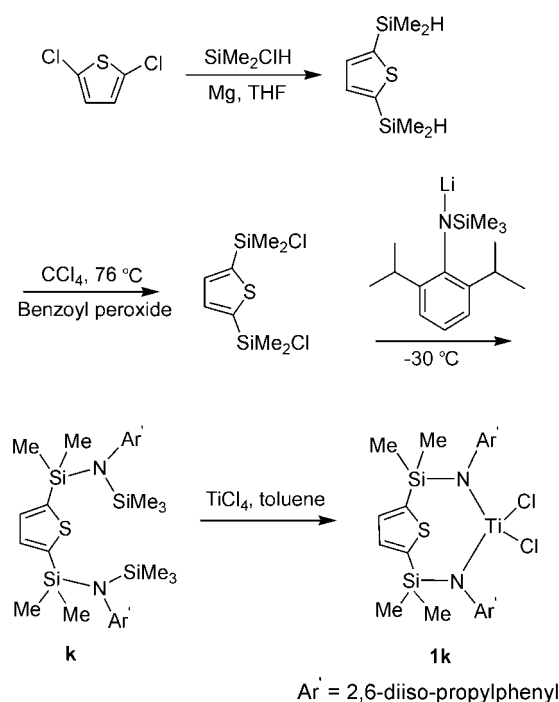


Table 1 Ethylene polymerization catalyzed by complexes **1a—1i**, **1k**/MAO system^a

Entry	Catalyst	$x_{Al/Ti}$	Activity (g
			PE/mol Ti•h)
1	1a (R ¹ =H, R ² =H)	1500 : 1	2.04 × 10 ⁴
2	1b (R ¹ =H, R ² =OCH ₃)	1500 : 1	0.59 × 10 ⁴
3	1c (R ¹ =H, R ² =Br)	1000 : 1	1.98 × 10 ⁴
4	1d (R ¹ =H, R ² =Bu- <i>t</i>)	1500 : 1	1.73 × 10 ⁴
5	1e (R ¹ =CH ₃ , R ² =H)	1000 : 1	0.98 × 10 ⁴
6	1f (R ¹ =CH ₃ , R ² =Br)	1500 : 1	3.94 × 10 ⁴
7	1g (R ¹ =CH ₃ , R ² =OCH ₃)	1000 : 1	0.85 × 10 ⁴
8	1h (R ¹ =H, R ² =CH ₃)	1500 : 1	0.84 × 10 ⁴
9	1i (R ¹ =H, R ² =Cl)	1500 : 1	1.00 × 10 ⁴
10	1k	1000 : 1	trace
11	Cp ₂ TiCl ₂	1500 : 1	3.11 × 10 ⁵

^a Polymerization condition: Cat.: 5 μmol; T_p=50 °C; solvent: toluene 50 mL; time: 0.5 h.

Unfortunately complex **1k** shows inactive to the ethylene polymerization, it is supposed that the complex containing sulfur atom seems not favorable to the catalytic activity.

As complex **1f** shows the highest activity, we further studied the activity influenced by Al/Ti molar ratio. The results are reported in Table 2. The higher the molar ratio of Al/Ti, the higher the activity, and the activity is increased greatly with the Al/Ti ratio from 500 : 1 to 1500 : 1, then shows a slightly increase. Even when the Al/Ti is 4000 : 1, the activity can not be greatly improved.

Table 2 Influence of Al/Ti molar ratio on the ethylene polymerization catalyzed by **1f**/MAO system^a

Entry	Catalyst	$x_{Al/Ti}$	Activity (g
			PE/mol Ti•h)
12	1f (R ¹ =CH ₃ , R ² =Br)	500 : 1	1.43 × 10 ⁴
6	1f (R ¹ =CH ₃ , R ² =Br)	1500 : 1	3.94 × 10 ⁴
13	1f (R ¹ =CH ₃ , R ² =Br)	2000 : 1	4.22 × 10 ⁴
14	1f (R ¹ =CH ₃ , R ² =Br)	4000 : 1	5.24 × 10 ⁴

^a Polymerization condition: Cat.: 5 μmol; T_p=50 °C; solvent: toluene 50 mL; time: 0.5 h.

The results of ethylene polymerization by using complexes **2a—2e** are summarized in Table 3. When activated by methylaluminoxane (MAO), all complexes are active for the polymerization of ethylene. The activity is moderate and relatively low in comparison with that of Cp₂ZrCl₂. As showed in Table 3, the bulk substituent (Bu-*t*) is not favorable to increase activity. In fact, complex **2a** without any substituent shows the highest activity in this series of catalysts.

Table 3 Ethylene polymerization catalyzed by complexes **2a—2e**/MAO system^a

Entry	Catalyst	$x_{Al/Zr}$	Activity (g
			PE/mol Ti•h)
1	2a (R ¹ =H, R ² =H)	1000 : 1	2.15 × 10 ⁴
2	2b (R ¹ =H, R ² =OCH ₃)	1000 : 1	1.56 × 10 ⁴
3	2c (R ¹ =H, R ² =Br)	1000 : 1	1.43 × 10 ⁴
4	2d (R ¹ =H, R ² =Bu- <i>t</i>)	1000 : 1	1.33 × 10 ⁴
5	2e (R ¹ =CH ₃ , R ² =H)	1000 : 1	1.98 × 10 ⁴
6	Cp ₂ ZrCl ₂	1000 : 1	2.45 × 10 ⁶

^a Polymerization condition: Cat.: 5 μmol; T_p=50 °C; solvent: toluene 50 mL; time: 0.5 h.

Polymerization of styrene by complexes **1a—1c** and **1e**

Styrene was polymerized by the complexes **1a—1c** and **1e** at 50 °C and Al/Ti molar ratio in 2000 : 1. The results are summarized of Table 4. The substituents on the ligand affect the catalytic activity slightly, and all these four complexes showed the moderate activity (Entries 1, 3, 5 and 9). The melting point of the resultant polymer was about 270 °C.

As showed in Table 4, when the complexes were preactivated by triethylaluminum (TEA), the activities increased greatly. By comparing Entry 1 [$A=1.21 \times 10^4$ g PS/(mol Ti•mol S•h)] and Entry 2 [$A=3.19 \times 10^5$ g PS/(mol Ti•mol S•h)], we observed that the activity was increased almost thirty-fold as well as the improvement of polymer syndiotacticity. Chien *et al.*²⁸ also found the similar result by the preactivation of the catalyst using trimethylaluminum (TMA). In this case, the alkoxy group (OPr-*i*) will be more easily displaced by TEA than MAO, which is then followed by MAO to produce Ti(III) active species which played an important role to the styrene polymerization.

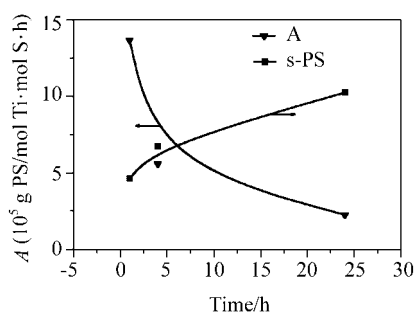
Polymerization time affects the activity greatly which can be seen from Entry 6, Entry 7 and Entry 8. As polymerization time increased from 1 to 24 h, the activity was decreased greatly from 137×10^4 g PS/(mol Ti•mol S•h) to 22.5×10^4 g PS/(mol Ti•mol S•h), however the syndiotacticity of the resultant polymer was improved from 37.8% to 71.5% as showed in Figure 4.

As showed in Table 4, when the complexes were preactivated by triethylaluminum (TEA), the activities increased greatly. By comparing Entry 1 [$A=1.21 \times 10^4$ g PS/(mol Ti•mol S•h)] and Entry 2 [$A=3.19 \times 10^5$ g PS/(mol Ti•mol S•h)], we observed that the activity was increased almost thirty-fold as well as the improvement of polymer syndiotacticity. Chien *et al.*²⁸ also found the similar result by the preactivation of the catalyst using trimethylaluminum (TMA). In this case, the alkoxy group (OPr-*i*) will be more easily displaced by TEA

Table 4 The syndiotactic polymerization of styrene catalyzed by complexes **1a**–**1c**, **1e**/MAO system^a

Entry	Catalyst	Time/h	Yield/mg	A ^b (×10 ⁴)	s-PS ^c /%	T _m /°C
1	1a (R ¹ =H, R ² =H)	24	25.4	1.21	58.3	269.1
2	1a +TEA	24	674	31.9	76.4	—
3	1b (R ¹ =H, R ² =OCH ₃)	24	21.1	1.01	50.7	271.1
4	1b +TEA	24	335	15.9	66.2	—
5	1c (R ¹ =H, R ² =Br)	24	21.3	1.02	86.8	271.6
6	1c +TEA	1	121	137	37.8	—
7	1c +TEA	4	197	55.9	50.4	—
8	1c +TEA	24	475	22.5	71.5	—
9	1e (R ¹ =CH ₃ , R ² =H)	24	27.9	1.34	79.2	272.0
10	1e +TEA	1	76.4	86.8	22.9	—
11	1e +TEA	4	256	72.7	63.1	—
12	1e +TEA	24	395	18.7	74.7	—
13	CpTiCl ₃	1	313	360	96.3	—

^a Polymerization condition: [Ti]=0.42 mmol·L⁻¹; Al/Ti=2000 : 1; T_p=50 °C; total volume=12 mL; styrene concentration=1.45 mol/L. The catalyst precursor was preactivated with 50 equivalent of triethylaluminum (TEA) where indicated. ^b Grams of PS/(mol Ti·mol S·h); ^c Grams of 2-butanone insoluble polymer/Grams of bulk polymer.

**Figure 4** Result of styrene polymerization affected by time.

than MAO, which is then followed by MAO to produce Ti(III) active species which played an important role in the styrene polymerization.

Polymerization time affects the activity greatly which can be seen from Entry 6, Entry 7 and Entry 8. As polymerization time increased from 1 to 24 h, the activity was decreased greatly from 137×10⁴ g PS/(mol Ti·mol S·h) to 22.5×10⁴ g PS/(mol Ti·mol S·h), however the syndiotacticity of the resultant polymer was improved from 37.8% to 71.5% as showed in Figure 4.

In Table 5, styrene was polymerized in bulk. It can be seen from Table 5, the catalytic activities of these four complexes were about 10⁵ g PS/(mol Ti·mol S·h) which showed a ten-fold increase in comparison with those in Table 4. Complexes **1a**–**1c** and **1e** were preactivated by 50 equivalent of TEA, and as showed in Table 5, the activities remained stable as well as the decrease of polymer syndiotacticity. That supposes the preactivation of catalyst by using TEA will not favor the improvement of both activity and polymer syndiotacticity to the styrene polymerization in bulk.

Table 5 Syndiotactic polymerization of styrene in bulk catalyzed by complexes **1a**–**1c**, **1e**/MAO system^a

Entry	Catalyst	Time/h	A ^b (×10 ⁵)	s-PS ^c /%
1	1a (R ¹ =H, R ² =H)	4	1.42	33.0
2	1a +TEA	4	1.34	13.3
3	1b (R ¹ =H, R ² =OCH ₃)	4	1.61	49.6
4	1b +TEA	4	1.38	14.3
5	1c (R ¹ =H, R ² =Br)	4	1.53	59.9
6	1c +TEA	4	1.81	40.4
7	1e (R ¹ =CH ₃ , R ² =H)	4	2.23	72.2
8	1e +TEA	4	1.28	32.2
9	CpTiCl ₃	1	14.8	62.8

^a Polymerization condition: [Ti]=0.42 mmol·L⁻¹; Al/Ti=300 : 1; T_p=50 °C; total volume=12 mL; styrene concentration=7.98 mol/L. The catalyst precursor was preactivated with 50 equivalent of triethylaluminum (TEA) where indicated. ^b Grams of PS/(mol Ti·mol S·h). ^c Grams of 2-butanone insoluble polymer/Grams of bulk polymer.

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