Syntheses of Titanium(IV) Complexes with Mono-Cp and Schiff Base Ligands and Their Catalytic Activities for Ethylene Polymerization and Ethylene/1-Hexene Copolymerization

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ABSTRACT: The syntheses of two kinds of titanium(IV) complexes with mono-Cp and Schiff base as the mixed ligands are reported. These complexes are synthesized by the reaction of $CpTiCl_3$ with the Schiff base lithium salt, and they are characterized by ^1H NMR, EA, IR, and MS. When activated by excess methylaluminoxane (MAO), all complexes are active for ethylene polymerization and ethylene/1-hexene copolymerization. **1/MAO** shows 3 times as active as complex **7** (Cp_2TiCl_2) to the ethylene/1-hexene copolymerization, and the molecular weight of the copolymer obtained by **1/MAO** is almost 2 times that of complex **3** and 5 times that of complex **7**. Complex **1** combines the advantages of non-metallocene (complex **3**) and metallocene (complex **7**) to the ethylene polymerization and ethylene/1-hexene copolymerization.

Introduction

The discovery of Ziegler−Natta catalysts and their use as homogeneous catalysts for the polymerization of ethylene greatly promoted the development of organometallic chemistry.[1] Research efforts have been devoted to understanding the way to control catalyst activity and selectivity with respect to polymer composition and structure. To date, many organometallic complexes have been synthesized, especially group 4 metal complexes supported by the ubiquitous cyclopentadienyl (Cp) ligand because of the motivation arising from academic research and ever increasing support from industry.[2−6] However, another branch of non-Cp complexes has also been extensively studied.[7,8] The non-Cp complexes may be supported by many kinds of ancillary ligands. McConville et al.[9] found that propylene-bridged aryl-substituted diamido group 4 complexes promote the living polymerization of α-olefins. More recently, Fujita and co-workers[10,11] discovered that group 4 complexes bearing the bidentate salicylaldimine chelate ligands show extremely high activity in ethylene polymerization.

In view of the homopolymerization and copolymeriation of olefins with metallocene and non-metallocene complexes,[10,12,13] it would be of interest to note that metallocene catalysts perform very actively in the catalytic copolymerization of ethylene with other α-olefins. This is the favored way of producing low-density polyethylene (LDPE) or elastomers. However, in the case of metallocene catalytic olefin polymerization, the molecular weight (MW) of prepared copolymers decreases greatly with the increase of inserted comonomers in the backbone of polyethylene so that it is difficult to obtain the polyethylene with very low density and relatively high MW at the same time. On the other hand, the MW of copolymers obtained by using non-metallocene catalysts exhibits good capability of copolymerization. To our interest, we think it would be possible to modify the catalysts by using greatly different types of ligands on the central metal to catalyze ethylene copolymerization producing high-MW and low-density polyethylene, which is a critical point for preparing bimodal molecular weight distribution (MWD) polyethylene successfully in a single reactor with a mixed catalyst system.

In this article, we report the syntheses of mono-Cp/Schiff base complexes and the study of their application in ethylene polymerization and ethylene/1-hexene copolymerization in the presence of methylaluminoxane (MAO). We found that the catalysts have an effective catalytic ability for ethylene copolymerization in the case of preparing high-MW and low-density polyethylene. Taking advantage of these novel catalysts, we have made promising progress in preparing bimodal MWD polyethylene with a mixed-catalyst system.

Results and Discussion

Syntheses of Titanium(IV) Complexes with Mono-Cp and Schiff Base Ligands. We set out with the plan of synthesizing complex **2** by the reaction of $CpTiCl_3$ and Schiff base lithium in a 1:1 molar ratio (Scheme 1) which has the structure with mono-Cp, mono Schiff-base ligand, and it is supposed to be a good precursor for olefin polymerization. Probably because of the electron deficiency of titanium(IV), complex **1** was readily obtained in good yield (50%) as fluffy crystals, containing one Cp ligand and two Schiff base ligands embedding the Ti(IV) in a six-coordinate environment.

We thought by changing the solvent to the less polar toluene and increasing the temperature to 80 °C, we may be successful. At the end we only isolated needle

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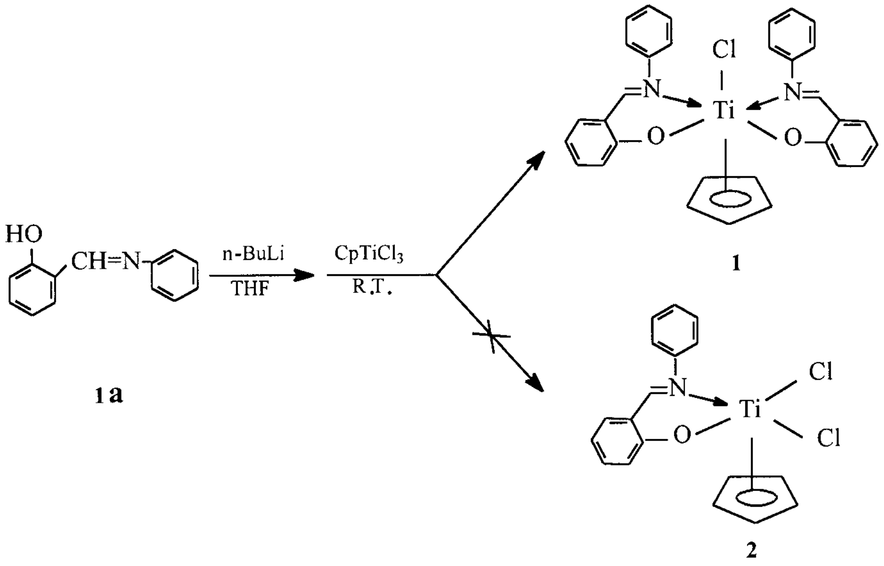
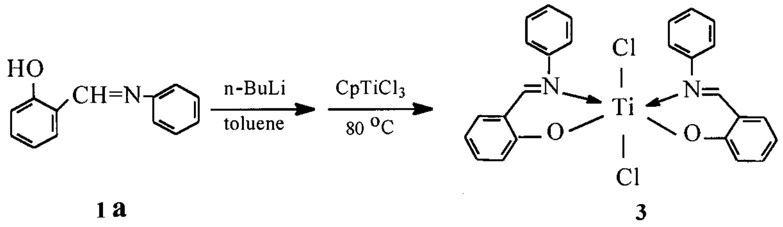
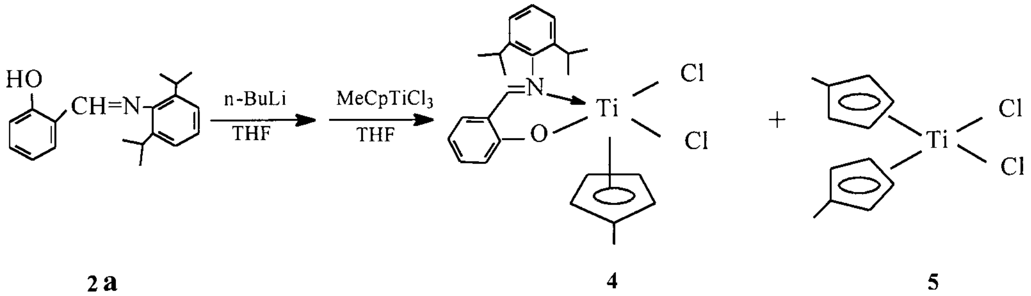
Scheme 1



Scheme 2



Scheme 3



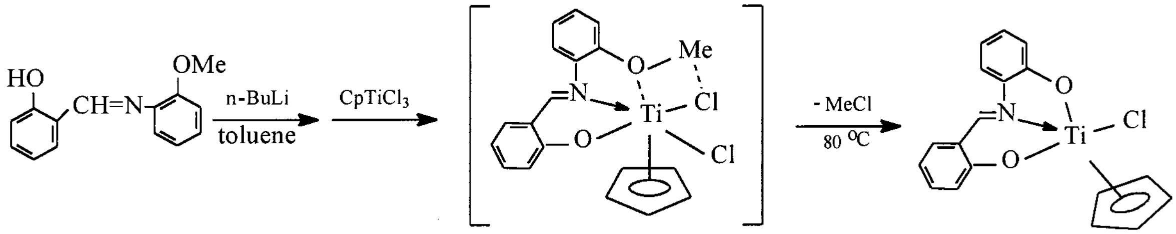
crystals **3** in 32% yield, and after characterization by ^{1}H NMR, EA, IR, and MS, it was found to be still different from our target complex **1** (Scheme 2). Fujita et al.[10] first reported the synthesis of complex **3** by the reaction of Schiff base lithium with $TiCl_4$. Scheme 2 is a new route to complex **3** by using an unorthodox procedure. It is assumed during the reaction ligand exchange takes place between Schiff base ligand and the Cp moiety.

Attempts to prepare analogues of complex **1** via changing the substituent on the Cp ring or phenyl group were unsuccessful, probably because of the increased steric bulk in comparison with **1**. In the first case the sterically bulky isopropyl group was introduced to the Schiff base ligand, and we obtained a result different from what was obtained in Scheme 1: mono-Cp, mono Schiff-base dichloride titanium complex **4** and compound **5**, which are hard to separate (Scheme 3). The ^{1}H NMR spectra contain peaks of compound **5** (6.71 (t, 4H), 6.59 (t, 4H), 2.47 (s, 6H)) which was different from that of the starting material $MeCpTiCl_3$ (6.95 (s, 2H), 6.83 (s, 2H), 2.53 (s, 3H)). ^{1}H NMR spectra indicate the molar ratio of **4**/**5** is 4:1. This supports our suggestion that Schiff base lithium will exchange with $MeCpTiCl_3$ to form compound **5**.

Another heteroatom group (MeO) was introduced to the Schiff base ligand (**3a**) in order to further stabilize the central metal. In this case, using toluene as solvent and maintaining the reaction mixture at 80 °C overnight produced the desired product, a mono-Cp and the tridentate Schiff-base titanoxacycle complex **6** (Scheme 4). In the ^{1}H NMR spectra of the complex, the peak of OCH_3, a strong singlet at 3.87 ppm visible in **3a**, has disappeared, indicating the bonding of the oxygen to the Ti metal. IR spectra of complex **6** indicate that the strong peak of C−O−C vibration which appeared about 1100 cm^{-1} has disappeared because of the loss of the methyl group. Further proof came from elemental analysis which perfectly matched the proposed structure. As proposed by Qian et al.,[14] we believe that complex **6** was obtained by thermocyclization via a four-membered transition state involving the Ti−Cl and O−Me groups and then followed by the elimination of CH_3Cl.

Polymerizarion of Ethylene. The results of ethylene polymerization using catalyst precursors (**1**, **3**, **6**,

Scheme 4



3a

6

Table 1. Ethylene Polymerizarion with Complexes 1, 3, 6, and 7/MAO[a]

entry	cat.	solvent	temp (°C)	yield (g)	activity (gPE/molTi·h)	M_w[d]	M_w/M_n[d]
1[b]	**1**	toluene	30	1.3	4.06×10^4		
2[b]	**1**	toluene	50	1.4	4.38×10^4	167×10^4	3.2
3[c]	**1**	toluene	50	0.3	1.88×10^4		
4[b]	**1**	hexane	30	0.7	2.19×10^4		
5[b]	**6**	toluene	50	0.5	1.56×10^4	163×10^4	4.77
6[b]	**3**	toluene	50	0.2	0.63×10^4	161×10^4	2.55
7[b]	**7**	toluene	50	0.39	1.22×10^4	52×10^4	2.65

[a] Conditions: solvent, 100 mL; Al/Ti = 1000:1; pressure, 1 atm; time, 1 h. [b] Catalyst, 32 μmol. [c] Catalyst, 16 μmol; catalyst **7**, Cp_2TiCl_2. [d] Determined by GPC.

Table 2. Ethylene/1-Hexene Copolymerizarion with Complexes 1, 3, 6 and 7/MAO[a]

entry	cat.	1-hexene (mL)	yield (g)	activity[f]	M_w[d]	M_w/M_n[d]	hexene[e] content
8[b]	**1**	3	3.3	1.03×10^5			
9[c]	**1**	5	2.8	1.75×10^5	57×10^4	2.73	4.34
10[b]	**6**	5	0.7	0.22×10^5	41×10^4	4.9	3.1
11[b]	**3**	5	1.9	0.59×10^5	34×10^4	2.55	3.27
12[b]	**7**	5	0.9	0.28×10^5	12×10^4	2.23	

[a] Conditions: solvent, toluene 100 mL; Al/Ti = 1000:1; pressure, 1 atm; time, 1 h. [b] Catalyst, 32 μmol. [c] Catalyst, 16 μmol; catalyst **7**, Cp_2TiCl_2. [d] Determined by GPC. [e] 1-Hexene content (mol %) in copolymer by ^{13}C NMR. [f] In g/(mol of Ti h).

and **7** (Cp_2TiCl_2)) are shown in Table 1. Different conditions including temperature (30 and 50 °C), solvent (toluene and hexane), and concentration of the catalyst are investigated.

The polymerization of ethylene with **1** in the presence of excess MAO at 50 °C exhibits a much higher activity (4.38×10^4 g of PE/(mol of Ti h)) in comparison with the activity of 0.63×10^4 (g of PE/(mol of Ti h)) for **3** and 1.22×10^4 (g of PE/(mol of Ti h)) for **7**; the activity of **1** is almost 7 times higher than that of **3** and 3 times higher than that of **7**. However, the activity of **6** is not as high as **1** due to the steric effect of the tridentate Schiff base ancillary ligand on titanium. The activity of the title complexes for ethylene polymerization is slightly dependent on temperature increase from 30 to 50 °C. Solvent polarity is an important factor for ethylene polymerization using the title complexes; the catalytic activity decreased significantly when hexane replaces toluene as the solvent (compare entry 1 and entry 4). Catalytic activity is a direct function of its concentration; comparing entry 2 and entry 3, we observe an increase of more than 2-fold in activity as catalyst concentration is doubled.

The resultant polymer obtained by using **1** as a catalyst has a high molecular weight ($M_w = 167 \times 10^4$) with a relatively narrow molecular weight distribution ($M_w/M_n = 3.2$). The molecular weight values of polymers obtained from all the catalysts are within a narrow range (entries 2, 5, and 6) and higher than that of Cp_2TiCl_2 (catalyst **7**, $M_w = 52 \times 10^4$). In the case of complex **6**, a significant increase in molecular weight distribution was observed ($M_w/M_n = 4.77$), probably due to the rigidity imposed by the tridentate Schiff base moiety.

We use complex **3** as the reference point for non-Cp complexes and complex **7** (Cp_2TiCl_2) for metallocenes. Complex **3** has a high molecular weight ($M_w = 161 \times 10^4$) but relatively low activity (0.63×10^4 g of PE/(mol of Ti h)), while complex **7** (Cp_2TiCl_2) has a high activity (1.22×10^4 g of PE/(mol of Ti h)) for ethylene polymerization, producing relatively low molecular weight PE ($M_w = 52 \times 10^4$). Complex **1** combines the advantages of complex **3** with high molecular weight and complex **7** (Cp_2TiCl_2) with high activity to ethylene polymerization.

Copolymerizarion of Ethylene/1-Hexene. Complexes **1**, **3**, **6**, and **7** were used to copolymerize ethylene/1-hexene in the presence of excess MAO. The results are summarized in Table 2.

The copolymerization activity increased in the order **1** (1.75×10^5 g/(mol of Ti h)) > **3** (0.59×10^5 g/(mol of Ti h)) > **7** (0.28×10^5 g/(mol of Ti h)) > **6** (0.22×10^5 g/(mol of Ti h)), and complex **1** shows much higher catalytic activity than **3**, **6**, and **7** (Cp_2TiCl_2). The observed M_w value of the resultant polymer did not change significantly among these copolymers ($M_w = (12-57) \times 10^4$). Although the activity of complex **6** is not high, the molecular weight distribution is particularly wide ($M_w/M_n = 4.9$). Compared to the homopolymer of ethylene, for complex **1**, the M_w value decreased greatly from 167×10^4 to 57×10^4, but the M_w value was still relatively high with a decreased M_w/M_n value from 3.2 to 2.73. It was also revealed that complex **1** exhibits the highest ability to incorporate 1-hexene into the PE backbone (4.34%).

From the ethylene/1-hexene coplymerization result, it is noteworthy that complex **1** exhibits attractive coplymerization properties in comparison with complexes **3** and **7**, including activity, molecular weight, molecular weight distribution, and 1-hexene incorporation ability.

Although compound **4** is impure, we still evaluated its activity toward ethylene polymerization ($A = 1.00 \times 10^4$ g of PE/(mol of Ti h)) and ethylene/1-hexene copolymerization ($A = 1.66 \times 10^5$ g/(mol of Ti h)) as reference under similar conditions as entries 2 and 9. The resultant polymers are determined by GPC with the following result: ethylene homopolymerization ($M_w = 368 \times 10^4$, $M_w/M_n = 3.92$) and ethylene/1-hexene copolymerization ($M_w = 150 \times 10^4$, $M_w/M_n = 2.49$, 1-hexene incorporation = 2.78%).

Experimental Section

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 before use. $CpTiCl_3$ was prepared as described in the literature.[15] The cocatalyst 10% methylaluminoxane (MAO) in toluene was purchased from Witco.

IR spectra were recorded on Nicolet Magna-IR 550 and Nicolet 5SXC spectrometers as KBr disks. Elemental analyses were carried out on an EA-1106 type analyzer. ^1H NMR and ^{13}C NMR spectra were recorded on a Bruker AVANCE 500 MHz spectrometer with TMS as internal standard. MS spectra were recorded on a HP 5989A instrument.

Syntheses of Schiff Base 1a, 2a, and 3a. A 250 mL three-neck flask charged with salicyaldehyde (12.2 g, 0.1 mol) and 70 mL of ethanol was heated to 80 °C. Then a solution of aniline (9.3 g, 0.1 mol) in 20 mL of ethanol was added dropwise. The reaction mixture was refluxed for 2 h and then cooled to room temperature. A precipitate was formed, which when recrystallized from ethanol afforded 17.6 g (89%) of a green-yellowish solid, which was characterized as **1a**: ^1H NMR ($CDCl_3$, 500 MHz) δ: 13.24 (br, 1H, exchangeable with D_2O, OH), 8.61 (s, 1H, CH═N), 7.44−6.91 (m, 9H, arom).

Compound **2a** was synthesized by a procedure similar to that used for **1a**; the green-yellowish compound **2a** was isolated in 88% yield, which was characterized as follows: ^1H NMR ($CDCl_3$, 500 MHz) δ: 13.31 (br, 1H, exchangeable with D_2O, OH), 8.31 (s, 1H, CH═N), 7.44−6.95 (m, 7H, arom), 3.00 (m, $J = 6.85$ Hz, 2H, $CH(CH_3)_2$), 1.24 (d, $J = 6.85$ Hz, 12H, $CH(CH_3)_2$).

Compound **3a** was synthesized by a procedure similar to that used for **1a**; a yellowish compound **3a** was isolated in 85% yield, which was characterized as follows: ^1H NMR ($CDCl_3$, 500 MHz) δ: 13.81 (br, 1H, exchangeable with D_2O, OH), 8.65 (s, 1H, CH═N), 7.50−6.92 (m, 8H, arom), 3.87 (s, 3H, OCH_3).

Synthesis of Complex 1. 6.77 mL (2.0113 M, 13.6 mmol) of *n*-BuLi was added dropwise to a 30 mL THF solution of **1a** (2.686 g, 13.6 mmol) at −70 °C for 30 min and stirred for a further 2 h. Then the above lithium salt solution in THF was added dropwise to the $CpTiCl_3$ (2.987 g, 13.6 mmol) dissolved in 30 mL of THF solution at −70 °C for 1 h. The dark red solution was allowed to warm to room temperature and stirred overnight. The solvent was removed in vacuo, and the oily mixture was extracted with diethyl ether, yielding a fluffy red crystal of **1** (1.84 g, 50%, base on **1a**). ^1H NMR ($CDCl_3$, 500 MHz) δ: 8.07−7.99 (m, 2H, CH═N), 7.42−6.05 (m, 18H, arom), 6.56 (s, 5H, C_5H_5). IR (KBr) ν: 1606, 1550, 1472, 1291, 1186, 1122, 906, 860, 696 cm^{-1}. MS (70 eV) *m*/*z* (%): 113 (2, $CpTi^+$), 93 (100), 65 (21, Cp^+). Anal. Calcd for $C_{31}H_{25}O_2N_2TiCl$: C, 68.83; H, 4.67; N, 5.18. Found: C, 68.51; H, 4.87; N, 5.30.

Synthesis of Complex 3. Compound **1a** (1.403 g, 7.11 mmol) in 50 mL of toluene was placed into a flask, and then 3.54 mL of *n*-BuLi (2.0113 M, 7.11 mmol) was added dropwise at −70 °C for 30 min and further stirred for 2 h at room temperature. Again the mixture was cooled to −70 °C, and $CpTiCl_3$ (1.56 g, 7.11 mmol) was added and stirred for 12 h at 80 °C. Filtration and concentration of the mixture gave **3** as a red needle crystal at −20 °C (0.58 g, 32%). ^1H NMR ($CDCl_3$, 500 MHz) δ: 8.05 (s, 2H, CH═N), 7.54−6.28 (m, 18H, arom). IR (KBr) ν: 1610, 1587, 1546, 1470, 1446, 1390, 1209, 1140, 1016, 865 cm^{-1}. MS (70 eV) *m*/*z* (%): 510 (M^+). Anal. Calcd for $C_{26}H_{20}O_2N_2TiCl_2$: C, 61.08; H, 3.95; N, 5.48. Found: C, 61.03; H, 3.94; N, 5.44.

Synthesis of Complex 6. To a 50 mL toluene solution of **3a** (1.745 g, 7.68 mmol) at −70 °C was slowly added 3.82 mL (2.0113 M, 7.68 mmol) of *n*-BuLi for 30 min. At the end of the addition, the temperature was increased slowly to room temperature and so maintained for 2 h. Again, the mixture was cooled to −70 °C, and $CpTiCl_3$ (1.684 g, 7.68 mmol) was added. The temperature was allowed to rise to room temperature and heated at 80 °C overnight. After filtration, the clear solution was maintained at −20 °C in the refrigerator. After 12 h a dark red precipitate formed, which was separated by filtration, washed with hexane, and dried in vacuo (0.995 g, 36% yield). ^1H NMR ($CDCl_3$, 500 MHz) δ: 9.17 (s, 1H, CH═N), 7.76−6.99 (m, 8H, arom), 6.20 (s, 5H, C_5H_5). IR (KBr) ν: 1603, 1581, 1538, 1463, 1438, 1372, 1296, 1146, 1025, 849, 747 cm^{-1}. MS (70 eV) *m*/*z* (%): 359 (24, M^+), 294 (100). Anal. Calcd for $C_{18}H_{14}O_2NTiCl$: C, 60.10; H, 3.93; N, 3.89. Found: C, 60.41; H, 3.98; N, 3.79.

Polymerization Procedure. A 250 mL flask was equipped with an ethylene inlet, a magnetic stirrer, and a vacuum line. The flask was filled with 100 mL of freshly distilled solvent, or the comonomer (1-hexene) was added. 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 a solution of the catalyst precursor with a syringe. The polymerization was carried out for 1 h and then quenched with 3% HCl in ethanol (250 mL). The precipitated polymer was filtered and then dried overnight in a vacuum oven at 80 °C. The M_w and M_w/M_n of the polymer were determined by GPC.

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