**Summary:** By a sidearm approach, a series of titanium complexes bearing an [O, N, S] tridentate ligand have been synthesized and proven to be highly active for ethylene polymerization. The complexes also show excellent ability to copolymerize ethylene with hex-1-ene and norbornene. The effects of the different sidearms on the catalytic behavior of the complexes were studied in detail.
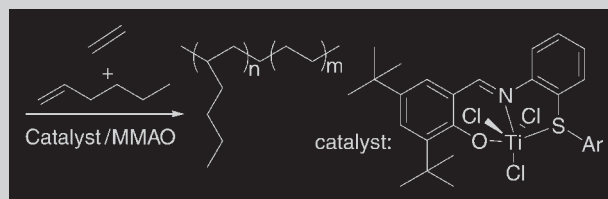
The copolymerization of ethylene with hex-1-ene using titanium complexes bearing [O, N, S] tridentate ligands as catalysts.

Novel Titanium Catalysts Bearing an [O, N, S] Tridentate Ligand for Ethylene Homo- and Copolymerization[a]

Cong Wang, Xiu-Li Sun, Yang-Hui Guo, Yuan Gao, Bo Liu, Zhi Ma, Wei Xia, Li-Ping Shi, Yong Tang*

State Key Laboratory of Organometallic Chemistry, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, 354 Fenglin Road, Shanghai 200032, P. R. China
Fax: +86-(0)-21-54925078; E-mail: tangy@mail.sioc.ac.cn

Introduction

The design and synthesis of novel catalysts for olefin polymerization plays a crucial role in the development of the polyolefin industry. Since the birth of the Kaminsky catalyst,[1] a variety of single-site catalysts, including metallocene catalysts[2] and non-metallocene catalysts,[2d–4] have been discovered for the preparation of polyolefin materials with well-defined architecture and high performance. Very recently, of the single-site catalysts developed, non-metallocene catalysts have attracted much attention both in academic research and industrial applications because of their own properties, e.g., high catalytic activity, easy synthesis, good thermal stability, low cocatalyst consumption, and capability for olefin copolymerization, especially in living olefin polymerization for the precise building of an olefin block polymer.[5]

Research into the discovery of single-site catalysts indicates that both electronic and steric effects of the ligand, as well as the choice of metal center, are very important. As such, the control of the coordination pattern between metal and ligands to tune the electronic properties and steric hindrance of the active site is crucial to develop a novel non-metallocene catalyst. Of the ligands employed as a highly active catalyst for olefin polymerization, heteroatom N and/or O and/or P species are common donors.[3,4,6] Recently, much attention has been paid to sulfur-containing ligands and several reports on their use as catalysts for olefin polymerization,[4j,7] as well as ethylene oligomerization,[8] showed that a sulfur donor was also powerful. In this communication, we wish to report the syntheses of a series of novel non-metallocene titanium complexes (**ST1**–**ST8**, as shown in Scheme 1) with an [O, N, S] tridentate ligand and their preliminary performance on ethylene homopolymerization and copolymerization with hex-1-ene and norbornene, respectively.

Experimental Part

Materials

All manipulations of air- and/or moisture-sensitive compounds were performed under an atmosphere of argon using standard

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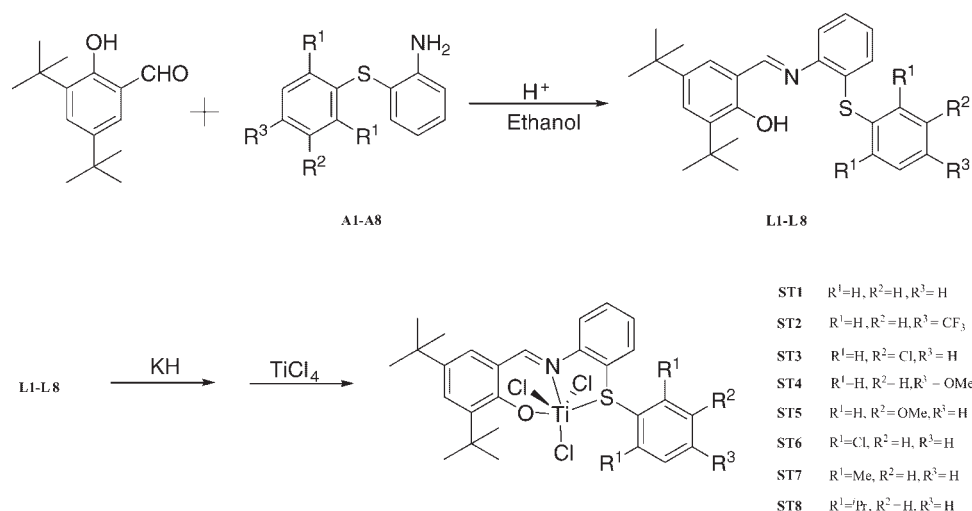
Scheme 1. Synthesis of ligands **L1–L8** and complexes **ST1–ST8**.

Schlenk techniques. ^{1}H and ^{13}C NMR spectra were recorded on a Varian XL-300 MHz spectrometer with tetramethylsilane as an internal standard. IR spectra were recorded using a Nicolet AV-360 spectrometer. Elemental analyses were performed by the Analytical Laboratory of Shanghai Institute of Organic Chemistry. Toluene, tetrahydrofuran (THF), hexane, and CH_2Cl_2 were each refluxed over sodium/benzophenone ketyl (CaH_2 in the case of CH_2Cl_2) and distilled prior to use. 3,5-Di-*tert*-butylsalicylaldehyde and the appropriate 2-phenylsulfanylanilines (**A1–A8**) were prepared in good yields according to published procedures,[9,10] and their structures were confirmed by ^{1}H NMR spectroscopy. Modified methylaluminoxane (MMAO) was purchased from Akzo Chemical as a 10 wt.-% solution in toluene. Polymerization-grade ethylene was purified before use. All other commercial chemicals are used as received. X-ray crystallographic data were collected using a Bruker AXSD8 X-ray diffractometer.

*Synthesis of Titanium Complexes **ST1–ST8***

All the ligands **L1–L8** were prepared by the condensation reaction of 3,5-di-*tert*-butylsalicylaldehyde with the appropriate 2-phenylsulfanylaniline (**A1–A8**) in good yields and were used in the synthesis of complexes **ST1–ST8**.

ST1: To a stirred suspension solution of KH (0.160 g, 4 mmol) in dried THF (10 mL) at −78 °C was added a solution of **L1** (1.670 g, 4 mmol) in dried THF (30 mL) dropwise over 10 min. The solution was allowed to warm to room temperature and stirred for 2 h. The solvent was removed under vacuum and the residue was redissolved in dried toluene (80 mL). To this transparent yellow solution, a solution of $TiCl_4$ (1.14 g, 1.5 equiv., 6 mmol) in toluene (20 mL) was added dropwise over 20 min at room temperature and the mixture was stirred overnight. The mixture was filtered and the residue was washed with dried CH_2Cl_2 (30 mL × 3). The combined organic filtrates were concentrated under vacuum to about 30 mL and were then kept at −30 °C overnight. Reddish crystals were collected and dried under vacuum, to give complex **ST1** (1.81 g) in 77% yield.

^{1}H NMR (CDCl$_3$): $\delta = 8.87$ (s, 1H, C*H*=N), 7.74–7.19 (m, 11H, H$_{Ar}$), 1.51 (s, 9H, ^{t}Bu), 1.36 (s, 9H, ^{t}Bu).

IR (KBr): 1 581 cm^{-1} (vs, C=N).

C$_{27}$H$_{30}$NOSCl$_3$Ti (570.8): Calcd. C 56.81, H 5.30, N 2.45; Found C 57.67, H 5.73, N 2.05.

ST2–ST8 were prepared according to a procedure similar to that for **ST1**.

ST2: 78% yield.

^{1}H NMR (CDCl$_3$): $\delta = 8.90$ (s, 1H, C*H*=N), 7.77–7.20 (m, 10H, H$_{Ar}$), 1.52 (s, 9H, ^{t}Bu), 1.34 (s, 9H, ^{t}Bu).

^{19}F NMR (282 MHz, CDCl$_3$): $\delta = 63.2$.

IR (KBr): 1 607 cm^{-1} (vs, C=N).

C$_{28}$H$_{29}$NOF$_3$S Cl$_3$Ti (638.8): Calcd. C 52.64, H 4.58, N 2.19; Found C 52.95, H 4.96, N 1.90.

ST3: 76% yield.

^{1}H NMR (CDCl$_3$): $\delta = 8.89$ (s, 1H, C*H*=N), 7.75–7.15 (m, 10H, Ar-H), 1.52 (s, 9H, ^{t}Bu), 1.37 (s, 9H, ^{t}Bu).

IR (KBr): 1 585 cm^{-1} (vs, C=N).

C$_{27}$H$_{29}$NOS Cl$_4$Ti (605.3): Calcd. C 53.58, H 4.83, N 2.33; Found C 54.36, H 5.22, N 2.11.

ST4: 71% yield.

^{1}H NMR (CDCl$_3$): $\delta = 8.90$ (s, 1H, C*H*=N), 7.74–6.88 (m, 10H, H$_{Ar}$), 3.79 (s, 3H, OC*H$_3$*), 1.52 (s, 9H, ^{t}Bu), 1.36 (s, 9H, ^{t}Bu).

IR (KBr): 1 614 cm^{-1} (vs, C=N).

C$_{28}$H$_{29}$NO$_2$S Cl$_3$Ti (600.8): Calcd. C 55.95, H 5.33, N 2.33; Found C 56.45, H 5.41, N 2.24

ST5: 85% yield.

^{1}H NMR (CDCl$_3$): $\delta = 8.85$ (s, 1H, C*H*=N), 7.73–6.83 (m, 10H, H$_{Ar}$), 3.73 (s, 3H, OC*H$_3$*), 1.52 (s, 9H, ^{t}Bu), 1.35 (s, 9H, ^{t}Bu).

IR (KBr): 1 591 cm^{-1} (vs, C=N).

C$_{28}$H$_{29}$NO$_2$S Cl$_3$Ti (600.8): Calcd. C 55.95, H 5.33, N 2.33; Found C 56.52, H 5.44, N 2.24.

ST6: 73% yield.

^{1}H NMR (CD$_2$Cl$_2$): $\delta = 8.85$ (s, 1H, C*H*=N), 7.83–7.27 (m, 9H, H$_{Ar}$), 1.54 (s, 9H, ^{t}Bu), 1.40 (s, 9H, ^{t}Bu).

IR (KBr): 1 645 cm^{-1} (vs, C=N).

$C_{27}H_{28}NOS\ Cl_5Ti$ (639.7): Calcd. C 52.80, H 4.47, N 2.24; Found C 52.26, H 4.93, N 1.70.

ST7: 64% yield.

^1H NMR (CD_2Cl_2): $\delta = 8.91$ (s, 1H, C*H*=N), 7.83–7.09 (m, 9H, H_{Ar}), 2.29 (s, 6H, C*H*$_3$), 1.53 (s, 9H, ^tBu), 1.41 (s, 9H, ^tBu).

IR (KBr): 1 582 cm^{-1} (vs, C=N).

$C_{29}H_{34}NOS\ Cl_3Ti$ (598.9): Calcd. C 58.14, H 5.68, N 2.33; Found C 57.84, H 5.43, N 2.09.

ST8: 70% yield.

^1H NMR ($CDCl_3$): $\delta = 8.54$ (s, 1H, C*H*=N), 7.74–6.47 (m, 9H, H_{Ar}), 3.66–3.48 (m, 2H, $J = 6.9$ Hz, C*H*$(CH_3)_2$), 1.62 (s, 9H, ^tBu), 1.35 (s, 9H, ^tBu), 1.15 (d, 12H, $J = 6.9$ Hz, CH(C*H*$_3)_2$).

IR (KBr): 1 598 cm^{-1} (vs, C=N).

$C_{33}H_{42}NOS\ Cl_3Ti$ (655): Calcd. C 60.51, H 6.46, N 2.14; Found C 59.38, H 7.04, N 1.58.

General Procedure of Ethylene Homo- and Copolymerization

A flame-dried Schlenk flask was twice purged with N_2 and charged with ethylene. The desired amount of freshly distilled toluene was transferred into the flask (placed in an oil bath at a desired temperature), and was saturated with ethylene. The comonomers (in the case of the copolymerization) and MMAO were injected into the flask in sequence using a syringe and the mixture was stirred for 5 min. The polymerization was started by adding a precursor catalyst solution in toluene with a syringe. After a desired time, the polymerization was quenched with acidified ethanol (100 mL, 10 vol.-% HCl in ethanol). The precipitated polymer was filtered off, washed with ethanol, and then dried under vacuum overnight at 50 °C to constant weight.

Polymer Characterization

The $\bar{M}_n$ and $\bar{M}_w/\bar{M}_n$ of the polymers were determined using a Waters alliance GPC 2000 series at 150 °C using a polystyrene calibration. 1,2,4-Trichlorobenzene was employed as a solvent at a flow rate of 1.0 mL · min^{-1}. ^{13}C NMR data for the ethylene copolymer was obtained using (D_4)-*o*-dichlorobenzene as a solvent at 110 °C. The melting points (T_m) of the polymers were determined by differential scanning calorimetry (DSC) on a Perkin-Elmer Pyris 1 instrument (heating rate = 10 °C · min^{-1}; temperature range = 20–230 °C).

Results and Discussion

Synthesis and Characterization of Ligands and Complexes

A general procedure for the synthesis of the ligands and complexes is shown in Scheme 1. Condensation of 3,5-di-*tert*-butylsalicylaldehyde with 2-phenylsulfanylaniline (**A1**–**A8**) afforded [O, N, S] tridentate ligands (**L1**–**L8**) in 70–90% yields. In general, the synthesis of the ligands is simple and efficient. It can be easily manipulated under mild reaction conditions. Good to high yields of the targeted ligands are obtained. It is worth noting that the condensation of salicylaldehyde with **A1**–**A8** is an environmentally

friendly reaction. When the reaction was finished, the produced imine crystallized upon cooling the reaction mixture to room temperature and was collected in high purity by only filtering and washing. The filtrate could be recycled and reused. The procedure is suitable for the synthesis of analogous ligands on a large scale. Titanium complexes **ST1**–**ST8** were prepared in high yields by treatment of the corresponding potassium salts of the ligands in toluene with a $TiCl_4$ (1.5 equiv.) solution in toluene at room temperature. This reaction proceeds quite smoothly and no bis-liganded complex was observed, even when the ratio of $TiCl_4$ to ligand was reduced to 0.5.

Single Crystal X-Ray Structure Analysis of Complex ST1

The X-ray structural analysis of an **ST1** crystal showed that the geometry around the titanium atom could be described as a distorted octahedron with the three chlorine atoms in a *mer* disposition (Cl(2)–Ti–Cl(3) angle, 163.3(8)°) (Figure 1). The Cl(1)–Ti–Cl(2) and Cl(1)–Ti–Cl(3) angles are 95.7(9) and 94.8(4)°, respectively, indicating that the three chlorine atoms are located *cis* to one another, which is favorable for the insertion of the monomer. The Ti–S bond length is 2.5908 Å, which is larger than the sum of the covalent radii, 0.11 Å ($r_{cov(Ti)} = 1.450$ Å, $r_{cov(S)} = 1.030$ Å). The Ti–Cl(1), Ti–Cl(2), and Ti–Cl(3) bond lengths are 2.2509, 2.2887, and 2.3430 Å, respectively.
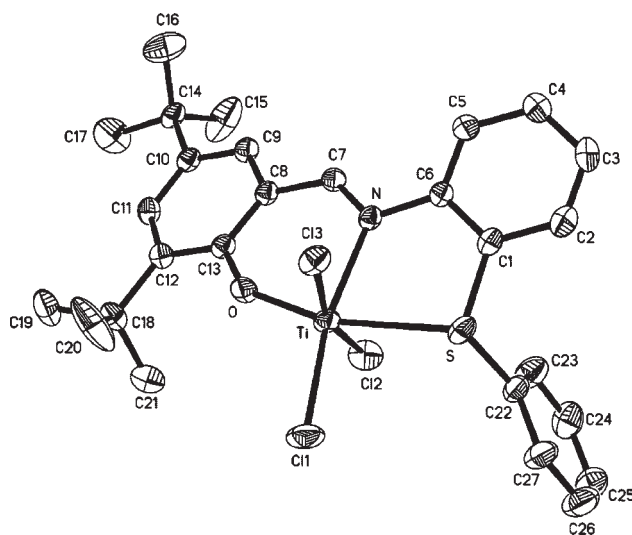

Figure 1. Molecular structure of complex **ST1**. Selected bond lengths (Å) and angles (deg.): Ti–O, 1.7910(19); Ti–N, 2.198(2); Ti–Cl(1), 2.2509(10); Ti–Cl(2), 2.2887(10); Ti–Cl(3), 2.3430(10); O–Ti–N, 86.44(8); O–Ti–Cl(1), 106.21(7); N–Ti–Cl(1), 167.35(7); O–Ti–Cl(2), 92.76(7); N–Ti–Cl(2), 83.81(7); Cl(1)–Ti–Cl(2), 95.79(4); O–Ti–Cl(3), 96.48(7); N–Ti–Cl(3), 83.01(6); Cl(1)–Ti–Cl(3), 94.84(4); Cl(2)–Ti–Cl(3), 163.38(4); O–Ti–S, 164.04(7); N–Ti–S, 77.79(6); Cl(1)–Ti–S, 89.55(4); Cl(2)–Ti–S, 87.99(4); Cl(3)–Ti–S, 79.36(3).

Table 1. Ethylene polymerization results with titanium complexes **ST1**–**ST8**.

Entry	Complex	Al/Ti ratio	T_p °C	Yield g	Activity[c]	$\bar{M}_w$[d] $\times 10^{-4}$	$\bar{M}_w/\bar{M}_n$[d]	T_m[e] °C
1[a]	**ST1**	500	50	1.560	1.95	5.02	2.04	130.6
2[a]	**ST2**	500	50	0.920	1.15	8.54	2.55	129.3
3[a]	**ST3**	500	50	0.610	0.76	12.73	3.07	132.0
4[a]	**ST4**	500	50	1.053	1.32	5.55	2.13	130.0
5[a]	**ST5**	500	50	0.847	1.06	4.45	2.49	131.3
6[a]	**ST6**	500	50	0.953	1.19	7.65	1.74	132.5
7[a]	**ST7**	500	50	0.171	0.21	18.41	1.87	132.0
8[a]	**ST8**	500	50	0.048	0.06	25.19	2.71	132.9
9[b]	**ST1**	1 000	50	1.149	3.94	2.03	2.36	132.3
10[b]	**ST1**	500	50	1.097	3.76	2.34	2.36	130.8
11[b]	**ST1**	100	50	0.550	1.89	4.02	1.78	133.1
12[b]	**ST1**	500	30	1.072	3.68	4.28	2.66	131.7
13[b]	**ST1**	500	80	0.420	1.44	1.37	2.47	–

[a] Reaction conditions: ethylene, 0.1 MPa; complexes, 3.2 µmol; toluene, 50 mL; reaction time, 15 min.
[b] Reaction conditions: ethylene, 0.1 MPa; complexes, 3.5 µmol; toluene, 20 mL; reaction time, 5 min.
[c] Activity: 10^6 g (PE) $\cdot$ mol^{-1}(Ti)) $\cdot$ h^{-1}.
[d] Determined by GPC relative to polystyrene standards.
[e] Determined by DSC.

Ethylene Polymerization

The titanium complexes **ST1**–**ST8** were examined for ethylene polymerization under different reaction conditions. In the presence of MMAO, all the complexes showed high activity for ethylene polymerization. As shown in Table 1, the electronic properties of the R^2 and R^3 substituents seem to have little influence on the activity of catalysts **ST2**–**ST5**. All complexes with an electron-withdrawing group (**ST2**, **ST3**) or an electron-donating group (**ST4**, **ST5**) were highly active for ethylene polymerization (Entry 2–5). **ST2** and **ST3** gave a higher molecular weight ($\bar{M}_w$) of polyethylene (**ST2**, $\bar{M}_w = 8.54 \times 10^4$, Entry 2; **ST3**, $\bar{M}_w = 12.73 \times 10^4$, Entry 3) in comparison with **ST1** ($\bar{M}_w = 5.02 \times 10^4$, Entry 1), whereas the $\bar{M}_w$'s of the polyethylenes produced by **ST4** and **ST5** were of the same degree of that by **ST1**. The independence of the catalyst activity on the electronic properties of the pendant sulfur group seems to be different from other single-site catalyst systems. The reason is waiting further investigation.

The R^1 substituent of the ligand significantly affected the behavior of the catalysts, such as their activity and product properties (**ST1**, **ST6**–**ST8**, Entry 1, 6–8). As shown in Table 1, increasing the steric hindrance of R^1 in the order of H < Cl < Me < ^{i}Pr resulted in an obvious decrease of catalytic activity (1.95, 1.19, 0.21, 0.06 $\times 10^6$ g (PE) $\cdot$ mol^{-1}(Ti) $\cdot$ h^{-1}) and an increase of molecular weight ($\bar{M}_w = 5.02$, 7.65, 18.41, 25.19 $\times 10^4$). The reason for the decrease of activity is probably because of the difficulty associated with the insertion of ethylene when the bulky group is around the active site, which slows down the ethylene polymerization. The steric effect would then reduce the rate of chain-transfer to result in the production of high-molecular-weight polymer. An interesting result of ethylene polymerization using **ST6** should be noted. Generally, compared with a H substituent in the R^1 position for **ST1**, the electron-withdrawing nature of a chlorine substituent in **ST6** results in a more electrophilic Ti center in the complex, which may increase the corresponding activity in the ethylene polymerization.[4d] However, the catalytic activity of **ST6** is lower than that of **ST1**. Considering the weak electronic effect on catalyst activity shown above (**ST2**–**ST5**), the possible explanation is that the steric effect of the Cl atom at the R^1 position plays a dominant role in the catalytic activity in the series of **ST** complexes.

The preliminary results about the effect of the amount of MMAO on catalyst activity showed that only an extremely low amount of MMAO was required to activate the catalysts and achieve a good activity in ethylene polymerizations. Complex **ST1**, for example, gave good activities (1.149, 1.097, and 0.550 $\times 10^6$ g (PE) $\cdot$ mol^{-1} (Ti) $\cdot$ h^{-1}, Entry 9–11 in Table 1) over an Al/Ti ratio range of 1 000 to 100. Noticeably, the $\bar{M}_w$ of the polyethylene was sensitive to the Al/Ti ratio. As investigated, the higher the Al/Ti ratio used, the lower the resulting $\bar{M}_w$ of the produced polyethylene (Entry 9–11, Table 1). This tendency is consistent with the mechanism of chain-transfer to aluminum compounds in an olefin polymerization process. It should be mentioned that **ST1** maintained a high activity even when the polymerization was performed at 80 °C (Entry 13). GPC analysis showed that the $\bar{M}_w$ of the polyethylene was temperature dependent. The decrease of the polymer's molecular weight from 4.28×10^4 to 1.37×10^4 with increasing reaction temperature from 30 to 80 °C is rationalized as the dependency of the chain transfer reaction on the polymerization temperature.

Table 2. Results of ethylene copolymerizations with hex-1-ene and norbornene.

Entry	Complex	Comonomer	Yield	Activity[c]	$\bar{M}_w^{[d]} \times 10^{-4}$	$\bar{M}_w/\bar{M}_n^{[d]}$	Comonomer content[e]	$T_m^{[f]}$
	μmol	mmol	g				mol-%	°C
1[a]	**ST1** (7.0)	Hex-1-ene (40.3)	0.680	38.9	14.59	3.87	30.0	100.9
2[a]	**ST2** (6.3)	Hex-1-ene (40.3)	0.684	43.4	19.56	3.26	28.2	115.7
3[a]	**ST4** (6.7)	Hex-1-ene (40.3)	0.627	37.4	17.42	2.46	25.9	97.4
4[b]	**ST1** (7.0)	Norbornene (11.7)	1.153	3.30	39.61	1.55	24.0	–
5[b]	**ST2** (6.3)	Norbornene (23.4)	0.636	2.03	39.84	1.90	27.4	–
6[b]	**ST4** (6.7)	Norbornene (23.4)	0.153	0.46	27.47	1.60	14.7	–

[a] Reaction conditions: ethylene, 0.1 MPa; reaction temperature, 25 °C; Al/Ti ratio, 500; reaction time, 15 min.
[b] Reaction conditions: ethylene, 0.1 MPa; reaction temperature, 25 °C; Al/Ti ratio, 500; reaction time, 30 min.
[c] Activity: 10^5 g · mol^{-1} (Ti) · h^{-1}.
[d] Determined by GPC relative to polystyrene standards.
[e] Determined by ^{13}C NMR spectroscopy.
[f] Determined by DSC.

Ethylene Copolymerization with Hex-1-ene and Norbornene

One of the greatest advantages of such novel complexes for polymerization is that they exhibit a promising capability to copolymerize ethylene with hex-1-ene and even with bulky norbornene. The preliminary results of the copolymerization are summarized in Table 2. Good catalytic activities for the ethylene/hex-1-ene copolymerization (Entry 1–3, Table 2) were obtained. The high incorporation of hex-1-ene in the copolymer, as calculated by ^{13}C NMR spectroscopy, a low T_m, as well as the high $\bar{M}_w$ of copolymer produced, indicated that a linear low-density polyethylene (LLDPE) with good properties could be produced by considered choice of catalyst and polymerization conditions.

The preliminary work on an ethylene/norbornene copolymerization (Entry 4–6 in Table 2) showed that, using such complexes described above, bulky norbornene could also be efficiently incorporated into the polyethylene backbone to produce an ethylene/norbornene copolymer that is of importance in the cycle of olefin copolymer materials for broad industrial applications.

Conclusion

A series of novel [O, N, S] tridentate titanium complexes have been developed as excellent catalysts for olefin polymerization. These complexes prove highly active for ethylene polymerization even in the presence of a considerably low amount of MMAO (Al/Ti ratio = 100). The electronic and steric effects of different substituents on the pendant sulfur group on the behavior of ethylene polymerization were investigated. It was found that the electronic effect of the pendant sulfur group had little influence either on the catalytic activity or on the $\bar{M}_w$ of the polymer. In contrast, steric effects affected both the activity and molecular weight. These complexes have shown a good capability to incorporate comonomers, such as hex-1-ene and norborn-

ene, into the polyethylene chain. Detailed investigations into the use of these catalysts to copolymerize ethylene with α-olefins and other steric olefins are in progress and will be reported in the near future.

[1] [1a] H. Sinn, W. Kaminsky, *Adv. Organomet. Chem.* **1980**, *18*, 99; [1b] H. Sinn, W. Kaminsky, H. J. Vollmer, R. Woldt, *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 390.

[2] For recent reviews, see: [2a] H. G. Alt, A. Köppl, *Chem. Rev.* **2000**, *100*, 1205; [2b] L. Resconi, L. Cavallo, A. Fait, F. Piemontesi, *Chem. Rev.* **2000**, *100*, 1253; [2c] G. Fink, B. Steinmetz, J. Zechlin, C. Przybyla, B. Tesche, *Chem. Rev.* **2000**, *100*, 1377; [2d] G. W. Coates, *Chem. Rev.* **2000**, *100*, 1223.

[3] For recent reviews, see: [3a] V. C. Gibson, S. K. Spitzmesser, *Chem. Rev.* **2003**, *103*, 283, and references therein; [3b] S. Mecking, *Angew. Chem., Int. Ed.* **2001**, *40*, 534, and references therein; [3c] S. D. Ittel, L. K. Johnson, M. Brookhart, *Chem. Rev.* **2000**, *100*, 1169, and references therein; [3d] G. J. P. Britovsek, V. C. Gibson, D. F. Wass, *Angew. Chem., Int. Ed.* **1999**, *38*, 428, and references therein.

[4] Selected recent references: [4a] B. S. Williams, M. D. Leatherman, P. S. White, M. Brookhart, *J. Am. Chem. Soc.* **2005**, *127*, 5132; [4b] J. Liu, Y. Li, J. Liu, Z. Li, *Macromolecules* **2005**, *38*, 2559; [4c] D. H. Camacho, E. V. Salo, J. W. Ziller, Z. Guan, *Angew. Chem., Int. Ed.* **2004**, *43*, 1821; [4d] Y. Chen, R. Chen, C. Qian, X. Dong, J. Sun, *Organometallics* **2003**, *22*, 4312; [4e] X. Mi, Z. Ma, L. Wang, Y. Ke, Y. Hu, *Macromol. Chem. Phys.* **2003**, *204*, 868; [4f] W. H. Sun, H. Yang, Z. Li, Y. Li, *Organometallics* **2003**, *22*, 3678; [4g] D. Zhang, G. X. Jin, *Organometallics* **2003**, *22*, 2851; [4h] S. E. Reybuck, A. L. Lincoln, S. Ma, R. M. Waymouth, *Macromolecules* **2005**, *38*, 2552;

[4i] R. Furuyama, M. Mitani, J. Mohri, R. Mori, H. Tanaka, T. Fujita, *Macromolecules* **2005**, *38*, 1546; [4j] D. C. H. Oakes, B. S. Kimberley, V. C. Gibson, D. J. Jones, A. J. P. White, D. J. Williams, *Chem. Commun.* **2004**, 2174.

[5] [5a] G. W. Coates, P. D. Hustad, S. Reinartz, *Angew. Chem., Int. Ed.* **2002**, *41*, 2236; [5b] M. Mitani, J. Mohri, Y. Yoshida, J. Saito, S. Ishii, K. Tsuru, S. Matsui, R. Furuyama, T. Nakano, H. Tanaka, S. Kojoh, T. Matsugi, N. Kashiwa, T. Fujita, *J. Am. Chem. Soc.* **2002**, *124*, 3327.

[6] [6a] E. Y. Tshuva, I. Goldberg, M. Kol, *J. Am. Chem. Soc.* **2000**, *122*, 10706; [6b] E. Y. Tshuva, I. Goldberg, M. Kol, H. Weitman, Z. Goldschmidt, *Chem. Commun.* **2000**, 379; [6c] W.-Q. Hu, X.-L. Sun, C. Wang, Y. Tang, L.-P. Shi, W. Xia, J. Sun, H.-L. Dai, X.-X. Li, X.-L. Yao, X.-R. Wang, *Organometallics* **2004**, *23*, 1684.

[7] [7a] T. Miyatake, K. Mizunuma, Y. Seki, M. Kakugo, *Makromol. Chem., Rapid Commun.* **1989**, *10*, 349; [7b] T. Miyatake, K. Mizunuma, M. Kakugo, *Makromol. Symp.* **1993**, *66*, 203; [7c] A. van der Linden, C. J. Schaverien, N. Meijboom, C. Ganter, A. G. Orpen, *J. Am. Chem. Soc.* **1995**, *117*, 3008; [7d] D. D. Graf, R. R. Schrock, W. M. Davis,

R. Stumpf, *Organometallics* **1999**, *18*, 843; [7e] V. C. Gibson, C. P. Nicholas, J. Long, J. Martin, G. A. Solan, J. C. Stichbury, *J. Organomet. Chem.* **1999**, *590*, 115; [7f] Z. Janas, L. B. Jerzykiewicz, K. Prybylak, P. Sobta, K. Szczegot, *Eur. J. Inorg. Chem.* **2004**, 1639; [7g] Z. Janas, L. B. Jerzykiewicz, R. L. Richards, P. Sobota, *Chem. Commun.* **1999**, 1015; [7h] K. Takaoki, T. Miyatake, *Macromol. Symp.* **2000**, *157*, 251; [7i] E. Y. Tshuva, S. Groysman, I. Goldberg, M. Kol, *Organometallics* **2002**, *21*, 662.

[8] [8a] R. D. Köhn, M. Haufe, G. Kociok-Köhn, S. Grimm, P. Wasserscheid, W. Keim, *Angew. Chem., Int. Ed.* **2000**, *39*, 4337; [8b] D. S. McGuinness, P. Wasserscheid, D. H. Morgan, J. T. Dixon, *Organometallics* **2005**, *24*, 552; [8c] D. S. McGuinness, P. Wasserscheid, W. Keim, D. Morgan, J. T. Dixon, A. Bollmann, H. Maumela, F. Hess, U. Englert, *J. Am. Chem. Soc.* **2003**, *125*, 5272; [8d] J. Huang, T. Wu, Y. Qian, *Chem. Commun.* **2003**, 2816.

[9] J. F. Larrow, E. N. Jacobsen, Y. Gao, Y. Hong, X. Nie, C. M. Zepp, *J. Org. Chem.* **1994**, *59*, 1939.

[10] D. G. Foster, E. E. Reid, *J. Am. Chem. Soc.* **1924**, *46*, 1936.