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Synthesis of monoalkoxy- and trialkoxy-substituted half-sandwich titanium complexes $PhCH_2CpTiCl_{3-n}(OR)_n$ ($n = 1$ or 3) as catalysts for syndiotactic styrene polymerization

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Two new series of various substituted half-sandwich titanium complexes $PhCH_2CpTiCl_2(OR)$ (R = Et (1), ^{i}Pr (2), ^{t}Bu (3), cyclohexyl (4), benzyl (5)) and $PhCH_2CpTi(OR)_3$ (R = Et (6), ^{i}Pr (7), ^{t}Bu (8), cyclohexyl (9), benzyl (10)) were prepared from $PhCH_2CpTiCl_3$ with lithium alkoxide or alcohol in the presence of triethylamine. All complexes were well characterized by ^{1}H NMR, MS, infrared spectroscopy and elemental analysis or high-resolution MS. Complexes 1–5 have two conformations, which were confirmed by temperature-dependent NMR. All complexes were tested as catalyst precursors for the syndiotactic polymerization of styrene. The syndiotactic polystyrene obtained exhibits low molecular weight ($M_w = 2.78 \times 10^4$) and narrow molecular weight distribution ($M_w/M_n = 1.50$). The different alkoxy ligands affected the activities slightly. The existence of the additional phenyl group on the cyclopentadienyl ligand stabilized the active species more effectively, which was reflected by the activities and syndiotacticities of all complexes, and even at high temperature the activities still kept high. The effects of Al/Ti and time on the syndiotactic styrene polymerization by complex 1 were investigated. Copyright © 2004 John Wiley & Sons, Ltd.

KEYWORDS: half-sandwich; syndiotactic polymerization; styrene; catalyst

INTRODUCTION

Ishihara and co-workers first obtained syndiotactic polystyrene (s-PS) by using half-sandwich titanium complexes activated by methylaluminoxane (MAO) in 1986.[1,2] Syndiotactic polystyrene is a new material with a high melting point of ~270 °C, a glass transition temperature similar to atactic polystyrene, a fast crystallization rate, a high modulus of elasticity and an excellent resistance to heat and chemical agents, thus it has attracted much attention from polymer scientists. Since then, many kinds of half-sandwich titanocenes $Cp'TiX_3$ and $Ind'TiX_3$ have been demonstrated to be the most effective syndiotactic catalyst precursors for syndiotactic styrene polymerization.[3–11]

Recently, many scientists have paid much attention to the study of monocyclopentadienyl titanium complexes bearing a weak coordination group.[12–15] Titanium complexes with an arene-pendant cyclopentadienyl ligand in the presence of MAO can selectively trimerize ethylene with high activity, which was reported by Hessen and co-workers.[16,17] The arene-pendant cyclopentadienyl ligand is likely to exhibit hemilabile behavior and stabilize the titanium center of the activated species by η6-coordination.[16,17] Chien *et al*.[18,19] and Schwecke and Kaminsky[20] have reported that half-sandwich titanocene containing an aromatic substituent on the cyclopentadienyl catalyzes syndiotactic polymerization of styrene, and the aromatic substituent plays a very important role in syndiotactic styrene polymerization.

Variation of substituents on the cyclopentadienyl ligand may result in changes of catalytic activity and physicochemical properties of the polymer[21–23] but the polymerization mechanism suggested by Zambelli *et al*. demonstrates

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chain-end control[24] similar to unsubstituted $CpTiCl_3$. The catalytic system containing the functional group would interact with the titanium center and influence the end of the polymer chain, which would affect the microstructure of the polymer. The active species of arene-substituted cyclopentadienyl titanium appear to be cationic titanium complexes in which the pendant arene group coordinates to the metal center.[16,19,20,25] Our previous work indicated that monoalkoxy-substituted $CpTiCl_2(OR)$ complexes showed high activities for the syndiotactic polymerization of styrene.[26,27] Trialkoxy ligand-substituted half-titanocenes also showed a strong increase in polymerization activity.[11] The polymerization behavior of alkoxy ligand-substituted titanium complexes could be attributed to electronic and steric effects, and this kind of complex could be prepared easily from $RCpTiCl_3$ and the corresponding alcohol in the presence of NEt_3.

In this study, we introduce two different functional ligands to titanium complexes at the same time and make further investigations into the effects of alkoxy ligands and benzyl substituents on cyclopentadienyl as a weak coordination system. Here, we report the synthesis, characterization and catalytic properties of $PhCH_2CpTiCl_2(OR)$ and $PhCH_2CpTi(OR)_3$.

RESULTS AND DISCUSSION

Synthesis of catalyst precursors

Complex $PhCH_2CpTiCl_3$ was prepared according to the modification of a literature method as shown in Scheme 1.[20] The benzyl-substituted cyclopentadiene was converted to the trimethylsilyl derivative by reaction of benzylcyclopentadiene with *n*-butyllithium followed by chlorotrimethylsilane. This trimethylsilyl derivative was then reacted with $TiCl_4$ in dichloromethane to obtain $PhCH_2CpTiCl_3$.

The $PhCH_2CpTiCl_2(OR)$ complexes (**1–5**) were prepared by the reaction of $PhCH_2CpTiCl_3$ with a stoichiometric amount of lithium alkoxide (see Scheme 2). The oil complexes could be separated out from the solvent by cooling and were element analysis pure.

In the ^{1}H NMR spectrum of complex **3**, the methylene bridge protons appear as two distinct singlets, the protons on cyclopentadienyl appear as three multiplets and the protons of *tert*-butyl appear as two singlets. Other complexes show the same phenomena as complex **3**. From the ^{1}H NMR spectrum,[28] complexes **1–5** may have two conformations as shown in Fig. 1: fully eclipsed and staggered. The chemical shift of the methylene bridge protons and the proportions of the two conformations are summarized in Table 1. The different alkoxy ligands show the different proportions of the two conformations at 20 °C. By increasing the temperature, the proportions of the two conformations of complex **3** were changed from 3.1 to 5.7, as shown in Table 1 and Fig. 2. Because of the bulky benzyl substituent on cyclopentadienyl,

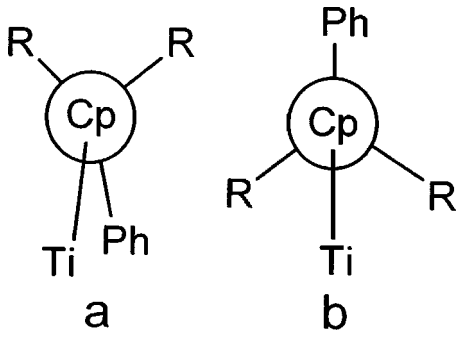
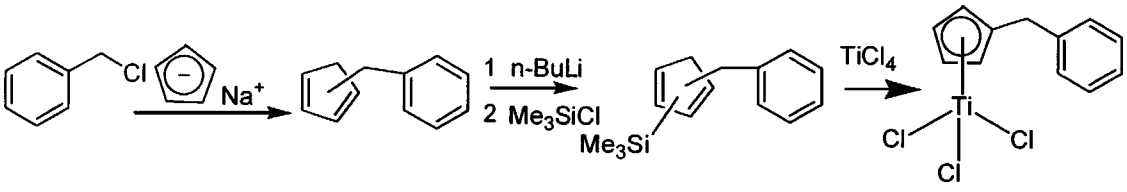
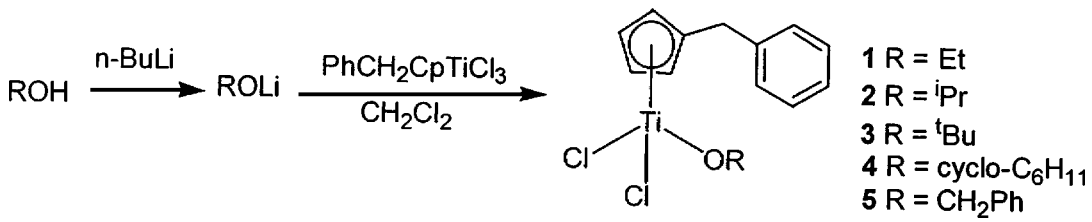


Figure 1. Newman projection of the two possible conformations of complexes $PhCH_2CpTiCl_2(OR)$: (**a**) fully eclipsed; (**b**) staggered.



Scheme 1.



Scheme 2.

Table 1. The ^{1}H NMR spectral data of the methylene group in complexes **1–5** and the proportions of the two conformations

Complexes	δ_1 (4.20 ppm)	δ_2 (4.14 ppm)	δ_2/δ_1
1	0.2382	0.7604	3.2
2	0.2015	0.8888	4.4
3[a]	0.2547	0.8002	3.1
3[b]	0.1744	1.0000	5.7
4	0.4105	2.2025	5.3
5	0.0790	0.1280[c]	1.6

[a] At 20 °C instead of 30 °C.
[b] At 45 °C instead of 50 °C.
[c] At 4.03 ppm instead of 4.14 ppm.

the rate of rotation is temperature-dependent and at the higher temperature the rate of rotation is quicker.

The $PhCH_2CpTi(OR)_3$ complexes (**6–10**) were prepared by the reaction of $PhCH_2CpTiCl_3$ with three equivalents of lithium alkoxide or alcohol in the presence of triethylamine (Scheme 3). Titanium complex **9** bearing three cyclohexyls was prepared by reflux in benzene, prolonging the reaction time to 24 h.

Syndiotactic polymerization of styrene

The $PhCH_2CpTiCl_2(OR)$ completes (**1–5**) were examined as catalyst precursors for syndiotactic polymerization of styrene in the solution using MAO as co-catalyst at various polymerization temperatures; the results are summarized in Table 2. The $PhCH_2CpTiCl_2(OR)$/MAO system shows high activities for styrene polymerization, and the highest activities for this series of complexes are found at 50 °C. The $PhCH_2CpTiCl_2(OR)$/MAO system is slightly more active than the corresponding $PhCH_2CpTiCl_3$/MAO system at 50 °C, and compared with the $CpTiCl_3$/MAO system shows low activities.

Although the nature of the active species in the syndiotactic polymerization of styrene is still under debate among researchers, compelling opinion is that the Ti(III) cationic species plays a very important role in this process.[29–31] The active catalytic site for syndiotactic styrene polymerization, illustrated in Scheme 4,[3] is thought to be $(RCpTiMe)^+(MAO{\cdot}X_2)^-$, where X is an alkoxy or chloride group. The alkoxy or chloride is stripped during formation of the active species but could still surround and stabilize the active species.[26] The alkoxy group is a better π-donor than chloride, which might lead to the generation of a more active site in the $PhCH_2CpTiCl_2(OR)$/MAO system than in the $PhCH_2CpTiCl_3$/MAO system, therefore $PhCH_2CpTiCl_2(OR)$ shows more activity than $PhCH_2CpTiCl_3$.

The steric effect of phenyl substitution could cause a reduction of stereochemical control, as evidenced by the low syndiotacticities and activities for complexes **1–5**

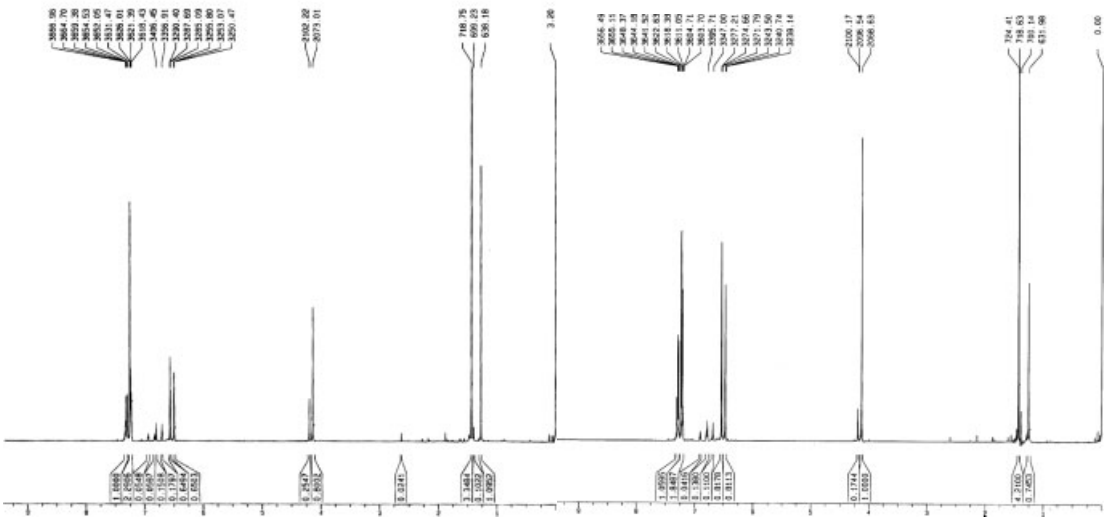
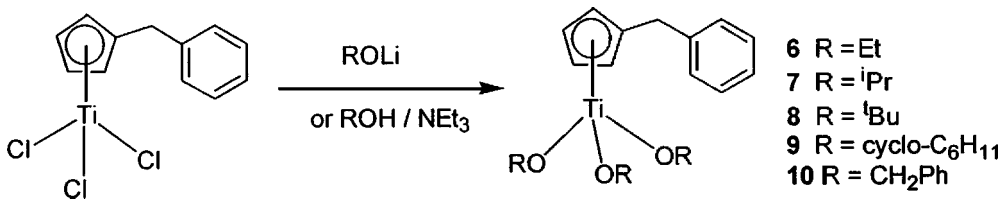


Figure 2. Temperature-dependent ^{1}H NMR spectrum of complex **3** $PhCH_2CpTiCl_2(O^tBu)$ (complex **3**): (i) 20 °C; (ii) 45 °C.

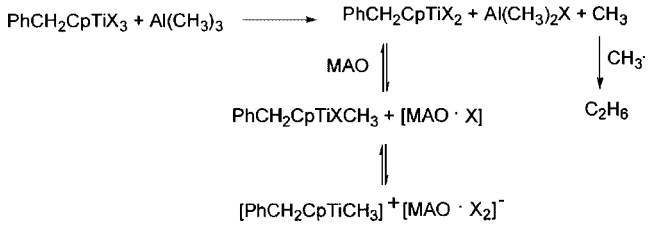


Scheme 3.

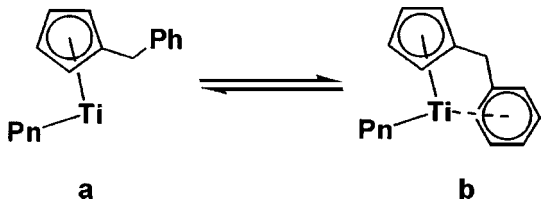
Table 2. Syndiotactic polymerization of styrene in the solution catalyzed by the $PhCH_2CpTiCl_2(OR)$ (complexes **1**–**5**)/MAO system[a]

Catalyst	T_P(°C)	Al/Ti	Time (h)	Yield (g)	Activity[b] ($\times 10^6$)	s-PS[c] (%)
R = Et (**1**)	30	2000	1	0.0578	1.32	93.9
	50	2000	1	0.2540	5.79	80.0
	70	2000	1	0.1071	2.44	73.7
	90	2000	1	0.1357	3.09	82.2
R = ^{i}Pr (**2**)	30	2000	1	0.1307	3.91	76.2
	50	2000	1	0.2627	5.99	79.4
	70	2000	1	0.2133	4.87	70.3
	90	2000	1	0.1453	3.31	57.1
R = ^{t} Bu (**3**)	30	2000	1	0.1867	4.26	92.3
	50	2000	1	0.2048	4.67	92.2
	70	2000	1	0.2042	4.66	78.8
	90	2000	1	0.1623	3.70	79.2
R = cyclo-C_6H_{11} (**4**)	30	2000	1	0.2127	4.85	69.7
	50	2000	1	0.2235	5.10	75.6
	70	2000	1	0.1344	3.07	84.5
	90	2000	1	0.1317	3.00	65.1
R = CH_2Ph (**5**)	30	2000	1	0.1980	4.52	79.5
	50	2000	1	0.2505	5.71	77.4
	70	2000	1	0.2042	4.66	87.7
	90	2000	1	0.1594	3.64	77.4
$PhCH_2CpTiCl_3$	30	2000	1	0.1525	3.48	87.3
	50	2000	1	0.1941	4.43	82.3
	70	2000	1	0.2142	4.89	84.0
	90	2000	1	0.1572	3.59	70.9
$CpTiCl_3$	50	2000	1	0.5655	12.9	90.3

[a] Polymerization conditions: 2 ml of styrene $V_{total} = 12$ ml, [Ti] = 0.21 mmol l^{-1}.
[b] Units: g PS mol^{-1} Ti mol^{-1} styrene h^{-1}.
[c] 2-Butanone-insoluble polymer (g)/bulk polymer (g).



Scheme 4. Formation of initiating species by the $PhCH_2CpTiX_3$/MAO system.



Scheme 5. Active species in equilibrium between states **a** and **b**: Ti represents the metal fagment of the active species.

relative to $CpTiCl_3$ (see Table 2). In a current study of the mechanism for syndiotactic styrene polymerization, the last benzyl group in the propagating chain and the styrene monomer are postulated to complex with the titanium center via multihapto interaction.[19,24,32–35] The active species of arene-substituted cyclopentadienyl titanium appears to be a cationic titanium complex in which the pendant arene group coordinates to the metal center.[16,20,25] The active species is in equilibrium between two states: state **b** with and state **a** without intramolecular phenyl coordination to the Ti center (Scheme 5). The phenyl and Ti interaction in state **b** interferes with styrene coordination so that the polymer chain is not able to grow as quickly as before.

In order to investigate the properties of the polymers obtained, the s-PS sample produced by complex **1** at 50 °C was selected for gel permeation chromatography (GPC) and ^{13}C NMR. The GPC analysis shows s-PS of low molecular weight ($M_w = 2.78 \times 10^4$) and narrow molecular weight distribution ($M_w/M_n = 1.50$), and ^{13}C NMR was used to verify the syndiotacticity of the polymer. The chemical shift of the phenyl C-1 carbon appeared at 145.24 ppm, and the

peak was single and sharp. According to a literature report,[1] we assigned this peak to the *rr* triad configuration, and the *rr* yield is >99%.

The highest activities of this catalyst system are observed at 50 °C. In general, increasing the temperature to 90 °C would lead to a decrease of activity[27] but the activity in this catalyst system did not change significantly from 50 °C to 90 °C. The phenyl group coordinates to the titanium center and provides steric hindrance to stabilize the active species against deactivation, such as reduction or β-hydride elimination at high temperature.[36,37] Even at a high temperature this catalyst system could still maintain a high activity.

Table 2 shows that the different alkoxy ligands affected the activity slightly. Previously, the *tert*-butoxy-substituted half-sandwich titanium complex showed the lowest activity compared with other alkoxy-substituted half-sandwich titanium complexes.[38] Here, the bulky group-substituted complex **3** does not show lower activity than the other complexes. As shown in Table 2, the benzyl substituent on cyclopentadienyl plays a more important role than the alkoxy ligand in syndiotactic styrene polymerization.

Taking complex **1** as a representative of this system, we investigated further the effects of variation of Al/Ti and time on the polymerization. The data in Table 3 show that the activity increases as Al/Ti increases from 500 to 3000 and then decreases slightly when Al/Ti increases further to 4000 together with a slight decrease in s-PS yield from 86.0% to 75.0%. However, with regard to polymerization time, activity is highest at the begining of polymerization and then decreases from 8.33×10^6 to 2.36×10^6g PS mol^{-1}Ti mol^{-1} styrene h^{-1} when the polymerization time is prolonged from 0.5 to 4 h. This behavior of the polymerization rate is similar to that of the Ziegler–Natta catalyst system and the decrease may be attributed to deactivation of the active centers or occlusion of part of the catalyst in the precipitated polymer.[2] It is also revealed from Table 4 that the syndiotacticity of the resultant polymer is affected by the polymerization time increase: the s-PS yield increases from 78.3% to 89.8%.

The $PhCH_2CpTi(OR)_3$ complexes (**6–10**) were also used as catalyst precursors in syndiotactic styrene polymerization in solution using MAO as co-catalyst at 50 °C; the results are presented in Table 5. The trialkoxy ligand-substituted titanium complexes show high activity and high syndiotacticity. The activities of the trialkoxy titanium complexes are slightly different: the *tert*-butoxy ligand titanium complex is the highest and the benzyloxy ligand titanium complex is the lowest. On comparing the two series of titanium complexes, the syndiotacticities of the trialkoxy titanium complexes are higher than the monoalkoxy titanium

Table 3. Syndiotactic polymerization of styrene in the solution catalyzed by the $PhCH_2CpTiCl_2(OEt)$ (complex **1**)/MAO system for different Al/Ti molar ratios[a]

Al/Ti	T_P (°C)	Time (h)	Yield (g)	Activity[b] ($\times 10^6$)	s-PS[c] (%)
500	50	1	0.0502	1.15	71.7
1000	50	1	0.1313	3.00	83.0
2000	50	1	0.2540	5.79	80.0
3000	50	1	0.2987	6.82	86.0
4000	50	1	0.2140	4.88	75.0

[a] Polymerization conditions: 2 ml of styrene, $V_{total} = 12$ ml, [Ti] = 0.21 mmol l^{-1}.
[b] Units: g PS mol^{-1} Ti mol^{-1} styrene h^{-1}.
[c] 2-Butanone-insoluble polymer (g)/bulk polymer (g).

Table 4. Syndiotactic polymerization of styrene in the solution catalyzed by the $PhCH_2CpTiCl_2(OEt)$ (complex **1**)/MAO system for different polymerization times[a]

Al/Ti	T_P (°C)	Time (h)	Yield (g)	Activity[b] ($\times 10^6$)	s-PS[c] (%)
2000	50	0.5	0.1827	8.33	78.3
2000	50	1	0.2540	5.79	80.0
2000	50	2	0.3746	4.27	88.7
2000	50	4	0.4137	2.36	89.8

[a] Polymerization conditions: 2 ml of styrene $V_{total} = 12$ ml, [Ti] = 0.21 mmol l^{-1}.
[b] Units: g PS mol^{-1} Ti mol^{-1} styrene h^{-1}.
[c] 2-Butanone-insoluble polymer (g)/bulk polymer (g).

Table 5. Syndiotactic polymerization of styrene in the solution catalyzed by the $PhCH_2CpTi(OR)_3$ (complexes **6–10**)/MAO system[a]

Catalyst	T_P (°C)	Time (h)	Yield (g)	Activity[b] ($\times 10^6$)	s-PS[c] (%)
$PhCH_2CpTi(OEt)_3$(**6**)	50	1	0.1326	3.03	90.5
$PhCH_2CpTi(O^iPr)_3$(**7**)	50	1	0.1360	3.10	92.5
$PhCH_2CpTi(O^tBu)_3$(**8**)	50	1	0.2389	5.45	87.5
$PhCH_2CpTi(O\text{-cyclo-}C_6H_{11})_3$(**9**)	50	1	0.1848	4.22	94.0
$PhCH_2CpTi(OCH_2Ph)_3$(**10**)	50	1	0.0560	1.29	91.3
$CpTiCl_3$	50	1	0.5655	12.9	90.3

[a] Polymerization conditions: 2 ml of styrene, $V_{total} = 12$ ml, [Ti] = 0.21 mmol l^{-1}, Al/Ti = 2000.
[b] Units: g PS mol^{-1} Ti mol^{-1} styrene h^{-1}.
[c] 2-Butanone-insoluble polymer (g)/bulk polymer (g).

complexes and, this can be attributed to the electronic and steric effects from the three alkoxy ligands, which affect the benzyl group coordination to the titanium center. The syndiotacticities of trialkoxy titanium complexes are also higher than $CpTiCl_3$.

EXPERIMENTAL

All manipulations were carried out under a dry argon atmosphere using standard techniques. Solvents were purified by distillation over sodium benzophenone (diethyl ether, THF, toluene and *n*-hexane) and CaH_2 (dichloromethane).

The MAO was purchased from Witco GmbH. Styrene was purified by washing several times with dilute NaOH solution, drying over anhydrous $CaCl_2$, vacuum distilling from CaH_2 and storing at −20 °C in the dark. The $PhCH_2CpTiCl_3$ complex was prepared by modified literature procedures.[20]

Mass spectra were measured on an HP5989A spectrometer, infrared spectra were recorded on a Nicolet FTIR 5SXC spectrometer and ^{1}H NMR was measured on a Brucker AVANCE-500Hz spectrometer using tetramethylsilane (TMS) as an internal standard. Elemental analyses were performed on an EA-1106 spectrometer.

$PhCH_2CpTiCl_2(OEt)$ (1)

A solution of *n*-BuLi (3.54 ml, 6.49 mmol) in *n*-hexane was added to a stirred solution of dry EtOH (0.299 g, 6.49 mmol) in 15 ml of *n*-hexane at room temperature under an argon atmosphere. The reaction mixture was stirred for 4 h. Then a solution of $PhCH_2CpTiCl_3$ (2.0 g, 6.49 mmol) in 70 ml of CH_2Cl_2 was added at −50 °C. The solution was warmed to room temperature and stirred overnight. The reaction mixture was filtered and the residue was washed with *n*-hexane (2 × 25 ml). All filtrates were combined and the solvent was removed under vacuum. The residue was extracted with *n*-hexane (50 ml) and the extracts were filtered. On cooling to −30 °C, the product was obtained as a yellow oil (1.12 g, 54%), b.p. 137–140 °C/0.2 mmHg. ^{1}H NMR (δ, ppm, $CDCl_3$): 7.34–7.24 (m, 5H), 6.95–6.51 (m, $J = 2.6$ Hz, 4H), 4.6 (q, $J = 7.0$ Hz, 2H), 4.20 (s, 0.5H), 4.13 (s, 1.5H), 1.34 (t, $J = 7.0$ Hz, 2.3H), 1.26 (br, 0.7H). MS (*m/e*): 318 (M^+). IR (cm^{-1}, Nujol mull): 3102m, 2977m, 2871m, 1602w, 1584w, 1493m, 1485w, 1453w, 1428w, 1380m, 1350s, 1240m, 1106w, 1071w, 1053m, 1039m, 936w, 829w, 769w, 704w. Analysis (calc.) for $C_{14}H_{16}Cl_2OTi$: C, 52.70; H, 5.05. Found: C, 52.48; H, 5.12.

$PhCH_2CpTiCl_2(O^iPr)$ (2)

Complex **2** was prepared using the same procedure as for complex **1**: 0.198 g (3.30 mmol) of ^{i}PrOH, 1.8 ml (3.30 mmol) of *n*-BuLi and 1.02 g (3.30 mmol) of $PhCH_2CpTiCl_3$ were used to give 0.55 g (32%) of yellow needle crystal, m.p. 103–105 °C. ^{1}H NMR (δ, ppm, $CDCl_3$): 7.34–7.24 (m, 5H), 6.95–6.50 (m, $J = 2.6$ Hz, 4H), 4.88 (sept, $J = 6.2$ Hz, 1H), 4.20 (s, 0.4H), 4.16 (s, 1.6H), 1.36 (d, $J = 6.2$ Hz, 4.8H), 1.21 (br, 1.2H). MS (*m/e*): 297 (M^+-HCl). IR (cm^{-1}, KBr): 3086m, 3026m, 2975m, 2926m, 1602m, 1493m, 1452m, 1430m, 1381s, 1365s, 1240m, 1112w, 1071w, 1050m, 1013m, 937w, 796w, 706w. Anal. (calc.) for $C_{15}H_{18}Cl_2OTi$: C, 54.09; H, 5.45. Found: C, 53.83; H, 5.45.

$PhCH_2CpTiCl_2(O^tBu)$ (3)

Complex **3** was prepared by the same procedure as for complex **1**: 0.51 g (6.80 mmol) of ^{t}BuOH, 3.71 ml (6.80 mmol) of *n*-BuLi and 2.11 g (6.80 mmol) of $PhCH_2CpTiCl_3$ were used to give 0.99 g (42%) of a yellow oil, b.p. 161–166° C/0.2 mmHg. ^{1}H NMR (δ, ppm, $CDCl_3$): 7.33–7.24 (m, 5H), 6.95–6.50 (m, $J = 2.6$ Hz, 4H), 4.20 (s, 0.5H), 4.15 (s, 1.5H), 1.44 (s, 6.8H), 1.28 (s, 2.2H). MS (*m/e*): 348 ($M^+ + 2$). IR (cm^{-1}, Nujol mull): 3101m, 3085m, 2977m, 2928m, 2867s, 1601w, 1584w, 1493s, 1485s, 1453w, 1429w, 1419m, 1387s, 1364s, 1237m, 1168s, 1071m, 1052m, 1038m, 1014s, 938w, 827s, 769s, 706s. Anal. (calc.) for $C_{16}H_{20}Cl_2OTi$: C, 55.36; H, 5.81. Found: C, 54.81; H, 5.69.

$PhCH_2CpTiCl_2(O\text{-}cyclo\text{-}C_6H_{11})$ (4)

Complex **4** was prepared by the same procedure as for complex **1**: 0.85 g (8.51 mmol) of cyclo-$C_6H_{11}OH$, 4.63 ml (8.51 mmol) of *n*-BuLi and 2.63 g (8.51 mmol) of $PhCH_2CpTiCl_3$ were used to give 1.52 g (48%) of a yellow needle crystal, m.p. 117–119°C. ^{1}H NMR (δ, ppm, $CDCl_3$): 7.34–7.24 (m, 5H), 6.95–6.50 (m, $J = 2.6$ Hz, 4H), 4.62 (m, 1H), 4.20 (s, 0.3H), 4.13 (s, 1.7H), 1.88–1.28 (m, 10H). MS (*m/e*): 372 (M^+). IR (cm^{-1}, KBr): 3097m, 3026m, 2932s, 2854m, 1630m, 1602m, 1493m, 1451m, 1431m, 1359w, 1342w, 1257w, 1125w, 1072m, 1050m, 1035m, 938w, 892w, 839s, 802s, 781s, 762s, 708s. Anal. (calc.) for $C_{18}H_{22}Cl_2OTi$: C, 57.94; H, 5.94. Found: C, 57.83; H, 5.99.

$PhCH_2CpTiCl_2(OCH_2Ph)$ (5)

Complex **5** was prepared using the same procedure as for complex **1**: 0.86 g (7.93 mmol) of $PhCH_2OH$, 4.33 ml (7.93 mmol) of *n*-BuLi and 2.44 g (6.49 mmol) of $PhCH_2CpTiCl_3$ were used to give 1.42 g (47%) of a yellow needle crystal, m.p. 138–141 °C. ^{1}H NMR (δ, ppm, $CDCl_3$): 7.36–7.17 (m, 10H), 6.93–6.39 (m, 4H), 5.49 (s, 1.2H), 4.7 (s, 0.8H), (4.20 s, 0.8H), 4.03 (s, 1.2H). MS (*m/e*): 344 (M^+-HCl). IR (cm^{-1}, KBr): 3096m, 3027m, 2933m, 1602w, 1493m, 1452m, 1432w, 1207w, 1072w, 1049m, 1030m, 940w, 840m, 805s, 782s, 708m. Anal. (calc.) for $C_{19}H_{18}Cl_2OTi$: C, 59.88; H, 4.76. Found: C, 59.78; H, 4.78.

$PhCH_2CpTi(OEt)_3$ (6)

Complex $PhCH_2CpTiCl_3$ (2.62 g, 8.47 mmol) was dissolved in 120 ml of diethyl ether to give a clear yellow solution. Both EtOH (1.37 g, 29.7 mmol) and Et_3N (3.00 g, 29.7 mmol) in 30 ml of diethyl ether were added dropwise over 1 h and stirred overnight. The mixture was filtered and the solvent was removed under vacuum. The residue was distilled under vacuum and the product was collected at 112–114 °C/0.2 mmHg. A yellow oil was obtained in the yield 52% (1.52 g). ^{1}H NMR (δ, ppm, $CDCl_3$): 7.31–7.19 (m,

5H), 6.20 (t, $J = 2.6$ Hz, 2H), 6.07 (t, $J = 2.6$ Hz, 2H), 4.30 (q, $J = 6.8$ Hz, 6H), 3.96 (s, 2 H), 1.20 (t, $J = 6.8$ Hz, 9H). MS (m/e): 338 (M^+). IR (cm^{-1}, Nujol mull): 3083m, 3060m, 3026m, 2969s, 2923m, 2850m, 1602m, 1584w, 1493m, 1452m, 1434m, 1375m, 1354w, 1116s, 1070s, 1052m, 922m, 794s, 705s. Anal. (calc.) for $C_{18}H_{26}O_3Ti$: C, 63.91; H, 7.75. Found: C, 63.77; H, 7.51.

$PhCH_2CpTi(O^iPr)_3$ (7)

Complex 7 was prepared by the same procedure as for complex **6**: 2.92 g (9.44 mmol) of $PhCH_2CpTiCl_3$, 1.70 g (28.3 mmol) of ^{i}PrOH and 2.86 g (28.3 mmol) of Et_3N were used to give 2.19 g (61%) of a yellow oil, b.p. 121–124°C/0.2mm Hg. ^{1}H NMR (δ, ppm, $CDCl_3$): 7.30–7.20 (m, 5H), 6.16 (t, $J = 2.7$ Hz, 2H), 6.01 (t, $J = 2.7$ Hz, 2H), 4.56 (sept, $J = 5.8$ Hz, 3H), 3.95 (s, 2H), 1.17 (t, $J = 5.8$ Hz, 18H). MS (m/e): 261 ($M^+ - 2^i$PrOH). IR (cm^{-1}, Nujol mull): 3085m, 3061m, 3030m, 2969s, 2922m, 2850m, 1601m, 1584w, 1495m, 1454m, 1432m, 1375m, 1354w, 1114s, 1070s, 1057m, 904m, 791s, 705s. Anal. (calc.) for $C_{21}H_{32}O_3Ti$: C, 66.31; H, 8.48. Found: C, 66.13; H, 8.24.

$PhCH_2CpTi(O^tBu)_3$ (8)

Complex **8** was prepared using the same procedure as for complex **6**: 3.34 g (10.81 mmol) of $PhCH_2CpTiCl_3$, 2.80 g (37.84 mmol) of ^{t}BuOH and 3.83 g (37.84 mmol) of Et_3N were used to give 2.10 g (46%) of a yellow oil, b.p. 128–132°C/0.2 mmHg. ^{1}H NMR (δ, ppm, $CDCl_3$): 7.30–7.17 (m, 5H), 6.15 (t, $J = 2.6$ Hz, 2H), 5.94(t, $J = 2.6$Hz, 2H), 3.94 (s, 2H), 1.24 (s, 27H). MS (m/e): 422 (M^+). IR (cm^{-1}, Nujol mull): 3085w, 3062w, 3028w, 2970s, 2924m, 2896m, 1604w, 1584w, 1494m, 1453m, 1382m, 1357s, 1227m, 1205s, 1177s, 1034s, 1002s, 853m, 794s, 704s. High-resolution MS for $C_{24}H_{38}O_3Ti$: calc., 422.2300; found, 422.1605.

$PhCH_2CpTi(O\text{-}cyclo\text{-}C_6H_{11})_3$ (9)

Complex $PhCH_2CpTiCl_3$ (1.19 g, 3.86 mmol) was dissolved in 50 ml of benzene to give a clear yellow solution and then cyclo-$C_6H_{11}OH$ (1.35 g, 13.51 mmol) and Et_3N (1.37 g, 13.51 mmol) in 30 ml of benzene were added dropwise over 1 h and reflexed for 24 h. The solvent was removed under vacuum and the residue was extracted with 100 ml of *n*-hexane and filtered. The filtrate was concentrated by removing the solvent under vacuum, the residue was distilled under vacuum and the product was collected at 160–168 °C/0.2 mmHg as a pale yellow oil in the yield 43% (0.83 g). ^{1}H NMR (δ, ppm, $CDCl_3$): 7.31–7.18 (m, 5H), 6.32 (t, $J = 2.6$Hz, 2H), 6.21 (t, $J = 2.6$ Hz, 2H), 4.40 (m, 1H), 4.03 (s, 2H), 2.00–1.18 (m, 30H). MS (m/e): 500 (M^+). IR (cm^{-1}, Nujol mull): 3105w, 3084w, 3027w, 2931s, 2854m, 1603m, 1584w, 1494m, 1451m, 1361m, 1345s, 1296w, 1260m, 1237w, 1172w, 1032w, 1070s, 1025s, 969m, 888m, 844s, 801s, 703s. High-resolution MS for $C_{30}H_{44}O_3Ti$: calc., 500.2770; found, 500.2866.

$PhCH_2CpTi(OCH_2Ph)_3$ (10)

Complex **10** was prepared using the same procedure as for complex **1**: 2.09 g (19.30 mmol) of $PhCH_2OH$, 10.54 ml (19.30 mmol) of BuLi and 1.87 g (6.03 mmol) of $PhCH_2CpTiCl_3$ were used to give 0.99 g (42%) of a yellow oil. ^{1}H NMR (δ, ppm, $CDCl_3$): 7.34–7.08 (m, 20H), 6.08–6.01 (m, 4H), 5.31 (s, 6H), 3.82 (s, 2H). MS (m/e): (524 (M^+)). IR (cm^{-1}, Nujol mull): 3086m, 3062m, 3028m, 2925m, 2874m, 1604w, 1495m, 1452s, 1365m, 1206m, 1080m, 1041m, 1022m, 910w, 801m, 805s, 734s, 699s. High-resolution MS for $C_{33}H_{32}O_3Ti$: calc., 524.1831; found, 524.1823.

Polymerization procedure and polymer characterization

Polymerization was conducted in small ampoules baked under vacuum and flushed with argon several times. Styrene, toluene and MAO were injected sequentially. After adding the catalyst precursor in toluene, the bottle was placed immediately in an oil bath at the desired polymerization temperature. After 1 h, the polymerization was quenched with 5% HCl in ethanol, filtered, washed with ethanol and dried under vacuum at 80 °C for 24 h to a constant weight. The polymer was extracted with refluxing 2-butanone for 12 h in order to determine the s-PS portion of the polymer obtained.

The ^{13}C NMR spectra were recorded on a Varian GRMINI-300 spectrometer in 1,2-dichlorobenzene at 130 °C. Molecular weight and molecular weight distribution (M_w/M_n) values were obtained from Waters-208 LC/GPC chromatograms employing polystyrene standards for calibration. Analysis was carried out using 1,2-dichlorobenzene at high temperature (140 °C).

CONCLUSION

We have prepared two new series of substituted half-sandwich titanium complexes $PhCH_2CpTiCl_2(OR)$ and $PhCH_2CpTi(OR)_3$. The $PhCH_2CpTiCl_2(OR)$ complexes (**1–5**) have two conformations, which are confirmed by temperature-dependent NMR. All complexes as catalyst precursors show high activities for styrene polymerization. The s-PS obtained exhibits low molecular weight ($M_w = 2.78 \times 10^4$) and narrow molecular weight distribution ($M_w/M_n = 1.50$). Low activities of all complexes relative to $CpTiCl_3$ were observed, indicating that the phenyl group might coordinate strongly to the active center, which interferes with the coordination and insertion of styrene. Introduction of a phenyl group on the cyclopentadienyl ligand increased the stability of the catalysts, which was reflected by activities staying high even at high temperature. The benzyl substituent plays a more important role than alkoxy ligands in syndiotactic styrene polymerization.

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