Styrene polymerization with half-sandwich titanium complexes bearing pendent alkenyl groups: From atactic to syndiotactic

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Abstract

A new series of substituted half-sandwich titanium complexes bearing bridged alkenyl groups $[\eta^5\text{-}C_5H_4\text{-(bridge)-(alkenyl)}]TiCl_3$ have been synthesized and characterized. All the titanium complexes display considerable catalytic activity towards the polymerization of styrene in the presence of methylaluminoxane (MAO). Bridging unit between the cyclopentadienyl moiety and the allyl groups plays a crucial role in reactivity and stereoselectivity of styrene polymerization. By modification of the bridging unit, the syndioselectivity of the polymer can be tailor-made, providing a new guideline to design catalyst for polymers having desired properties.
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Keywords: Alkenyl; Atactic; Syndiotactic; Polystyrene

1. Introduction

Design and synthesis for efficient transition metal catalyst towards precisely controlled polymer properties have attracted considerable attention in the field of organometallic chemistry [1,2]. Since Ishihara and coworkers succeeded in the synthesis of syndiotactic polystyrene (s-PS) in 1985 [3,4] based on titanium compounds and methylaluminoxane (MAO), the cyclopentadienyl ring of the titanium complexes Cp'TiX$_3$ (Cp' = substituted or unsubstituted cyclopentadienyl (Cp) or indenyl ligand; X = halogen, alkoxy, phenoxy) has experienced a wide structure variation in the search for catalysts with higher activity and stereoselectivity [5–9].

It is found that the introduction of electron-donating groups to the Cp ring usually leads to catalysts with higher activity due to the long-term stability of the active species and a lower probability of chain termination [7]. In contrast, introduction of a heteroatom containing substituent leads to a dramatic reduction of polymerization activity. It is believed that the pendant heteroatom intramolecularly coordinates to the active center reducing its electrophilicity, and sterically hinders the coordination and insertion of the styrene molecule [10,11].

Recently, the use of ligands substituted by weaker donors has focused attention on olefin polymerization [11,12]. Hessen [13] reported that titanium complexes with an arene-pendant Cp ligand could selectively trimerize ethylene with high activity. The arene-pendant moiety is likely to exhibit hemilabile behavior by η^6-coordination. Chien [14] demonstrated that the aromatic substituent also plays a very important role in styrene polymerization. We previously reported that introduction of an alkenyl group into the Cp ring can remarkably influence the catalyst's activity [15].

As a part of study of the influence of double bond on the styrene polymerization, herein, we report a new series of titanium complexes bearing bridged alkenyl groups, and investigate the relationship between the structure and their catalytic behavior. By modification of the bridging unit, the syndioselectivity of the polymer can be tailor-made, providing a new guideline to design catalyst for polymers having desired properties.
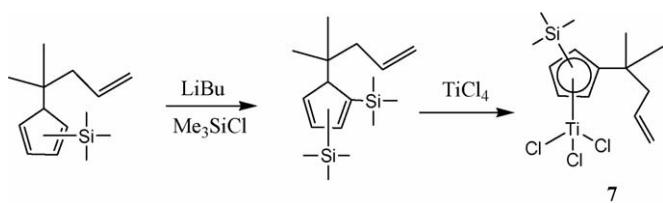
2. Results and discussion

2.1. Synthesis of catalyst precursors

The titanium complexes used in this study can all be described by the general formula $[\eta^5\text{-}C_5H_4\text{-(bridge)-(alkenyl)}]TiCl_3$ (alkenyl = allyl or butenyl). The routes employed for the synthe-

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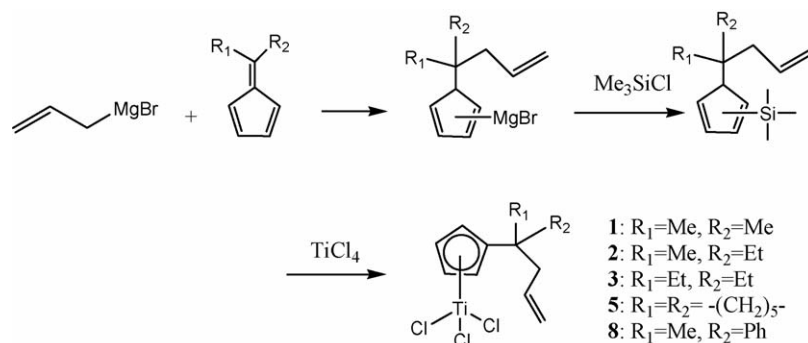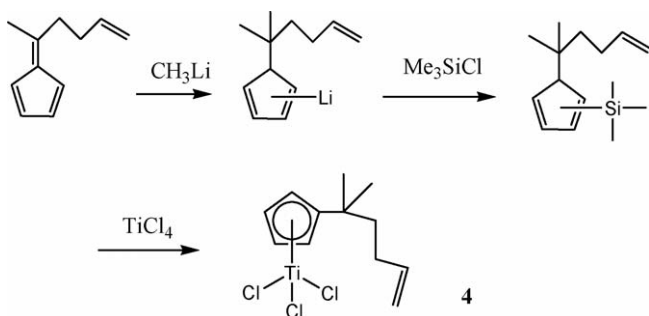
Scheme 1.

Scheme 2.

sis of the [η^5-C$_5$H$_4$-(bridge)-(alkenyl)]TiCl$_3$ compounds were summarized in Schemes 1–3.

Cyclopentadienyl ligands with [-(bridge)-(alkenyl)] substituents were readily accessible from the reaction of 6,6-dialkylfulvenes [16,17] with the appropriate alkenyl magnesium bromide [18] or methyllithium. The resulting addition products reacted with trimethylsilyl chloride to afford the corresponding [C$_5$H$_4$-(bridge)-(alkenyl)]SiMe$_3$ as yellow oils, which were used for subsequent reactions.

The various (cyclopentadienyl) titanium trichlorides were readily prepared via Me$_3$SiCl elimination upon reaction of the appropriate (trimethylsilyl) cyclopentadienyl intermediates with TiCl$_4$. All titanium compounds were characterized by ^{1}H NMR, elemental analysis, MS and IR.

2.2. Polymerization results

The procedure of polymerization reported by Kaminsky [19] was used in our experiment. Constant amounts of MAO were used to ensure the same scavenger effect in each polymerization [19]. All polymerizations were carried out for 30 min and the results are summarized in Table 1.

Scheme 3.

As shown in Table 1, all the catalysts exhibited considerable activities in styrene polymerization. The activities of the catalysts and the syndiotacticity of the polymers located in a wide range of distribution.

2.2.1. Effect of the bridge between the cyclopentadienyl and allyl groups

To probe the structure–performance relationship in the polymerization, the effect of the bridging unit was investigated. We

Table 1
Polymerization of styrene catalyzed by [η^5-C$_5$H$_4$-(bridge)-(alkenyl)]TiCl$_3$/MAO systems[a]

Run	Catalyst	Al/Ti (mol/mol)	Activity[b] (×10^5)	s-PS[c] (%)
1	1 (R$_1$ = R$_2$ = Me)	2000	37.0	88.3
2		4000	52.4	79.5
3		8000	63.8	81.3
4	2 (R$_1$ = Me, R$_2$ = Et)	2000	4.0	45.2
5		4000	4.8	55.9
6		8000	16.0	66.6
7	3 (R$_1$ = R$_2$ = Et)	2000	2.6	13.9
8		4000	4.6	9.5
9		8000	3.2	5.8
10	4	2000	23.1	89.8
11		4000	30.2	94.0
12		8000	31.9	81.5
13	5 (R$_1$ = R$_2$ = cyclo-C$_5$H$_{10}$)	2000	17.9	96.4
14		4000	27.7	99.9
15		8000	13.1	85.6
16	6 (R$_1$ = R$_2$ = H)	2000	108.3	86.4
17		4000	173.1	92.8
18		8000	310.4	89.0
19	7 (CpSiMe$_3$)	2000	35.2	91.3
20		4000	89.8	84.3
21		8000	122.3	75.5
22	8 (R$_1$ = Me, R$_2$ = Ph)	2000	5.14	8.5
23		4000	2.34	2.9
24		8000	0.73	6.2

[a] Polymerization conditions: 50 °C for 0.5 h; styrene = 4 ml; MAO = 6.6 ml [MAO] = 1.53 M; V_{total} = 12 ml.
[b] g PS/(mol Ti·mol S·h).
[c] (g of 2-butanone insoluble polymer)/(g of bulk polymer).

found that, with the increase of steric bulkiness of the substituents on the tertiary carbon between the Cp and allyl moiety, the activities of the catalysts reduced dramatically and the proportion of atactic polystyrene increased significantly.

The catalyst with unsubstituted CH_2 bridge (complex **6** ($R_1=R_2=H$)) between Cp ligand and the allyl moiety exhibited extraordinary high activity, which was about 5 times higher than that of **1** at Al/Ti ratio 8000. We early reported that the activity of complex **6**/MAO system was even higher than that of $CpTiCl_3$/MAO system [15], which implied that the double bond of complex **6** did not coordinate to the active center and could not affect the coordination and insertion of monomer.

When CH_2 bridge between Cp ligand and the allyl moiety was substituted by alkyl groups (Me, Et, etc.), the activities of the catalysts reduced significantly. Intramolecular coordination might rationalize the phenomena.

The evidence is the variation of the chemical shifts of the terminal protons attached to the double bond. According to ^1H NMR, if the double bond is near the titanium atom, the highly electrophilic titanium center will attract the electrons of double bond towards itself and away from the spinning nucleus. This deshielding effect lead to the NMR signal occurring at a lower magnetic field. Table 2 summarised the chemical shifts of the terminal protons attached to the double bond.

It shows that, with the increase of steric bulkness of the substituents, the chemical shifts slightly move to downfield in the order **1 < 2 < 3**. This implies that the tendency of coordination of the double bond to the titanium center is strengthened. As a result, the catalytic activity of the complex and syndiotacticity of the polymer should reduce in the order: **1 > 2 > 3**. As shown in Table 2, the experiment result is consistent perfectly with this presumption. The influence of the substituents on the tertiary carbon is so remarkable that the activity of complex **3** is nearly twenty times lower than that of complex **1**, and the polymer produced by **3**/MAO system is nearly atactic polystyrene.

Unexpectedly, the chemical shift of complex **5** bearing $C(cyclo-C_5H_{10})$ bridge (Table 2) is even smaller in value than that of complex **1**. This implies that the interaction between the double bond and the titanium center in complex **5** is weaker than that of complex **1**, because the rigid 6-member ring skelecton of cyclohexane limit the double bond coordinate to the titanium

Table 2
The chemical shifts of the terminal protons attached to the double bond

Complex	Chemical shift of H_a, H_b (δ, ppm)	Activity[a] ($\times 10^5$)	s-PS[a] (%)
1 (R_1 = Me, R_2 = Me)	5.06–4.94	63.8	81.3
2 (R_1 = Me, R_2 = Et)	5.08–5.00	16.0	66.6
3 (R_1 = Et, R_2 = Et)	5.10–5.07	3.2	5.8
5 [R_1 = R_2 = (cyclo-C_5H_{10})]	4.97–4.89	13.1	85.6

[a] Under the same condition. See also Table 1.

center. As a result, the polystyrene catalyzed by **5**/MAO exhibited the highest syndiotacticity (99.9%, Table 1, run 14).

In our early research, we reported another evidence that the increasing steric bulkiness of the substituents on the tertiary carbon between the Cp ligand and arene moiety forced the arene group move to titanium center. In the preparaion of *o*-MeO-containing benzyl-substituted cyclopentadienyl titanium complexes, when the C_1 bridge is substituted by ethyl or bigger group, the reaction always gives titanoxacycle complexes [20]. Hessen also indicated that disubstituted C_1 bridge between the cyclopentadienyl and arene moieties in $[\eta^5-C_5H_3R-(bridge)-Ar]TiCl_3$ was much more prone to arene coordination, which was the prerequisite for ethylene trimerization [13].

On the basis of experiment result, we propose that, with the increase of steric bulkiness of the substituents on the tertiary carbon between the Cp and allyl moiety, the tendency of intramolecular coordination of the double bond to the titanium center is increased.

The intramolecular coordination, according to the mechanism supposed by Mahanthappa and Waymouth [21], Jo et al. [22], Nifant'ev et al. [23], Cavallo and co-workers [24,25], limits the optimization of the chirality of titanium center and disorder the styrene monomer inserting at a syn position, leading to a result that the atactic proportion is increased in the polymerization.

There might be an intramolecular competition of coordination between the phenyl moiety and the alkenyl moiety in catalyst **8**/MAO. The **8**/MAO system displayed significantly lower polymerization activity and afforded predominantly atactic polystyrene, presumably due to stronger arene coordination to the titanium center [26].

To investigate the intramolecular coordination further, we prolong the chain length between the double bond and the Cp moiety. Complex **4** was synthesized and compared with its C(Me, Me) bridge analogue (complex **1**). The activity of complex **4** is relatively slower than that of complex **1**. Although the prolonged double bond is less prone to coordination, the effect of steric hindrance is also increased remarkably.
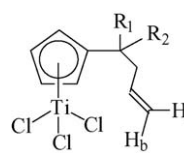
2.2.2. Effect of substituents on the cyclopentadienyl group

The effect of the attachment of substituents on the cyclopentadienyl moiety was probed by the catalytic behavior of the precatalyst $CH_2=CHCH_2C(CH_3)_2Cp(SiMe_3)TiCl_3$. As expected, the activity of **7**/MAO can reach 1.22×10^7 g PS/(mol Ti·mol S·h) which is remarkably higher than that of **1**/MAO under the same condition. Obviously, the electron-donating trimethylsilyl group of **7** increases the electron density on the titanium center, and better stabilizes the electrophilic titanium center. As a result, the concentration of active species increases, which leads to higher activity. Furthermore, chain transfer via β-H elimination is likely to be suppressed, because of the stronger electron-donating ability of the substituent Cp ligand as compared to unsubstituent Cp ligand [24,25].

2.2.3. The influence of temperature

Generally, the activities of complexes, which contain intramolecular coordination groups, increase with the tempera-
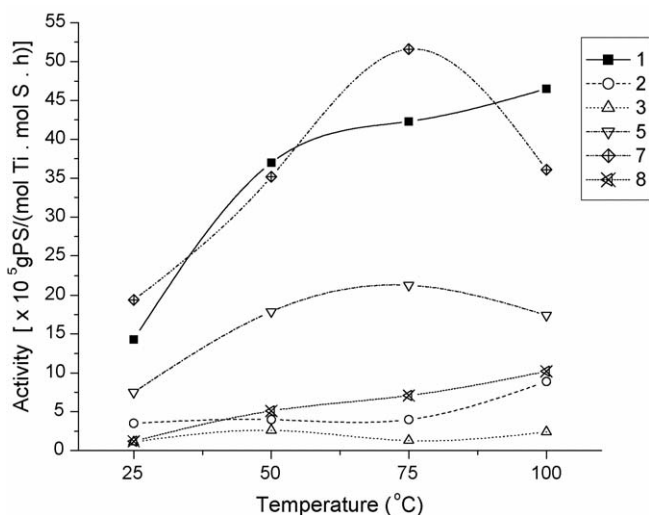
Fig. 1. Dependence of the activity on polymerization temperatures. Polymerization conditions: catalyst = 5 μmol; Al/Ti = 2000; T_P = 0.5 h; styrene = 4 ml; MAO = 6.6 ml; [MAO] = 1.53 M; V_{total} = 12 ml.

ture, because the intramolecular coordination is less tight at high temperatures. The dependence of activity and syndiotacticity on the temperatures is summarized in Figs. 1 and 2. Within the range of 25–75 °C, the activities of the most of catalysts increase with the temperature, which is consistent with the $[\eta^5$-C_5H_4-(bridge)-Ar]TiCl$_3$/MAO system reported by Zambelli and co-workers [26]. It was noteworthy pointing out that complex **7** exhibited the highest activity at 75 °C. We presume that, the tendency of the intramolecular coordination of the double bond to the titanium center is weakened at higher temperatures.

At 100 °C, the activity of some of the catalysts (**5**, **7**) somewhat decreased. This decrease is attributed to decomposition of the catalyst or to deactivation of the active centers. Basically, all the complexes exhibited remarkable thermal stability at high temperatures.
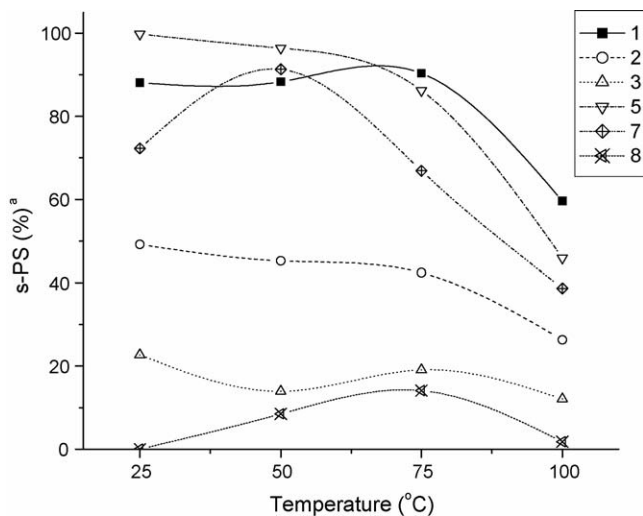

Fig. 2. Dependence of the syndiotacticity on polymerization temperatures. [a](g of 2-butanone insoluble polymer)/(g of bulk polymer); polymerization conditions: catalyst = 5 μmol; Al/Ti = 2000; T_P = 0.5 h; styrene = 4 ml; MAO = 6.6 ml; [MAO] = 1.53 M; V_{total} = 12 ml.
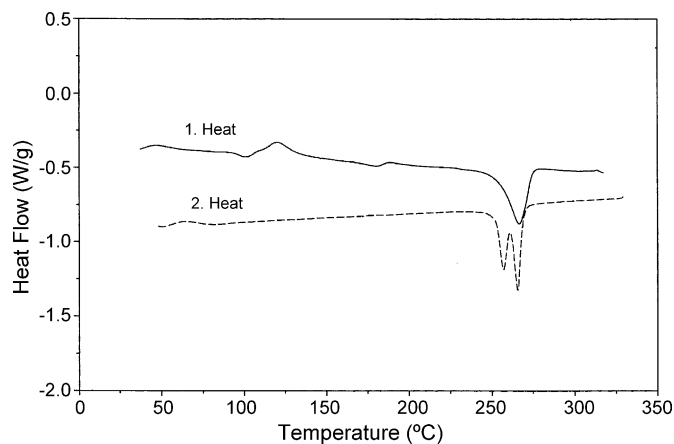

Fig. 3. First and second heatings of a DSC thermogram of an s-PS sample produced with **2**/MAO.

2.2.4. Polymer analyses

Thermal property of s-PS produced by **1**/MAO and **2**/MAO were measured using differential scanning calorimetry (DSC). A melting point of 267 °C was observed for s-PS produced by complex **1** (Table 1, run 1). However, s-PS produced by **2**/MAO (Table 1, run 4) shows a more complex behavior. A melting point of 266 °C was observed during the first heating, but two melting points (256 and 265 °C) were observed during the second heating (Fig. 3). Kaminsky and co-workers have reported that the s-PS produced by BzCpTiCl$_3$/MAO have three melting points during the second heating [19]. We presume this may be owing to different crystalline polymorphic structure of s-PS produced by $[\eta^5$-C_5H_4-(bridge)-(alkenyl)]TiCl$_3$/MAO catalytic systems.

2.2.5. Combination effects of ligand and polymerization condition

Three major parameters in the styrene polymerization: activity, selectivity, and stability can be remarkably influenced by the substituents on the key positions (backbone, cyclopentadienyl, and alkene). Combined with the polymerization condition, the styrene polymerization can be adjusted within syndiotactic and atactic polymerization. The syndiotactic proportion range from 0–99.9% (Fig. 2). Catalyst **8** afforded atactic polystyrene, whereas catalyst **5** afforded syndiotactic polystyrene (99.9%). Other catalysts exhibited the behavior of transition states. These adjustable results provided a possibility that the polymer can be tailor-made, providing a new guideline to design catalyst for polymers having desired properties.

3. Experimental part

3.1. Materials and general procedures

All manipulations were carried out under a dry argon atmosphere using standard Schlenk techniques. Solvents were purified by distillation over sodium benzophenone (diethyl ether, tetrahydrofuran(THF), toluene and *n*-hexane) and P$_2$O$_5$ (dichloromethane). MAO was produced by Witco GmbH. Styrene was purified by washing several times with dilute NaOH solution, dried over anhydrous CaCl$_2$, vacuum distillation from

CaH$_2$ and stored at −20 °C in darkness. Complex **6** was synthesized according to the literature [15].

Mass spectra were measured on an HP5989A spectrometer. IR spectra were recorded on a Nicolet FTIR 5SXC spectrometer. ^{1}H NMR was measured on a Brucker AVANCE-500 Hz spectrometer using tetramethylsilane (TMS) as an internal standard.

Elemental analyses were performed on an EA-1106 spectrometer. DSC was performed on a TA DSC 2910. The samples (10 mg) were heated to 330 °C, cooled at 5 °C/min to 30 °C, and heated again to 330 °C at a heating rate of 20 °C/min.

3.2. Polymerization procedure

Polymerization was conducted in small ampoules heated under vacuum and flushed with argon several times. Styrene, toluene, and MAO were sequentially injected, and the catalyst precursor in toluene was then added. The bottle was immediately placed in an oil bath at the desired polymerization temperature. After 30 min, the polymerization was quenched with 10% HCl in ethanol, filtered, and dried under vacuum at 80 °C for 24 h to a constant weight. The syndiotacticity of s-PS was calculated according to the equation: s-PS(%) = [(g of 2-butanone insoluble polymer)/(g of bulk polymer)] × 100.

3.3. Synthesis of complexes

3.3.1. Synthesis of complex 1
3.3.1.1. Synthesis of CH$_2$=CHCH$_2$C(CH$_3$)$_2$CpSiMe$_3$. To the solution of CH$_2$=CHCH$_2$MgCl (94 mmol) in 100 ml of diethyl ether, was added dropwise 10.1 g (94 mmol) of dimethylfulene. The mixture was stirred overnight, and 10.2 g (94 mmol) Me$_3$SiCl in 50 ml of THF was slowly added. The reaction mixture was stirred for 4 h. Subsequently, the mixture was poured into ice water and extracted with petroleum. The organic phase was dried over magnesium sulphate. The volatiles were removed in vacuo, and the residue was distilled at 48 °C/9 Pa to give a yellow oil. Yield 10 g, 48.4%. ^{1}H NMR (δ, ppm, CDCl$_3$): 6.61 (d, J = 4.8 Hz, 1H, Cp–H), 6.45 (d, J = 4.8 Hz, 1H, Cp–H), 6.06 (s, 1H, Cp–H), 5.76–5.64 (m, 1H, CH=), 5.01–4.96 (m, 2H, CH$_2$=), 3.24 (s, 1H, Cp–H), 2.26–2.21 (m, 2H, CH$_2$), 1.16 (s, 6H, CH$_3$), 0.16–0.05 (m, 9H, SiMe$_3$).

3.3.1.2. Synthesis of CH$_2$=CHCH$_2$C(CH$_3$)$_2$CpTiCl$_3$ (1). To the solution of 1 ml (9 mmol) of TiCl$_4$ was added dropwise 2 g (9 mmol) CH$_2$=CHCH$_2$C(CH$_3$)$_2$CpSiMe$_3$ in 30 ml of CH$_2$Cl$_2$. The colour changed to dark red. The mixture was stirred overnight and the solvent was removed in vacuo to give a dark-red oil which solidified after 1 day. Recrystallization in hexane afforded bright yellow crystals. Yield: 1.59 g, 58.4%. ^{1}H NMR (δ, ppm, CDCl$_3$): 7.02 (t, J = 2.7 Hz, 2H, Cp–H), 6.89 (t, J = 2.7 Hz, 2H, Cp–H), 5.63–5.54 (m, 1H, CH=), 5.06–4.94 (m, 2H, CH$_2$=), 2.30 (d, J = 7.2 Hz, 2H, CH$_2$), 1.43 (s, 6H, CH$_3$). EIMS (m/e): 259 (M^+–CH$_2$=CHCH$_2$, 18), 223 (M^+–CH$_2$=CHCH$_2$–HCl, 100), 224 (M^+–CH$_2$=CHCH$_2$–Cl, 19). IR (KBr, cm^{-1}): 3100 m, 3080 m, 2990 s, 1640 m, 1480 m,

1050 s, 1000 m, 700 s. Anal. calc. for C$_{11}$H$_{15}$Cl$_3$Ti: C, 43.82; H, 5.01; found C, 43.85; H, 5.29.

3.3.2. Synthesis of complex 2
3.3.2.1. Synthesis of CH$_2$=CHCH$_2$C(CH$_3$) (C$_2$H$_5$) CpSiMe$_3$. To the solution of CH$_2$=CHCH$_2$MgCl (58 mmol) in 100 ml of diethyl ether, was added dropwise 7 g (58 mmol) of 6-methyl-6-ethylfulene in 10 ml of diethyl ether. The mixture was stirred overnight, and 6.5 g (60 mmol) of Me$_3$SiCl in 20 ml of THF was slowly added. The reaction mixture was stirred for 4 h. Subsequently, the mixture was poured into ice water and extracted with petroleum. The organic phase was dried over magnesium sulphate. The volatiles were removed in vacuo, and the residue was distilled at 51–52 °C/10 Pa to give a yellow oil. Yield: 8.7 g, 62.0%. ^{1}H NMR (δ, ppm, CDCl$_3$): 6.59 (d, J = 4.8 Hz, 1H, Cp–H), 6.47 (d, J = 4.8 Hz, 1H, Cp–H), 6.08 (s, 1H, Cp–H), 5.76–5.68 (m, 1H, CH=), 5.04–4.98 (m, 2H, CH$_2$=), 3.25 (s, 1H, Cp–H), 2.35–2.21 (m, 2H, CH$_2$), 1.63–1.48 (m, 2H, CH$_2$), 1.13 (s, 3H, CH$_3$), 0.79–0.74 (m, 3H, CH$_3$), 0.18–0 (m, 9H, SiMe$_3$).

3.3.2.2. Synthesis of CH$_2$=CHCH$_2$C (CH$_3$) (C$_2$H$_5$) Cp TiCl$_3$ (2). To the solution of 1.1 ml (10 mmol) of TiCl$_4$ in 10 ml of CH$_2$Cl$_2$ was added dropwise 2 g (8.5 mmol) of CH$_2$=CHCH$_2$C (CH$_3$) (C$_2$H$_5$) CpSiMe$_3$ in 30 ml CH$_2$Cl$_2$. The colour changed to dark-red. The mixture was stirred overnight and the solvent was removed in vacuo to give a dark-red oil which solidified after 1 day. Recrystallization in hexane afforded bright brown crystals. Yield: 1.113 g, 41.5%. ^{1}H NMR (δ, ppm, CDCl$_3$): 7.04–7.02 (m, 2H, Cp–H), 6.91–6.88 (m, 2H, Cp–H), 5.67–5.59 (m, 1H, CH=), 5.08–5.00 (m, 2H, CH$_2$=), 2.46 (d, J = 7.3 Hz, 2H, CH$_2$), 1.76–1.71 (m, 2H, CH$_2$), 1.40 (s, 3H, CH$_3$), 0.77 (m, 3H, CH$_3$). EIMS (m/e): 273 (M^+–CH$_2$=CHCH$_2$, 11), 237 (M^+–CH$_2$=CHCH$_2$-HCl, 100), 238 (M^+–CH$_2$=CHCH$_2$-Cl, 23). IR (KBr, cm^{-1}): 2890 s, 1640 m, 1380 m, 1050 s, 1000 m, 890 s, 700 s. Anal. calc. for C$_{12}$H$_{17}$Cl$_3$Ti: C, 45.68; H, 5.43; found C, 45.98; H, 5.65.

3.3.3. Synthesis of complex 3
3.3.3.1. Synthesis of CH$_2$=CHCH$_2$C (C$_2$H$_5$)$_2$CpSiMe$_3$. To the suspension of CH$_2$=CHCH$_2$MgCl (60 mmol) in 100 ml of diethyl ether was added dropwise 7 g (60 mmol) of diethylfulene. The mixture was stirred overnight, and 6.5 g (60 mmol) of Me$_3$SiCl in 20 ml of THF was slowly added. The reaction mixture was stirred for 4 h. Subsequently, the mixture was poured into ice water and extracted with petroleum. The organic phase was dried over magnesium sulphate. The volatiles were removed in vacuo, and the residue was distilled at 51–52 °C/10 Pa to give a yellow oil. Yield 9.1 g, 61.1%. ^{1}H NMR (δ, ppm, CDCl$_3$): 6.56 (d, J = 4.8 Hz, 1H, Cp–H), 6.47–6.46 (m, 1H, Cp–H), 6.08 (d, J = 1.2 Hz, 1H, Cp–H), 5.72–5.64 (m, 1H, CH=), 5.06–4.97 (m, 2H, CH$_2$=), 3.23 (s, 1H, Cp–H), 2.31–2.28 (m, 2H, CH$_2$), 1.56–1.50 (m, 4H, CH$_2$), 0.74–0.69 (m, 6H, CH$_3$), 0.17–0 (m, 9H, SiMe$_3$).

3.3.3.2. Synthesis of CH$_2$=CHCH$_2$C (C$_2$H$_5$)$_2$ CpTiCl$_3$ (3). To the solution of 1 ml (9 mmol) of TiCl$_4$ in 10 ml of CH$_2$Cl$_2$

was added dropwise 2 g (8.1 mmol) of $CH_2=CHCH_2C$ $(C_2H_5)_2$ $CpSiMe_3$ in 30 ml CH_2Cl_2. The colour changed to dark-red. The mixture was stirred overnight and the solvent was removed in vacuo to give a dark-red oil which solidified after 1 day. Recrystallization in hexane afforded bright yellow crystals. Yield: 1.0 g, 38%. ^{1}H NMR (δ, ppm, $CDCl_3$): 7.06 (t, $J = 2.7$ Hz, 2H, Cp–H), 6.91 (t, $J = 2.7$ Hz, 2H, Cp–H), 5.81–5.73 (m, 1H, CH=), 5.10–5.07 (m, 2H, CH_2=), 2.53 (d, $J = 7.3$ Hz, 2H, CH_2), 1.81 (q, $J = 7.5$, 4H, CH_2), 0.86 (t, $J = 7.5$, 6H, CH_3). EIMS (*m/e*): 287 (M^+–$CH_2=CHCH_2$, 8), 251 (M^+–$CH_2=CHCH_2$–HCl, 100), 252 (M^+–$CH_2=CHCH_2$–Cl, 18). IR (KBr, cm^{-1}): 2890 s, 1640 m, 1380 m, 1050 s, 1000 m, 920 s, 700 s. Anal. calc. for $C_{13}H_{19}Cl_3Ti$: C, 47.38; H, 5.81; found C, 47.44; H, 6.10.

3.3.4. Synthesis of complex 4

3.3.4.1. Synthesis of $CH_2=CHCH_2$ $CH_2C(CH_3)_2CpSiMe_3$. To the solution of CH_3Li in diethyl ether (82 ml, 59 mmol) was added dropwise 7.8 g (53.4 mmol) of ($CH_2=CHCH_2CH_2$) $(CH_3)C=C_5H_4$ fulvene. The mixture was stirred overnight, and 5.8 g (53.4 mmol) of Me_3SiCl in 20 ml of THF was slowly added. The reaction mixture was stirred for 4 h. Subsequently, the mixture was poured into ice water and extracted with petroleum. The organic phase was dried over magnesium sulphate. The volatiles were removed in vacuo, and the residue was distilled at 58 °C/7.5 Pa to give a yellow oil. Yield 6.5 g, 48.4%. ^{1}H NMR (δ, ppm, $CDCl_3$): 6.58–6.55 (m, 1H, Cp–H), 6.44–6.43 (m, 1H, Cp–H), 6.05 (s, 1H, Cp–H), 5.83–5.74 (m, 1H, CH=), 4.97–4.85 (m, 2H, CH_2=), 3.23 (s, 1H, Cp–H), 1.93–1.87 (m, 2H, CH_2), 1.60–1.51 (m, 2H, CH_2), 1.16 (s, 6H, CH_3), 0.18–0.00 (m, 9H, $SiMe_3$).

3.3.4.2. Synthesis of $CH_2=CHCH_2$ $CH_2C(CH_3)_2CpTiCl_3$ (4). To the solution of 1 ml (9 mmol) of $TiCl_4$ was added dropwise 1 g (4.3 mmol) $CH_2=CHCH_2C(CH_3)_2CpSiMe_3$ in 25 ml of toluene. The colour changed to dark-red. The mixture was stirred overnight and the solvent was removed in vacuo to give a dark-red oil which solidified after 1 day. Recrystallization in hexane afforded bright red crystals. Yield: 339 mg, 25%. ^{1}H NMR (δ, ppm, $CDCl_3$): 7.01 (m, 2H, Cp–H), 6.88 (m, 2H, Cp–H), 5.76–5.66 (m, 1H, CH=), 4.98–4.88 (m, 2H, CH_2=), 1.89–1.81 (m, 2H, CH_2), 1.67–1.61 (m, 2H, CH_2), 1.43 (s, 6H, CH_3). EIMS (*m/e*): 259 (M^+–$CH_2=CHCH_2$, 28), 223 (M^+–$CH_2=CHCH_2$–HCl, 100), 224 (M^+–$CH_2=CHCH_2$–Cl, 24). IR (KBr, cm^{-1}): 3100 m, 3080 m, 2890 s, 1640 m, 1370 m, 1050 s, 1000 m, 920 s, 690 s. Anal. calc. for $C_{12}H_{17}Cl_3Ti$: C, 45.68; H, 5.43; found C, 46.05; H, 5.67.

3.3.5. Synthesis of complex 5

3.3.5.1. Synthesis of $CH_2=CHCH_2C$ (cyclo-C_5H_{10}) $CpSiMe_3$. To the solution of $CH_2=CHCH_2MgCl$ (68.4 mmol) in 100 ml of diethyl ether was added dropwise 10 g (68.4 mmol) of (cyclo-C_5H_{10}) $C=C_5H_4$ fulvene. The mixture was stirred overnight, and 7.4 g (60 mmol) Me_3SiCl in 40 ml of THF was slowly added. The reaction mixture was stirred for 4 h. Subsequently, the mixture was poured into ice water and extracted with petroleum. The organic phase was dried over magnesium sulphate. The volatiles were removed in vacuo, and the residue was distilled at

69–85 °C/20 Pa to give a yellow oil. Yield 7.2 g, 40.5%. ^{1}H NMR (δ, ppm, $CDCl_3$): 6.58–6.55 (m, 1H, Cp–H), 6.46–6.44 (m, 1H, Cp–H), 6.11 (s, 1H, Cp–H), 5.67–5.59 (m, 1H, CH=), 4.97–4.92 (m, 2H, CH_2=), 3.26 (s, 1H, Cp–H), 2.21 (d, $J = 7.2$ Hz, 2H, CH_2), 1.52–1.35 (m, 10H, CH_2), 0.17–0 (m, 9H, $SiMe_3$).

3.3.5.2. Synthesis of $CH_2=CHCH_2C$ (cyclo-C_5H_{10}) $CpTiCl_3$ (5). To the solution of 0.72 ml (4.2 mmol) of $TiCl_4$ in 10 ml of CH_2Cl_2 was added dropwise 1 g (3.8 mmol) of $CH_2=CHCH_2C$ (cyclo-C_5H_{10}) $CpSiMe_3$ in 10 ml of CH_2Cl_2. The colour changed to dark red. The mixture was stirred overnight and the solvent was removed in vacuo to give a dark-red oil which solidified after 1 day. Recrystallization in hexane afforded bright yellow crystals. Yield: 29 mg, 40.8%. ^{1}H NMR (δ, ppm, $CDCl_3$): 7.01 (t, $J = 2.7$ Hz, 2H, Cp–H), 6.88 (t, $J = 2.7$ Hz, 2H, Cp–H), 5.42–5.34 (m, 1H, CH=), 4.97 (m, 1H, CH_2=), 4.89 (m, 1H, CH_2=), 2.44 (d, $J = 7.4$ Hz, 2H, CH_2), 1.99–1.22 (m, 10H, CH_2). EIMS (*m/e*): 299 (M^+–$CH_2=CHCH_2$, 7), 263 (M^+–$CH_2=CHCH_2$–HCl, 100). IR (KBr, cm^{-1}): 2890 s, 1640 w, 1420 m, 920 w, 800 m, 700 m. Anal. calc. for $C_{14}H_{19}Cl_3Ti$: C, 49.23; H, 5.61; found C, 49.04; H, 5.74.

3.3.6. Synthesis of complex 7

3.3.6.1. Synthesis of $CH_2=CHCH_2C(CH_3)_2Cp(SiMe_3)_2$. To the solution of $CH_2=CHCH_2C(CH_3)_2CpSiMe_3$ (36 mmol) in 50 ml diethyl ether and 20 ml THF was added dropwise 19.5 ml (36 mmol) of BuLi. The mixture was stirred overnight, and 4.34 g (40 mmol) of Me_3SiCl in 20 ml of THF was slowly added. The reaction mixture was stirred for 4 h. Subsequently, the mixture was poured into ice water and extracted with petroleum. The organic phase was dried over magnesium sulphate. The volatiles were removed in vacuo, and the residue was distilled at 57–71 °C/2 Pa to give a red oil. Yield 8.1 g, 77.1%. ^{1}H NMR (δ, ppm, $CDCl_3$): 6.66 (m, 1H, Cp–H), 6.41 (m, 1H, Cp–H), 6.06 (t, $J = 1.7$ Hz, 1H, Cp–H), 5.74–5.65 (m, 1H, CH=), 4.99–4.93 (m, 2H, CH_2=), 2.25 (d, $J = 7.3$ Hz, 2H, CH_2), 1.14 (s, 6H, CH_3), 0 (m, 18H, $SiMe_3$).

3.3.6.2. Synthesis of $CH_2=CHCH_2C(CH_3)_2Cp(SiMe_3)TiCl_3$ (7). To a solution of 0.4 ml (3.6 mmol) of $TiCl_4$ in 15 ml of CH_2Cl_2 was added dropwise 1 g (3.4 mmol) of $CH_2=CHCH_2C(CH_3)_2Cp(SiMe_3)_2$ in 25 ml CH_2Cl_2. The colour changed to dark red. The mixture was stirred overnight and the volatiles were removed in vacuo to yield the dark-red oil, which was 95% pure, as seen by NMR spectroscopy. Yield: 457 mg, 36%. ^{1}H NMR (δ, ppm, $CDCl_3$): 7.11 (s, 1H, Cp–H), 7.00 (m, 1H, Cp–H), 6.95 (m, 1H, Cp–H), 5.56–5.47 (m, 1H, CH=), 4.98–4.80 (m, 2H, CH_2=), 2.28–2.15 (m, 2H, CH_2), 1.39 (s, 3H, CH_3), 1.32 (s, 3H, CH_3), 0.28 (s, 9H, $SiMe_3$). EIMS (*m/e*): 331 (M^+–$CH_2=CHCH_2$, 22), 295 (M^+–$CH_2=CHCH_2$–HCl, 100), 296 (M^+–$CH_2=CHCH_2$–Cl, 22). IR (KBr, cm^{-1}): 3100 m, 3080 m, 2890 s, 1640 m, 1370 m, 1050 s, 920 s, 690 s.

3.3.7. Synthesis of complex 8

3.3.7.1. Synthesis of $CH_2=CHCH_2C(CH_3)$ (C_6H_5) $CpSiMe_3$. To the solution of $CH_2=CHCH_2MgCl$ (26.8 mmol) in 30 ml

of diethyl ether was added dropwise 4.5 g (26.8 mmol) of $(CH_3)(C_6H_5)C=C_5H_4$. The mixture was stirred overnight, and 3.0 g (26.7 mmol) of Me_3SiCl in 25 ml of THF was slowly added. The reaction mixture was stirred for 4 h. Subsequently, the mixture was poured into ice water and extracted with petroleum. The organic phase was dried over magnesium sulphate. The volatiles were removed in vacuo, and the residue was distilled at 97–100 °C/25 Pa to give a yellow oil. Yield 3.0 g, 39.7%. ^{1}H NMR (δ, ppm, $CDCl_3$): 7.40–7.15 (m, 5H, Ph-H), 6.42–6.21 (m, 3H, Cp–H), 5.62–5.53 (m, 1H, CH=), 5.05–4.95 (m, 2H, CH_2=), 3.27 (m, 1H, Cp–H), 2.80–2.73 (m, 2H, CH_2), 1.53–1.50 (m, 3H, CH_3), 0.12–0 (m, 9H, $SiMe_3$).

3.3.7.2. Synthesis of $CH_2=CHCH_2CH(CH_3)$ (C_6H_5) $CpTiCl_3$ (8). To a solution of 1 ml (9.1 mmol) of $TiCl_4$ in 15 ml of CH_2Cl_2 was added dropwise 2.2 g (7.7 mmol) of $CH_2=CHCH_2C(CH_3)_2CpSiMe_3$ in 25 ml of CH_2Cl_2. The colour changed to dark red. The mixture was stirred overnight and the solvent was removed in vacuo to give a dark-red oil which solidified after 1 day. Recrystallization in hexane afforded bright yellow crystals. Yield: 379 mg, 13.9%. ^{1}H NMR (δ, ppm, $CDCl_3$): 7.32 (m, 2H, Ph-H), 7.27–7.22 (m, 3H, Ph-H), 7.18 (m, 1H, Cp–H), 6.95 (m, 1H, Cp–H), 6.88 (m, 1H, Cp–H), 6.77 (m, 1H, Cp–H), 5.47–5.38 (m, 1H, CH=), 5.11–5.02 (m, 2H, CH_2=), 3.16 (m, 1H, CH_2), 2.93 (m, 1H, CH_2), 1.81 (s, 3H, CH_3). EIMS (*m/e*): 321 (M^+–$CH_2=CHCH_2$, 34), 285 (M^+–$CH_2=CHCH_2$–HCl, 100), 286 (M^+–$CH_2=CHCH_2$–Cl, 25). IR (KBr, cm^{-1}): 3070 s, 2920 s, 1640 m, 1600 m, 1380 m, 1250 s, 920 s, 700 s. Anal. calc. for $C_{16}H_{17}Cl_3Ti$: C: 52.86 H: 4.71; found C: 51.99 H: 4.98.

4. Conclusion

A new series of substituted half-sandwich titanium complexes bearing bridged alkenyl groups [η^5-C_5H_4-(bridge)-(alkenyl)]$TiCl_3$ have been synthesized and characterized. All the titanium complexes display considerable catalytic activity towards the polymerization of styrene in the presence of methylaluminoxane (MAO). The highest activity of 1.22×10^7 g PS/(mol Ti·mol S·h) was obtained in **7**/MAO catalytic system. Bridging unit between the cyclopentadienyl moiety and the allyl groups plays a crucial role in reactivity and stereoselectivity of styrene polymerization. By modification of the bridging unit, the syndioselectivity of the polymer can be tailor-made, providing a new guideline to design catalyst for polymers having desired properties.

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