

# Synthesis of double silylene-bridged binuclear titanium complexes and their use as catalysts for ethylene polymerization

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## Abstract

Five new double silylene-bridged binuclear titanium complexes were synthesized by the reaction of  $\text{RCpTiCl}_3$  and  $\text{Li}_2[\mu, \mu\text{-(SiMe}_2)_2(\text{C}_5\text{H}_3)_2]$  in toluene. They were all well characterized. These complexes activated with methylaluminoxane (MAO) are highly active catalysts ( $2.33 \times 10^5$  g PE/mol Cat h) for the polymerization of ethylene even at low Al/Ti (Al/Ti = 300). The molecular weight distribution of the polymer indicates broad or bimodal (MWD = 26.76) distribution.

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**Keywords:** Double silylene-bridged; Binuclear; Titanocene; Catalysis; Polyethylene

## 1. Introduction

Recently, there is much interest in the binuclear catalysts because of the cooperative electronic and chemical interaction between the two catalytic centers. This interaction could affect catalysis behavior, for example, the catalytic activities and molecular weight of the obtained polymer different from that of mononuclear catalyst [1]. To control the distance between the coordination sites will require a certain degree of rigidity of ligand. If two cyclopentadienyl rings bridged by a single unit, the relative orientation between the two metals may vary in an uncontrolled manner because of the rotation about the Si–Cp bond. With two  $\text{Me}_2\text{Si}$  between the two cyclopentadienyl rings, a less flexible system would fasten the position between the two metals [2].

The chemistry of mononuclear Group 4 complexes (Fig. 1) with symmetric and asymmetric rings bridged by doubly  $\text{Me}_2\text{Si}$  and their potential application as catalysts in stereo-selective hydrogenation and polymerization of olefins has been extensively studied [3].

Different mono- and bi-nuclear transition metal derivatives containing  $[\mu, \mu\text{-(SiMe}_2)_2(\text{C}_5\text{H}_3)_2]^{2-}$  have been reported [4,2(a)], but few Group 4 binuclear complexes are known

[2(b),5]. In 1994, Royo and co-workers [3(a)] reported the first trichloride titanium complex containing  $[\mu, \mu\text{-(SiMe}_2)_2(\text{C}_5\text{H}_3)_2]^{2-}$  (Fig. 2).

In 1995, Corey et al. [2(b)] synthesized binuclear titanium complexes (Fig. 3).

The first complexes containing unsymmetrical-bridged binuclear titanium complexes was prepared by Huhmann et al. [5(b)] in 1996 (Fig. 4).

Lang et al. [5(a)] first studied the double silylene-bridged binuclear titanium complexes as efficient catalyst precursors for ethylene polymerization in 1995 (Fig. 5).

Recently, Wang and co-workers [6] reported the effective polymerization of ethylene with mixed-bridged binuclear metallocene complexes (Fig. 6).

All the results revealed that these types of complexes polymerize olefins effectively. In our previous work, we found that mono-bridged hetero-binuclear or homo-binuclear titanium complexes with different substituted cyclopentadienyl ring gave good result on the polymerization of olefin [7]. We are always interest in studying the reactivity of cyclopentadienyl Group 4 metal complexes which using the  $[\mu, \mu\text{-(SiMe}_2)_2(\text{C}_5\text{H}_4)_2]$  as a unit to increase the stereo rigidity of the complexes. Here, we report the synthesis of a series of double silylene-bridged binuclear titanium complexes, which contain alkyl and potential coordination group (allyl and benzyl) on the Cp ring. Their application for ethylene polymerization under low ratio of Al/Ti was also studied.

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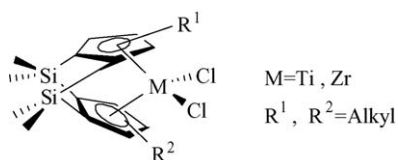
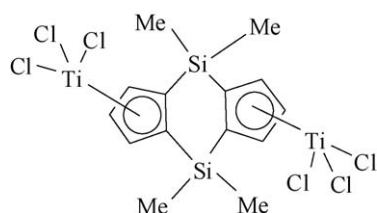
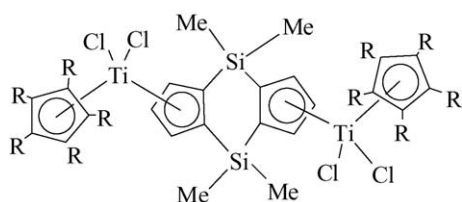


Fig. 1. Double silylene-bridged mononuclear group 4 complexes.

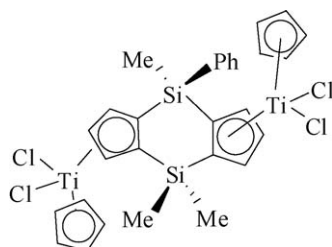


Pascual Royo, 1994

Fig. 2. Complex of  $[\text{TiCl}_3]_2[\mu, \mu\text{-(Me}_2\text{Si)}_2(\text{C}_5\text{H}_3)_2]$ .

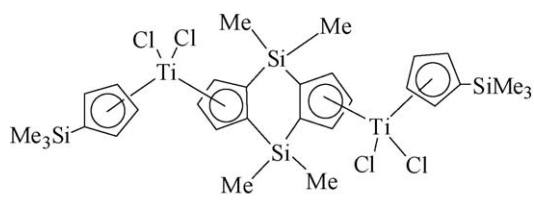
Joyce Y. Corey, 1995

Fig. 3. Binuclear titanium complex.

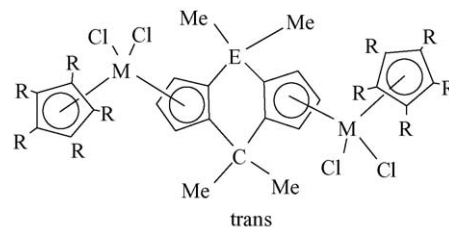


Jean L. Huhmann, 1996

Fig. 4. Asymmetrical-bridged binuclear titanium complex.



Heinrich Lang, 1995

Fig. 5. Complex of  $[(\text{Me}_3\text{SiCp})\text{TiCl}_2]_2[\mu, \mu\text{-(Me}_2\text{Si)}_2(\text{C}_5\text{H}_3)_2]$ .

R=H, Me E=Si, Ge, M=Ti, Zr

Wang, 2002

Fig. 6. Mixed-bridged binuclear metallocene.

## 2. Results and discussion

### 2.1. Synthesis of complexes 1–5

The general synthetic route to prepare complexes **1–5** was the reaction of 2 equiv. of  $\text{RCpTiCl}_3$  with  $\text{Li}_2[\mu, \mu\text{-(Me}_2\text{Si)}_2(\text{C}_5\text{H}_3)_2]$  in toluene as shown as Scheme 1, all the complexes were characterized by  $^1\text{H NMR}$ , MS, IR and EA.

The complexes are soluble in  $\text{CH}_2\text{Cl}_2$  and toluene, sensitive to moisture and air. They have two isomers in theory but only trans one was obtained. The *cis*- and *trans*-isomers can be easily distinguished by the  $^1\text{H}$  signals of the bridging  $\text{SiMe}_2$  units, for the trans isomer all four methyl groups are equivalent and only one methyl resonance signal is observed. Affected by doubly bridge, a significant upfield shift (0.2 ppm) is observed for the signal of the  $\text{Me}_2\text{Si}$  linked to cyclopentadienyl ring compared with the corresponding signal of single  $\text{Me}_2\text{Si}$ -bridged titanium complexes [7(b)].

### 2.2. Polymerization results

The synthesized binuclear complexes **1–5** were used for the homogeneous polymerization of ethylene and it was found they are effective catalysts. The result of ethylene polymerization using these binuclear complexes is shown in Table 1.

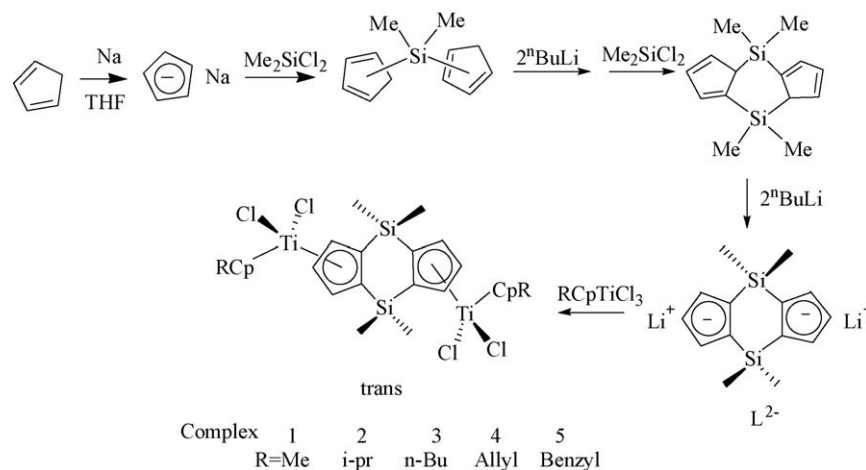
All the complexes show high activity for the polymerization of ethylene especially at low ratio Al/Ti which similar to the result of Lang et al. [5(a)].

The activity reaches to its maximum when R is *n*-Bu (complex **3**,  $A = 2.33 \times 10^5$  g PE/mol Cat h). Compared with  $\text{Cp}_2\text{TiCl}_2$ , alkyl substituted group on cyclopentadienyl ring would keep

Table 1  
Results of olefin polymerization catalyzed by complexes **1–5**/MAO

Cat.	Al/Ti	Act. ( $\times 10^5$ g PE/mol Cat h)	$M_n$ ( $\times 10^5$ g/mol)
$\text{Cp}_2\text{TiCl}_2$	300	2.15	1.28
<b>1</b>	300	2.08	1.91
<b>2</b>	300	2.16	3.06
<b>3</b>	300	2.33	5.73
<b>4</b>	300	1.38	1.37
<b>5</b>	300	1.62	3.67

Conditions:  $T = 75^\circ\text{C}$ ,  $t = 30$  min,  $V = 25$  ml, catalyst = 0.002 mmol, and  $P_{\text{C}_2\text{H}_4} = 1.0$  MPa.



Scheme 1. Route for the synthesis of complexes 1–5.

Table 2  
The effect of pressure to the MWD

$P_{\text{ethylene}}$ (MPa)	$M_n$	$M_w$	Polydispersity
0.1	190896	437256	2.2905
1.0	7164	191683	26.7574

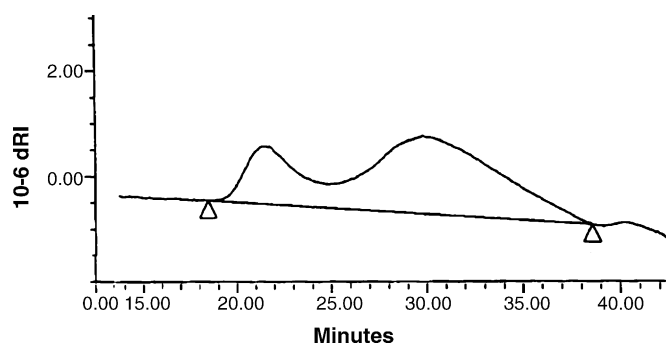
Conditions:  $t = 30$  min,  $V = 25$  ml, catalyst = 0.002 mmol, Al/Ti = 1000, and  $T = 60$  °C.

high activity of polymerization while the potential coordinate group (**4** allyl, **5** benzyl) decreased the activity. It is possible that the coordination [5(d)] between the potential coordinate group and active Ti atom would remarkably reduce the space where ethylene monomer inserted.

The molecular weight of the polymer is similar to that of mono-bridged binuclear titanium complexes [7(c)].

Molecular weight distribution (MWD) curves of obtained polyethylene appeared broad and bimodal distribution. The GPC results of the polymer obtained from **3** are shown in Table 2 and Fig. 7.

These results may indicate that the interaction between two metals creates more than one kind of active species during the polymerization. When activated with MAO, it is possible that the activities of the two Ti atoms are not equal, so bimodal (MWD = 26.76) PE was obtained under 1.0 MPa.

Fig. 7. GPC of ethylene polymerization by complex **3**,  $P_{\text{ethylene}} = 1.0$  MPa.Table 3  
The effects of temperature to the polymerization of ethylene by complex **3**

Temperature (°C)	30	45	60	75	90
Activity	1.48	2.39	2.47	3.34	1.10
$M_n$	2.65	5.95	6.03	5.43	3.03

Conditions:  $t = 30$  min,  $V = 25$  ml, catalyst = 0.002 mmol, act.:  $\times 10^5$  g PE/mol Cat h,  $M_n$ :  $\times 10^5$  g/mol,  $P_{\text{C}_2\text{H}_4} = 1.0$  MPa, and Al/Ti = 1000.

Complex **3** was used to test the effect of different polymerization conditions. The result on temperature variation with activity is presented in Table 3.

It is obvious that 75 °C is an optimum temperature below or above which the activity is lower. We supposed that the catalytic system was not stable under high temperature, so the activity decreased when the temperature was above optimum point.

The effect of time on polymerization is presented in Table 4.

From the table it can be seen that catalytic activity decreases gradually with time, after about 1.5 h a sharp decline happens, probably due to the deactivation of catalyst. Compared with the single-bridged system [7(b)], the catalytic system was much more stable.

The dependence of activity (A) on the Al/Ti molar ratio is presented in Table 5.

There is a direct relationship between activities and ratio of Al/Ti. The result implies that for practical purpose Al/Ti molar ratio (150–500) is the ideal for polymerization, and any increase will have little impact on activity as we can see. The increase of Al/Ti molar ratio from 150 to 3000 only increases the activ-

Table 4  
The effect of time to the polymerization of ethylene by complex **3**

Time (h)	0.5	1.0	1.5	2.0
Activity ( $\times 10^5$ g PE/mol Cat h)	3.34	2.74	2.72	1.42
$M_n$ ( $\times 10^5$ g/mol)	5.43	2.79	2.95	2.96

Conditions:  $t = 30$  min,  $V = 25$  ml, catalyst = 0.002 mmol,  $P_{\text{ethylene}} = 1.0$  MPa, Al/Ti = 1000/1, and  $T = 75$  °C.

Table 5  
The effect of Al/Ti to the polymerization of ethylene by complex 3

Al/Ti	150	300	500	750	1000	2000	3000
Activity	1.18	2.33	3.03	3.22	3.34	4.01	4.68
$M_n$	4.08	5.73	5.26	5.67	5.43	4.88	3.76

Conditions:  $T = 75^\circ\text{C}$ ,  $t = 30$  min,  $V = 25$  ml, catalyst = 0.002 mmol,  $P_{\text{ethylene}} = 1.0$  Mpa, act.:  $\times 10^5$  g polymer/mol Cat h, and  $M_n$ :  $\times 10^5$  g/mol.

ity to  $4.68 \times 10^5$  g PE/mol Cat h. Actually, commercialization of the metallocene-based catalysts process suffers from some difficulties such as the excessive amounts of expensive MAO required for activation. This is impractical both commercially in terms of cost and technologically because of the amount of residues left in the polymer, so design and synthesis high activity metallocene-based catalysts with less co-catalysts is a very important work.

**Conclusion.** The double-bridged binuclear titanium complexes are high activity catalyst for ethylene polymerization under comparable low ratio of Al/Ti and bimodal PE was obtained.

### 3. Experimental

#### 3.1. General conditions

All manipulations were carried out under an argon atmosphere using standard Schlenk techniques. Solvents (THF, toluene, and *n*-hexane) were dried over the sodium-benzophenone ketyl and distilled. Halogenated solvents were distilled from  $\text{P}_2\text{O}_5$ . The titanium complexes  $\text{RCpTiCl}_3$  were synthesized from the reaction of  $\text{RCpSiMe}_3$  with  $\text{TiCl}_4$  in toluene as the literature [8].  $[\mu, \mu\text{-(SiMe}_2)_2(\text{C}_5\text{H}_4)_2]$  and  $\text{Li}_2[\mu, \mu\text{-(SiMe}_2)_2(\text{C}_5\text{H}_3)_2]$  was synthesized by the procedure described by Huhmann et al. [5(b)].  $^1\text{H NMR}$  spectra were measured on a Gemini-300 NMR Spectrometer using  $\text{DMSO-}d_6$  as solvent and  $\text{Me}_4\text{Si}$  as an internal standard. Mass spectra were performed on a HP-5989A Mass Spectrometer (EI/70 eV). IR spectra were recorded on a Nicolet Magna-IR550 IR Spectrometer.

#### 3.2. Preparation of complex 1 $[\text{MeCpTiCl}_2]_2$ $[\mu, \mu\text{-(SiMe}_2)_2(\text{C}_5\text{H}_3)_2]$

To a solution of 668 mg (2.74 mmol) of  $[\mu, \mu\text{-(SiMe}_2)_2(\text{C}_5\text{H}_4)_2]$  in 50 ml of THF, 3.4 ml (1.60 M, 5.4 mmol) of *n*-BuLi in hexane was added dropwise at r.t. A gradually color change from colorless to white was happened and then stirred for extra 3 h. Then, 1.315 g (5.63 mmol)  $\text{MeCpTiCl}_3$  was added at  $-30^\circ\text{C}$ . A rapid color change from white to red was observed. The mixture warmed to r.t. and stirred over night than settled. After that, the solvent was removed under reduced pressure, the residue was washed with THF 20 ml  $\times$  2 and hexane 20 ml  $\times$  2, then dried under reduced pressure, red crystals (153 mg) were obtained by recrystallization from THF/hexane (8% yield based on Ti). Mp  $224^\circ\text{C}$ . Anal. Calc. for  $\text{C}_{26}\text{H}_{32}\text{Cl}_4\text{Si}_2\text{Ti}_2$ ; Calc.:

C 48.93%, H 5.05%; found: C 48.66%, H 5.06%;  $^1\text{H NMR}$  (500 MHz,  $\text{DMSO-}d_6$ ) 7.37 (d,  $J = 2.5$ , 4H), 6.70–6.78 (m, 6H), 6.18 (t,  $J = 2.3$ , 4H), 2.17 (s, 6H), 0.38 (s, 12H). IR (KBr,  $\text{cm}^{-1}$ ): 3180 (w), 3093 (w), 3079 (w), 2988 (w), 2950 (w), 2923 (w), 2896 (w), 2855 (w), 1496 (m), 1448 (m), 1407 (w), 1373 (m), 1243 (m), 1210 (m), 1070 (w), 1052 (m), 1041 (w), 1023 (w), 975 (m), 900 (w), 845 (s), 818 (vs), 782 (s), 698 (w), 678 (m), 645 (w), 597 (w), 514 (m). MS:  $m/z$  636 (2,  $M^+$ ); 601 (2,  $M^+ - \text{Cl}$ ); 566 (1,  $M^+ - 2\text{Cl}$ ).

#### 3.3. Preparation of complex 2 $[\text{i-PrCpTiCl}_2]_2$ $[\mu, \mu\text{-(SiMe}_2)_2(\text{C}_5\text{H}_3)_2]$

The same procedure as described for complex 1 was used. 576 mg (2.36 mmol) of  $[\mu, \mu\text{-(SiMe}_2)_2(\text{C}_5\text{H}_4)_2]$ , 2.95 ml (1.60 M, 4.72 mmol) of *n*-BuLi, and 1.236 g (4.72 mmol) *i*-PrCpTiCl<sub>3</sub> were reacted to give 255 mg (15.6% yield based on Ti) complex 2 of deep red crystals. Mp  $264^\circ\text{C}$ . Anal. Calc. for  $\text{C}_{30}\text{H}_{40}\text{Cl}_4\text{Si}_2\text{Ti}_2$ ; Calc.: C 51.88%, H 5.82%; found: C 51.96%, H 5.85%;  $^1\text{H NMR}$  (500 MHz,  $\text{DMSO-}d_6$ ) 7.37 (d,  $J = 2.3$ , 4H), 6.71 (t,  $J = 2.3$ , 2H), 6.72 (s, 4H), 6.27 (s, 4H), 3.01–3.04 (m,  $J = 6.9$ , 2H), 1.13 (d,  $J = 6.9$ , 12H), 0.39 (s, 12H). IR (KBr,  $\text{cm}^{-1}$ ): 3105 (w), 3080 (m), 2975 (m), 2970 (m), 2890 (w), 2880 (w), 1495 (m), 1146 (m), 1430 (m), 1400 (w), 1380 (m), 1215 (m), 1240 (m), 1080 (w), 1070 (m), 970 (m), 910 (w), 930 (w), 870 (m), 850 (s), 815 (vs), 780 (s), 680 (m), 600 (w), 520 (m). MS:  $m/z$  692 (0.2,  $M^+$ ); 657 (1,  $M^+ - \text{Cl}$ ); 622 (1,  $M^+ - 2\text{Cl}$ ).

#### 3.4. Preparation of complex 3 $[\text{n-BuCpTiCl}_2]_2$ $[\mu, \mu\text{-(SiMe}_2)_2(\text{C}_5\text{H}_3)_2]$

The same procedure as described for complex 1 was used. 1.247 g (4.75 mmol) of  $[\mu, \mu\text{-(SiMe}_2)_2(\text{C}_5\text{H}_4)_2]$ , 6.0 ml (1.60 M, 9.60 mmol) of *n*-BuLi, and 2.605 g (9.50 mmol) *n*-BuCpTiCl<sub>3</sub> were reacted to give 957 mg (27.9% yield based on Ti) complex 3 of red crystals. Mp  $254^\circ\text{C}$ . Anal. Calc. for  $\text{C}_{32}\text{H}_{44}\text{Cl}_4\text{Si}_2\text{Ti}_2$ ; Calc.: C 53.19%, H 6.15%; found: C 53.21%, H 6.14%;  $^1\text{H NMR}$  (500 MHz,  $\text{DMSO-}d_6$ ) 7.36 (s, 4H), 6.72 (m, 6H), 6.21 (s, 4H), 2.55 (t,  $J = 7.3$ , 4H), 1.44–1.50 (m,  $J = 7.3$ , 4H), 1.24–1.30 (m,  $J = 7.3$ , 4H), 0.86 (t,  $J = 7.3$ , 6H), 0.40 (s, 12H). IR (KBr,  $\text{cm}^{-1}$ ): 3100 (m), 3090 (m), 3070 (m), 2945 (m), 2930 (m), 2850 (m), 1495 (m), 1470 (w), 1460 (w), 1450 (w), 1430 (w), 1400 (w), 1380 (w), 1240 (s), 1210 (s), 1100 (w), 1080 (w), 1050 (m), 960 (m), 870 (m), 850 (s), 840 (s), 810 (vs), 780 (s), 680 (m), 520 (m). MS:  $m/z$  720 (0.2,  $M^+$ ); 685 (0.4,  $M^+ - \text{Cl}$ ); 650 (1,  $M^+ - 2\text{Cl}$ ).

#### 3.5. Preparation of complex 4 $[\text{CH}_2=\text{CHCH}_2\text{CpTiCl}_2]_2$ $[\mu, \mu\text{-(SiMe}_2)_2(\text{C}_5\text{H}_3)_2]$

The same procedure as described for complex 1 was used. 605 mg (2.48 mmol) of  $[\mu, \mu\text{-(SiMe}_2)_2(\text{C}_5\text{H}_4)_2]$ , 3.1 ml (1.60 M, 4.96 mmol) of *n*-BuLi, and 1.287 g (4.96 mmol)  $\text{CH}_2=\text{CHCH}_2\text{CpTiCl}_3$  were reacted to give 641 mg (37.4% yield based on Ti) complex 4 of red crystals. Mp  $271^\circ\text{C}$ . Anal. Calc. for  $\text{C}_{30}\text{H}_{36}\text{Cl}_4\text{Si}_2\text{Ti}_2$ ; Calc.: C 52.20%, H 5.26%; found: C 52.33%, H 5.30%;  $^1\text{H NMR}$  (500 MHz,  $\text{DMSO-}d_6$ ) 7.39 (d,

$J=2.5$ , 4H), 6.74–6.76 (m, 6H), 6.22 (t,  $J=2.5$ , 4H), 5.88 (m, 2H), 4.99–5.05 (m, 4H), 3.35 (d,  $J=7.3$ , 4H), 0.39 (s, 12H). IR (KBr,  $\text{cm}^{-1}$ ): 3098 (m), 2954 (m), 2924 (s), 2853 (m), 1638 (m), 1494 (m), 1462 (w), 1427 (m), 1409 (w), 1379 (w), 1242 (s), 1211 (s), 1080 (w), 1052 (m), 996 (w), 961 (m), 906 (w), 859 (s), 840 (vs), 814 (vs), 778 (s), 752 (w), 733 (w), 695 (w), 678 (m), 642 (w), 623 (w), 588 (w), 571 (w), 515 (m). MS:  $m/z$  688 (1,  $M^+$ ); 653 (1,  $M^+ - \text{Cl}$ ); 618 (2,  $M^+ - 2\text{Cl}$ ).

### 3.6. Preparation of complex **5** [ $\text{PhCH}_2\text{CpTiCl}_2$ ]<sub>2</sub> [ $\mu, \mu$ -( $\text{SiMe}_2$ )<sub>2</sub> ( $\text{C}_5\text{H}_3$ )<sub>2</sub>]

The same procedure as described for complex **1** was used. 564 mg (2.31 mmol) of [ $\mu, \mu$ -( $\text{SiMe}_2$ )<sub>2</sub> ( $\text{C}_5\text{H}_4$ )<sub>2</sub>], 2.9 ml (1.60 M, 4.64 mmol) of *n*-BuLi, and 1.4349 g (4.63 mmol)  $\text{PhCH}_2\text{CpTiCl}_3$  were reacted to give 490 mg (26.9% yield based on Ti) complex **5** of red crystals. Mp 277 °C. Anal. Calc. for  $\text{C}_{38}\text{H}_{40}\text{Cl}_4\text{Si}_2\text{Ti}_2$ ; Calc.: C 57.73%, H 5.11%; found: C 57.66%, H 5.20%;  $^1\text{H}$  NMR (500 MHz,  $\text{DMSO}-d_6$ ) 7.43 (d,  $J=2.5$ , 4H), 7.16–7.29 (m, 10H), 6.76 (t,  $J=2.4$ , 4H), 6.74 (t,  $J=2.5$ , 2H), 6.30 (t,  $J=2.4$ , 4H), 3.88 (s, 4H), 0.42 (s, 12H). IR (KBr,  $\text{cm}^{-1}$ ): 3110 (w), 3080 (w), 3025 (w), 2920 (w), 1720 (w), 1600 (w), 1480 (m), 1460 (w), 1450 (w), 1420 (w), 1400 (w), 1370 (w), 1250 (m), 1215 (m), 1080 (w), 1060 (m), 1035 (m), 960 (m), 850 (s), 820 (vs), 780 (s), 705 (s), 680 (m), 520 (m). MS:  $m/z$  788 (0.1,  $M^+$ ); 753 (0.1,  $M^+ - \text{Cl}$ ); 718 (3,  $M^+ - 2\text{Cl}$ ).

### 3.7. Olefin polymerization

Ethylene was purified by passage through 4 Å molecular sieves. Polymerization was carried out in a reactor placed in a thermostatically heated bath and equipped with a magnetic stirrer. MAO, toluene solution of metallocene and more toluene to bring the final volume to 25 ml were added to the reactor in that sequence. The reaction mixture was stirred vigorously at desirable temperature and pre-dried ethylene at desirable pressure was pumped in for a 30 min and a small amount of ethanol/HCl was added to quench the polymerization. The polymer was fil-

tered and then dried in vacuum at 60 °C over night to constant weight.

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