

# Disiloxane bridged indenyl metallocene catalysts for olefin polymerizations <sup>☆</sup>

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## Abstract

Two new disiloxanyl-bridged bis(indenyl) Group 4 metallocenes, [*rac*-1,3-bis( $\eta^5$ -indenyl)-1,1,3,3-tetramethyldisiloxane]dichlorotitanium (**2**) and -zirconium (**3**), have been synthesized from the corresponding ligand 1,1,3,3-tetramethyl-1,3-bis(indenyl)disiloxane (**5**), which in turn was obtained by the hydrolysis of (1-indenyl)chlorodimethylsilane (**4**). Both **2** and **3** exhibit unusual and unexpected catalysis behaviors for olefin polymerization. They polymerize ethylene only when activated by methyl aluminoxane (MAO) but not by  $\text{Ph}_3\text{C}^+\text{B}(\text{C}_6\text{F}_5)_4^-$ -tri-isobutylaluminum (**7**). The Ti precursor **2** does not polymerize propylene with either cocatalyst, whereas the Zr precursor **3** exhibited moderate activity to produce atactic polypropylene, even though **3** is  $C_2$  symmetric. The propylene polymerization activities of **3**-MAO increased strongly while that of **3**-**7** decreased slightly with the increase in  $T_p$ . These catalytic behaviors may be the result of  $\sigma$  donation from oxygen atom of the siloxane bridge to metal center.

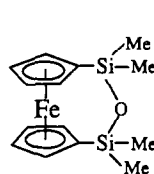
**Keywords:** Titanium; Zirconium; Disiloxane bridged indenyl metallocene; Catalysis

## 1. Introduction

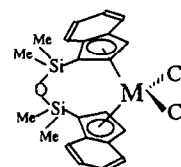
The discoveries of stereospecific  $\alpha$ -olefin polymerizations by 14-electron *ansa*-metallocene cations of Group 4 elements [1] have revolutionized Ziegler–Natta catalysis. Various types of ring-bridging group have been developed to investigate the influence of the corresponding *ansa*-metallocene precursor on the olefin polymerization behavior of the catalyst derived from it [2]. It is now generally recognized that metallocenes having a single-atom rigid bridge structure exhibit good activity and high stereoselectivity in propylene polymerization [2f,3]. Metallocenes with a two-atom, more flexible bridge perform less well by comparison. Thus far, only a few Group 4 metallocenes with a three-atom bridge have been synthesized, including those with a trimethylene group [4], and none of these studies has dealt with their polymerization catalysis. Compared with one- or two-atom bridges, the trimethylene group is exceedingly flexible. However, another triatomic bridge, 1,1,3,3-tetramethyldisiloxanediy,  $-\text{Me}_2\text{SiOSiMe}_2-$ , is

less likely to be as flexible as  $-(\text{CH}_2)_3-$  in a metallocene complex, because of conformational effects resulting from the four methyl substituents.

The first disiloxane-bridged metallocene, a ferrocene derivative [1,3-bis-( $\eta^5$ -cyclopentadienyl)-1,1,3,3-tetramethyldisiloxane]iron (**1**), was prepared by



**1**



**2** M = Ti

**3** M = Zr

Schaaf et al. [5] in 1961. Curtis et al. [6] subsequently reported a Group 4 tetramethyldisiloxane-bridged metallocene  $[\text{O}(\text{Me}_2\text{SiC}_5\text{H}_4)_2]\text{TiCl}_2$  and determined its X-ray structure. More recently, Royo and coworkers [7] have prepared the analogous zirconium compound  $[\text{O}(\text{Me}_2\text{SiC}_5\text{H}_4)_2]\text{ZrCl}_2$  and demonstrated that its

<sup>☆</sup> Dedicated to Professor Herbert Schumann on the occasion of his 60th birthday.

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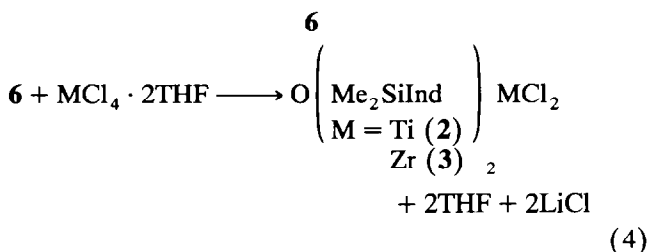
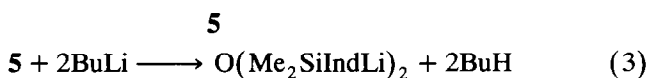
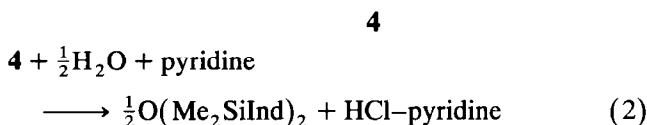
molecular structure was similar to that of the titanium analog. Fischer and coworkers [8] have also recently synthesized several stable tetramethyldisiloxane-bridged "lanthanocene" halides, including  $[O(Me_2SiC_5H_4)_2]PrCl \cdot THF$  (THF = tetrahydrofuran) and  $\{[O(Me_2SiC_5H_4)_2]YbCl\}_2$ , and carried out a low temperature X-ray diffraction study of the Yb analog.

We report here the syntheses and characterization of the first disiloxane-bridged bis(indenyl)metallocenes, [*rac*-1,3-bis( $\eta^5$ -indenyl)-1,1,3,3-tetramethyldisiloxane]-dichlorotitanium (**2**) and -zirconium (**3**), as well as a study of their properties as catalysts for ethylene and propylene polymerizations.

## 2. Results

### 2.1. Synthesis of **2** and **3**

The syntheses of **2** and **3** involve the following reactions:



The synthesis of  $Me_2SiIndCl$  (**4**) from indenyllithium and dichlorodimethylsilane proceeded at high conversion (Eq. (1)). The hydrolysis of **4** (Eq. (2)) was carried out at  $-30^\circ C$  and continued overnight at room temper-

ature. Shortly after the product **5** was distilled from the reaction mixture, it changed from colorless to yellow. Elemental analysis of **5** therefore had to be performed immediately after its synthesis in order to obtain satisfactory results. Conversion of **5** to its dilithium salt **6** was carried out in THF solution (Eq. (3)). The final step (Eq. (4)) afforded the *ansa*-metallocene complexes **2** and **3** with approximately 30–40% yields, owing to side reactions leading to polymeric products. The latter were minimized by the simultaneous addition of dianion solution **6** and  $MCl_4 \cdot THF$  adduct into THF solvent with vigorous stirring. Both **2** and **3** were purified by recrystallization from toluene at low temperature.

$^1H$  NMR spectra of **2** and **3** both show only two sharp singlets for the four methyl groups. Earlier studies have shown that the *meso* form of a bis(indenyl) Group 4 *ansa*-metallocene has chemical shifts of the vinylic H(2) and H(3) protons on the five-member ring that differ by less than 0.2 ppm [9]. In contrast, **2** and **3** have chemical shift differences of 0.84 ppm and 0.46 ppm respectively for their vinylic H(2) and H(3) resonances and can thus be assigned as racemic structures.

### 2.2. Polymerizations of ethylene and propylene

It has been established [10] that methyl aluminoxane (MAO) converts metallocene dichloride precursors into metallocenium species which catalyze olefin polymerization. The results of ethylene polymerization catalyzed by **2**-MAO and **3**-MAO are summarized in Table 1.

The polymerizations were performed under the following conditions: [precursor] = 50  $\mu M$ , [Al]/[precursor] = 4000. Runs 1–3 show that, at a polymerization temperature of  $20^\circ C$ , catalyst **2** has a moderate activity  $A$  of  $4.91 \times 10^6$  g polyethylene (mol Ti) $^{-1}[C_2H_4]^{-1}h^{-1}$  which decreases to  $0.21 \times 10^6$  g polyethylene (mol Ti) $^{-1}[C_2H_4]^{-1}h^{-1}$  at  $T_p = -20^\circ C$ . Catalyst **3** is less sensitive to  $T_p$ . The highest activity,  $5.46 \times 10^6$  g polyethylene (mol Zr) $^{-1}[C_2H_4]^{-1}h^{-1}$ , was reached at  $T_p = 0^\circ C$  with slightly smaller  $A$  at higher or lower  $T_p$ . The molecular weight (MW) of the

Table 1  
Ethylene polymerization using MAO as cocatalyst

Run	Catalyst	[Al]/[catalyst]	$T_p$ ( $^\circ C$ )	Time (min)	Yield (g)	$A$ ( $\times 10^6$ g polyethylene (mol catalyst) $^{-1}$ $[C_2H_4]^{-1}h^{-1}$ )	$T_m$ ( $^\circ C$ )	MW <sup>a</sup> ( $\times 10^5$ )	
	Compound	Concentration ( $\mu M$ )							
1	<b>2</b>	50	4000	20	10	1.36	4.91	135.57	0.39
2	<b>2</b>	50	4000	0	10	1.13	3.01	136.76	0.49
3	<b>2</b>	50	4000	-20	10	0.10	0.21	137.08	1.23
4	<b>3</b>	50	4000	20	10	0.68	2.48	134.86	0.16
5	<b>3</b>	50	4000	0	10	2.05	5.46	136.50	0.91
6	<b>3</b>	50	4000	-20	10	0.73	1.55	137.31	2.50

<sup>a</sup> By the intrinsic viscosity method [11].

Table 2  
Propylene polymerization using MAO as cocatalyst

Run	Catalyst		[Al]/[Zr]	$T_p$ (°C)	Time (min)	Yield (g)	$A^a$ ( $\times 10^5$ g polypropylene (mol catalyst) $^{-1}$ [C <sub>2</sub> H <sub>4</sub> ] $^{-1}$ h $^{-1}$ )	MW <sup>a</sup> ( $\times 10^3$ )
	Compound	Concentration ( $\mu$ M)						
1	3	50	4000	20	15	0.36	8.66	0.43
2	3	50	4000	0	15	0.18	3.20	1.54
3	3	50	4000	-20	15	0.14	1.98	2.41
4	3	50	4000	-50	15	0.09	1.24	3.19

<sup>a</sup> By the intrinsic viscosity method [11].

polyethylene obtained by these two catalysts showed different  $T_p$  dependences. Changing  $T_p$  from 20 to -20 °C only slightly increased the MW from  $0.39 \times 10^5$  to  $1.23 \times 10^5$  for the system 2–MAO, while a much larger increment of 15 times was observed for 3–MAO. The melting temperature  $T_m$  matches the MW of the polymer.

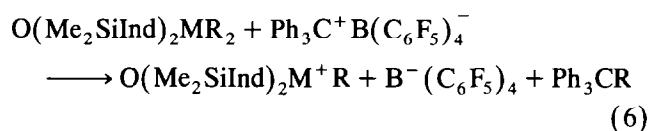
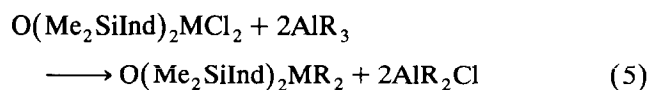
$\text{Ph}_3\text{C}^+\text{B}(\text{C}_6\text{F}_5)_4^-$ -TIBA (7) (TIBA = tri-isobutyl-aluminum) was developed by Chien and coworkers [12] as a cocatalyst. The reaction conditions in the present study were as follows: [precursor] = 50  $\mu$ M; [ $\text{Ph}_3\text{C}^+\text{B}(\text{C}_6\text{F}_5)_4^-$ ] = 50  $\mu$ M; [TIBA] = 1.0–2.0 mM;  $T_p$  = 20.0 and -20 °C. Remarkably, neither 2 nor 3 was active toward ethylene polymerization under these conditions.

As for propylene polymerizations, the Ti complex 2 did not produce any polymers no matter whether 7 or MAO was used as the cocatalyst. The Zr complex 3 showed moderate propylene polymerization activities using either cocatalyst, as summarized in Table 2 and Table 3.

### 3. Discussion

The catalytic activity of a metallocenium catalyst is strongly influenced by the nature of the counter-ion, the electrophilicity of the metal center and the stability of the olefin  $\pi$  complex. The effect of the counter-ion has been previously investigated by us [13]. In the present study the two cocatalysts have different counter-ions. In

the case of 7, the reactions between 2 or 3 and  $\text{Ph}_3\text{C}^+\text{B}(\text{C}_6\text{F}_5)_4^-$ -TIBA to form cationic metallocenium species are rapid (M = Ti or Zr; R = isobutyl):



The  $\text{B}(\text{C}_6\text{F}_5)_4^-$  counter-ion is both inert and non-coordinating, and the metallocenium ion may be considered to be a “naked” ion.

Marks and coworkers [10] have recorded <sup>13</sup>C NMR spectra of  $\text{Cp}'_2\text{Zr}(\text{CH}_3)_2$  and MAO showing the formation of  $\text{Cp}'_2\text{Zr}^{+13}\text{CH}_3$  species. It is reasonable to assume that there is alkylation of Zr followed by abstraction of an anionic ligand from it by MAO, even though the exact sequence of events is not known with certainty. We can write

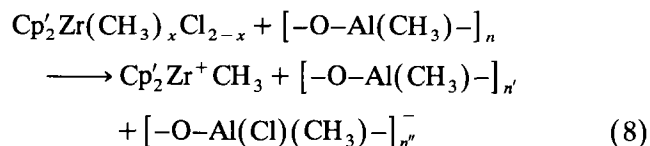
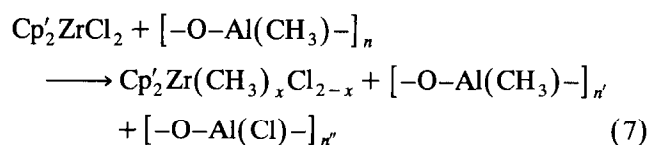


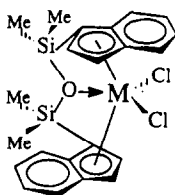
Table 3  
Propylene polymerization using  $\text{Ph}_3\text{C}^+\text{B}(\text{C}_6\text{F}_5)_4^-$ -TIBA as cocatalyst

Run	Catalyst		TIBA (mM)	$T_p$ (°C)	Time (min)	Yield (g)	$A$ ( $\times 10^5$ g polypropylene (mol catalyst) $^{-1}$ [C <sub>3</sub> H <sub>6</sub> ] $^{-1}$ h $^{-1}$ )	MW <sup>a</sup> ( $\times 10^3$ )
	Compound	Concentration ( $\mu$ M)						
1	3	50	1.0	20	20	0.10	1.73	0.68
2	3	50	1.5	0	20	0.09	1.20	2.02
3	3	50	2.0	-20	20	0.30	3.18	3.21
4	3	50	2.0	-50	20	0.24	2.48	4.50

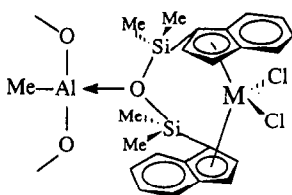
<sup>a</sup> By the intrinsic viscosity method [11].

where  $x = 1, 2$  and  $n = n' + n''$  which are all integers. Both MAO and MAO<sup>-</sup> are weak but none the less coordinating. Furthermore, MAO is amphiphilic in its interaction.

The catalyst systems 2-MAO and 3-MAO have only modest ethylene polymerization activities. Many Group 4 metallocenes starting with the non-bridged Cp<sub>2</sub>ZrCl<sub>2</sub> first investigated by Kaminsky and coworkers [14] to various bridged *ansa*-zirconocenium catalysts studied by Chien and coworkers [2j–2t] have *A* values which are 10<sup>2</sup>–10<sup>4</sup> times greater. A very unusual behavior in the present study is the effect of the cocatalyst. In numerous comparisons of metallocene-MAO and metallocene-7 systems, the latter are always more active than the former, and the difference is greater the lower *T<sub>p</sub>*. The present systems are the first observed to act in a contrary way. One possible reason for this difference may be the  $\sigma$  donation of the bridging oxygen atom represented below to the “naked” ion:



This effect would greatly decrease the electrophilicity of the metal center and tend to destabilize the olefin  $\pi$  complex and M–C bond. If instead the cocatalyst is MAO, then one may consider a  $\sigma$ -complexation structure like



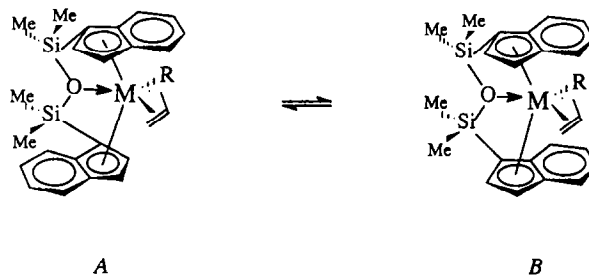
to restore the electron deficiency at the metal center and ethylene polymerization activity. Residual electronic effects of donation from oxygen and steric effects such as centroid–metal–centroid angle and distance all can contribute toward lower activities of the 2-MAO and 3-MAO systems and low MW of the polyethylene that they produce.

The propylene polymerization results are also unexpected and interesting. Precursor 2 with Ti as the metal is inactive using either MAO or 7 as the cocatalyst. The first metallocene catalyst Cp<sub>2</sub>TiCl<sub>2</sub>–Et<sub>2</sub>AlCl deactivated rapidly in ethylene polymerization [15] owing to reduction of Ti(IV) to Ti(III) species. The structures of the latter have been determined by X-ray diffraction

[16] and electron paramagnetic resonance [17]. Kinetic studies showed the reduction to be a second-order process [18]. This early catalyst also did not polymerize propylene at all, probably because of faster reduction for Ti–CH<sub>2</sub>–CH(CH<sub>3</sub>)–R as compared with Ti–CH<sub>2</sub>–CH<sub>2</sub>–R. It has been reported that the stability decreases strongly in the order of M–CH<sub>3</sub> > M–C<sub>2</sub>H<sub>5</sub> > M–C(CH<sub>3</sub>)<sub>3</sub> etc., and benzyl, neopentyl, neophyl norbornyl and camphryl derivatives are much more stable, where M is Ti, V or Cr [19].

Precursor 3 exhibits low activity toward propylene polymerization, however. Reduction of zirconium is more difficult than titanium because Zr(III) is not very accessible. The low propylene polymerization of 3-7 has a slight negative dependence on *T<sub>p</sub>*. This suggests that the  $\pi$ -propylene complex is relatively unstable for the “naked” 3<sup>+</sup>. The MW has a strongly negative *T<sub>p</sub>* dependence because of additional contribution from activated  $\beta$ -hydrogen elimination. As explained above, the  $\sigma$  donation from the bridging oxygen atom to the metal center is suppressed by interaction with MAO. Therefore the polymerizations of propylene by 3-MAO has strong positive variation of *A* with *T<sub>p</sub>*, indicating a more stable propylene  $\pi$  complex in this system. The MW still decreases with increase in *T<sub>p</sub>* owing to the independent  $\beta$ -hydride elimination process.

Compound 3 is C<sub>2</sub> symmetric and similar *ansa*-metallocenes having one or two atom bridges are usually isospecific. The stereoselectivity is attributed to non-bonded interactions. However, 3 has a non-rigid ligand frame work. One can imagine conformational changes such as



Structure B may have little or no stereoselectivity. Because of the flexibility of the three-atom bridge and low non-bonded interactions to form a particular orientation of the complexed monomer or of the growing chain, even structure A may be very low in stereodiscrimination. The stereoaccessibility to the metal center would favor  $\beta$ -hydrogen elimination and processes leading to reduction of the transition metal as pointed out above. There are of course many other processes which could contribute toward the loss of stereospecificity because of the geometries of 2 and 3.

## 4. Experimental section

### 4.1. General procedure

All operations were carried out under an argon atmosphere using Schlenk and glove-box techniques except where specified. Argon was deoxygenated with activated BTS catalyst and dried with molecular sieves and  $P_2O_5$ . Pentane, hexane, toluene, THF and diethyl ether were distilled under argon from sodium–potassium alloy. Methylene chloride was purified by  $CaH_2$ . Indene (90%) was obtained from Fluka Chemika.  $Me_2SiCl_2$  (99%) was from Aldrich, pyridine was from Fischer Chemical, and MAO was purchased from Akzo.

Polymerizations of ethylene and propylene were run in 250 ml crown-capped glass pressure reactors containing 50 ml of toluene saturated with the monomer at 15 lbf in<sup>-2</sup> (103 kPa). An excess amount of MAO was introduced first into the reactor, followed by the metallocene precursor. The reaction formed in situ the metallocenium ion together with an anion of MAO. Polymerizations were quenched with methanol containing 2 vol.% HCl and the polymer was worked up as described previously [19–21].

### 4.2. Synthesis of (1-indenyl)chlorodimethylsilane (4)

Indene (14.5 ml, 0.124 mol) was dissolved in 125 ml of hexane to form a clear solution. At 0 °C, 77.2 ml of butyllithium (0.124 mol, 1.6 M) was added dropwise with stirring into the solution. After the addition the mixture was allowed to warm to room temperature and stirred overnight. The resulting solid was isolated, washed with two 100 ml portions of hexane and then dissolved in 150 ml of diethyl ether. At 0 °C, 30.0 ml of  $Me_2SiCl_2$  (0.248 mol) was added to the solution in one portion. The mixture was then refluxed for 20 h. The LiCl that formed was removed by filtration over Celite and the solid was washed with two extra 50 ml portions of ether. Vacuum removal of the ether and excess  $Me_2SiCl_2$  from the filtrate resulted in an oily liquid. Distillation through a 30 cm Vigreux column produced 17.56 g (68%) of product (boiling point (b.p.), 108–110°C 2.6 Torr). <sup>1</sup>H NMR ( $CDCl_3$ , 200 MHz): δ 0.18 (s, 3H,  $CH_3$ ); 0.23 (s, 3H,  $CH_3$ ); 3.75 (s, 1H, methine H); 6.66 (d, 1H, vinylic H); 7.02 (d, 1H, vinylic H); 7.21–7.30 (m, 2H, aromatic H); 7.46 (d, 1H, aromatic H); 7.59 (d, 1H, aromatic H) ppm. Anal. Found: C, 63.77; H, 6.49.  $C_{11}H_{13}ClSi$  calc.: C, 63.29; H, 6.28%.

### 4.3. Synthesis of 1,1,3,3-tetramethyl-1,3-bis(indenyl)disiloxane (5)

Compound 4 (17.0 g, 0.081 mol) was dissolved in 150 ml of diethyl ether. At –30 °C, 6.58 ml of pyridine (0.081 mol) and then 0.73 ml of  $H_2O$  (0.041 mol) were added dropwise with stirring to the solution, resulting in

a precipitate. The mixture was allowed to warm to room temperature and stirred overnight. After filtration through Celite and removal of the ether under vacuum, a slightly milky oil was formed. The oil was distilled twice and one portion was collected (b.p., 121–123 °C (0.002 Torr); yield, 10.74 g (73%)). <sup>1</sup>H NMR ( $CDCl_3$ , 200 MHz): δ –0.09 (s, 6H,  $CH_3$ ); –0.02 (s, 6H,  $CH_3$ ); 3.51 (s, 2H, methine H); 6.65 (d, 2H, vinylic H); 6.72 (d, 2H, vinylic H); 7.17–7.54 (m, 8H, aromatic H) ppm. Anal. Found: C, 72.72; H, 7.02.  $C_{22}H_{26}OSi_2$  calc.: C, 72.87; H, 7.23%.

### 4.4. Preparation of (1,3-bis( $\eta^5$ -indenyl)-1,1,3,3-tetramethylidisiloxane)titanium(IV) dichloride (2)

At –30 °C 14.8 ml of butyllithium (0.024 mol, 1.6 M) was added to a stirred solution of 4.26 g of 5 (0.012 mol) in 100 ml of THF. The solution was stirred for 4 h in the bath. In a second flask, 1.26 ml of  $TiCl_4$  (0.012 mol) was added to 100 ml of THF at 0 °C to form a suspension. Both solutions were transferred by cannula simultaneously to a third flask containing 50 ml THF at room temperature, and the reaction mixture was stirred overnight. Removal of THF under vacuum, extraction of the residue with 100 ml of toluene and filtration through Celite resulted in a deep-red solution. The toluene was removed and the solid residue was washed with two 50 ml portions of pentane to give 2.07 g (37%) of burgundy crystals that were pure by NMR. Recrystallization from toluene gave an analytically pure sample. <sup>1</sup>H NMR ( $CDCl_3$ , 200 MHz): δ 0.39 (s, 6H,  $CH_3$ ); 0.70 (s, 6H,  $CH_3$ ); 5.87 (d, 2H, vinylic H); 6.71 (d, 2H, vinylic H); 7.30–7.49 (m, 4H, aromatic H); 7.59 (d, 2H, aromatic H); 7.86 (d, 2H, aromatic H) ppm. Anal. Found: C, 54.86; H, 4.97.  $C_{22}H_{24}Cl_2OSi_2Ti$  calc.: C, 55.12; H, 5.05%.

### 4.5. Preparation of (1,3-bis( $\eta^5$ -indenyl)-1,1,3,3-tetramethylidisiloxane) zirconium(IV) dichloride (3)

Following the same procedure as for the synthesis of 2, 4.30 g of 5 (0.012 mol), 14.8 ml of butyllithium (0.024 mol, 1.6 M) and 2.75 g of  $ZrCl_4$  (0.012 mol) produced 1.87 g of 3 (30%). An analytically pure sample was obtained by recrystallization from toluene as a yellow crystalline solid. <sup>1</sup>H NMR ( $CDCl_3$ , 200 MHz): δ 0.52 (s, 6H,  $CH_3$ ); 0.59 (s, 6H,  $CH_3$ ); 6.58 (d, 2H, vinylic H); 7.04 (d, 2H, vinylic H); 7.10–7.27 (m, 4H, aromatic H); 7.50 (d, 2H, aromatic H); 7.66 (d, 2H, aromatic H) ppm. Anal. Found: C, 50.94; H, 4.70.  $C_{22}H_{24}Cl_2OSi_2Zr$  calc.: C, 50.54; H, 4.64%.

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