

Synthesis, characterization, and reactivities of the polysiloxane-bridged binuclear metallocenes tetramethyldisiloxanediylbis(cyclopentadienylnitium trichloride) and hexamethyltrisiloxanediylbis(cyclopentadienylnitium trichloride)

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Abstract

The reaction of dithallium salts of tetramethyldisiloxanediylbis(cyclopentadienyl), **3**, and hexamethyltrisiloxanediylbis(cyclopentadienyl), **4**, with two equivalents of TiCl_4 gives the title compounds tetramethyldisiloxanediylbis(cyclopentadienylnitium trichloride), **5** and hexamethyltrisiloxanediylbis(cyclopentadienylnitium trichloride), **6** respectively. The stoichiometric reaction of **5** and **6** with water results in the formation of new oxygen-bridged metallocenes $[(\text{TiCl}_2)_2(\mu^2\text{-O})-(\eta^5\text{-C}_5\text{H}_4)_2-\mu^2\text{-(SiMe}_2)_2\text{O}]$, **7**, and $[(\text{TiCl}_2)_2(\mu^2\text{-O})-(\eta^5\text{-C}_5\text{H}_4)_2-\mu^2\text{-(SiMe}_2)_3\text{O}_2]$, **8**. In addition, further reaction of **7** and **8** with another one equivalent of water or the treatment of **5** and **6** with an excess amount of water gives rise to the formation of the metallocene compounds having Ti_4O_4 rings $[(\text{TiCl})_2(\mu^2\text{-O})-(\eta^5\text{-C}_5\text{H}_4)_2-\mu^2\text{-(SiMe}_2)_2\text{O}]_2(\mu^2\text{-O})_2$, **9**, and $[(\text{TiCl})_2(\mu^2\text{-O})-(\eta^5\text{-C}_5\text{H}_4)_2-\mu^2\text{-(SiMe}_2)_3\text{O}_2]_2(\mu^2\text{-O})_2$, **10**. All the new kinds of metallocenes prepared have been characterized by IR, NMR, mass spectrometry, or elemental analysis. Especially an investigation of the $\Delta\delta$ values in ^1H NMR and a comparison between the theoretical and observed isotopic ratio in a mass spectra among the synthesized bridged compounds have been very conveniently utilized to study their structures. Polymerization experiments with the dinuclear complexes in the presence of methylaluminoxane as a cocatalyst indicate that the compounds **5** and **6** do exhibit catalytic activity for syndiotactic polymerization of styrene.

Keywords: Silicon; Binuclear; Metallocene; Polysiloxane; Oxygen bridge

1. Introduction

Since Kaminsky's discovery of the soluble zirconocene-methylaluminoxane as a suitable catalyst for ethylene polymerization, many efforts have been devoted to the investigation and development of metallocene catalyst systems for polymerizing various olefins [1]. As a consequence of these efforts, there have been very important and valuable advances on both academic and industrial sides that allow a better understanding of the polymerization mechanism and of the correlation between the metallocene structure and the polymer

properties. In spite of these improvements, still there are some difficulties that need to be resolved for the practical application of these remarkable catalysts. Heterogenation is one of those difficulties. The researches concerning heterogenation so far indicate that a simple and physical impregnation or mixing of metallocenes to the support (such as silica) does not seem to be an appropriate way to make the practically applicable heterogenized catalyst, mainly due to a drastic reduction of the catalyst activity [2].

As a result of those studies, a more direct immobilization method has been proposed recently to get a chemical attachment between metallocene compounds and surface of the supporting material [3]. We have been interested not only in preparing anchored metal-

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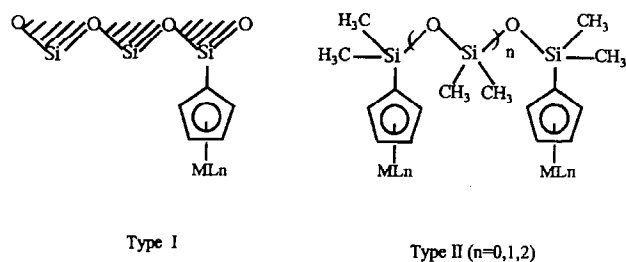


Fig. 1. Silica surface-anchored metallocene and polysiloxane-bridged metallocene.

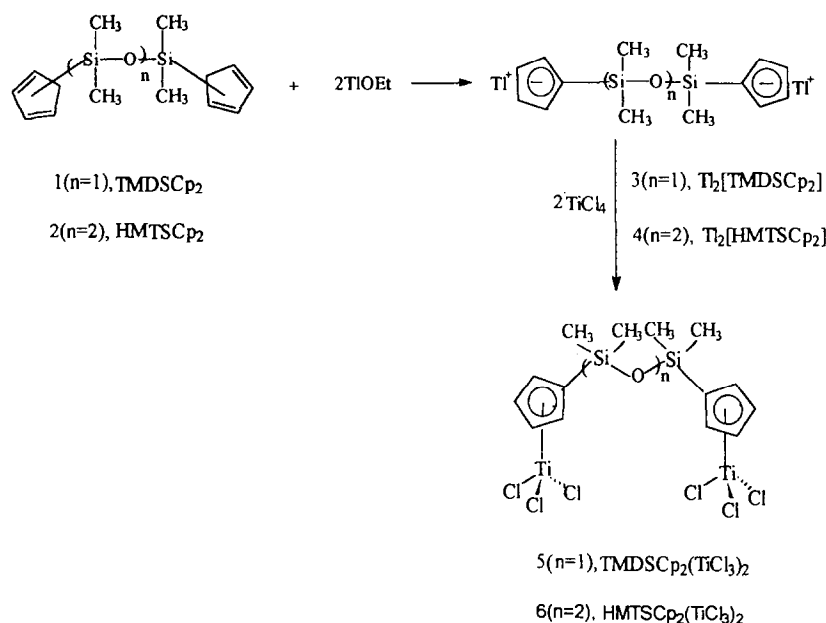
locene complexes at a silica surface through the pendant cyclopentadienyl group or its derivatives, type I, but also in model compounds for those catalysts synthesizing the metallocenes with a polysiloxane bridge between cyclopentadienyl rings, type II, to look at the chemistry of the surface-anchored metallocenes (Fig. 1). Based on this idea we have successfully prepared a variety of new kinds of metallocene [4] and here describe synthesis, characterization, and reactions of the polysiloxane-bridged dinuclear metallocene complexes.

2. Results and discussion

2.1. Synthesis and characterization of polysiloxane-bridged dinuclear metallocene complexes

Synthesis of disiloxane- and trisiloxane-bridged dinuclear metallocene complexes **5** and **6** is realized by the reaction of thallium salts of the corresponding ligands tetramethyldisiloxanediybis(cyclopentadienyl) **1** and hexamethyltrisiloxanediybis(cyclopentadienyl) **2** with two equivalents of TiCl_4 in toluene. The thallium com-

pounds **3** and **4** were prepared in 95% yield by treatment of the corresponding cyclopentadienyl compounds **1** and **2** with thallium ethoxide in diethyl ether. Use of dilithium or disodium salts instead of dithallium salts was found to be unsuccessful for obtaining the desired binuclear complexes. As shown in Scheme 1, the procedure is general and applicable to various polysiloxane-bridged compounds. The yield of the metallation step is about 30% in both reactions. It is important to use toluene as a solvent since other solvents, such as THF and diethyl ether, did not produce the expected compounds. Both dinuclear complexes **5** and **6** are separated as a yellow solid but the solubility properties of the two are slightly different. The complex **5** is soluble in diethyl ether, THF, methylene chloride and aromatic hydrocarbons such as benzene and toluene, but is poorly soluble in hexane. In contrast, the complex **6** is soluble in most of the organic solvents. These new compounds are characterized by ^1H NMR, IR, mass spectrometry and elemental analysis. ^1H NMR spectra of complex **5** show the expected resonances for the bridging TMDSCp_2 which appear as two sets of pseudotriplets at $\delta 7.06$ and 7.22 ppm with a coupling constant of 2.5 Hz due to an AA'BB' system along with a singlet at 0.46 ppm for Si-CH_3 . ^1H NMR spectra of the complex **6** also has two sets of pseudotriplets at $\delta 7.05$ and 7.23 ppm for the bridging cyclopentadienyl fragment and two singlet at $\delta 0.08$ and 0.43 ppm for Si-CH_3 protons. The observed chemical shifts and coupling patterns for **5** and **6** are very similar to the value reported for the dimethylsilyl-bridged dinuclear complex $[(\text{TiCl}_3)_2-(\eta^5\text{-C}_5\text{H}_4)_2-\mu^2(\text{SiMe}_2)]$ by Royo and co-workers [5]. This result suggests that the three types of bridge introduced between two CpTiCl_3 fragments do not affect the



Scheme 1.

electronic circumstances at the metal center much. The value of $\Delta\delta = [\delta_d - \delta_p]$, where δ_d and δ_p are the chemical shifts for 'distal protons' and 'proximal protons' respectively, is 0.16 for compound **5** [6]. This value is found to be smaller than that observed for the complex containing TMDSCp₂ as a chelating ligand (0.41 for TiCl₂[Cp(SiMe₂)₂OCp]) [7]; this is consistent with Peterson's suggestion for distinguishing between the bridging and chelating (ansa-type) disposition of the ligand; although the difference is only 0.25, this is much smaller for other systems [5,6]. On the contrary, the value of $\Delta\delta$ for compound **6** is 0.18, which is actually the same as the observed value of 0.18 for the complex containing HMTSCp₂ as a chelating ligand, TiCl₂-[Cp(SiMe₂O)₂SiMe₂Cp] [4]. This kind of trend seems to be attributed to the small $\Delta\delta$ value for ansa-metalloenes with a long bridge between cyclopentadienyl groups. This shows that one should be very careful in applying $\Delta\delta$ values as an appropriate spectroscopic

parameter for distinguishing modes of coordination, especially for ansa-metalloenes with a relatively longer bridge than the well-known dimethylsilyl or ethylene bridge. Since the compound **5** is extremely moisture sensitive, **5** is contaminated with variable amounts of the dinuclear μ -oxo compound (vide infra) unless rigorously anhydrous conditions are maintained. Owing to this reason a successful elemental analysis for **5** could not be obtained. Instead, the EI mass spectrum for **5** was very informative and was used as a decisive tool to identify its formulation, because in **5** there are six chlorines and two silicones showing a prominent second isotope appearance in the spectrum. Even though the mass spectrum of **5** does not show a molecular ion of 566, it clearly shows a mass of (M⁺ - 15) generated from the CH₃ group liberation from the molecular ion. The peak spectrum for **5** based on the (M⁺ - 15) is easily recognized from the characteristic isotopic ratio of the ions separated by two mass units due principally to the presence of six chlorines, as shown in Fig. 2. The observed isotopic ratio is reasonably well in agreement with the computed one based on its given formulation by taking into account the extreme water sensitivity of **5**. The compound **6** is also moisture sensitive, but not as much as compound **5**; therefore, its formulation could be confirmed by elemental analysis.

2.2. Formation of oxo-bridged dinuclear metallocene from the reaction of water with complexes **5** and **6**

Treatment of the polysiloxane-bridged metallocene complexes **5** and **6** in toluene with one equivalent of water results in the formation of an oxygen bridge between the titanium center. The new oxo-bridge complexes **7** and **8** (Scheme 2) can be isolated as a yellow powder-like solid in moderate yield (30% for **7** and 35% for **8**) after several recrystallizations. Both compounds are soluble in most of the organic solvents. The reaction is conveniently monitored by IR. One additional strong broad band is observed at about 800 cm⁻¹ due to the vibration of the (Ti-O-Ti) linkage. The ¹H NMR spectrum for **7** reveals a single sharp peak at 0.46 ppm from the Si-CH₃ groups and two sets of pseudotriplets at 7.14 and 6.98 ppm, which are about 0.08 ppm higher than those for the nonoxo-bridged complex **5**, due to an AA'BB' system for the TMDSCp₂. The ¹H NMR spectrum for **8** also shows two sets of pseudotriplets at 7.08 and 7.01 ppm for the bridging HMTSCp₂ and two sharp singlets at 0.42 and 0.14 ppm with an integration ratio of 2 to 1 for the two inequivalent Si-CH₃ groups. Values of $\Delta\delta$ have also been investigated for these new μ -oxo metallocene complexes; 0.18 was found for **7** which is similar to the value before oxygen bridging between metal centers. In the case of **8**, the value of $\Delta\delta$ is found to be only 0.07, which is much smaller than the value of 0.18 before

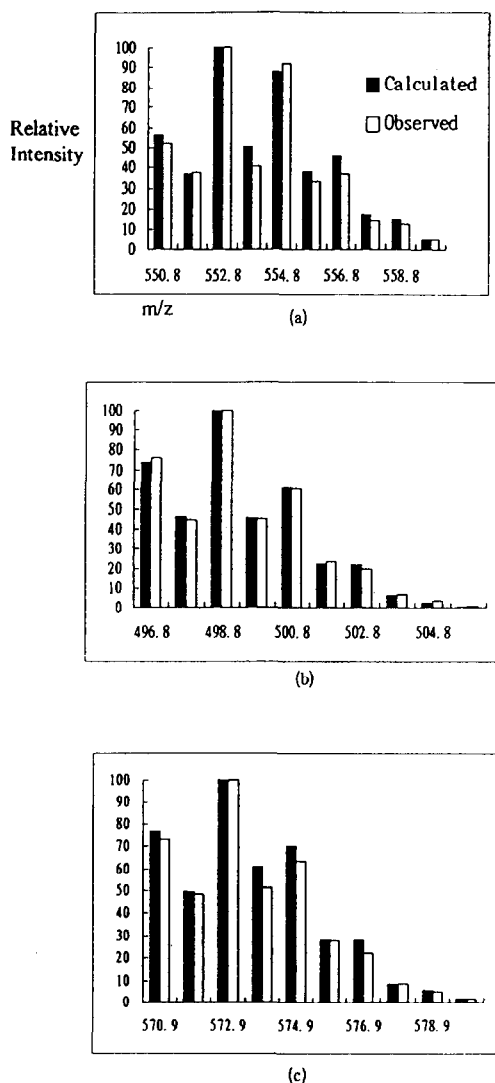
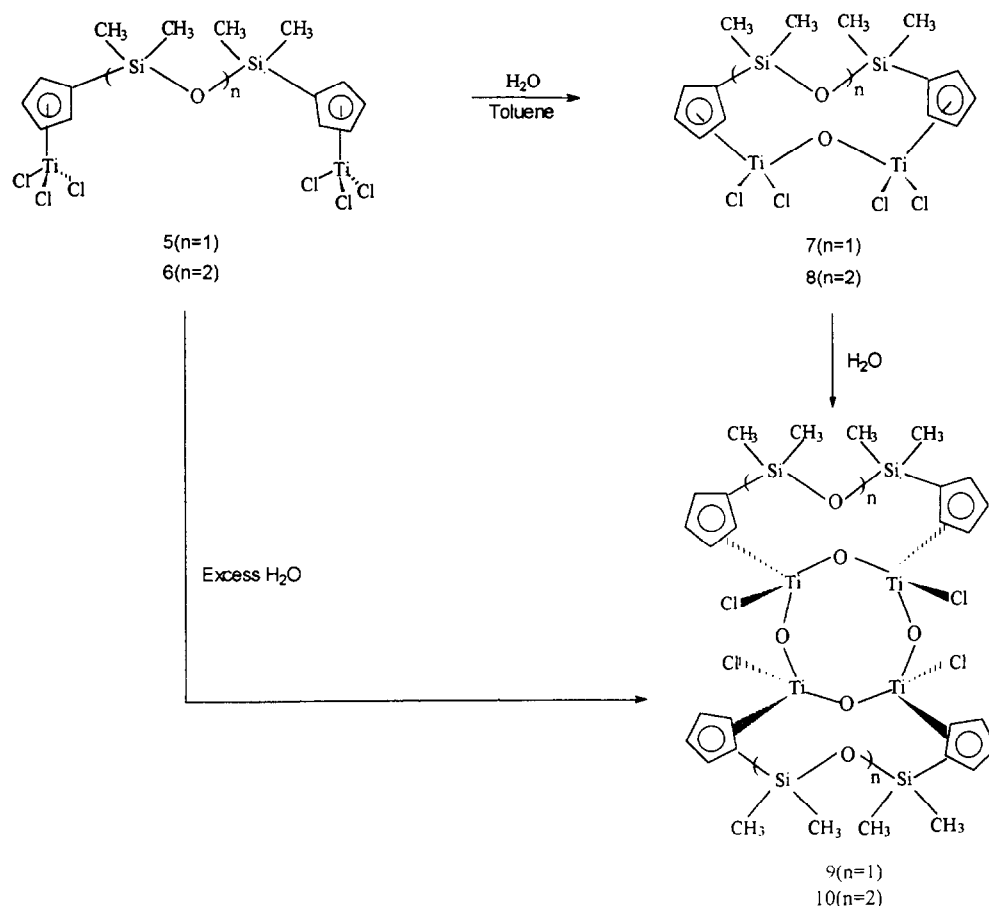


Fig. 2. Observed and calculated isotope patterns for (M⁺ - 15) of (a) **5**, (b) **7**, and (c) **8**.

oxygen bridging. It is instructive to compare these values and trends with their corresponding dimethylsilyl bridging analogs. Recently Royo and co-workers prepared the dinuclear oxo-bridged compound $[(\text{TiCl}_2)_2(\mu^2\text{-O})(\eta^5\text{-C}_5\text{H}_4)_2-\mu^2\text{-SiMe}_2]$ by controlled hydrolysis of $[(\text{TiCl}_3)_2-(\eta^5\text{-C}_5\text{H}_4)_2-\mu^2\text{-SiMe}_2]$ with a stoichiometric amount of water [5]. In these compounds the value of $\Delta\delta$ is 0.28 for nonoxo-bridged and 0.33 for oxo-bridged compounds, which indicates that the oxo-bridge cause a small increase in $\Delta\delta$. This result has a clear analogy in **5** to **7** transformation, but is just the opposite in the **6** to **8** transformation. This contradiction between the two compounds can be explained in terms of the steric hinderance around the metal center. Generally, it is known that $\Delta\delta$ decreased as the steric hinderance around the metal center is increased in the dinuclear complexes [5,6,8]. Even though the molecular structure of complexes **7** and **8** are not determined, it is easily understandable that the presence of one or two more (SiMe_2O) groups in addition to the SiMe_2 between the cyclopentadienyl rings has a significant effect on the structural parameters in chelation. The resultant increase in the distance between the linked cyclopentadienyl rings consistently leads to a lengthening of the Ti–Ti separation and gives rise to the formation of the

sterically strained Ti–O–Ti bond. In the case of **7** this effect may not be serious and the $\Delta\delta$ difference caused by the oxygen bridge follows a general trend as reported. However, it is expected that the steric hinderance of the resultant chelate in **8**, which includes two Cps, a trisiloxane bridge, and a (Ti–O–Ti) bond, will be much more severe than that of nonoxo-bridged dinuclear complex **6**. As expected, $\Delta\delta$ for **8** is reduced to 0.07, which is less than half the $\Delta\delta$ (0.18) for **6**; this observation can actually be good evidence for the presence of an oxygen bridge between the titaniums in complex **8**. Mass spectra for the μ -oxo complexes **7** and **8** have been carefully examined and these are also in fairly good agreement with the predicted formulations. Mass spectra of **7** show not only the molecular ion peak at 512 but also the peak from $(\text{M}^+ - 15)$ as a base peak. Both peaks demonstrate the expected peak pattern and isotopic ratio separated by two mass units due to the presence of four chlorines and two silicones (Fig. 2). The complex **8** also exhibits a molecular ion at 586 and $(\text{M}^+ - 15)$ at 571 along with the consistent isotopic ratio.

It is found that further reaction of water with the above complexes gives rise to the formation of other compounds. This behavior is very analogous to that



Scheme 2.

reported for other dinuclear complexes [5]. Based on the report, we assigned these compounds as the tetranuclear μ -oxo complexes **9** and **10**. The protons in **9** exhibit four multiplets at 7.03, 6.97, 6.80, and 6.42 ppm corresponding to an ABCD system and two singlets at 0.53 and 0.34 ppm for Si–CH₃ protons because the formation of Ti₄O₄ makes both the cyclopentadienyl protons and methyl protons of the siloxane bridging groups inequivalent. Similarly, the protons in **10** appear as three multiplet at 6.98, 6.71, and 6.59 ppm with an integration ratio of 2 : 1 : 1 for the cyclopentadienyl protons (probably due to the accidental chemical shift coincidence of two protons) and three singlets at 0.45, 0.27 and 0.17 ppm for the methyl protons of the trisiloxane bridging groups. We have investigated the catalytic properties of **5–10** in methylaluminoxane-activated olefin polymerization and preliminary results have already been reported [9]. The detailed story will be reported soon, but some points can be noted. The dinuclear complexes **5** and **6** do show a reasonable activity for styrene polymerization, similar to CpTiCl₃. The syndiotactic index values for the synthesized polystyrene from those catalysts are greater (95.6) than that from CpTiCl₃ (82.2).

3. Experimental section

All reactions were carried out under a dry, oxygen-free atmosphere using standard Schlenk techniques with a double manifold vacuum line. Nitrogen gas was purified by passage through the column of molecular sieve (4A) and Drierite (8 mesh). Tetrahydrofuran, diethyl ether, toluene, hexane, and pentane were distilled from sodium–benzophenone ketyl prior to use. Methylene chloride was distilled from phosphorus pentoxide prior to use. White filtering aid (celite) was stored in a 130°C oven. 1,3-Dichlorotetramethyldisiloxane and 1,5-dichlorohexamethyltrisiloxane purchased from United Chemical Technologies were used after distilling from calcium hydride. CpLi, CpNa (2 M solution in THF), and TIOEt were used as-purchased from Aldrich. NMR spectra were recorded at 300 MHz on a Bruker WM-300 FT-NMR spectrometer. Mass spectra were obtained with a Finnigan MAT 95Q spectrometer. IR spectra were recorded on a Jasco FT/IR-5300 spectrophotometer between 4000 and 200 cm⁻¹. Elemental analyses were performed by Hanwha Group R & E Center.

3.1. Synthesis of dithallium tetramethyldisiloxanedicyclopentadienide (**3**)

To a diethyl ether solution (50 ml) of dicyclopentadienyltetramethyldisiloxane, **1**, (2.74 g) at –78°C was added two equivalents of TIOEt. Then the bath was allowed to warm to room temperature and the mixture was stirred for 3 h. The resulting solution was filtered to

get a gray powder on a glass frit. The solid powder was washed with 2 × 30 ml of diethyl ether to give 6.7 g (96%) of **1**. Anal. Found: C, 25.26; H, 3.28. C₁₄H₂₀OSi₂Tl₂. Calc.: C, 25.13; H, 3.01%.

3.2. Synthesis of dithallium hexamethyltrisiloxanedicyclopentadienide (**4**)

This compound was prepared in an analogous fashion to the dithallium tetramethyldisiloxanedicyclopentadiene, **3**, except that dicyclopentadienylhexamethyltrisiloxane, **2**, was used in place of **1**. Washing of the resultant solid gave a product in 95% yield. Anal. Found: C, 25.70; H, 3.65. C₁₆H₂₆O₂Si₃Tl₂. Calc.: C, 25.85; H, 3.35%.

3.3. Synthesis of tetramethyldisiloxanediylbis(cyclopentadienyltitanium trichloride) (**5**)

TiCl₄ (6.8 mmol) was dissolved in 50 ml toluene. A suspension of dithallium tetramethyldisiloxanedicyclopentadienide (3.3 mmol) was added to the TiCl₄ solution at –78°C. The color of the solution turned from orange to dark green. The solution was warmed to room temperature. After stirring for 4 h the solvent was evaporated to dryness to give a dark reddish sticky material. Addition of a 1 : 1 mixture of ether–hexane gave a dark red solution together with black solids which were removed by filtration. After removal of the black solid several times by using fractional recrystallization in ether–hexane at –20°C, the desired product was obtained in 25% yield by washing out oxygen-bridged by-product with hexane. IR (KBr, cm⁻¹): 3094, 2961, 1408, 1370, 1256, 1182, 1103, 1045, 842, 798, 760. ¹H NMR (CDCl₃): δ 7.22 (t, 2.5 Hz, C₅H₄), 7.06 (t, 2.5 Hz, C₅H₄), 0.46 (s, 12H). EI/MS (70 eV): 550.8 (M⁺ – CH₃, 52%), 552.8(100%), 554.8(91.8%), 556.8-(33.3%), 516 (M⁺ – CH₃–Cl), 122 (CpSiMe₂), 72 (SiMe₂). Theoretical isotopic ratio: 550.8(56%), 552.8-(100%), 554.8(88.1%), 556.8(45.8%).

3.4. Synthesis of hexamethyltrisiloxanediylbis(cyclopentadienyltitanium trichloride) (**6**)

To a solution of TiCl₄ (4.2 mmol) in 50 ml toluene at –78°C was added a suspension of dithallium hexamethyltrisiloxanedicyclopentadienide (2 mmol) in 50 ml toluene. The color of the solution turned from orange to dark green immediately. After addition, the solution was warmed to room temperature and stirred for 2 h followed by heating another 2 h at 60°C. A purification method similar to that used to purify **5** (with the exception of hexane washing) was used to give a product as a bright yellow solid in 35% yield. Anal. Found: C, 30.37; H, 4.27%. C₁₆H₂₆C₁₆O₂Si₃Ti₂. Calc.: C, 29.88; H, 4.07%. IR (KBr, cm⁻¹) 3098, 2959, 1408, 1370, 1260, 1179, 1045, 799, 764. ¹H NMR (CDCl₃): δ 7.23

(t, 2.5 Hz, C₅H₄), 7.06 (t, 2.5 Hz, C₅H₄), 0.43 (s, 12H), 0.09 (s, 6H).

3.5. The reaction of tetramethyldisiloxanediylbis(dicyclopentadienyltitanium trichloride) (5) with water-formation of 7

A solution of complex **5** (0.38 g) in 50 ml toluene was treated with a stoichiometric amount of water in THF at room temperature. After being stirred for 12 h, the solvent was evaporated to give a yellow solid. A couple of recrystallizations of the solid from hexane at –20°C gave a bright yellow product **7** in 40% yield. IR (KBr, cm⁻¹): 3094, 2955, 2897, 1416, 1368, 1256, 1087, 875, 820, 804, 754. ¹H NMR (CDCl₃): δ 7.14 (t, 2.5 Hz, C₅H₄), 6.98 (t, 2.5 Hz, C₅H₄), 0.46 (s, 12H). EI/MS (70 eV): 512 (M⁺, 20%), 496.8 (M⁺ – Me, 7.4%), 500.8 (60.86%), 502.8 (22.03%), 462 (M⁺ – Me – Cl), 167 (Cp–Si(Me)₂–O), 122 (Cp–SiMe₂). Theoretical isotopic ratio: 496.8 (75.8%), 498.8 (100%), 500.8 (60.4%), 502.8 (19.9%).

3.6. The reaction of hexamethyltrisiloxanediylbis(dicyclopentadienyltitanium trichloride) (6) with water-formation of 8

This reaction proceeded in an analogous fashion to the above reaction with the exception that 0.46 g hexamethyltrisiloxanediylbis(dicyclopentadienyltitanium trichloride, **6**, was used in place of **5**. Recrystallization from hexane gave 0.18 g of yellow solid of **8** (43% yield). IR (KBr, cm⁻¹): 3094, 2957, 2901, 1408, 1367, 1258, 1180, 1084, 1050, 898, 850, 800, 698. ¹H NMR (CDCl₃): δ 7.09 (t, 2.5 Hz, C₅H₄), 7.01 (4, 2.5 Hz, C₅H₄), 0.42 (s, 12H), 0.14 (s, 6H). EI/MS (70 eV): 586 (M⁺, 9%), 570.9 (M⁺ – Me, 76.8%), 572.9 (100%), 574.9 (69.9%), 576.9 (28%), 555 (M⁺ – Cl, 9%), 122 (Cp–Si(Me)₂). Theoretical isotopic ratio: 570.0 (73.1%), 572.9 (100%), 574.9 (63.6%), 576.8 (22.6%).

3.7. Preparation of [(TiCl)₂(μ₂-O)-(η⁵-C₅H₄)₂(SiMe₂-O)₂(μ₂-O)₂ (9)

Method A: to a solution of **7** (0.6 g, 1.17 mmol) in 50 ml toluene at room temperature was added one equivalent of H₂O in 30 ml THF. After stirring overnight, solvent was evaporated followed by addition of 40 ml of hexane. The solution was filtered to obtain a product as a yellow solid on a frit. Recrystallization (two or more) from Et₂O–hexane or toluene–hexane resulted in 0.3 g (50% yield) of **9**.

Method B: complex **7** was dissolved in 50 ml toluene and treated with an excess amount of water (more than three equivalents) at room temperature. After being stirred for 12 h, the same basic purification procedure was used to give a yellow solid product.

IR (KBr, cm⁻¹): 3096, 2957, 1408, 1368, 1257, 1182, 1084, 1062, 860, 804, 698. ¹H NMR (CDCl₃): δ 7.03 (m, C₅H₄), 6.97 (m, C₅H₄), 6.80 (m, C₅H₄), 6.42 (m, C₅H₄), 0.53 (s, 6H), 0.34 (s, 6H).

3.8. Preparation of [(TiCl)₂(μ₂-O)-(η⁵-C₅H₄)₂(SiMe₂)₃O₂]₂(μ₂-O)₂ (10)

Two methods similar to those used to make **9** were applied. The only exception was introduction of **8** in place of **7**. The final product **10** was separated in 40% yield as a needle-like crystalline solid. IR (KBr, cm⁻¹): 3096, 2958, 1405, 1370, 1257, 1184, 1082, 860, 802, 698. ¹H NMR (CDCl₃): δ 6.89 (m, C₅H₄, 2H), 6.71 (m, C₅H₄), 6.59 (m, C₅H₄), 0.45 (s, 6H), 0.27 (s, 6H), 0.17 (s, 6H).

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