

Cis- and *trans*-titanium complexes with doubly silyl-bridged dicyclopentadienyl ligands: molecular structure of $[(\text{TiCl})_2(\mu\text{-O})\{(\text{SiMe}_2)_2(\eta^5\text{-C}_5\text{H}_3)_2\}]_2(\mu\text{-O})_2$

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Dedicated to the memory of an outstanding scientist and good friend, Mark E. Vol'pin

Abstract

The reaction of TiCl_4 with $\text{Li}_2[(\text{SiMe}_2)_2(\eta^5\text{-C}_5\text{H}_3)_2]$ in toluene at room temperature afforded a mixture of *cis*- and *trans*- $[(\text{TiCl})_2(\text{SiMe}_2)_2(\eta^5\text{-C}_5\text{H}_3)_2]$ in a molar ratio of 1/2 after recrystallization. The complex *trans*- $[(\text{TiCl})_2(\text{SiMe}_2)_2(\eta^5\text{-C}_5\text{H}_3)_2]$ was hydrolyzed immediately by the addition of water to THF solutions to give *trans*- $[(\text{TiCl})_2(\mu\text{-O})\{(\text{SiMe}_2)_2(\eta^5\text{-C}_5\text{H}_3)_2\}]_2$ as a solid insoluble in all organic solvents, whereas hydrolysis of *cis*- $[(\text{TiCl})_2(\text{SiMe}_2)_2(\eta^5\text{-C}_5\text{H}_3)_2]$ under different conditions led to the dinuclear μ -oxo complex *cis*- $[(\text{TiCl})_2(\mu\text{-O})\{(\text{SiMe}_2)_2(\eta^5\text{-C}_5\text{H}_3)_2\}]_2$ and two oxo complexes of the same stoichiometry $[(\text{TiCl})_2(\mu\text{-O})\{(\text{SiMe}_2)_2(\eta^5\text{-C}_5\text{H}_3)_2\}]_2(\mu\text{-O})_2$ as crystalline solids. Alkylation of *cis*- and *trans*- $[(\text{TiCl})_2(\text{SiMe}_2)_2(\eta^5\text{-C}_5\text{H}_3)_2]$ with MgClMe led respectively to the partially alkylated *cis*- $[(\text{TiMe}_2\text{Cl})_2\{(\text{SiMe}_2)_2(\eta^5\text{-C}_5\text{H}_3)_2\}]_2$ and the totally alkylated *trans*- $[(\text{TiMe}_2)_2\{(\text{SiMe}_2)_2(\eta^5\text{-C}_5\text{H}_3)_2\}]_2$ compounds. The crystal and molecular structure of the tetranuclear oxo complex $[(\text{TiCl})_2(\mu\text{-O})\{(\text{SiMe}_2)_2(\eta^5\text{-C}_5\text{H}_3)_2\}]_2(\mu\text{-O})_2$ was determined by X-ray diffraction. © 1998 Elsevier Science S.A. All rights reserved.

Keywords: Crystal structures; Titanium complexes; Silyl-bridged cyclopentadienyl complexes

1. Introduction

Extensive studies have been carried out on complexes containing the so-called *ansa*-ligands, with relation to their catalytic applications [1] in Ziegler–Natta polymerization of olefins to produce highly stereoregular *iso*- and *syndio*-tactic polymers. The use of bridged silyldicyclopentadienyl ligands provides access to new types of mono- and bent dicyclopentadienyl-type metal complexes. Doubly silyl-bridged cyclopentadienyl compounds [2] and some of their transition metal complexes [3,4] have been reported. Related ring-substituted group 4 metal derivatives have also been described more recently [5]. The use of these silyl-bridged ligands provides more rigid systems [3,6] which avoid the participation of ring carbon–hydrogen activation reactions; in addition, the presence of electron-withdrawing silyl groups enhances the accessibility of lower oxidation states [3,7]. We have reported previously the isolation of new group 4

metal monocyclopentadienyl- [8], *ansa*-dicyclopentadienyl- [8b,9] and dicyclopentadienyl-type [10] complexes containing singly and doubly SiMe_2 bridged cyclopentadienyl ligands. Dinuclear dicyclopentadienyl-type complexes [11] with the doubly bridged ligand and with only one of the rings coordinated to the metal [12] have also been reported.

In this paper we report the synthesis and structural characterization of new *cis*- and *trans*-dinuclear chloro-, oxo- and methyl-titanium monocyclopentadienyl-type complexes and the X-ray molecular structure of the oxo-derivative $[(\text{TiCl})_2(\mu\text{-O})\{(\text{SiMe}_2)_2(\eta^5\text{-C}_5\text{H}_3)_2\}]_2(\mu\text{-O})_2$.

2. Results and discussion

Whereas the reaction of TiCl_4 with the dilithium salt of the ligand [8b] in toluene led to the selective formation of *trans*- $[(\text{TiCl})_2\{(\text{SiMe}_2)_2(\eta^5\text{-C}_5\text{H}_3)_2\}]_2$ (1) in 30% yield, a similar reaction with the dilithium salt in toluene always afforded a mixture with a variable proportion of the *cis*-I and *trans*-I isomers, as shown in Scheme 1. All attempts made

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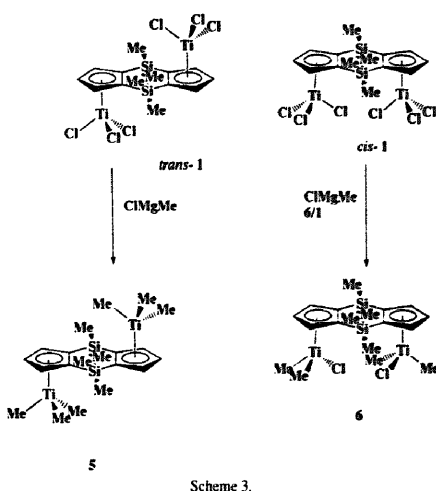
¹ X-ray diffraction studies.

2 polymer represented in Scheme 2, formed by one μ -oxo bridge between each dinuclear unit, whose molecular weight could not be determined.

When an NMR tube containing a solution of *cis*-1 in wet benzene- d_6 (0.01% H_2O) was allowed to stand for 1 week, yellow crystals formed, which were identified as $[(TiCl)_2-(\mu-O)\{(SiMe_2)_2(\eta^5-C_5H_3)_2\}]_2(\mu-O)_2$ (**3**) by 1H NMR spectroscopy; the molecular structure was determined by X-ray diffraction methods.

When a similar reaction was carried out on a preparative level by the addition of 1 equiv. of water to a toluene solution of *cis*-1, the dinuclear oxo-complex *cis*-2 was isolated on evaporation as a yellow crystalline solid soluble in hexane and toluene. Further hydrolysis was observed when toluene or acetonitrile solutions of *cis*-1 were treated with 2 equiv. of water in the presence of NEt_3 , leading to the isolation of complex **4** as a yellow microcrystalline solid soluble in chloroform, benzene and toluene but less soluble in hexane, although crystals of good quality for X-ray diffraction could not be obtained. The 1H and ^{13}C NMR spectra of complex *cis*-2 show two resonances for the two pairs of equivalent $SiMe_2$ groups and the expected AA'B spin system for the ring protons, indicating that the bridging oxygen is in the plane of symmetry of the molecule. The 1H NMR spectra of both oxo-complexes **3** and **4** show the same pattern (see Section 4), with four resonances for the $SiMe_2$ groups and an ABC spin system for the ring protons, which is not resolved in chloroform- d_1 but was observed in benzene- d_6 and confirmed by the ^{13}C NMR spectrum of **4**. This is consistent with the molecular structure determined by X-ray diffraction for complex **3**, which shows symmetric dicyclopentadienyl ligands each also containing symmetric rings with an ABC spin system. The similar NMR behavior found for complex **4** suggests that this compound may be a conformational isomer of **3** with all four chlorine atoms on the same side of the Ti_2 plane, and the two bridged cyclopentadienyl systems on the opposite side instead of the alternating disposition observed for complex **3**, as discussed below.

The alkylation of complexes *cis*-1 and *trans*-1 was studied using $MgClMe$ as alkylating agent (Scheme 3). The addition of 6 equiv. of $MgClMe$ to a hexane solution of *trans*-1 gave a yellow solution from which the hexamethyl ditanium $[(TiMe_3)_2\{(SiMe_2)_2(\eta^5-C_5H_3)_2\}]$ *trans*-5 complex was isolated as a crystalline very air sensitive yellow solid, very soluble in hexane, which was characterized by elemental analysis and NMR spectroscopy. As the *trans*- μ -oxo complex **2** could not be characterized structurally because of its poor solubility in all organic solvents, we tried to obtain the expected more soluble methylated compound by reacting complex **2** with 4 equiv. of $MgClMe$. This reaction takes place readily to give a yellow-green solution, which contains three different components, one being the hexamethylated derivative **5**, together with an unresolvable mixture of oxo-compounds, which show $\nu(M-O)$ IR absorptions at 800 cm^{-1} and 860 cm^{-1} .



Scheme 3.

The analogous reaction carried out with *cis*-1 led to the tetramethyl ditanium derivative $[(TiMe_2Cl)\{(SiMe_2)_2(\eta^5-C_5H_3)_2\}]_2$ *cis*-6, even in the presence of 2 equiv. excess of the alkylating agent. Both complexes **5** and **6** are air sensitive and partial hydrolysis takes place on exposure to air. Complex **6** is soluble in hexane from which it can be recrystallized as a yellow microcrystalline solid; this was characterized by elemental analysis and NMR spectroscopy. The presence of only one signal for all the $SiMe_2$ protons and one signal for all the $Ti-Me$ groups confirms the expected *trans* disposition of the two metal fragments in complex **5**. The 1H NMR spectrum of complex **6** shows two resonances for the $SiMe_2$ groups and only one resonance for all the four equivalent $Ti-Me$ groups, indicating the presence of a plane of symmetry and consistent with a formulation with two independent metal fragments which could also be connected by two chloro bridges, as would be expected to alleviate the electron deficiency of the metal centers.

3. X-ray molecular structure of $[Ti_2\{(SiMe_2)_2(\eta^5-C_5H_3)_2\}Cl_2(\mu-O)]_2(\mu-O)_2$ (**3**)

The molecular structure of **3** based on its X-ray structural analysis is shown in Fig. 1 with the numbering scheme employed. Selected bond angles and distances are given in Table 1.

The crystallographic molecular symmetry is $\bar{1}$, whereas the approximate symmetry is even higher ($2/m$). The molecular structure confirms that **3** can be regarded as the dimer of the dinuclear fragment $[(TiCl)_2(\mu_2-O)\{(SiMe_2)_2(\eta^5-C_5H_3)_2\}]$ affording a tetranuclear derivative showing a non-planar Ti_4O_4 core with a chair conformation in which the oxygen bridges in each dinuclear fragment are located

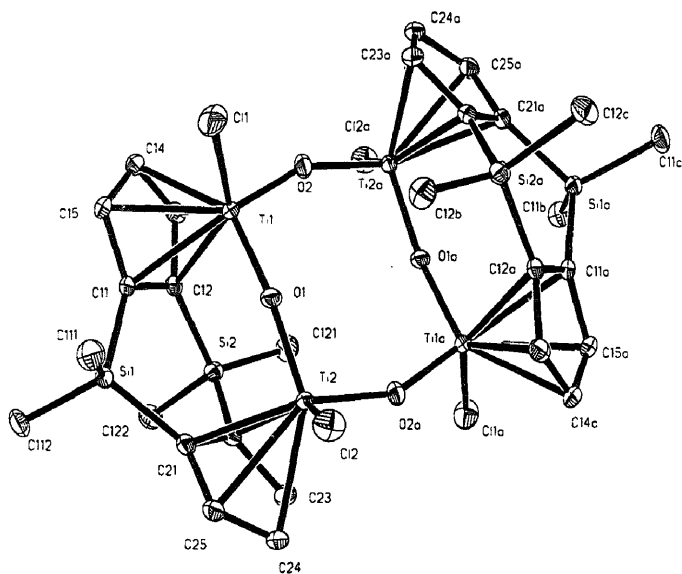


Fig. 1. ORTEP drawing of the molecular structure of compound 3 together with the atomic labeling scheme.

Table 1
Selected bond lengths (Å) and angles (°) for complex 3

Ti(1)–O(2)	1.798(4)
Ti(1)–Cl(1)	2.268(2)
Ti(1)–C(11)	2.352(5)
Ti(1)–C(15)	2.382(5)
Ti(2)–O(2a)	1.812(4)
Ti(2)–Cl(2)	2.270(2)
Ti(2)–C(21)	2.354(5)
Ti(2)–C(24)	2.388(6)
O(2)–Ti(2a)	1.812(4)
Si(1)–C(112)	1.867(6)
Si(1)–C(21)	1.876(6)
Si(2)–C(22)	1.868(6)
Si(2)–C(12)	1.876(6)
C(11)–C(12)	1.451(8)
C(13)–C(14)	1.397(9)
C(21)–C(25)	1.411(8)
C(22)–C(23)	1.427(8)
C(24)–C(25)	1.423(9)
Ti(1)–O(1)	1.803(4)
Ti(1)–C(12)	2.329(5)
Ti(1)–C(13)	2.370(5)
Ti(1)–C(14)	2.394(5)
Ti(2)–O(1)	1.814(4)
Ti(2)–C(22)	2.326(6)
Ti(2)–C(23)	2.360(6)
Ti(2)–C(25)	2.395(6)
Si(1)–C(111)	1.848(7)
Si(1)–C(11)	1.874(5)
Si(2)–C(121)	1.850(7)
Si(2)–C(122)	1.870(6)

Table 1 (continued)

C(11)–C(15)	1.416(7)
C(12)–C(13)	1.409(8)
C(14)–C(15)	1.409(8)
C(21)–C(22)	1.441(8)
C(23)–C(24)	1.384(9)
O(2)–Ti(1)–O(1)	104.5(2)
O(1)–Ti(1)–Cl(1)	102.61(14)
O(2a)–Ti(2)–Cl(2)	101.40(14)
Ti(1)–O(1)–Ti(2)	160.7(2)
C(111)–Si(1)–C(112)	110.7(3)
C(112)–Si(1)–C(11)	108.6(3)
C(112)–Si(1)–C(21)	110.5(3)
C(121)–Si(2)–C(22)	113.9(3)
C(22)–Si(2)–C(122)	106.8(3)
C(22)–Si(2)–C(12)	104.0(3)
O(2)–Ti(1)–Cl(1)	101.5(2)
O(2a)–Ti(2)–O(1)	103.3(2)
O(1)–Ti(2)–Cl(2)	104.34(14)
Ti(1)–O(2)–Ti(2a)	153.0(2)
C(111)–Si(1)–C(11)	111.8(3)
C(111)–Si(1)–C(21)	110.6(3)
C(11)–Si(1)–C(21)	104.5(2)
C(121)–Si(2)–C(122)	111.4(3)
C(121)–Si(2)–C(12)	111.8(3)
C(122)–Si(2)–C(12)	108.5(3)

(continued)

above and below the plane formed by the four Ti atoms, whereas the oxygen bridges between the titanium atoms of different fragments are very close to the plane. The two chloro atoms and the dicyclopentadienyl system of each fragment

occupy alternate sides with respect to the Ti_2O_4 core. This disposition is similar to the chair conformation found for $[\text{Ti}_2\{(\text{SiMe}_2)(\eta^5\text{-C}_5\text{H}_4)_2\}\text{Cl}_2(\mu\text{-O})]_2(\mu\text{-O})$ [8a], containing a singly bridged dicyclopentadienyl system, and the planar conformation found for $[\text{Ti}(\eta^5\text{-C}_5\text{HMe}_3)_2\text{Br}(\mu\text{-O})]_4$ [13] and $[\{\text{Ti}(\eta^5\text{-C}_5\text{H}_4\text{SiMe}_3)(\text{NCS})(\mu\text{-O})\}_4]$ [14] with non-bridged cyclopentadienyl rings. All the titanium–oxygen distances in the Ti_2O_4 core are similar (between 1.798(4) and 1.814(4) Å) and the $\text{Ti}(1)\text{O}(1)\text{Ti}(2)$ and $\text{Ti}(1)\text{O}(2)\text{Ti}(2a)$ angles are very close, their values being $160.7(2)^\circ$ and $153.0(2)^\circ$ respectively. Each titanium is coordinated tetrahedrally to two oxygen atoms, one chlorine atom and one cyclopentadienyl ring, with angles between 101.5° and 115.9° . The two silicon bridging atoms and the carbon atoms of their methyl groups are located in the same plane with the two cyclopentadienyl rings in a necessarily eclipsed configuration. The dihedral angle between the ring planes of each bridging cyclopentadienyl ligand is closer ($32.5(2)^\circ$) than that found ($64.35(6)^\circ$) for $[\text{Ti}\{(\text{SiMe}_2)_2(\eta^5\text{-C}_5\text{H}_3)_2\}\text{Cl}_2]$ [8b], owing to the presence of one oxygen bridge between both bridged titanium atoms with a $\text{Ti}(1)\text{O}(1)\text{Ti}(2)$ angle of $160.7(2)^\circ$, and the two silicon atoms are coplanar with the cyclopentadienyl carbon atoms of each of these rings. The mean Ti–Cl distance 2.269(2) Å is between those found for the related monocyclopentadienyl- and metallocene-type chloride complexes.

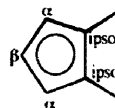
4. Experimental

All manipulations were performed under an inert atmosphere of argon or nitrogen using syringes or cannulae through Subaseals in Schlenk tubes using high vacuum line techniques or a VAC model HE 63P glovebox. Solvents were dried and distilled under nitrogen, CH_2Cl_2 over P_2O_{10} , diethyl ether and tetrahydrofuran from sodium benzophenone ketyl, benzene and toluene from sodium, and hexane from sodium–potassium alloy. 4,4,8,8-Tetramethyltetrahydro-4,8-disila-s-indacene and $\text{Li}_2\{(\text{SiMe}_2)_2(\eta^5\text{-C}_5\text{H}_3)_2\}$ were prepared according to literature procedures [2]. MeLi (1.6 M solution in diethyl ether), MeMgCl, and TiCl_4 (Aldrich) were obtained commercially and used as received. The ^1H and ^{13}C NMR spectra were recorded at 299.95 and 75.43 MHz respectively on a Varian Unity 300 spectrometer; chemical shifts, in ppm, are positive downfield with respect to external SiMe_4 ; coupling constants are in Hz. IR spectra were recorded in Nujol mulls for solids on a Perkin-Elmer 583 spectrophotometer. C and H analyses were performed with a Perkin-Elmer 240-B microanalyzer. Mass spectra were recorded in a Hewlett-Packard 5988A spectrometer.

4.1. Reaction of TiCl_4 with $\text{Li}_2\{(\text{SiMe}_2)_2(\eta^5\text{-C}_5\text{H}_3)_2\}$

A suspension of 2.41 g (9.42 mmol) of $\text{Li}_2\{(\text{SiMe}_2)_2(\eta^5\text{-C}_5\text{H}_3)_2\}$ in 75 ml of toluene was treated with a solution of 2.17 ml (19.77 mmol) of TiCl_4 in 25 ml of toluene. After

being stirred for 5 h at room temperature the LiCl formed was removed by filtration and the red solution was concentrated, under vacuum, to a final volume of 20 ml. The solution was then cooled at -35°C for 12 h to give a yellow crystalline solid which after being filtered, washed with hexane and dried under vacuum, was characterized as *trans*- $[(\text{TiCl}_3)_2\{(\text{SiMe}_2)_2(\eta^5\text{-C}_5\text{H}_3)_2\}]$ (**1**) (2.07 g, 3.75 mmol, 40% yield). The residual solution was evaporated to dryness to give a solid which was then recrystallized repeatedly from toluene to give yellow crystals of *cis*- $[(\text{TiCl}_3)_2\{(\text{SiMe}_2)_2(\eta^5\text{-C}_5\text{H}_3)_2\}]$ (**1**) (1.55 g, 2.81 mmol, 30% yield). When the same reaction was carried out heating the mixture at 60°C , the molar ratio of *cis/trans* isomers was 1/1 but the total yield was decreased owing to the presence of unrecovered decomposition products. Data for *cis*-**1**. Anal. Calc. for $\text{C}_{14}\text{H}_{18}\text{Si}_2\text{Ti}_2\text{Cl}_6$: C, 30.52; H, 3.29. Found: C, 31.03; H, 3.61%. ^1H NMR (300 MHz, CDCl_3 , 25°C): δ 0.45 (s, 6H, Me–Si), 0.70 (s, 6H, Me–Si), 6.93 (t, $J = 2.9$ Hz, 2H, C_3H_3 β), 7.55 (d, $J = 2.9$ Hz, 4H, C_3H_3 α). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3): -4.2 (Si–Me), 1.4 (Si–Me), 124.5 (C_3H_3 β), 132.7 (C_3H_3 α), 136.8 (C_3H_3 ipso). Data for *trans*-**1**. ^1H NMR (300 MHz, CDCl_3 , 25°C): δ 0.65 (s, 12H, Me–Si), 7.13 (t, $J = 2.9$ Hz, 2H, C_3H_3 β), 7.57 (d, $J = 2.9$ Hz, 4H, C_3H_3 α). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3): 1.4 (Si–Me), 129.7 (C_3H_3 β), 132.7 (C_3H_3 α), 141.9 (C_3H_3 ipso). The following labels are used in the text.



4.2. Preparation of $[(\text{TiCl}_3)_2(\mu\text{-O})\{(\text{SiMe}_2)_2(\eta^5\text{-C}_5\text{H}_3)_2\}]$ *trans*-**2**

Deoxygenated and distilled water (21 μl , 1.20 mmol) and NEt_3 (0.33 ml, 2.40 mmol) were added by syringe to a stirred solution of 0.66 g (1.20 mmol) of *trans*-**1** in THF and a yellow precipitate was formed immediately. The reaction mixture was maintained at room temperature for 8 h and then the solvent was removed under vacuum. The ammonium salt contained in the residual solid was removed by extraction into CH_2Cl_2 (3×20 ml) to leave a yellow solid, insoluble in all organic solvents, which was characterized as *trans*- $[(\text{TiCl}_3)_2(\mu\text{-O})\{(\text{SiMe}_2)_2(\eta^5\text{-C}_5\text{H}_3)_2\}]$ (**2**) (0.60 g, 1.08 mmol, 90% yield). Data for **2**. Anal. Calc. for $\text{C}_{14}\text{H}_{18}\text{Si}_2\text{Ti}_2\text{Cl}_6$: C, 33.90; H, 3.66. Found: C, 34.05; H, 3.87%.

4.3. Preparation of $[(\text{TiCl}_3)_2(\mu\text{-O})\{(\text{SiMe}_2)_2(\eta^5\text{-C}_5\text{H}_3)_2\}]$ *cis*-**2**

Deoxygenated and distilled water (19.6 μl , 1.09 mmol) was added by syringe to a stirred solution of 0.60 g (1.09

mmol) of *cis-1* in toluene. The dark red reaction mixture was maintained at room temperature for 12 h giving a green solution; the solvent was then removed under vacuum. The *cis-2* compound was obtained by extraction into hexane (2 × 30 ml) from the green oil formed. Solvent was removed from the yellow solution under vacuum and a yellow microcrystalline solid was characterized as *cis*-[(TiCl₂)₂(μ-O){(SiMe₂)₂(η⁵-C₅H₃)₂}] (2) (0.46 g, 0.83 mmol, 85% yield).

Data for *cis-2*. Anal. Calc. for C₁₃H₁₈Si₂Ti₂Cl₆: C, 33.90; H, 3.66. Found: C, 34.53; H, 3.92%. ¹H NMR (300 MHz, CDCl₃, 25°C): δ 0.30 (s, 6H, *Me-Si*), 0.59 (s, 6H, *Me-Si*), 7.17 (t, *J* = 2.9 Hz, 2H, C₅H₃), 7.36 (d, *J* = 2.9 Hz, 4H, C₅H₃). ¹³C{¹H} NMR (CDCl₃): 0.9 (*Si-Me*), 2.5 (*Si-Me*), 123.7 (C₅H₃ β), 129.1 (C₅H₃ α), 133.7 (C₅H₃ ipso).

4.4. Preparation of [(TiCl₂)₂(μ-O){(SiMe₂)₂(η⁵-C₅H₃)₂}]₂-(μ-O)₂ (3), (4)

4.4.1. Method A

A solution of [(TiCl₂)₂(SiMe₂)₂(η⁵-C₅H₃)₂] *cis-1* in wet benzene-d₆ (0.01% H₂O) was maintained in an NMR tube for 6 days to give yellow crystals which after being filtered, washed with hexane and dried under vacuum, were characterized as complex 3. Data for 3. ¹H NMR (300 MHz, CDCl₃, 25°C): δ 0.31 (s, 6H, *Me-Si*), 0.39 (s, 6H, *Me-Si*), 0.62 (s, 6H, *Me-Si*), 1.01 (s, 6H, *Me-Si*), 6.67 (m, 4H,

C₅H₃ β), 7.06 (m, 4H, C₅H₃ α, α'), 7.27 (m, 4H, C₅H₃ α, α').

4.4.2. Method B

Deoxygenated and distilled water (33.7 μl, 1.87 mmol) and NEt₃ (0.51 ml, 3.74 mmol) were added by syringe to a stirring solution of 0.51 g (0.94 mmol) of *cis-1* in toluene. The reaction mixture was maintained at room temperature for 12 h and the solvent was then removed under vacuum. Extraction of the residual solid into hexane (2 × 30 ml) gave a solution which provided yellow crystals after removal of solvent under vacuum. They were characterized as complex 4 (0.4 g, 0.70 mmol, 74% yield).

Data for 4. Anal. Calc. for C₂₈H₃₆Si₄Ti₄O₄: C, 38.12; H, 4.11. Found: C, 38.09; H, 4.55%. ¹H NMR (300 MHz, CDCl₃, 25°C): δ 0.37 (s, 6H, *Me-Si*), 0.47 (s, 6H, *Me-Si*), 0.53 (s, 6H, *Me-Si*), 0.67 (s, 6H, *Me-Si*), 6.87 (m, 4H, C₅H₃ β), 7.38 (m, 8H, C₅H₃ α, α'). ¹H NMR (300 MHz, C₆D₆, 25°C): δ 0.18 (s, 6H, *Me-Si*), 0.36 (s, 6H, *Me-Si*), 0.38 (s, 6H, *Me-Si*), 0.64 (s, 6H, *Me-Si*), 6.33 (m, 4H, C₅H₃ β), 6.99 (m, 4H, C₅H₃ α, α'), 7.02 (m, 4H, C₅H₃ α, α'). ¹³C{¹H} NMR (CDCl₃): -0.5 (*Si-Me*), 0.9 (*Si-Me*), 1.7 (*Si-Me*), 3.0 (*Si-Me*), 123.7 (C₅H₃ β), 135.5, 136.1 (C₅H₃ α, α'), 135.1, 136.8 (C₅H₃ ipso).

4.5. Synthesis of *trans*-[(TiMe₃)₂{(SiMe₂)₂(η⁵-C₅H₃)₂}] (5)

MgClMe (3.63 ml of a 3 M THF solution, 10.89 mmol) was added at -78°C to a suspension of *trans-1* (1.05 g, 1.81

Table 2

Crystal data and structure refinement for complex 3

Empirical formula	C ₂₈ H ₃₆ Ti ₄ O ₄ Cl ₄ · 1/2C ₆ H ₆
Formula weight	469.69
Temperature (K)	293(2)
Wavelength (Å)	0.71073
Crystal system	monoclinic
Space group	<i>P</i> 2 ₁ / <i>n</i>
Unit cell dimensions	
<i>a</i> (Å)	9.709(4)
<i>b</i> (Å)	15.112(3)
<i>c</i> (Å)	14.700(5)
β (°)	100.60(2)
Volume (Å ³)	2120. (1)
<i>Z</i>	2
Density (calc.) (g cm ⁻³)	1.443
Absorption coefficient (cm ⁻¹)	11.23
<i>F</i> (000)	938
Crystal size (mm)	0.2 × 0.2 × 0.3
θ Range for data collection (°)	2 to 25
Index ranges	-11 < <i>h</i> < 11, 0 < <i>k</i> < 17, 0 < <i>l</i> < 17
Reflections collected	3878
Independent reflections	3727 (<i>R</i> _{int} = 0.0421)
Refinement method	full-matrix least-squares on <i>F</i> ²
Data, restraints, parameters	3727, 0, 226
Goodness-of-fit on <i>F</i> ²	1.053
Final <i>R</i> indices (<i>I</i> > 2σ(<i>I</i>)) ^a	<i>R</i> 1 = 0.0487, ω <i>R</i> 2 = 0.1598
<i>R</i> indices (all data)	<i>R</i> 1 = 0.0848, ω <i>R</i> 2 = 0.1691
Weighting scheme	calc. ω = 1/[σ ² (<i>F</i> _o ²) + (0.0944 <i>P</i>) ² + 3.0549 <i>P</i>] where <i>P</i> = (<i>F</i> _o ² + 2 <i>F</i> _c ²)/3
Largest difference peak, hole (e Å ⁻³)	1.004, -0.306

^a *R*1 = Σ||*F*_o|| - |*F*_c||/Σ|*F*_o||, ω*R*2 = {Σω(*F*_o² - *F*_c²)} / {Σω(*F*_o²)^{1/2}}

mmol) in hexane (50 ml). The reaction mixture was warmed to room temperature and stirred for 12 h. After filtration the solvent was removed under vacuum and the resulting solid was recrystallized from hexane to give **5** (0.56 g, 1.30 mmol, 73% yield).

Data for **5**. Anal. Calc. for $C_{20}H_{30}Si_2Ti_2$: C, 56.07; H, 8.47. Found: C, 55.75; H, 8.53%. 1H NMR (300 MHz, $CDCl_3$, 25°C): δ 0.21 (s, 12H, *Me-Si*), 1.29 (s, 18H, *Me-Ti*), 6.17 (t, $J = 2.9$ Hz, 2H, $C_5H_3 \beta$), 6.35 (d, $J = 2.9$ Hz, 4H, $C_5H_3 \alpha$, α'). $^{13}C\{^1H\}$ NMR ($CDCl_3$): 1.6 (*Si-Me*), 64.4 (*Ti-Me*), 120.7 ($C_5H_3 \beta$), 124.3 ($C_5H_3 \alpha$), 129.8 (C_5H_3 ipso).

4.6. Synthesis of *cis*-[(*TiMe_2Cl*)₂{(*SiMe_2*)₂(η^5 - C_5H_5)₂}] (**6**)

MgClMe (3.84 ml of a 3 M THF solution, 11.58 mmol) was added at $-78^\circ C$ to a suspension of *cis*-**1** (1.05 g, 1.92 mmol) in hexane (50 ml). The reaction mixture was warmed to room temperature and stirred for 12 h. After filtration the solvent was removed under vacuum and the resulting solid was recrystallized from hexane to give **6** (0.48 g, 1.02 mmol, 58% yield).

Data for **6**. Anal. Calc. for $C_{14}H_{18}Si_2Ti_2Cl_4O$: C, 46.07; H, 6.44. Found: C, 46.45; H, 6.31%. 1H NMR (300 MHz, $CDCl_3$, 25°C): δ 0.04 (s, 6H, *Me-Si*), 0.17 (s, 6H, *Me-Si*), 0.92 (s, 12H, *Me-Ti*), 6.63 (t, $J = 2.9$ Hz, 2H, $C_5H_3 \beta$), 6.71 (d, $J = 2.9$ Hz, 4H, $C_5H_3 \alpha$). $^{13}C\{^1H\}$ NMR ($CDCl_3$): -3.4 (*Si-Me*), 2.9 (*Si-Me*), 53.2 (*Ti-Me*), 121.8 ($C_5H_3 \beta$), 124.0 ($C_5H_3 \alpha$), 126.8 (C_5H_3 ipso).

4.7. X-ray structural determination for compound **3**

Crystallographic and experimental details of the crystal structure determination are given in Table 2. Suitable crystals of complex **3** were mounted on an Enraf-Nonius Cad4 automatic four-circle diffractometer with bisecting geometry, equipped with a graphite-oriented monochromator and Mo $K\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$). Data were collected at room temperature. Intensities were corrected for Lorentz and polarization effects in the usual manner. No absorption or extinction corrections were made.

The structures were solved by direct methods (SHELXS 90) [15] and refined by full-matrix least-squares against F^2 (SHELXL 93) [16]. All non-hydrogen atoms were refined anisotropically. In the last cycle of refinement the hydrogen atoms were positioned geometrically and refined using a riding model with thermal parameters equivalent to that of the carbon atom to which they were attached. Calculations were carried on an ALPHA AXP (Digital) workstation.

5. Supplementary material

Tables of atomic coordinates and isotropic displacement parameters, full lists of bond distances and angles, anisotropic displacement parameters, hydrogen coordinates and structure factors have been deposited with the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK.

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