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Journal of Organometallic Chemistry 663 (2002) 134–144

Journal  
of Organo  
metallic  
Chemistry[www.elsevier.com/locate/jorgchem](http://www.elsevier.com/locate/jorgchem)

# Synthesis and crystal structures of thermally stable titanocenes

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Received 28 May 2002; accepted 18 July 2002

Dedicated to Professor Pascual Royo on the occasion of his 65th birthday in recognition of his outstanding contributions to organometallic chemistry

## Abstract

Reduction of fully substituted titanocene dichlorides  $[\text{TiCl}_2(\eta^5\text{-C}_5\text{Me}_4\text{R})_2]$  ( $\text{R} = \text{SiMe}_2\text{CH}_2\text{CH}_2\text{Ph}$ , **3**;  $\text{SiMe}_2\text{Ph}$ , **4**; and  $\text{SiMePh}_2$ , **5**) with magnesium in THF proceeds via the formation of titanocene monochlorides  $[\text{TiCl}(\eta^5\text{-C}_5\text{Me}_4\text{R})_2]$  **6–8** to afford monomeric titanocenes,  $[\text{Ti}(\eta^5\text{-C}_5\text{Me}_4\text{R})_2]$ , **9–11**. Titanocene monochlorides give the expected EPR spectra in toluene solution and glass. The structure of **7** was further corroborated by single-crystal X-ray diffraction. Titanocenes **9–11** are EPR silent down to  $-196^\circ\text{C}$  but exhibit paramagnetic broadening of the signals in solution NMR spectra. The positions of the NMR signals are temperature-dependent, obeying the Curie Law in the range investigated ( $0\text{--}60^\circ\text{C}$ ). As revealed by X-ray crystallography, titanocenes **9** and **11** possess bent metallocene structures with the cyclopentadienyl rings tilted at an angle of  $9.8(1)$  and  $14.4(2)^\circ$ , respectively. Titanocenes **9–11** are easily oxidized with  $\text{PbCl}_2$  to the parent dichloride complexes **3–5**. Titanocenes **9** and **10** react with bis(trimethylsilyl)ethyne (btmse) only in large excess of the alkyne to give an equilibrium concentration of the respective  $[\text{Ti}(\eta^5\text{-C}_5\text{Me}_4\text{R})_2(\eta^2\text{-Me}_3\text{SiC}\equiv\text{CSiMe}_3)]$  complexes. On the other hand, titanocene **11** does not observably react with btmse.

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**Keywords:** Titanium; Titanocenes; Bent titanocenes; Silyl substituents; X-ray crystallography

## 1. Introduction

Electron-deficient, monomeric titanocenes are thermally unstable due to their strong tendency to acquire more valence electrons by means of various rearrangements which generally result in a conversion of Ti(II) to Ti(III) or Ti(IV) [1]. Accordingly, the parent titanocene,  $[\text{Ti}(\eta^5\text{-C}_5\text{H}_5)_2]$ , rearranges to green ‘dimeric titanocene’,  $[(\mu\text{-}\eta^5\text{-}\eta^5\text{-C}_5\text{H}_4\text{C}_5\text{H}_4)\{\text{Ti}(\mu\text{-H})(\eta^5\text{-C}_5\text{H}_5)\}_2]$ , very rapidly under ambient conditions [2]. Thermal stability of methyl-substituted titanocenes increases with the number of electron donating methyl groups on the cyclopentadienyl ligands; however, compounds analogous to dimeric titanocene are obtained from transiently formed titanocenes containing mono- up to trimethy-

lated cyclopentadienyl ligands [3]. The coordination-stabilized titanocene  $[(\mu\text{-N}_2)\{\text{Ti}(\eta^5\text{-C}_5\text{Me}_4\text{H})_2\}_2]$  readily eliminates dinitrogen and, subsequently, dihydrogen to give a paramagnetic dimer with bridging  $\text{Ti}\text{--}\text{C}^{\text{CP}}\sigma$  bonds  $[\{\text{Ti}(\eta^1\text{-}\eta^5\text{-C}_5\text{Me}_4)(\eta^5\text{-C}_5\text{Me}_4\text{H})\}_2]$  [4]. Even the relatively stable decamethyltitanocene, prepared by an elimination of dinitrogen from  $[(\mu\text{-N}_2)\{\text{Ti}(\eta^5\text{-C}_5\text{Me}_5)_2\}_2]$ , is inherently contaminated by hydride species  $[\text{TiH}(\eta^5\text{-C}_5\text{Me}_5)(\eta^1\text{-}\eta^5\text{-C}_5\text{Me}_4\text{CH}_2)]$  [5]. Thus, so far only silicon-modified fully ring-substituted titanocenes  $[\text{Ti}(\eta^5\text{-C}_5\text{Me}_4\text{SiMe}_2\text{R})_2]$  ( $\text{R} = \text{Bu}^t$  **1** [6] or  $\text{Me}$  **2** [7]) were found to be stable at ambient temperature. Titanocene **1** resulted from the reduction of  $[\text{TiCl}(\eta^5\text{-C}_5\text{Me}_4\text{SiMe}_2\text{Bu}^t)_2]$  with sodium amalgam [6]. An analogous reduction of  $[\text{TiCl}_2\{\eta^5\text{-C}_5\text{Me}_4(\text{SiMe}_3)\}_2]$  with magnesium metal is complicated by side reactions [8] and, hence, compound **2** was obtained alternatively by thermolysis of bis(trimethylsilyl)ethyne (btmse) complex  $[\text{Ti}\{\eta^5\text{-C}_5\text{Me}_4(\text{SiMe}_3)\}_2(\eta^2\text{-btmse})]$  [7]. Here, we report

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the synthesis and crystal structures of thermally stable titanocenes containing other silyl substituents on otherwise fully methylated cyclopentadienyl ligands.

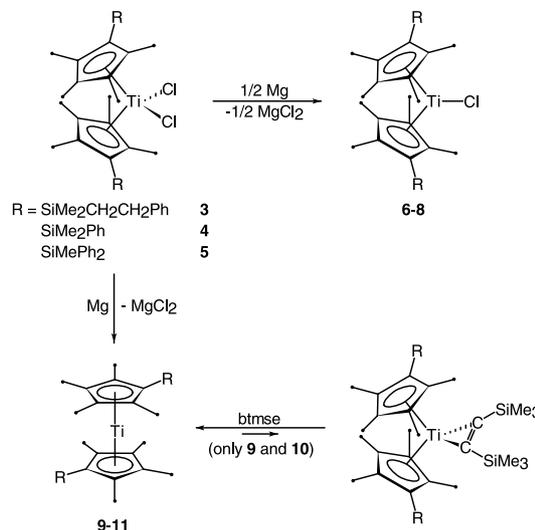
## 2. Results and discussion

### 2.1. Synthesis of ring-silylated titanocene dichlorides 3–5

Cyclopentadienes  $C_5HMe_4(SiMe_2CH_2CH_2Ph)$ ,  $C_5HMe_4(SiMe_2Ph)$ , and  $C_5HMe_4(SiMePh_2)$  were obtained in good yields from the metathesis of lithium tetramethylcyclopentadienide with commercially available chlorosilanes  $ClSiMe_2CH_2CH_2Ph$ ,  $ClSiMe_2Ph$ , and  $ClSiMePh_2$ , respectively. Their  $^1H$ - and  $^{13}C$ -NMR spectra revealed the presence of only one double-bond isomer with the silicon group attached to the  $C-sp^3$  ring-carbon atom. The synthesis of titanocene dichlorides thereof followed the procedure used for the preparation of analogous alkenyldimethylsilyl titanocene dichlorides [9]: in situ generated  $[TiCl_3(THF)_3]$  and the respective lithium cyclopentadienide were reacted to give Ti(III) intermediates, which were without isolation oxidized with  $AgCl$  to titanocene dichlorides  $[TiCl_2(\eta^5-C_5Me_4R)_2]$  ( $R = SiMe_2CH_2CH_2Ph$ , **3**;  $SiMe_2Ph$ , **4**; and  $SiMePh_2$ , **5**) in 16–28% isolated yields. Compounds **3–5** were characterized by NMR, IR, and EI-MS spectra. The latter showed an elimination of one cyclopentadienyl ligand as the major fragmentation process with the elimination of chloride ligand being less abundant. Molecular ion was observed in neither case.

### 2.2. Preparation and properties of titanocene monochlorides 6–8

Reduction of titanocene dichlorides **3–5** by half molar equivalent of activated magnesium in THF affords the corresponding titanocene monochlorides,  $[TiCl(\eta^5-C_5Me_4R)_2]$ , **6–8** in high yields (Scheme 1). When all the magnesium was consumed the product **6** was worked-up by extraction with hexane whereas compounds **7** and **8**, due to their low solubility in hexane, were extracted and crystallized from toluene. Crystalline **8** obtained in this manner is contaminated by the formed  $MgCl_2$  which is also slightly soluble in toluene. Compounds **6** and **7** form blue solutions in both THF and toluene, while the solutions of **8** are turquoise. Electronic absorption spectra of **6–8** in toluene and THF have the same appearance, showing an absorption band at 550–570 nm accompanied by a broad shoulder at 650–670 nm. These bands of low intensity (molar extinction coefficient ca.  $1 \times 10^2$ ) have been attributed to  $1a_1 \rightarrow 2a_1$  transitions [12]. EI-MS spectra of **6–8** showed the silyl group ions as base peaks, however, the molecular ions of **7** and **8** fragmented with the loss of the cyclopentadienyl ligands while that of **6** showed in addition a



Scheme 1.

minor loss of the chlorine atom, thus resembling the behaviour of  $[TiCl\{\eta^5-C_5Me_4(SiMe_3)\}_2]$  [13].

The monochloride  $d^1$  complexes are paramagnetic, showing in toluene solution EPR spectra consist of one broad single line whose  $g$ -factor decreases in the order **6** (1.959), **7** (1.950), and **8** (1.948). In keeping with a growing anisotropy of the high-field  $g$ -tensor component ( $g_3$ ) in toluene glass [10], the linewidth ( $\Delta H_{pp}$ ) increases in the same order. The  $g$ -factor values for **7** and **8** belong amongst the lowest ones reported for fully substituted titanocene monochlorides (cf. [11]). Compounds **6–8** display very similar EPR spectra in both THF and toluene solutions. This proves an absence of the solvent coordination; otherwise the EPR signal of THF-adducts should occur at  $g = 1.979$  [10]. In the presence of active magnesium the complexes are reduced both in the presence and the absence of btmse to the respective titanocenes **9–11** (see below).

### 2.3. Crystal structure of 7

Compound **7** crystallizes with the symmetry of  $C2/c$  space group, so that the crystallographic twofold axis passes through the titanium and chlorine atoms what makes only one-half of the molecule crystallographically independent. The molecular structure of **7** (Fig. 1) corroborates the pseudotrigonal coordination around the titanium atom. Its molecular parameters (Table 1) do not differ markedly from those found for the closely related  $[TiCl\{\eta^5-C_5Me_4(SiMe_3)\}_2]$  [13]. The cyclopentadienyl rings are in a staggered conformation, and a steric congestion induced by the bulky silyl groups is largely relieved by their placement in side positions on the opposite sides of the  $Cg-Ti-Cg'$  plane (Fig. 2). The silicon substituents are directed towards the chlorine atom forming a torsion angle ( $\tau$ )  $Si-Cg-Cg'-Si'$  of  $104.0(2)^\circ$ . The angle subtended by the least-squares

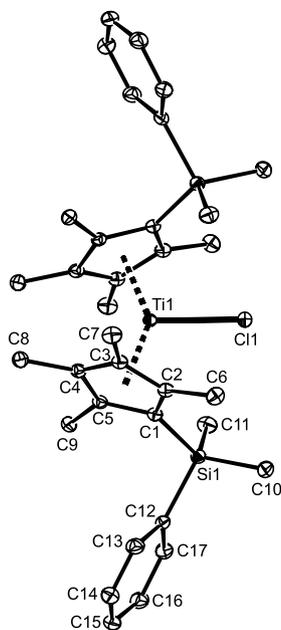


Fig. 1. Molecular structure of **7** (30% probability ellipsoids) with the atom numbering scheme. The non-labelled atoms are generated by the symmetry operation  $(1-x, y, 1/2-z)$ . For clarity, hydrogen atoms are omitted.

Table 1  
Selected bond lengths (Å) and bond angles (°) for **7**

Bond lengths			
Ti–Cg <sup>a</sup>	2.066(2)	Ti–Cl	2.3640(7)
Ti–C(1)	2.3704(16)	Ti–C(2)	2.3930(16)
Ti–C(3)	2.3901(17)	Ti–C(4)	2.4340(17)
Ti–C(5)	2.3916(16)	C(1)–C(2)	1.436(2)
C(1)–C(5)	1.436(2)	C(2)–C(3)	1.416(2)
C(3)–C(4)	1.419(2)	C(4)–C(5)	1.419(2)
C(1)–Si	1.8779(17)	Si–C(10)	1.865(2)
Si–C(11)	1.872(2)	Si–C(12)	1.889(2)
C <sub>ring</sub> –C <sub>Me</sub>	1.503(2)– 1.509(2)	C–C <sub>Ph ring</sub>	1.375(3)– 1.400(3)
Bond angles			
Cg–Ti–Cg <sup>b</sup>	141.4(2)	C(2)–C(1)–C(5)	106.34(15)
C(1)–C(2)–C(3)	108.64(15)	C(2)–C(3)–C(4)	108.22(15)
C(3)–C(4)–C(5)	107.90(15)	C(1)–C(5)–C(4)	108.75(15)
$\phi$ <sup>c</sup>	36.0(1)	$\tau$ <sup>d</sup>	104.0(2)

<sup>a</sup> Cg denotes the centroid of the C(1–5) cyclopentadienyl ring atoms; Cg' is the centroid of the symmetry generated ring.

<sup>b</sup> Symmetry transformation used to generate equivalent positions:  $(1-x, y, 1/2-z)$ .

<sup>c</sup> Dihedral angle between the least-squares cyclopentadienyl planes.

<sup>d</sup> Torsion angle Si–Cg–Cg'–Si'.

planes of cyclopentadienyl rings of  $36.0(1)^\circ$  is virtually the same as in the mentioned reference compound  $35.8(1)^\circ$ .

#### 2.4. Preparation and properties of titanocenes **9–11**

Titanocenes  $[\text{Ti}\{\eta^5\text{-C}_5\text{Me}_4(\text{SiMe}_2\text{CH}_2\text{CH}_2\text{Ph})\}_2]$  (**9**),  $[\text{Ti}\{\eta^5\text{-C}_5\text{Me}_4(\text{SiMe}_2\text{Ph})\}_2]$  (**10**), and  $[\text{Ti}\{\eta^5\text{-C}_5\text{Me}_4(\text{Si-$

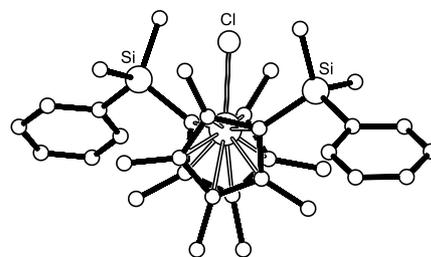


Fig. 2. Structure of **7** viewed along the Cg–Cg' line.

$\text{MePh}_2\}_2]$  (**11**) were obtained from reduction of titanocene dichlorides **3–5**, respectively, with one molar equivalent of activated magnesium in THF as the only isolated products in high yields (Scheme 1). In no case, however, the reduction leads quantitatively to titanocenes, and their purification is inevitable. After consumption of magnesium all volatiles were evaporated under vacuum, and the residue was extracted with hexane. The titanocenes were purified by crystallisation from hexane; mother liquors were separated and discarded for **9** and **10** whereas all the hexane solution was removed from **11** which is low soluble in hexane, and the compound was re-crystallized from toluene. Even so, EPR spectroscopy revealed the presence of trace amounts of titanocene monochlorides (see above) and alkoxy derivatives, characterized by a single line at  $g = 1.976$ ,  $\Delta H = 4.0$  G (in toluene glass  $g_1 = 1.998$ ,  $g_2 = 1.860$ ,  $g_3 = 1.954$ ,  $g_{\text{av}} = 1.977$ ). These paramagnetic impurities were estimated to be present in less than 2% of total titanium content. The crystalline compounds melted at: **9**,  $75^\circ\text{C}$ ; **10**,  $85^\circ\text{C}$ , and **11**,  $105^\circ\text{C}$ , all without decomposition; the values may be subject of change at eventual lower content of the above mentioned impurities.

In  $\text{C}_6\text{D}_6$  solution, compounds **9–11** show a remarkable paramagnetic broadening of  $^1\text{H-NMR}$  resonances, however, no signal is observed in their EPR spectra down to  $-196^\circ\text{C}$  in toluene solution. In  $^1\text{H-NMR}$  spectra, titanocenes **9–11** feature very broad resonances in a range ca.  $0\text{--}85$  ppm. Positions of the signals change with temperature and the relative chemical shifts,  $\Delta_i = \delta - \delta(\text{C}_6\text{D}_6)$ , obey the Curie Law in the accessible temperature range of  $0\text{--}60^\circ\text{C}$ . This behaviour is similar to that of compounds **1** and **2**, and is compatible with magnetic moments of  $\mu = 2.4\mu_{\text{B}}$  determined for **1** [6] and  $\mu = 2.48\text{--}2.60\mu_{\text{B}}$  for  $[\text{Ti}(\eta^5\text{-C}_5\text{Me}_5)_2]$  [5b].

Electron impact mass spectra of **9–11** show the molecular ion  $[\text{M}]^+$  of lower intensity relative to the  $[\text{M-H}]^+$  peak which dominates a cluster of isotope and hydrogen deficient peaks. This contrasts with spectra of **2** which are dominated by  $[\text{M}]^+$  species [7] and also with spectra of **1** where  $[\text{M}]^+$  shows only 3% relative abundance [6]. In **9–11**, the loss of hydrogen atom from  $[\text{M}]^+$  is the main fragmentation process leading to a more stable methylene-containing ion. The presence of neutral  $[\text{M-H}]$  complexes as an impurity in the bulk

samples was unequivocally excluded by the absence of any EPR signal attributable to these presumably paramagnetic compounds. Well-defined compounds of this type  $[\text{Ti}\{\eta^5\text{-C}_5\text{Me}_4(\text{SiMe}_3)\}\{\eta^1:\eta^5\text{-C}_5\text{Me}_4\text{SiMe}_2\text{CH}_2\}]$  [8] and  $[\text{Ti}(\eta^5\text{-C}_5\text{Me}_5)(\eta^1:\eta^5\text{-C}_5\text{Me}_4\text{CH}_2)]$  [14] display EPR spectra which would differ from EPR spectra of the above mentioned impurities. Electronic absorption spectra of **9–11** correspond well to spectra of **1** and **2** showing the absorption band at 580–590 nm in both toluene and THF. This rules out any strong coordination of THF molecule(s) to the titanium centre.

Compounds **9** and **10** exert only a very low affinity to btmse. Even with a 28 molar excess of btmse added to a solution of **9** in hexane, complex  $[\text{Ti}\{\eta^5\text{-C}_5\text{Me}_4(\text{SiMe}_2\text{CH}_2\text{CH}_2\text{Ph})\}_2(\eta^2\text{-btmse})]$  (**12**) formed slowly during 2 h at 22 °C, finally reaching a concentration comparable to that of unreacted **9**. Similarly, compound **10** in toluene and btmse (btmse:**10** = 20) was converted to  $[\text{Ti}\{\eta^5\text{-C}_5\text{Me}_4(\text{SiMe}_2\text{Ph})\}_2(\eta^2\text{-btmse})]$  (**13**) in  $25 \pm 5\%$ . The presence of **12** and **13** was detected by the occurrence of their electronic absorption bands at  $940 \pm 5$  and  $935 \pm 5$  nm, respectively, that are typical for titanocene complexes with  $\eta^2$ -coordinated alkene and alkyne ligands [3,7,15,16]. Complexes **12** and **13** could not be isolated because they decomposed upon removal of the solvent and excess btmse under vacuum at room temperature, affording quantitatively the parent titanocenes. At variance, titanocene **11** in toluene did not observably react with a similar excess of btmse. The reaction of **9–11** with  $\text{PbCl}_2$  in THF [17] cleanly recovered titanocene dichlorides **3–5**.

The observed low affinity of **9** and **10** towards btmse and the absence of such an affinity for **11** contrast with the behaviour of **2** which readily forms  $\eta^2$ -alkyne complex  $[\text{Ti}\{\eta^5\text{-C}_5\text{Me}_4(\text{SiMe}_3)\}_2(\eta^2\text{-btmse})]$  stable up to 70 °C [7]. This apparently results from a rotation of the cyclopentadienyl ligands bearing bulky dimethyl(phenethyl)silyl, dimethylphenylsilyl, and methyl-diphenylsilyl substituents, sweeping up the coordination space around the titanium centre with the effect increasing in the above order of ligands.

### 2.5. Crystal structures of **9** and **11**

The structures of **9** and **11** were determined by single crystal X-ray diffraction analysis. In contrast to both structurally characterized titanocenes **1** and **2**, which showed exactly parallel cyclopentadienyl rings, compounds **9** and **11** are asymmetric (Figs. 3 and 4). The geometric parameters of both compounds are very similar (Tables 2 and 3). The  $\text{Cg1-Ti-Cg2}$  (Cg denotes cyclopentadienyl ring centroid) angle in **9** amounts to  $166.0(2)$  and  $162.2(2)^\circ$  in **11** whilst the least-squares cyclopentadienyl ring planes subtend an angle of  $9.8(1)$  and  $14.4(2)^\circ$ , respectively. The cyclopentadienyl ligands are mutually rotated at the torsion angle  $\text{Si1-Cg1-}$

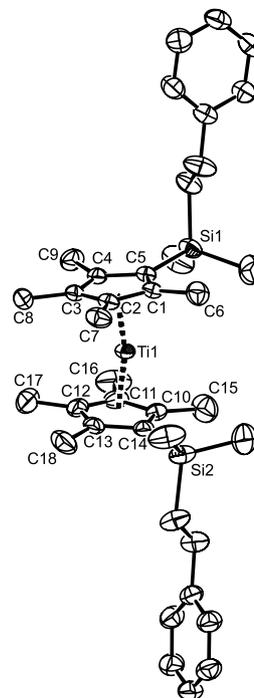


Fig. 3. Molecular structure of **9** (30% probability ellipsoids) showing the atom numbering scheme. For clarity, all hydrogen atoms are omitted.

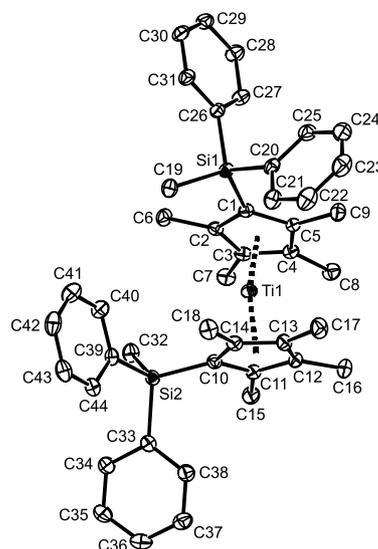


Fig. 4. Molecular structure of **11** (30% probability ellipsoids) showing the atom numbering scheme. For clarity, all hydrogen atoms are omitted.

$\text{Cg2-Si2}$  of  $98.3(2)^\circ$  for **9** and  $88.2(2)^\circ$  for **11** (see Fig. 5). The angle between the least-squares phenyl planes in the molecule of **9** is  $88.7(1)^\circ$ . In **11**, the least-squares planes of phenyl rings at Si(1) and Si(2) atoms are mutually rotated at different angles  $84.5(1)$  and  $71.4(1)^\circ$ , respectively. A closer inspection at the parameters of titanocene moieties shows that the ring angle at the carbon atom bearing the silyl group is more acute

Table 2  
Selected bond lengths (Å) and bond angles (°) for **9**

Bond lengths			
Ti–Cg(1) <sup>a</sup>	2.004(3)	Ti–Cg(2) <sup>a</sup>	2.001(3)
Ti–C(1)	2.325(3)	Ti–C(2)	2.378(3)
Ti–C(3)	2.376(3)	Ti–C(4)	2.326(3)
Ti–C(5)	2.298(3)	Ti–C(10)	2.301(3)
Ti–C(11)	2.370(3)	Ti–C(12)	2.379(3)
Ti–C(13)	2.334(3)	Ti–C(14)	2.294(3)
C–C <sub>Cp ring</sub>	1.404(5)– 1.445(4)	C <sub>ring</sub> –C <sub>Me</sub>	1.501(5)– 1.511(5)
Si(1)–C(5)	1.862(3)	Si(1)–C(19)	1.869(5)
Si(1)–C(20)	1.854(5)	Si(1)–C(21)	1.887(4)
Si(2)–C(14)	1.869(3)	Si(2)–C(29)	1.874(5)
Si(2)–C(30)	1.854(5)	Si(2)–C(31)	1.903(4)
C(21)–C(22)	1.475(5)	C(22)–C(23)	1.524(5)
C(31)–C(32)	1.471(6)	C(32)–C(33)	1.535(5)
C–C <sub>Ph ring</sub>	1.354(5)– 1.382(5)		
Bond angles			
Cg(1)–Ti–Cg(2) <sup>a</sup>	166.0(2)	C(2)–C(1)–C(5)	108.5(3)
C(1)–C(2)–C(3)	108.5(3)	C(2)–C(3)–C(4)	108.2(3)
C(3)–C(4)–C(5)	108.7(3)	C(1)–C(5)–C(4)	106.1(3)
C(11)–C(10)–C(14)	109.3(3)	C(11)–C(12)–C(13)	108.7(3)
C(10)–C(14)–C(13)	105.6(3)	C(12)–C(13)–C(14)	108.8(3)
C(10)–C(11)–C(12)	107.7(3)	$\phi^b$	9.8(1)
$\omega_1^c$	88.8(1)	$\tau^d$	98.3(2)

<sup>a</sup> Cg(1) and Cg(2) are centroids of the C(1–5) and C(10–14) cyclopentadienyl rings, respectively.

<sup>b</sup> Dihedral angle between the least-squares cyclopentadienyl planes.

<sup>c</sup> Dihedral angle between the least-squares planes of phenyl rings.

<sup>d</sup> Torsion angle Si(1)–Cg(1)–Cg(2)–Si(2).

(106.1(3) and 105.6(3)° for **9**; 106.0(2) and 106.1(2)° for **11**) compared to analogous angles at other ring carbon atoms (107.7(3)–109.3(3)°). This appears to be a general feature of silyl-substituted permethylated cyclopentadienyltitanium compounds since a similar cyclopentadienyl ring angles were also found for symmetric titanocene **2** [7], monochloride **7** (106.3(2)°) as well as for eight titanocene complexes bearing  $\eta^5\text{-C}_5\text{Me}_4\text{SiMe}_2\text{R}$  with R being a methylene linked to a bridging *ansa*-chain or to a titanacycle [9]. The least-squares cyclopentadienyl ring planes are nearly perpendicular to the Ti–Cg vectors, and maximum deviations of the Si atoms from the least-squares planes of cyclopentadienyl rings in outward direction (0.194(4) Å for Si(2) of **11**) are comparable with analogous maximum deviations of methyl carbon atoms (0.182(4) Å for C(6) of **11**). It shows that bulky substituents of the silyl groups do not impose any steric hindrance into these titanocene molecules. The bending of the titanocene structures and the overall asymmetry in the solid state result most likely from crystal packing effects induced by steric demands of the bulky silyl groups. This corresponds to recent DFT calculations which indicate that only a small change of the overall energy is associated with tilting the cyclopentadienyl rings [18].

Table 3  
Selected bond lengths (Å) and bond angles (°) for **11**

Bond lengths			
Ti–Cg(1) <sup>a</sup>	2.017(2)	Ti–Cg(2) <sup>a</sup>	2.010(2)
Ti–C(1)	2.310(2)	Ti–C(2)	2.358(2)
Ti–C(3)	2.393(2)	Ti–C(4)	2.381(2)
Ti–C(5)	2.330(2)	Ti–C(10)	2.296(2)
Ti–C(11)	2.327(2)	Ti–C(12)	2.389(2)
Ti–C(13)	2.390(2)	Ti–C(14)	2.335(2)
C–C <sub>Cp ring</sub>	1.410(3)– 1.451(3)	C <sub>ring</sub> –C <sub>Me</sub>	1.504(3)– 1.509(3)
C(1)–Si(1)	1.866(2)	C(10)–Si(2)	1.862(2)
Si(1)–C(19)	1.868(2)	Si(1)–C(20)	1.881(2)
Si(1)–C(26)	1.881(2)	Si(2)–C(32)	1.876(2)
Si(2)–C(33)	1.880(2)	Si(2)–C(39)	1.884(2)
C–C <sub>Ph ring</sub>	1.374(4)– 1.405(3)		
Bond angles			
Cg(1)–Ti–Cg(2) <sup>a</sup>	162.2(2)	C(2)–C(1)–C(5)	106.0(2)
C(1)–C(2)–C(3)	108.6(2)	C(2)–C(3)–C(4)	108.4(2)
C(3)–C(4)–C(5)	108.5(2)	C(1)–C(5)–C(4)	108.5(2)
C(11)–C(10)–C(14)	106.1(2)	C(11)–C(12)–C(13)	108.4(2)
C(10)–C(14)–C(13)	108.0(2)	C(12)–C(13)–C(14)	108.7(2)
C(10)–C(11)–C(12)	108.8(2)	$\phi^b$	14.4(2)
$\omega_1^c$	84.5(1)	$\omega_2^d$	71.4(1)
$\tau^e$	88.8(2)		

<sup>a</sup> Cg(1) and Cg(2) are centroids of the C(1–5) and C(10–14) cyclopentadienyl rings, respectively.

<sup>b</sup> Dihedral angle between the least-squares cyclopentadienyl planes.

<sup>c</sup> Dihedral angle between the least-squares planes of phenyl rings at Si(1) atom.

<sup>d</sup> Dihedral angle between the least-squares planes of phenyl rings at Si(2) atom.

<sup>e</sup> Torsion angle Si(1)–Cg(1)–Cg(2)–Si(2).

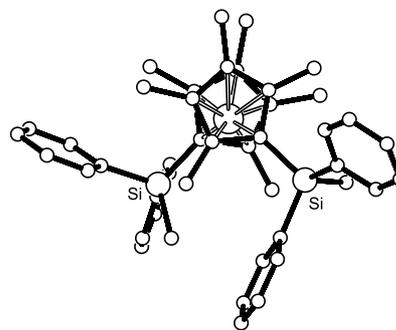


Fig. 5. A view of structure of **11** along the Cg(1)–Cg(2) direction.

### 3. Conclusions

In addition to so far known thermally stable titanocenes **1** and **2** another complexes of this type **9**, **10**, and **11** have been prepared. The common feature of all thermally stable titanocenes is the presence of a bulky silyl group on tetramethyl-substituted cyclopentadienyl ligands. At variance with the solid-state structures of **1** and **2** which show exactly parallel cyclopentadienyl rings titanocenes **9** and **11** are asymmetric and bent. The Cg–Ti–Cg angles of 166.0(2)° for **9** and 162.2(2)° for **11** are much larger than typical angles of bent fully substituted

titanocene derivatives, e.g.  $[\text{TiCl}_2(\eta^5\text{-C}_5\text{Me}_4\text{R})_2]$   $\text{R} = \text{Me}$ ,  $137.4(3)^\circ$  [19],  $\text{R} = \text{SiMe}_3$ ,  $137.6(5)^\circ$  [4],  $\text{R} = \text{Ph}$ ,  $137.6(2)^\circ$  [11];  $[\text{TiCl}(\eta^5\text{-C}_5\text{Me}_4\text{R})_2]$   $\text{R} = \text{Me}$ ,  $143.6(2)^\circ$  [20];  $\text{R} = \text{SiMe}_3$ ,  $144.4(1)^\circ$  [4],  $\text{R} = \text{Ph}$ ,  $143.4(1)^\circ$  [11];  $[\text{Ti}(\eta^5\text{-C}_5\text{Me}_4\text{R})_2(\eta^2\text{-btmse})]$   $\text{R} = \text{Me}$ ,  $138.6(3)^\circ$  [21],  $\text{R} = \text{SiMe}_3$ ,  $142.2(1)^\circ$  [7], and  $\text{R} = 4\text{-F-phenyl}$   $138.9(1)^\circ$  [22]. The angles between the least-squares planes of cyclopentadienyl rings  $\phi$  are correspondingly low:  $9.8(1)^\circ$  for **9** and  $14.4(2)^\circ$  for **11**. Similar angles were found in methylene-stabilized titanocene  $[\text{Ti}(\eta^5\text{-C}_5\text{Me}_5)(\eta^5\text{-}\eta^1\text{-C}_5\text{Me}_4\text{CH}_2)]$  [23] and dimethylene-stabilized titanocenes  $[\text{Ti}(\eta^5\text{-C}_5\text{Me}_4\text{R})\{\eta^4\text{:}\eta^3\text{-C}_5\text{Me}_2(\text{CH}_2)_2\text{R}\}]$  ( $\text{R} = \text{Ph}$ , benzyl) [22], and in  $[\text{Ti}\{\eta^5\text{-C}_5\text{Me}_3(\text{CH}_2\text{CH}(t\text{-Bu})\text{CH}=\text{CHCH}(t\text{-Bu})\text{CH}_2)\}\{\eta^4\text{:}\eta^3\text{-C}_5\text{Me}_3(\text{CH}_2)_2\}]$  [24] and  $[\text{Ti}\{\eta^5\text{-C}_5\text{Me}_2\text{Ph}(\text{CH}_2\text{CH}(t\text{-Bu})\text{CH}=\text{CHCH}(t\text{-Bu})\text{CH}_2)\}\{\eta^4\text{:}\eta^3\text{-C}_5\text{Me}_2\text{Ph}(\text{CH}_2)_2\}]$  [22], however, the angles are opened on the side of the methylene groups. These compounds are thermally stable to  $150\text{--}200^\circ\text{C}$  [22,24,25] which means that bending of their cyclopentadienyl ligands does not remarkably facilitate the activation of methyl groups on an inclined side. On the other hand, the hydrogen abstraction from ligand to titanium is a feasible process in permethyltitanocene [5], the hydrogen atom is accommodated in  $[\text{TiH}(\eta^5\text{-C}_5\text{Me}_5)_2]$  and  $[\text{TiH}(\eta^5\text{-C}_5\text{Me}_4\text{Ph})_2]$  at large Cg–Ti–Cg angles of  $152.0$  and  $152.3^\circ$  (two molecules in unit cell) [26a] and  $150.8(1)^\circ$  [26b], respectively, and structures of bent titanocenes show that such a hydride intermediate could be formed upon intramolecular hydrogen abstraction by titanium in **9–11**. However, bent titanocenes **9**, **10**, and **11** melt at temperature of  $75$ ,  $85$ , and  $105^\circ\text{C}$ , respectively, without observable decomposition unlike permethyltitanocene where the hydrogen abstraction process occurs even at ambient temperature [5]. The stabilizing effect of silyl groups is difficult to account for only by electronic effects as there is apparently no direct through space Ti–Si interaction at the distance of about  $3.70\text{ \AA}$ , and there is no remarkable difference in the ‘silicon effect’ resulting from replacement of silicon alkyl substituents by phenyl groups. A steric congestion between  $\text{SiMe}_2$  methyl groups of one cyclopentadienyl ligand and methyl groups attached to the other cyclopentadienyl ligand at the opposite position, which was suggested to stabilize the molecule **1** with parallel cyclopentadienyl rings does not apply to **9** where the torsion angle Si(1)–Cg(1)–Cg(2)–Si(2) amounts to  $98.3(2)^\circ$ , the silicon atoms are at a longer distance from titanium and yet the compound is thermally stable. Thus, the only specific effect of the silyl groups lies in the planar deformation of the cyclopentadienyl ring forming a more acute ring angle at the carbon atom bearing the silicon atom (ca.  $106^\circ$ ) and correspondingly, all other angles of the ring are more obtuse (av.  $108^\circ$ ). It is difficult, however, to estimate the relevance of this structural change for the ease of C–H bond activation in all the above titanocenes. The steric congestion at the

titanium atom due to rotating cyclopentadienyl ligands is apparently the reason for a low stability of the titanocene–btmse complexes, decreasing in the order of titanocenes  $2 \gg 9 \approx 10 > 11$ . On the other hand, the titanium atom is accessible for chlorine atom as all these titanocenes are oxidized by  $\text{PbCl}_2$  in THF to the corresponding dichlorides. Investigations on thermal activation of C–H bonds and on oxidative addition reactions of the silyl-containing titanocenes are in progress.

## 4. Experimental

### 4.1. Methods

Syntheses of cyclopentadienyl ligands and titanocene dichlorides **3–5** thereof were carried out under argon. All manipulations with Ti(III) compounds **6–8** and Ti(II) compounds **9–11** were performed under vacuum on an all-glass high vacuum line using sealed glass devices equipped with breakable seals.  $^1\text{H}$ - ( $399.95\text{ MHz}$ ) and  $^{13}\text{C}$ - ( $100.58\text{ MHz}$ ) NMR spectra were recorded on a Varian UNITY Inova 400 spectrometer in  $\text{C}_6\text{D}_6$  solutions at  $25^\circ\text{C}$ . The spectra of **9–11** were further investigated over the temperature range  $0\text{--}60^\circ\text{C}$ . Chemical shifts ( $\delta/\text{ppm}$ ) are given relative to the solvent signal ( $\delta_{\text{H}} 7.15$ ,  $\delta_{\text{C}} 128.0$ ). EI-MS spectra were obtained on a VG-7070E mass spectrometer at  $70\text{ eV}$ . Crystalline samples in sealed capillaries were opened and inserted into the direct inlet under argon. EPR spectra were recorded on an ERS-220 spectrometer (Center for Production of Scientific Instruments, Academy of Sciences of GDR, Berlin, Germany) operated by a CU-1 unit (Magnetech, Berlin, Germany) in the X-band.  $g$ -Values were determined by using an  $\text{Mn}^{2+}$  standard at  $g = 1.9860$  ( $M_1 = -1/2$  line). A variable temperature unit STT-3 was used for measurements in the range  $-140\text{--}+25^\circ\text{C}$ . Concentrations of paramagnetic species in samples of **9–11** were estimated by comparison of integrated peak areas with that of a  $[(\eta^5\text{-C}_5\text{H}_5)_2\text{Ti}(\mu\text{-Cl})_2\text{Al}(\text{C}_2\text{H}_5)\text{Cl}]$  standard solution ( $c = 5.275\text{ mM}$  in  $\text{C}_6\text{H}_6$ ). UV–near IR spectra in the range of  $280\text{--}2000\text{ nm}$  were measured on a Varian Cary 17D spectrometer in all-sealed quartz cells (Hellma). IR spectra were measured in an air-protecting cuvette on a Nicolet Avatar FTIR spectrometer in the range  $400\text{--}4000\text{ cm}^{-1}$ . With the exception of air-stable titanocene dichlorides **3–5** all studied titanium compounds are extremely air- and moisture-sensitive and therefore their solid samples were handled in a glovebox Labmaster 130 (mBraun) under purified nitrogen. Crystalline samples for EI-MS measurements and determination of m.p.s were placed in glass capillaries and sealed out. KBr pellets were prepared and placed into an air-protecting cuvette in the glovebox.

#### 4.2. Chemicals

The solvents THF, C<sub>6</sub>H<sub>14</sub>, and C<sub>6</sub>H<sub>5</sub>CH<sub>3</sub> were dried by refluxing over LiAlH<sub>4</sub> and stored as solutions of dimeric titanocene [(μ-η<sup>5</sup>:η<sup>5</sup>-C<sub>5</sub>H<sub>4</sub>C<sub>5</sub>H<sub>4</sub>){Ti(μ-H)(η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>)}<sub>2</sub>] [27]. TiCl<sub>4</sub> (International Enzymes) was purified by refluxing over copper wire and distilled in vacuum. Butyllithium (2.5 M in C<sub>6</sub>H<sub>14</sub>, Aldrich), 1,2,3,4-tetramethylcyclopentadiene (mixture of isomers) and chlorodimethylphenethylsilane, chlorodimethylphenylsilane, and chloromethyldiphenylsilane (all Aldrich) were transferred via syringe under Ar. Magnesium turnings (Aldrich, purum for Grignard reactions) were firstly used in large excess for the preparation of [Ti(η<sup>5</sup>-C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>(η<sup>2</sup>-btmse)] [3]. Unreacted activated magnesium was separated from the reaction mixture, washed thoroughly with THF and stored in ampoules equipped with breakable seals. Bis(trimethylsilyl)ethyne (btmse, Fluka) was degassed, stored as a solution of dimeric titanocene for 4 h, and finally distributed into ampoules by distillation on a vacuum line.

#### 4.3. Synthesis of 1,2,3,4-tetramethyl-5-(dimethylphenethylsilyl)cyclopenta-1,3-diene and titanocene dichloride (3)

1,2,3,4-Tetramethyl-5-(dimethylphenethylsilyl)cyclopenta-1,3-diene was obtained from 1,2,3,4-tetramethylcyclopentadiene (13.8 g, 0.113 mol) by the reaction of its lithium salt (generated from stoichiometric amounts of 1,2,3,4-tetramethylcyclopentadiene and 2.5 M LiBu) with the equimolar amount of chlorodimethylphenethylsilane (22.5 g, 0.113 mol) in THF. The reaction mixture was stirred overnight (voluminous Li<sup>+</sup>(C<sub>5</sub>HMe<sub>4</sub>)<sup>-</sup> salt largely disappeared) and the solution was reduced to volume of ca. 30 ml by distilling off THF. After evaporation of volatiles in vacuum the product was distilled from oil bath (150 °C) under vacuum of a rotary pump. Yield of yellow liquid 28.0 g (87%).

<sup>1</sup>H-NMR (C<sub>6</sub>D<sub>6</sub>): δ -0.02 (s, 6H, SiMe<sub>2</sub>), 0.79–0.84 (m 2H, CH<sub>2</sub>Si), 1.81 (d, *J* ≈ 1.3 Hz, 6H, Me<sub>4</sub>C<sub>5</sub>), 1.91 (s, 6H, Me<sub>4</sub>C<sub>5</sub>), 2.50–2.55 (m, 2H, CH<sub>2</sub>Ph), 7.05–7.21 (m, 5H, Ph). <sup>13</sup>C{<sup>1</sup>H}-NMR (C<sub>6</sub>D<sub>6</sub>): δ -3.1 (SiMe<sub>2</sub>), 11.3, 14.7 (Me<sub>4</sub>C<sub>5</sub>); 17.1 (CH<sub>2</sub>Si), 30.6 (CH<sub>2</sub>Ph), 54.4 (C<sub>5</sub>Me<sub>4</sub>H, CH), 125.9, 128.1, 128.6 (Ph, CH); 133.0, 135.7 (Me<sub>4</sub>C<sub>5</sub>, C<sub>ipso</sub>); 145.4 (Ph, C<sub>ipso</sub>). IR (neat, cm<sup>-1</sup>): 3084 (w), 3062 (w), 3026 (m), 2959 (s), 2915 (vs), 2858 (s), 1631 (w), 1603 (w), 1495 (m), 1453 (s), 1410 (w), 1379 (w), 1249 (vs), 1219 (w), 1176 (m), 1123 (w), 1110 (w), 1046 (w), 1021 (w), 984 (m), 952 (w), 899 (w), 837 (vs), 772 (s), 754 (m), 725 (w), 698 (vs), 632 (w), 560 (w), 487 (m), 418 (m).

Titanocene dichloride [TiCl<sub>2</sub>{(η<sup>5</sup>-C<sub>5</sub>Me<sub>4</sub>(SiMe<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>Ph)}<sub>2</sub>] (3) was prepared by reacting [TiCl<sub>3</sub>(THF)<sub>3</sub>] [generated in situ by adding LiBu in hexanes (22.5 ml of 1.6 M, 36.0 mmol) to TiCl<sub>4</sub> (4.0 ml,

36.0 mmol) in THF (50 ml) followed by a short reflux] with lithium cyclopentadienide obtained by reacting LiBu (30 ml of 2.5 M in hexanes, 75.0 mmol) with the above cyclopentadiene (20.7 g, 73.0 mmol) in THF (500 ml) for 24 h at room temperature under stirring. After refluxing this mixture for 30 h and subsequent stirring with AgCl (5.16 g, 36.0 mmol) at 40 °C for 5 h, the product was worked up as described for [TiCl<sub>2</sub>{η<sup>5</sup>-C<sub>5</sub>Me<sub>4</sub>(SiMe<sub>3</sub>)<sub>2</sub>}<sub>2</sub>] [13]. Yield of brown crystals of 3 was 9.8 g (42%).

<sup>1</sup>H-NMR (C<sub>6</sub>D<sub>6</sub>): δ 0.57 (s, 6H, SiMe<sub>2</sub>), 1.16–1.25 (m 2H, CH<sub>2</sub>Si), 1.63, 2.11 (2 × s<sub>1</sub> 6H, Me<sub>4</sub>C<sub>5</sub>); 2.56–2.63 (m, 2H, CH<sub>2</sub>Ph), 7.00–7.15 (m, 5H, Ph). <sup>13</sup>C{<sup>1</sup>H}-NMR (C<sub>6</sub>D<sub>6</sub>): δ 0.5 (SiMe<sub>2</sub>), 12.1, 16.9 (Me<sub>4</sub>C<sub>5</sub>); 19.9 (CH<sub>2</sub>Si), 30.8 (CH<sub>2</sub>Ph), 125.7 (Ph, CH), 127.5 (Me<sub>4</sub>C<sub>5</sub>, C<sub>ipso</sub>), 128.4 (Ph, CH), 135.5, 137.8 (Me<sub>4</sub>C<sub>5</sub>, C<sub>ipso</sub>); 145.4 (Ph, C<sub>ipso</sub>) (one CH resonance of Ph group not found). EI-MS (150 °C): *m/z* (relative abundance,%) [684 [M]<sup>+</sup> not observed], 651 (8), 650 (9), 649 ([M-Cl]<sup>+</sup>; 15), 335 (10), 334 (7), 333 (26), 332 (8), 331 (25), 284 ([Cp<sup>+</sup>+H]<sup>+</sup>; 9), 180 (8), 179 (19), 178 ([C<sub>5</sub>Me<sub>4</sub>SiMe<sub>2</sub>]<sup>+</sup>; 50), 177 (13), 164 (15), 163 ([PhCH<sub>2</sub>CH<sub>2</sub>SiMe<sub>2</sub>]<sup>+</sup>; 88), 147 (14), 136 (10), 135 ([C<sub>5</sub>Me<sub>5</sub>]<sup>+</sup>, 71), 121 (6), 119 (13), 105 (12), 91 (13), 73 (12), 60 (7), 59 ([SiMe<sub>2</sub>H]<sup>+</sup>; 100), 43 (10). IR (KBr, cm<sup>-1</sup>): 3083 (w), 3035 (w), 3027 (m), 2984 (w), 2958 (s), 2895 (vs), 1602 (m), 1494 (s), 1473 (w), 1450 (s), 1412 (m), 1375 (s), 1356 (m), 1342 (m), 1253 (s), 1243 (vs), 1166 (w), 1123 (m), 1024 (s), 948 (w), 927 (w), 910 (w), 892 (s), 878 (m), 834 (vs, b), 808 (s), 773 (s), 752 (m), 725 (m), 696 (s), 670 (w), 647 (w), 575 (vw), 558 (vw), 489 (w), 417 (s). Anal. Calc. for C<sub>38</sub>H<sub>54</sub>Cl<sub>2</sub>Si<sub>2</sub>Ti (*M* 685.81): C, 66.55; H, 7.94. Found: C, 66.48; H, 7.90%.

#### 4.4. Synthesis of 1,2,3,4-tetramethyl-5-(dimethylphenylsilyl)cyclopenta-1,3-diene and titanocene dichloride (4)

1,2,3,4-Tetramethyl-5-(dimethylphenylsilyl)cyclopenta-1,3-diene was obtained from 1,2,3,4-tetramethylcyclopentadiene (13.7 g, 0.113 mol) by the reaction of its lithium salt (generated from stoichiometric amounts of 1,2,3,4-tetramethylcyclopentadiene and 2.5 M LiBu) with the equimolar amount of chlorodimethylphenylsilane (19.3 g, 0.113 mol) in THF as described above. After evaporation of all volatiles in vacuum the product was distilled from oil bath at 140 °C under vacuum of a rotary pump. Yield of yellow liquid 24.2 g (84%).

<sup>1</sup>H-NMR (C<sub>6</sub>D<sub>6</sub>): δ 0.16 (s, 6H, SiMe<sub>2</sub>), 1.75 (s, 12H, C<sub>5</sub>Me<sub>4</sub>); 2.99 (s, 1H, C<sub>5</sub>Me<sub>4</sub>H), 7.15–7.43 (m, 5H, Ph). <sup>13</sup>C{<sup>1</sup>H}-NMR (C<sub>6</sub>D<sub>6</sub>): δ -3.8 (SiMe<sub>2</sub>), 11.3, 14.6 (C<sub>5</sub>Me<sub>4</sub>); 54.7 (C<sub>5</sub>Me<sub>4</sub>H, CH), 127.8, 129.1 (Ph, CH); 132.8 (Ph or C<sub>5</sub>Me<sub>4</sub>, C<sub>ipso</sub>), 134.0 (Ph, CH); 135.9, 139.2 (Ph or C<sub>5</sub>Me<sub>4</sub>, C<sub>ipso</sub>). IR (neat, cm<sup>-1</sup>): 3069 (m), 3050 (w), 2963 (s), 2912 (vs), 2857 (s), 1950 (vw), 1879 (vw), 1814 (vw), 1775 (vw), 1633 (w), 1590 (vw), 1487 (w),

1442 (m), 1427 (s), 1379 (w), 1335 (vw), 1302 (w), 1248 (s), 1218 (m), 1190 (vw), 1113 (vs), 1047 (w), 1023 (w), 983 (m), 952 (w), 919 (vw), 832 (s), 817 (vs), 795 (w), 776 (m), 731 (s), 700 (s), 642 (m), 559 (vw), 494 (m), 469 (w).

Titanocene dichloride [ $\text{TiCl}_2\{(\eta^5\text{-C}_5\text{Me}_4(\text{SiMe}_2\text{Ph})_2)\}_2$ ] (**4**) was prepared from  $\text{TiCl}_4$  (4.0 ml, 36 mmol) and  $\text{C}_5\text{HMe}_4(\text{SiMe}_2\text{Ph})$  (18.6 g, 73 mmol) by the above described procedure. Yield of brown, finely crystalline **4** 4.6 g (20%).

$^1\text{H-NMR}$  ( $\text{C}_6\text{D}_6$ ):  $\delta$  0.87 (s, 6H,  $\text{SiMe}_2$ ), 1.58, 2.10 ( $2 \times$  s, 6H,  $\text{C}_5\text{Me}_4$ ); 7.09–7.45 (m, 5H, Ph).  $^{13}\text{C}\{^1\text{H}\}$ -NMR ( $\text{C}_6\text{D}_6$ ):  $\delta$  1.5 ( $\text{SiMe}_2$ ), 12.1, 16.9 ( $\text{C}_5\text{Me}_4\text{H}$ ); 128.0, 128.7 (CH, Ph); 134.0 (Ph/ $\text{C}_5\text{Me}_4$ ,  $\text{C}_{\text{ipso}}$ ), 134.3 (Ph, CH), 138.2, 141.7 (Ph/ $\text{C}_5\text{Me}_4$ ,  $\text{C}_{\text{ipso}}$ ). EI-MS (160 °C):  $m/z$  (relative abundance, %) [628  $[\text{M}]^+$  not observed], 593 ( $[\text{M}-\text{Cl}]^+$ ; 4), 558 ( $[\text{M}-2\text{Cl}]^+$ ; 2), 557 (2), 373 ( $[\text{M}-\text{Cp}]^+$ ; 4), 338 ( $[\text{Cp}^+\text{TiCl}]^+$ ; 7), 303 ( $[\text{Cp}^+\text{Ti}]^+$ ; 3), 256 (9), 255 ( $[\text{Cp}]^+$ ; 6), 254 (9), 239 ( $[\text{Cp}^+-\text{Me}]^+$ ; 6), 176 (7), 137 (7), 136 (15), 135 ( $[\text{SiMe}_2\text{Ph}]^+$ ; 100), 121 (14), 120 (8), 107 (7), 105 (10), 91 (9), 73 (7), 59 (16), 57 (8), 55 (7), 44 (7), 43 (9), 43 (18), 41 (12). IR (KBr,  $\text{cm}^{-1}$ ): 3067 (m), 3047 (w), 3000 (m), 2959 (m), 2901 (s), 1588 (vw), 1479 (m), 1443 (w), 1427 (m), 1407 (w), 1374 (m), 1352 (vw), 1337 (w), 1246 (s), 1124 (w), 1108 (s), 1022 (m,b), 825 (sh), 814 (vs), 774 (s), 736 (s), 702 (s), 656 (w), 475 (m), 433 (s), 406 (w). Anal. Calc. for  $\text{C}_{34}\text{H}_{46}\text{Cl}_2\text{Si}_2\text{Ti}$  (M 629.70): C, 64.85; H, 7.36. Found: C, 64.79; H, 7.32%.

#### 4.5. Synthesis of 1,2,3,4-tetramethyl-5-(diphenylmethylsilyl)cyclopenta-1,3-diene and titanocene dichloride (**5**)

The cyclopentadiene was obtained by the above described procedure from 0.113 mol (26.3 g) of  $\text{ClSiMePh}_2$ . The product distilled from oil bath at 170 °C under vacuum of a rotary pump. Yield of viscous yellow liquid 27.6 g (77%).  $^1\text{H-NMR}$  ( $\text{C}_6\text{D}_6$ ):  $\delta$  0.35 (s, 3H,  $\text{SiMe}$ ), 1.65, 1.74 ( $2 \times$  s, 6H,  $\text{C}_5\text{Me}_4$ ); 3.39 (s, 1H,  $\text{C}_5\text{Me}_4\text{H}$ ), 7.08–7.69 (m, 10H, Ph).  $^{13}\text{C}\{^1\text{H}\}$ -NMR ( $\text{C}_6\text{D}_6$ ):  $\delta$  -6.6 ( $\text{SiMe}$ ), 11.3, 14.8 ( $\text{C}_5\text{Me}_4$ ); 53.0 ( $\text{C}_5\text{Me}_4\text{H}$ , CH), 128.1, 128.3, 129.6, 130.1 (Ph, CH); 133.2 (Ph or  $\text{C}_5\text{Me}_4$ ,  $\text{C}_{\text{ipso}}$ ), 134.6, 135.2 (Ph, CH); 136.8, 137.4 (Ph or  $\text{C}_5\text{Me}_4$ ,  $\text{C}_{\text{ipso}}$ ). IR (neat,  $\text{cm}^{-1}$ ): 3069 (m), 3049 (w), 3026 (vw), 3010 (w), 2997 (vw), 2959 (m), 2930 (m), 2911 (s), 2868 (w), 2855 (m), 1957 (vw), 1884 (vw), 1820 (vw), 1763 (vw), 1633 (m), 1589 (w), 1567 (vw), 1486 (w), 1442 (m), 1427 (vs), 1382 (w), 1329 (vw), 1302 (vw), 1254 (s), 1215 (m), 1192 (vw), 1169 (w), 1157 (vw), 1109 (vs), 1069 (vw), 1047 (w), 1021 (w), 998 (vw), 981 (m), 953 (w), 918 (vw), 785 (vs), 767 (m), 735 (s), 719 (m), 699 (vs), 675 (vw), 659 (vw), 562 (w), 511 (vs), 476 (m), 463 (s), 438 (w), 423 (m).

Titanocene dichloride [ $\text{TiCl}_2\{(\eta^5\text{-C}_5\text{Me}_4(\text{SiMePh})_2)\}_2$ ] (**5**) was prepared from  $\text{TiCl}_4$  (4.0 ml, 36 mmol) and  $\text{C}_5\text{HMe}_4(\text{SiMePh}_2)$  (23.2 g, 73 mmol) according to the

above protocol. Yield of brown, finely crystalline **5** 4.4 g (16%).

$^1\text{H-NMR}$  ( $\text{C}_6\text{D}_6$ ):  $\delta$  1.29 (s, 3H,  $\text{SiMe}$ ), 1.56, 1.95 ( $2 \times$  s, 6H,  $\text{C}_5\text{Me}_4$ ); 7.12–7.17 (m, 6H, Ph), 7.59–7.64 (m, 4H, Ph).  $^{13}\text{C}\{^1\text{H}\}$ -NMR ( $\text{C}_6\text{D}_6$ ):  $\delta$  0.1 ( $\text{SiMe}$ ), 12.1, 17.2 ( $\text{C}_5\text{Me}_4$ ); 127.9 (Ph, CH), 129.0 (Ph/ $\text{C}_5\text{Me}_4$ ,  $\text{C}_{\text{ipso}}$ ), 129.1 (Ph, CH), 132.4 (Ph/ $\text{C}_5\text{Me}_4$ ,  $\text{C}_{\text{ipso}}$ ), 136.4 (Ph, CH), 138.6, 138.8 (Ph/ $\text{C}_5\text{Me}_4$ ,  $\text{C}_{\text{ipso}}$ ). EI-MS (190 °C):  $m/z$  (relative abundance, %) [752  $[\text{M}]^+$  not observed], 719 (6), 718 (6), 717 ( $[\text{M}-\text{Cl}]^+$ ; 9), 400 ( $[\text{M}-\text{Cp}'-\text{Cl}]^+$ ; 10), 395 (10), 393 (10), 318 (12), 317 ( $[\text{Cp}]^+$ ; 11), 316 (7), 198 (20), 197 ( $[\text{SiMePh}_2]^+$ ; 100), 121 (10), 105 (10). IR (KBr,  $\text{cm}^{-1}$ ): 3067 (m), 3051 (m), 2997 (w), 2956 (w), 2901 (m), 1588 (w), 1567 (w), 1483 (m), 1428 (s), 1376 (m), 1335 (m), 1250 (m), 1190 (w), 1125 (w), 1105 (s), 1026 (m), 826 (w), 791 (vs), 738 (s), 715 (s), 702 (s), 669 (w), 486 (s), 481 (s), 452 (m), 438 (m). Anal. Calc. for  $\text{C}_{44}\text{H}_{50}\text{Cl}_2\text{Si}_2\text{Ti}$  (M 753.84): C, 70.11; H, 6.69. Found: C, 69.06; H, 6.65%.

#### 4.6. Preparation of [ $\text{TiCl}\{\eta^5\text{-C}_5\text{Me}_4(\text{SiMe}_2\text{CH}_2\text{CH}_2\text{Ph})\}_2$ ] (**6**)

The solution of **3** (1.37 g, 2.0 mmol) in THF (30 ml) was added to activated Mg (25 mg, 1.03 mmol) and the mixture was stirred at 60 °C until the color turned blue and all magnesium disappeared. All volatiles were distilled off in vacuum and the residue was extracted with  $\text{C}_6\text{H}_{14}$  (20 ml). The extract was concentrated to ca. 10 ml and cooled at -18 °C overnight to afford pale blue aggregates of fibrous crystals. Yield of [ $\text{TiCl}\{\eta^5\text{-C}_5\text{Me}_4(\text{SiMe}_2\text{CH}_2\text{CH}_2\text{Ph})\}_2$ ] (**6**) was 1.13 g (87%).

EPR ( $\text{C}_6\text{H}_{14}$ , 23 °C):  $g = 1.959, \Delta H = 15$  G. EPR ( $\text{C}_6\text{H}_5\text{CH}_3$ , -140 °C):  $g_1 = 1.9995, g_2 = 1.9822, g_3 = 1.8916, g_{\text{av}} = 1.958$ ; (THF, 22 °C):  $g = 1.958, \Delta H = 14$  G. EI-MS (170 °C):  $m/z$  (relative abundance, %) 653 (10), 652 (20), 651 (51), 650 (44), 649 ( $[\text{M}]^+$ ; 86), 648 (11), 647 (9), 633 ( $[\text{M}-\text{Me}]^+$ ; 6), 614 ( $[\text{M}-\text{Cl}]^+$ ; 3), 544 ( $[\text{M}-\text{Ph}(\text{CH}_2)_2]^+$ ; 5), 451 (7), 368 (6), 367 (8), 366 ( $[\text{M}-\text{Cp}]^+$ ; 14), 365 (7), 264 (7), 263 (12), 262 (23), 261 ( $[\text{M}-\text{Cp}'-\text{CH}_2\text{CH}_2\text{Ph}]^+$ ; 20), 260 (11), 259 (12), 257 (10), 178 ( $[\text{C}_5\text{Me}_4\text{SiMe}_2]^+$ ; 10), 164 (17), 163 ( $[\text{Ph}(\text{CH}_2)_2\text{SiMe}_2]^+$ ; 100), 135 ( $[\text{C}_5\text{Me}_5]^+$ ; 78), 73 (11), 59 (87). IR (KBr,  $\text{cm}^{-1}$ ): 3100 (vw), 3082 (w), 3061 (w), 3022 (m), 2999 (m), 2953 (s), 2910 (vs), 1602 (m), 1494 (s), 1480 (m), 1453 (s), 1413 (m), 1379 (s), 1349 (w), 1332 (vs), 1253 (vs), 1178 (m), 1126 (m), 1026 (s), 1003 (w), 909 (w), 899 (m), 835 (vs), 809 (vs), 768 (s), 751 (m), 719 (m), 697 (s), 643 (w), 561 (w), 492 (w), 423 (s). UV-vis ( $\text{C}_6\text{H}_5\text{CH}_3$ , 22 °C, nm): 555 > 670 (sh) nm.

#### 4.7. Preparation of [ $\text{TiCl}\{\eta^5\text{-C}_5\text{Me}_4(\text{SiMe}_2\text{Ph})\}_2$ ] (**7**)

Compound **4** (0.5 g, 0.8 mmol) and magnesium turnings (10.0 mg, 0.42 mmol) were placed into an ampoule, evacuated on a vacuum line, and THF (20 ml)

was distilled in. The solution of **4** was then heated to 60 °C until all the magnesium disappeared (5 days). The solvent was distilled off, the residue was washed with 10 ml of C<sub>6</sub>H<sub>14</sub> and dissolved in 30 ml of C<sub>6</sub>H<sub>5</sub>CH<sub>3</sub>. The solvent was then slowly distilled from one ampoule into another leaving blue crystalline material over white layer of MgCl<sub>2</sub>. This residue was then extracted by condensing vapour of C<sub>6</sub>H<sub>5</sub>CH<sub>3</sub> to leave majority of MgCl<sub>2</sub> on an ampoule wall. The saturated toluene solution afforded turquoise crystals of **7** for EI-MS, IR, and m.p. measurements and for X-ray single crystal analysis. The reduction of **4**–**7** proceeded apparently quantitatively but only the first partial crop of crystals (0.080 g) was isolated and used for characterization.

EPR (C<sub>6</sub>H<sub>5</sub>CH<sub>3</sub>, 22 °C):  $g = 1.950$ ,  $\Delta H = 17$  G; (C<sub>6</sub>H<sub>5</sub>CH<sub>3</sub>, -140 °C):  $g_1 = 1.999$ ,  $g_2 = 1.981$ ,  $g_3 = 1.856$ ,  $g_{av} = 1.945$ ; (THF, 22 °C):  $g = 1.949$ ,  $\Delta H = 17$  G. EI-MS (180 °C):  $m/z$  (relative abundance, %) 597 (8), 596 (19), 595 (43), 594 (42), 593 ([M]<sup>+</sup>; 76), 592 (11), 591 (8), 578 ([M-Me]<sup>+</sup>; 6), 577 (9), 341 (10), 340 (33), 339 (39), 338 ([M-Cp]<sup>+</sup>; 76), 337 (48), 336 (12), 322 (8), 136 (14), 135 ([SiMe<sub>2</sub>Ph]<sup>+</sup>; 100), 121 (9), 59 (10), 43 (10). IR (KBr, cm<sup>-1</sup>): 3063 (m), 3048 (w), 2995 (m), 2957 (s), 2904 (s), 1959 (vw), 1944 (vw), 1888 (vw), 1873 (vw), 1809 (vw), 1759 (vw), 1588 (vw), 1566 (vw), 1484 (w), 1450 (w), 1427 (m), 1410 (w), 1379 (m), 1334 (m), 1243 (s), 1187 (vw), 1157 (vw), 1126 (w), 1106 (s), 1065 (vw), 1023 (m), 998 (vw), 835 (s), 821 (s), 808 (vs), 774 (m), 753 (w), 727 (s), 699 (s), 655 (m), 572 (vw), 542 (vw), 471 (m), 447 (s), 424 (s). UV-vis (C<sub>6</sub>H<sub>5</sub>CH<sub>3</sub>, 22 °C, nm): 568 > 670 (sh).

#### 4.8. Preparation of [TiCl{( $\eta^5$ -C<sub>5</sub>Me<sub>4</sub>(SiMePh<sub>2</sub>))<sub>2</sub>}] (**8**)

Compound **5** (0.5 g, 0.66 mmol) and magnesium turnings (8.0 mg, 0.33 mmol) were reacted in THF as described for **7**. Dark green crystalline product was obtained by crystallization from hot C<sub>6</sub>H<sub>5</sub>CH<sub>3</sub> solution. Only the first crop of crystals was used for characterization as further crops should contain more MgCl<sub>2</sub> which is also soluble in C<sub>6</sub>H<sub>5</sub>CH<sub>3</sub> (although much less than **8**). Yield of crystalline **8** 0.13 g (18%).

EPR (C<sub>6</sub>H<sub>5</sub>CH<sub>3</sub>, 22 °C):  $g = 1.948$ ,  $\Delta H = 20.0$  G; (C<sub>6</sub>H<sub>5</sub>CH<sub>3</sub>, -140 °C):  $g_1 = 1.998$ ,  $g_2 = 1.980$ ,  $g_3 = 1.850$ ,  $g_{av} = 1.943$ ; (THF, 22 °C):  $g = 1.947$ ,  $\Delta H = 21$  G. EI-MS (250 °C):  $m/z$  (relative abundance, %) 721 (9), 720 (21), 719 (41), 718 (44), 717 ([M]<sup>+</sup>; 66), 716 (11), 715 (8), 485 (9), 403 (11), 402 (34), 401 (36), 400 ([M-Cp]<sup>+</sup>; 75), 399 (29), 398 (10), 198 (20), 197 ([SiMePh<sub>2</sub>]<sup>+</sup>; 100), 121 (13), 105 (14), 91 (10). UV-vis (C<sub>6</sub>H<sub>5</sub>CH<sub>3</sub>, 22 °C, nm): 575 > 680 (sh).

#### 4.9. Preparation of titanocene **9**

Complex **3** (1.37 g, 2.0 mmol) in THF (30 ml) was added to activated magnesium (50 mg, 2.06 mmol) and

the mixture was stirred at 60 °C until the color turned turquoise and all magnesium disappeared (after 1–3 days). Then, all volatiles were distilled off under vacuum and the residue was extracted with C<sub>6</sub>H<sub>14</sub>. Partial solvent removal and cooling to -18 °C overnight gave **9** as grey prisms. Yield: 1.02 g (83%).

M.p. 75 °C. EI-MS (160 °C):  $m/z$  (relative abundance, %) 616 (9), 615 (31), 614 ([M]<sup>+</sup>; 50), 613 ([M-H]<sup>+</sup>; 100), 612 (14), 611 (13), 509 ([M-Ph(CH<sub>2</sub>)<sub>2</sub>]<sup>+</sup>; 8), 445 (5), 331 ([M-Cp]<sup>+</sup>; 10), 163 ([PhCH<sub>2</sub>CH<sub>2</sub>SiMe<sub>2</sub>]<sup>+</sup>; 5), 135 ([C<sub>5</sub>Me<sub>5</sub>]<sup>+</sup>; 9), 59 (21). IR (KBr, cm<sup>-1</sup>): 3082 (w), 3059 (w), 3025 (m), 2951 (s), 2907 (vs), 1602 (m), 1494 (s), 1452 (s), 1379 (m), 1332 (m), 1315 (s), 1246 (vs), 1166 (m), 1130 (m), 1021 (s), 894 (s), 832 (vs), 801 (s), 764 (s), 751 (m), 697 (s), 445 (m). UV-vis (C<sub>6</sub>H<sub>14</sub>, 22 °C, nm): 590.

#### 4.10. Preparation of [Ti{( $\eta^5$ -C<sub>5</sub>Me<sub>4</sub>(SiMe<sub>2</sub>Ph))<sub>2</sub>}] (**10**)

Complex **10** was obtained from 1.25 g (2.0 mmol) of **4** and 2.0 mmol of activated magnesium as described for **9**. A concentrated C<sub>6</sub>H<sub>14</sub> extract afforded a crystalline yellowish green product by cooling to -18 °C. A yellow mother liquor was separated and discarded, and the product was recrystallized from C<sub>6</sub>H<sub>14</sub>. Yield of grey crystalline material was 0.56 g (50%).

M.p. 85 °C. EI-MS (160 °C):  $m/z$  (relative abundance, %) 560 (9), 559 (28), 558 ([M]<sup>+</sup>; 57), 557 ([M-H]<sup>+</sup>; 100), 556 (41), 555 (15), 304 (13), 303 ([M-Cp]<sup>+</sup>; 40), 302 (19), 301 (11), 136 (10), 135 ([SiMe<sub>2</sub>Ph]<sup>+</sup>; 67), 73 (29), 59 (10). IR (KBr, cm<sup>-1</sup>): 3065 (m), 3051 (m), 2952 (s), 2912 (vs), 2860 (m), 1971 (w), 1896 (vw), 1880 (vw), 1819 (vw), 1765 (vw), 1588 (vw), 1567 (vw), 1485 (w), 1450 (w), 1427 (s), 1410 (w), 1379 (m), 1328 (m), 1314 (m), 1246 (s), 1188 (vw), 1129 (m), 1107 (s), 1065 (vw), 1022 (m), 998 (vw), 830 (sh), 822 (sh), 811 (vs), 769 (m), 727 (s), 701 (s), 656 (m), 580 (w), 514 (w), 469 (m), 436 (s). UV-vis (C<sub>6</sub>H<sub>5</sub>CH<sub>3</sub>, 22 °C, nm): 580.

#### 4.11. Preparation of [Ti{( $\eta^5$ -C<sub>5</sub>Me<sub>4</sub>(SiMePh<sub>2</sub>))<sub>2</sub>}] (**11**)

Complex **11** was obtained from **5** (1.50 g, 2.0 mmol) and activated magnesium as for **9** and **10**. The residue after evaporation of THF in high vacuum was repeatedly extracted by C<sub>6</sub>H<sub>14</sub> in order to separate the low-soluble product from MgCl<sub>2</sub>. The concentrated C<sub>6</sub>H<sub>14</sub> solution was poured away from a residue, and this was dissolved in toluene to give a yellow-green solution. Greenish brown prism crystals were obtained by cooling the concentrated solution to -18 °C. Yield: 1.0 g (73%).

M.p. 105 °C. EI-MS (190 °C):  $m/z$  (relative abundance, %) 683 (8), 682 ([M]<sup>+</sup>; 16), 681 ([M-H]<sup>+</sup>; 26), 680 ([M-2H]<sup>+</sup>; 31), 679 (6), 365 ([M-Cp]<sup>+</sup>; 7), 364 (6), 318 ([Cp'H]<sup>+</sup>; 9), 199 (9), 198 (20), 197 ([SiMePh<sub>2</sub>]<sup>+</sup>; 100), 121 (6), 105 (9). IR (KBr, cm<sup>-1</sup>):

Table 4  
Crystal and structure refinement data for **7**, **9** and **11**

Compound	<b>7</b>	<b>9</b>	<b>11</b>
Chemical formula	C <sub>34</sub> H <sub>46</sub> ClSi <sub>2</sub> Ti	C <sub>38</sub> H <sub>54</sub> Si <sub>2</sub> Ti	C <sub>44</sub> H <sub>50</sub> Si <sub>2</sub> Ti
M <sub>w</sub> (g mol <sup>-1</sup> )	594.24	614.88	682.92
T (K)	150(2)	293(2)	150(2)
Crystal system	Monoclinic	Triclinic	Triclinic
Space group	C2/c (No. 15)	P1̄ (No. 2)	P1̄ (No. 2)
a (Å)	19.5550(7)	10.010(1)	10.0770(3)
b (Å)	11.9460(4)	13.583(2)	11.6870(4)
c (Å)	14.5450(5)	14.550(2)	17.1540(4)
α (°)	90	104.46(1)	70.777(2)
β (°)	111.263(2)	95.32(1)	82.920(2)
γ (°)	90	105.46(1)	80.470(2)
V (Å <sup>3</sup> )	3166.5(2)	1819.3(4)	1876.1(1)
Z	4	2	2
D <sub>calc</sub> (g cm <sup>-3</sup> )	1.247	1.121	1.209
μ(Mo–Kα) (mm <sup>-1</sup> )	0.452	0.324	0.322
F(000)	1268	662	728
Crystal colour	Blue	Grey	Brown
Crystal size (mm <sup>3</sup> )	0.47 × 0.45 × 0.20	0.7 × 0.6 × 0.5	0.5 × 0.2 × 0.18
θ-Range (°)	3.28–27.48	1.47–24.98	3.37–25.04
hkl range	–25/25, –15/15, –18/18	–11/11, 0/16, –17/16	–11/11, –13/13, –19/20
Unique diffractions	3613	6375	6520
Observed diffractions <sup>a</sup>	2871	4437	5566
Parameters	179	382	434
R(F), wR(F <sup>2</sup> ) (all data) <sup>b</sup>	0.0521, 0.0927	0.0906, 0.1652	0.0523, 0.1088
R(F), wR(F <sup>2</sup> ) (observed diffractions) <sup>b</sup>	0.0370, 0.0856	0.0535, 0.1459	0.0420, 0.1021
S (all data) <sup>c</sup>	1.031	1.041	1.039
(Δρ) <sub>max</sub> , (Δρ) <sub>min</sub> (e Å <sup>-3</sup> )	0.313, –0.270	0.618, –0.257	0.473, –0.418

<sup>a</sup> Diffractions with  $I_o > 2\sigma(I_o)$ .

<sup>b</sup>  $R(F) = \sum ||F_o| - |F_c|| / \sum |F_o|$ ,  $wR(F^2) = [\sum (w(F_o^2 - F_c^2)^2) / \sum w(F_o^2)^2]^{1/2}$ .

<sup>c</sup>  $S = [\sum (w(F_o^2 - F_c^2)^2) / (N_{\text{diffractions}} - N_{\text{parameters}})]^{1/2}$ .

3065 (m), 3046 (m), 2993 (w), 2955 (s), 2910 (vs), 2858 (m), 1971 (w), 1882 (vw), 1820 (vw), 1766 (vw), 1587 (w), 1566 (w), 1485 (m), 1427 (vs), 1381 (m), 1310 (m), 1249 (m), 1187 (w), 1128 (w), 1107 (vs), 1066 (vw), 1023 (m), 998 (w), 818 (m), 787 (vs), 737 (s), 714 (s), 700 (vs), 670 (m), 493 (s), 471 (m), 456 (m). UV–vis (C<sub>6</sub>H<sub>5</sub>CH<sub>3</sub>, 22 °C, nm): 590.

#### 4.12. Reaction of **9**–**11** with btmse

Btmse (1.0 ml, 4.47 mmol) was added to a solution of **9** (0.10 g, 0.16 mmol; molar ratio btmse:Ti = 28.0) in C<sub>6</sub>H<sub>5</sub>CH<sub>3</sub> (4.0 ml). An absorption band at 940 nm in UV–near IR spectrum of the mixture occurred and grew in intensity during 1.5 h while, simultaneously, the band due to **9** at 590 nm showed a moderate decrease and its maximum moved to 620 nm as a result of increasing background absorption at shorter wavelengths. After 2 h the intensity ratio did not change further. Attempted isolation of [Ti{(η<sup>5</sup>-C<sub>5</sub>Me<sub>4</sub>(SiMe<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>Ph))<sub>2</sub>(η<sup>2</sup>-btmse)] (**12**) by evaporation of all volatiles under vacuum and redissolution of the residue in C<sub>6</sub>H<sub>14</sub> (4.0 ml) lead to a complete recovery of **9** as indicated by UV–near IR spectrum. Replacement of C<sub>6</sub>H<sub>14</sub> with THF did not change the spectrum either.

Compound **10** (0.12 g, 0.22 mmol) in 4.0 ml of C<sub>6</sub>H<sub>5</sub>CH<sub>3</sub> was reacted with 1.0 ml of btmse (btmse:Ti = 20) for 2 h and UV–near IR spectra were measured. A new absorption band of **13** at 930 nm occurred while the band at 580 nm due to **10** diminished. A final estimate molar fraction of **13** in the **10/13** mixture was 25 ± 5%. Twice repeated evaporation of volatiles followed by dissolution of the residue in C<sub>6</sub>H<sub>14</sub> afforded a solution showing only the band at 580 nm. Analogous experiment of **11** with btmse in C<sub>6</sub>H<sub>5</sub>CH<sub>3</sub> did not result in occurring any band in the region 800–1200 nm.

#### 4.13. Oxidation of **9**–**11** with PbCl<sub>2</sub>

Crystalline **9** (0.21 g, 0.34 mmol) was dissolved in THF (20 ml) and the solution was poured on vacuum-dried, solid PbCl<sub>2</sub> (0.095 g, 0.34 mmol). The mixture was stirred at 60 °C for 4 h while the colour changed to reddish brown. Volatiles were evaporated in vacuum, and the residue was extracted with C<sub>6</sub>H<sub>14</sub> (20 ml). The solution was concentrated to crystallisation and cooled overnight to –18 °C. Crystalline **3** (0.20 g, 87%) was identified by EI-MS and <sup>1</sup>H- and <sup>13</sup>C-NMR spectra. Analogous reactions of **10** (0.20 g, 0.36 mmol) and **11**

(0.20 g, 0.32 mmol) with equimolar amounts of  $\text{PbCl}_2$  in THF afforded **4** (0.18 g, 79%) and **5** (0.20 g, 84%), respectively.

#### 4.14. X-ray crystallography

Fragments of a blue crystal of **7**, a grey prism of **9**, and a brown platelet of **11** were inserted into Lindemann glass capillaries in a glove box. Diffraction data for **9** were collected on an Enraf–Nonius four-circle CAD4 and the data for **7** and **11** on a Nonius KappaCCD diffractometers. The structures were solved by direct methods (SIR-92, [28]) and refined by weighted full-matrix least-squares on  $F^2$  (SHELXL-97, [29]). All non hydrogen atoms were refined with anisotropic thermal motion parameters. The hydrogen atoms were included in calculated positions. Relevant crystallographic data are given in Table 4.

### 5. Supplementary materials

Crystallographic data for the structural analysis have been deposited at the Cambridge Crystallographic Data Centre, CCDC nos. 186411, 173171, 186443 for compounds **7**, **9** and **11**. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: <http://www.ccdc.cam.ac.uk>).

### Acknowledgements

Financial support of Grant Agency of the Czech Republic (projects No. 203/02/0774 and No. 203/99/M037) is gratefully acknowledged.

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