

Synthesis and structure of isopropylidimethylsilyl-substituted octamethyltitanocene

Lenka Lukešová^a, Jiří Pinkas^a, Michal Horáček^a, Róbert Gyepes^b,
Jiří Kubišta^a, Karel Mach^{a,*}

^a J. Heyrovský Institute of Physical Chemistry, Academy of Sciences of the Czech Republic, Dolejškova 3, 182 23 Prague 8, Czech Republic

^b Department of Inorganic Chemistry, Faculty of Science, Charles University, Hlavova 2030, 128 40 Prague 2, Czech Republic

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Abstract

Reduction of isopropylidimethylsilyl-substituted titanocene dichloride $[\text{TiCl}_2(\eta^5\text{-C}_5\text{Me}_4\text{SiMe}_2\text{Pr}^i)_2]$ (**1**) by excess magnesium in the presence of excess bis(trimethylsilyl)ethyne (btmse) in tetrahydrofuran at 60 °C yielded a mixture of products amongst them only the trinuclear Ti–Mg–Ti hydrido-bridged complex $\text{Mg}[\text{Ti}(\mu\text{-H})_2(\eta^5\text{-C}_5\text{Me}_4\text{SiMe}_2\text{Pr}^i)_2]$ (**3**) was isolated and characterized. The precursor of titanocene, $[\text{Ti}(\eta^5\text{-C}_5\text{Me}_4\text{SiMe}_2\text{Pr}^i)_2(\eta^2\text{-btmse})]$ (**6**), was obtained from the identical system which, after initial formation of $[\text{TiCl}(\eta^5\text{-C}_5\text{Me}_4\text{SiMe}_2\text{Pr}^i)_2]$ (**2**), reacted at –18 °C overnight and then the solution was rapidly separated from the remaining magnesium. Titanocene $[\text{Ti}(\eta^5\text{-C}_5\text{Me}_4\text{SiMe}_2\text{Pr}^i)_2]$ (**7**) was obtained by thermolysis of **6** at 75 °C in vacuum. Crystal structures of **1**, **2**, **3**, **6**, and **7** were determined.

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1. Introduction

Thermally stable, well-defined crystalline titanocenes are known only a few, all of them containing triorganylsilyl group in addition to four methyl groups on each of the two cyclopentadienyl ligands [1–3]. The titanocene containing *tert*-butyldimethylsilyl group was obtained from the appropriate titanocene monochloride by the reduction with sodium amalgam [1], that one containing trimethylsilyl group by thermolysis of its bis(trimethylsilyl)ethyne (btmse) complex [2], and the titanocenes containing phenethyldimethylsilyl and methyl-diphenylsilyl groups were prepared by a direct reduction of the particular titanocene dichloride by magnesium in tetrahydrofuran (thf) [3] (Chart 1). Decamethyltitanocene [4] seems to be further

stabilized by the replacement of one methyl group on each cyclopentadienyl ligand by a more bulky group, like *iso*-propyl or *tert*-butyl [5]. Although none of these solely carbonaceous titanocenes has been crystallographically characterized the crystal structures of their nitrogen complexes $[\{\text{Ti}(\eta^5\text{-C}_5\text{Me}_5)_2(\mu\text{-}\eta^1\text{-}\eta^1\text{-N}_2)\}]$ [6] and $[\text{Ti}(\eta^5\text{-C}_5\text{Me}_4\text{Pr}^i)_2(\eta^1\text{-N}_2)_2]$ were determined [5]. The stability of titanocenes $[\text{Ti}(\eta^5\text{-C}_5\text{Me}_4\text{R})_2]$ and their nitrogen complexes follow opposite trends. The thermal stability of the nitrogen complexes was found to be decreasing in the order of R: Me > Prⁱ > SiMe₃ > Bu' [5], and for the titanocenes it is only known that the titanocene for R = SiMe₃ is stable at 70 °C [2] whereas that for R = Me forms an equilibrium with its hydride at room temperature [4]. A similar trend applies also to titanocene–btmse complexes. The $[\text{Ti}(\eta^5\text{-C}_5\text{Me}_4\text{R})_2(\eta^2\text{-btmse})]$ complex for R = Me thermolyzes at 150 °C to give the double tucked-in (allyl-diene) titanocene $[\text{Ti}\{\eta^5\text{-C}_5\text{Me}_3(\text{CH}_2)_2\}(\eta^5\text{-C}_5\text{Me}_5)]$ [7] whereas for R = SiMe₃ it eliminates smoothly btmse to give the titanocene

* Corresponding author. Tel.: +420 2 6605 3735; fax: +420 2 858 2307.
E-mail address: mach@jh-inst.cas.cz (K. Mach).

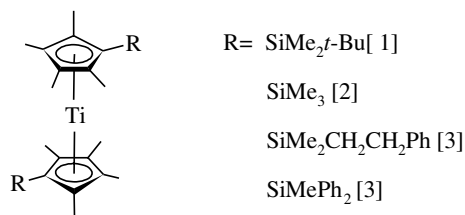


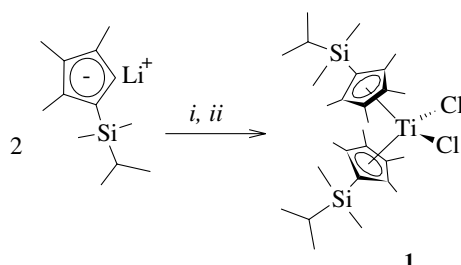
Chart 1.

at only 80 °C [2]. On the other hand, the titanocene for R = SiMePh₂ coordinates btmse reluctantly forming an observable equilibrium concentration of the adduct only at a large excess of free btmse [3], and neither the titanocene nor its btmse complex was found for R = SiMe₂(CH₂CH₂CF₃) [8].

In this work, we investigate the preparation of the titanocene for R = SiMe₂Pr^{*i*} attempting a direct reduction by magnesium as well as the route via thermolysis of its btmse complex.

2. Results and discussion

The synthesis of 5-(isopropylidimethylsilyl)-1,2,3,4-tetramethylcyclopenta-1,3-diene (Cp'^{*H*}) and the corresponding titanocene dichloride [TiCl₂(η⁵-C₅Me₄SiMe₂-Pr^{*i*})₂] (**1**) thereof followed in all respects the synthesis of the trimethylsilyl derivatives (Scheme 1) [9]. Both the compounds were characterized by ¹H and ¹³C NMR, IR, and EI-MS spectra and compound **1** by X-ray diffraction analysis. The EI-MS spectra of the both compounds showed fragmentations with the loss of Pr^{*i*} and Me groups. Com-



i TiCl₃(thf)₃, thf, boil for 20h.

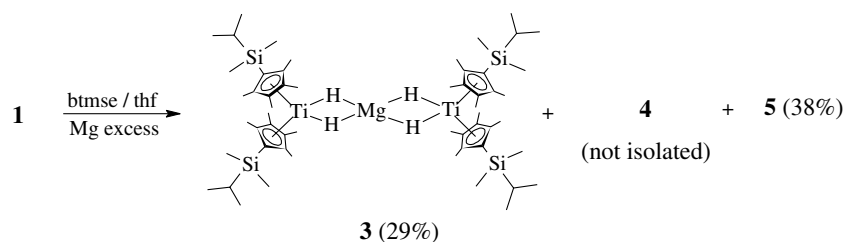
ii 0.5 PbCl₂, workup

Scheme 1.

pound **1** did not exert its molecular ion but gave a fragment ion arising from the loss of one cyclopentadienyl ligand as a base peak. The IR spectra showed absorption bands typical for the SiMe₂Pr^{*i*} group at 1247 (vs) and 881 (s) cm⁻¹ and very strong bands at 815 and 830 cm⁻¹ for Cp'^{*H*} or 811 (vs), 825 (s), and 834 (s) cm⁻¹ for **1**. These bands vary only slightly in all the other titanocene derivatives.

The reduction of **1** by a half molar equivalent of Mg rapidly afforded the blue, paramagnetic monochloride [TiCl(η⁵-C₅Me₄Pr^{*i*})₂] (**2**) which displayed typical ESR and electronic absorption spectra common for highly methyl-substituted titanocene monochlorides [10,11]. The EI-MS spectra showed the molecular ion base peak which fragmented with a loss of Me or Pr^{*i*} group. These fragments were then losing the SiMe₂Pr^{*i*} or the whole Cp' ligand. Surprisingly, elimination of Cl or Cp' from the molecular ion was not observed at all. The monomeric chemical formula of **2** was confirmed by X-ray crystal structure analysis (vide infra).

The clue complex for the thermolytic synthesis of titanocene, its btmse complex, could not be obtained by a standard procedure [7,12], i.e., the reduction of **1** with excess magnesium in thf in the presence of a 5-fold molar excess of btmse at 60 °C. Such a reaction resulted in the formation of a complex mixture of products (Scheme 2) from which the products low-soluble in hexane (**3**, **4**) and those contained in the mother liquor (**5**) were separated. The former products were dissolved in toluene and characterized by EPR spectra. The EPR spectra in solution and in the frozen glass indicated the presence of two titanocene–magnesium complex hydrides of known structural types. The trinuclear Ti–Mg–Ti hydrido complex Mg[Ti(μ-H)₂{η⁵-C₅Me₄(SiMe₂Pr^{*i*})₂}₂] (**3**) was easily recognized by EPR spectrum of the frozen glass showing an electronic triplet state of axial symmetry and its solid state structure was proved by X-ray diffraction analysis (vide infra). Compounds of the general formula Mg[Ti(μ-H)₂(η⁵-Cp'^{*H*})₂]₂ are known for Cp' = C₅Me₅ [13], C₅HMe₄, C₅H₂Me₃ [14], C₅Me₄Ph [15], and C₅Me₄(SiMe₂CH₂CH₂CF₃) [8]. For this type of compounds the magnitude of the zero-field splitting *D* spans a narrow range of values (*D*_{max} = 0.0133 cm⁻¹ for Cp' = C₅HMe₄ [14] and *D*_{min} = 0.0116 cm⁻¹ for Cp' = C₅Me₄(SiMe₂CH₂CH₂CF₃) [8]) because the distance between the spin-unpaired electrons residing on the Ti(III) atoms varies within 0.2 Å only. The present value of *D* = 0.0117 cm⁻¹ is close to that for the above mentioned



Scheme 2.

silyl-substituted derivative, and corresponds well with the crystallographic Ti–Ti distance of 5.779(1) Å for **3** (vide infra). The molecule of **3** could not be evaporated without decomposition in mass spectrometer, and hence, the EI-MS spectra show only the titanocene fragment ions arising from the loss of hydrogen. The presence of bridging hydrogen atoms in **3** is evidenced by a broad absorption band in IR spectrum at 1200 cm^{-1} which is typical for this species [8,13–15].

The evidence for the other, very minor titanocene component **4** in the low-hexane soluble fraction was obtained by ESR spectroscopy only. The ESR spectrum of the toluene solution displayed a triplet 1:2:1 characterized by $g = 1.990$ and coupling constant $a = 7.7\text{ G}$. Such a signal is typical for $[\text{Cp}'_2\text{Ti}(\mu\text{-H})_2]\text{M}$ species where M can be an alkali metal [16] or magnesium [17]. The magnesium complexes were further shown to be dimeric, bridged by halogen atoms and coordinating either diethyl ether [18a] or thf by their magnesium atoms (Chart 2, A) [18b]. The other alternative is the bridging of magnesium atoms by methylene carbon atoms as it was found in the main product of the reduction of $[\text{TiCl}_2(\eta^5\text{-C}_5\text{Me}_4\text{SiMe}_3)_2]$ with excess magnesium at $60\text{ }^\circ\text{C}$ in the absence of btmse (Chart 2, B) [19]. Since compound **4** could not be isolated for X-ray diffraction analysis and the ESR spectra are not sensitive enough to determine the nature of the bridging elements between the magnesium atoms it has to be concluded that compound **4** is a dimeric titanocene–magnesium hydride of type A or B depicted in Chart 2.

The hexane mother liquor of the above reduction contained a highly soluble product **5** which did not form crystals suitable for X-ray analysis. This khaki-colored product is paramagnetic, giving ESR spectra in toluene solution and glass compatible with a monomeric species $\text{Cp}'_2\text{TiL}$ where L is carbyl. Its EI-MS spectra show the $[\text{Cp}'_2\text{Ti} - \text{H}]^+$ molecular ion (m/z 489 at 88% abundance) accompanied by a rich fragment pattern arising from losses of hydrogen atoms thereof, e.g., m/z 485 (100). The molecular peak, however, became a base peak when the measurement was carried out at low ionization potential of 15 eV. Since the similar $[\text{TiCl}_2(\eta^5\text{-C}_5\text{Me}_4\text{SiMe}_3)_2]/\text{Mg}(\text{excess})/\text{thf}/\text{btmse}(\text{excess})$ system at $60\text{ }^\circ\text{C}$ produced the compound C [19] depicted in Chart 2 we can assume that the structure of **5** is also similar. However, in the absence of X-ray crystal structure it is impossible to establish whether the intramolecular Ti–carbyl bond is generated from the methyl

group (as in C, Chart 2) or from the internal carbon atom of the isopropyl group.

The formation of **3** in the present system, which was not observed in analogous system with $[\text{TiCl}_2(\eta^5\text{-C}_5\text{Me}_4\text{SiMe}_3)_2]$ [19], is probably due to the presence of a bulky isopropyl dimethylsilyl group promoting an easier dissociation of MgCl_2 from compound **4** (structure A in Chart 2) to give **3**. The trinuclear Ti–Mg–Ti hydride complex analogous to **3** was previously obtained from $[\text{TiCl}_2(\eta^5\text{-C}_5\text{Me}_4\text{SiMe}_2\text{CH}_2\text{CH}_2\text{CF}_3)_2]$ although in a very low yield [8]. The further analogous experiment carried out at $-5\text{ }^\circ\text{C}$ in a refrigerator for 2 days afforded a similar mixture of products, therefore the synthesis of the titanocene–btmse complex was attempted at a yet lower temperature.

2.1. Preparation of bis{(isopropyl dimethylsilyl)-tetramethylecyclopentadienyl}titanium(II) (**7**)

The required precursor to titanocene, $[\text{Ti}(\eta^5\text{-C}_5\text{Me}_4\text{SiMe}_2\text{Pr}^i)_2(\eta^2\text{-btmse})]$ (**6**), was obtained following the protocol for the synthesis of $[\text{Ti}(\eta^5\text{-C}_5\text{Me}_4\text{SiMe}_3)_2(\eta^2\text{-btmse})]$ [2] and using a 5-fold molar excess of btmse. When compound **1** was reduced to **2**, which was manifested by turning to blue color, the reaction mixture was placed into a freezer at $-18\text{ }^\circ\text{C}$ overnight. Then, the solution was rapidly poured away from excessive magnesium, evaporated, and yellow product **6** was extracted by a minimum amount of hexane. Crystalline **6** was obtained by cooling of its concentrated solution. This was used for all characterization. Its EI-MS spectra showed the spectra of titanocene **7** (m/z 490) and btmse, the latter decreasing in intensity during the sample evaporation. This is due to the ease of thermal dissociation of **6** (see below) and high volatility of btmse. On the other hand, the IR spectrum of **6** did not indicate its low thermal stability. The $\nu(\text{C}\equiv\text{C})$ vibration of **6** gives rise to three absorption bands at 1634 (w), 1599 (s), and 1562 (w) cm^{-1} which differ only negligibly in wavenumbers and shape from other highly substituted $[\text{Ti}(\eta^5\text{-C}_5\text{Me}_4\text{R})_2(\eta^2\text{-btmse})]$ complexes: R = SiMe₃, 1620 (w), 1595 (s), and 1560 (w) [2]; Me, 1638 (w), 1595 (m), and 1562 (w); H, 1658 (w), 1602 (s), and 1568 (w) [7]. Since these complexes lose btmse at temperatures $80\text{ }^\circ\text{C}$ for R = SiMe₃, 1,2-bis(trimethylsilyl)ethene at $130\text{ }^\circ\text{C}$ for R = Me, and at $>130\text{ }^\circ\text{C}$ for R = H [7] these figures show that the thermolytic temperature of these compounds can-

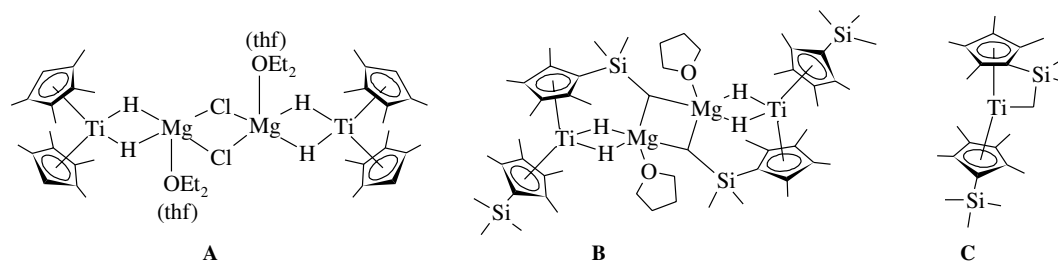


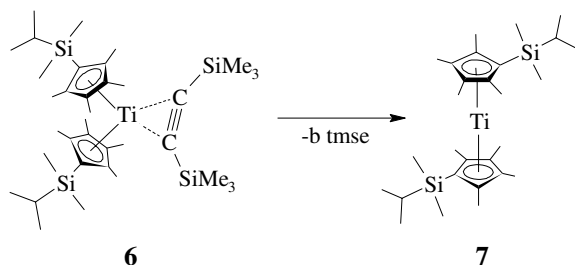
Chart 2.

not be predicted from the wavenumbers of the $\nu(\text{C}\equiv\text{C})$ absorption bands. The similar conclusion stems also from electronic absorption spectrum of **6** whose absorption band at 940 nm occurs in a narrow range 920–980 nm for the above mentioned btmse complexes [2,7]. The ^1H and ^{13}C NMR spectra of **6** were not measured because when diluting solid **6** in C_6D_6 the yellow color of its solution was rapidly turning to a turquoise color typical for titanocenes $[\text{Ti}(\eta^5\text{-C}_5\text{Me}_4\text{SiMe}_3)_2]$ (**8**) or $[\text{Ti}(\eta^5\text{-C}_5\text{Me}_4\text{SiMe}_2\text{Pr}^i)_2]$ (**7**) (see below). Then, it turned out that a dilution of the hexane or benzene solution of **6** induces its dissociation quite reproducibly. In such solutions, containing an equimolar concentration of free btmse, equilibrium concentrations of **6** were observed displaying a weak electronic absorption band at 940 nm.

Titanocene **7** was obtained analogously to titanocene **8** by thermolysis of solid **6** at 75°C in a high vacuum (Scheme 3). The samples of **6** which dissociated in diluted solutions were evaporated and thermolyzed in vacuum at 75°C as well in order to complete the dissociation of btmse. The non-volatile titanocene was crystallized from hexane to give prisms which were turquoise in incident light and red in transmitted light, similarly to **8**. The compound was further characterized by IR spectrum, EI-MS spectra with the molecular ion to be a base peak, and by electronic absorption spectrum showing a distinct absorption band at 578 nm, in line with the spectrum of **8** (570 nm) [2] and $[\text{Ti}(\eta^5\text{-C}_5\text{Me}_4\text{SiMe}_2\text{Bu}^i)_2]$ (**9**) (580 nm) [1]. The ^1H NMR spectra of **7** showed four broad signals, whose half-widths and chemical shifts were temperature dependent. The chemical shifts obeyed Curie law fitting to linear dependence $\delta = a + bT^{-1}$. The signals were tentatively assigned to ring methyl protons, silylmethyl and isopropyl protons based on previous assignments for **8** [2], **9** [1], and $[\text{Ti}(\eta^5\text{-C}_5\text{Me}_5)_2]$ [4a]. Although the dissociation of the **8**-btmse complex to give **8** by the dilution of its solutions was also previously described [2] compound **6** seems to be dissociating easier, and correspondingly, the titanocene **7** is probably slightly more stable than titanocene **8**.

2.2. X-ray crystal structures of isopropyldimethylsilyl titanocene complexes

The titanocene dichloride **1**, monochloride **2**, and titanocene-btmse complex **6** possess crystallographically asymmetrical molecules crystallizing in monoclinic space



Scheme 3.

groups. The PLATON representations of **1**, **2** (molecule 1 of the two independent molecules), and **6** are depicted in Figs. 1–3, respectively, and their important geometric parameters are given in Table 1. Compared with structures of their trimethylsilyl [2,9] or dimethyl(3,3,3-trifluoropropyl)silyl [8] analogs the compounds show very similar overall geometric parameters, like Ti–Cg, Ti–Cl or Ti–C(btmse) distances and Cg–Ti–Cg or φ angles. The molecule 1 and molecule 2 of **2** differ by mutual positions of their cyclopentadienyl ligands characterized by torsion angles C(101)–Cg(1)–Cg(2)–C(110) $106.3(2)^\circ$ (see Fig. 2) and C(201)–Cg(3)–Cg(4)–C(210) $179.6(2)^\circ$. The placement of the silyl substituents on the opposite sides of the Cg(3), Ti(2), Cg(4) plane found in molecule 2 was also observed in $[\text{TiCl}(\eta^5\text{-C}_5\text{Me}_4\text{SiMe}_3)_2]$ [9] or $[\text{TiCl}(\eta^5\text{-C}_5\text{Me}_4\text{SiMe}_2\text{CH}_2\text{-CH}_2\text{CF}_3)_2]$ [8] whereas the situation of the silyl groups closer to the open titanocene shell, as in molecule 1, was found in $[\text{TiCl}(\eta^5\text{-C}_5\text{Me}_4\text{SiMe}_2\text{Ph})_2]$ (torsion angle of $104.0(2)^\circ$) [3]. The crystal packing in **2** apparently “compresses” molecule 1 since both the Ti(1)–Cl(1) bond length of 2.3157(11) Å and average Ti(1)–Cg distance of 2.0710(15) Å are shorter than the corresponding values for molecule 2 Ti(2)–Cl(2) 2.3394(10) Å and Ti(2)–Cg of 2.0741(15) Å. The average values for both molecules of **2** do not differ significantly from the values observed in the above mentioned titanocene monochlorides. The bonding and structure of the btmse ligand in **6** do not differ from those of highly substituted $[(\text{TiCp}'_2)\text{-btmse}]$ complexes [12]: Cp' = C_5Me_5 [20], $\text{C}_5\text{Me}_4\text{H}$ [7], $\text{C}_5\text{Me}_4\text{SiMe}_3$ [2], $\text{C}_5\text{Me}_4(4\text{-fluorophenyl})$ [21] or $[\text{TiMe}_2\text{Si}(\text{C}_5\text{Me}_4)_2\text{-btmse}]$ [22]. Examination of the cyclopentadienyl ligand structures confirmed the general feature of the silyl-substituted tetramethylcyclopentadienyl ligands that the ring angle at the carbon atom bearing the silicon atom is acute (av. 105°) compared with the other ring angles (av. 108°). The

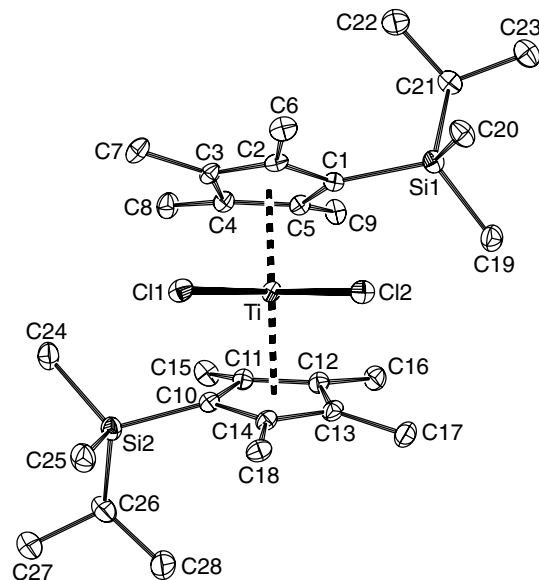


Fig. 1. The molecular structure of compound **1** (30% probability thermal motion ellipsoids) showing the atom numbering scheme. Hydrogen atoms are omitted for clarity.

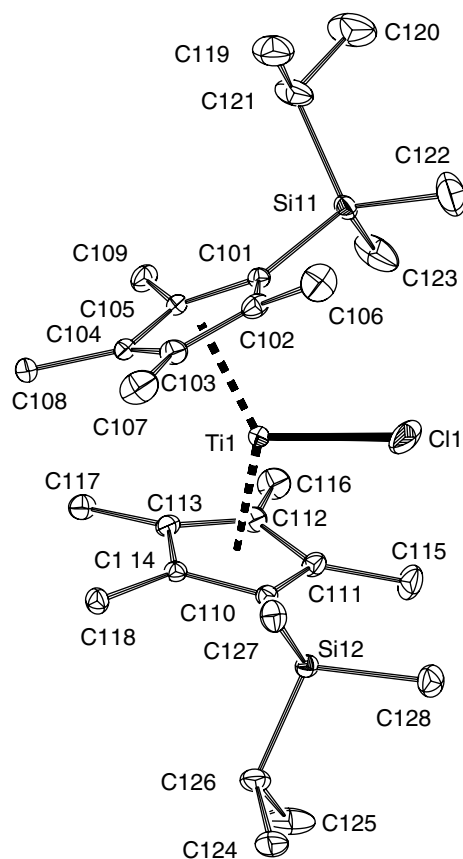


Fig. 2. The molecular structure of molecule 1 of **2** (30% probability thermal motion ellipsoids) showing the atom numbering scheme. Hydrogen atoms are omitted for clarity.

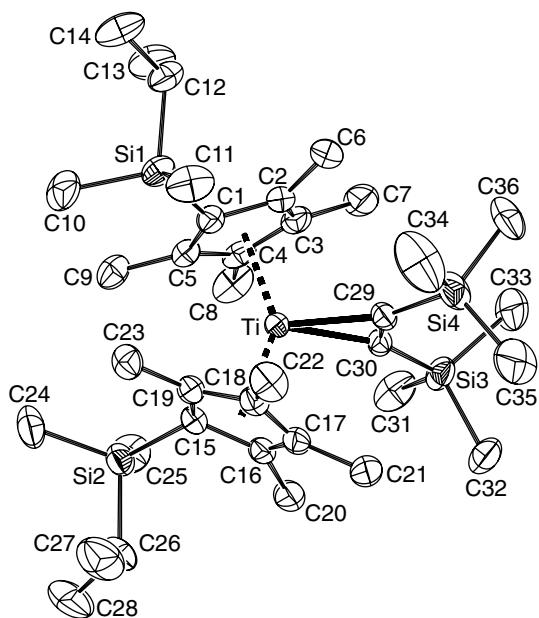


Fig. 3. The molecular structure of **6** (30% probability thermal motion ellipsoids) showing the atom numbering scheme. Hydrogen atoms are omitted for clarity.

Table 1
Selected bond lengths (Å) and angles (°) for molecules of **1**, **2**, and **6**^a

Atoms	1	2 ^b	6
<i>Bond lengths</i>			
Ti–Cl(1)	2.3576(7)	2.3157(11)	2.129(3) ^c
Ti–Cl(2)	2.3709(7)	–	2.132(3) ^c
Ti–Cg(1)	2.128(1)	2.0726(15)	2.128(2)
Ti–Cg(2)	2.128(1)	2.0694(15)	2.143(2)
C–C(ring) _{av}	1.420(3)	1.420(5)	1.416(5)
C–C(Me) _{av}	1.503(3)	1.508(5)	1.506(6)
Si(1)–C(1)	1.893(2)	1.875(3)	1.879(4)
<i>Bond angles</i>			
Cg(1)–Ti–Cg(2)	137.92(5)	142.23(6)	142.21(7)
Si(1)–C(1)–C(2)	128.0(2)	128.8(2)	121.4(3)
Si(1)–C(1)–C(5)	124.7(2)	124.5(2)	127.6(3)
C(2)–C(1)–C(5)	105.9(2)	106.3(3)	104.8(3)
C(1)–C(2)–C(3)	108.7(2)	109.0(3)	109.2(3)
C(2)–C(3)–C(4)	108.5(2)	107.7(3)	109.2(3)
C(3)–C(4)–C(5)	107.7(2)	108.3(3)	107.4(3)
C(1)–C(5)–C(4)	109.0(2)	108.7(3)	109.5(3)
φ ^d	40.9(1)	36.1(1)	41.4(2)
Cl(1)–Ti–Cl(2)	90.78(2)	–	35.59(13) ^c

^a The geometric data are given for the cyclopentadienyl ring denoted by lower numbers and Cg(1); the data for the ring denoted by higher numbers which determine Cg(2) do not differ remarkably and are not listed.

^b The data are given for molecule **1** out of two independent molecules present in the unit cell. Atoms in molecule **1** of Fig. 1 are labeled with numbers increased by 10 for Si and by 100 for C.

^c For compound **6** read C(29) instead of Cl(1) and C(30) instead of Cl(2). The bond length C(29)–C(30) is 1.302(5) Å.

^d Dihedral angle between least-squares planes of the cyclopentadienyl rings.

silicon atom is further substantially deviated from the axis of this angle depending on the steric hindrance of the silyl substituent with neighbouring methyl groups (see difference in the Si(1)–C(1)–C(2) and Si(1)–C(1)–C(5) angles in Table 1).

The trinuclear complex **3** crystallizes in orthorhombic space group *Pbcn*, and its molecules are symmetrical with respect to a 2-fold rotation axis involving Ti and Mg atoms (Fig. 4). In the so far known symmetrical molecules of this type complexes with ligands (η^5 -C₅Me₄H) [14] or (η^5 -C₅Me₄SiMe₂CH₂CH₂CF₃) [8] the 2-fold rotation axis was perpendicular to the present one. Important geometric parameters for **3** are listed in Table 2. The two Cp₂Ti(μ-H)₂Mg moieties are mutually rotated by nearly 90°, the bridging metal-hydride bonds form planes with virtually equal Ti–H and Mg–H bond lengths of 1.83(2) Å. Compared with the above dimethyl(3,3,3-trifluoropropyl)silyl complex where the Ti–Ti distance was 5.919(2) Å [8] compound **3** is more strongly bonded showing the Ti–Ti distance of only 5.779(2) Å.

Compound **7** crystallizes in monoclinic space group, the unit cell contains two molecules which are centrosymmetric. The precision of geometric data is low due to high thermal parameters and a disorder imposed over the isopropyl group (see Fig. 5). The most valuable data on the structure of the titanocene skeleton are given in Table 3. They show that the Ti–Cg distance of 2.0135(16) Å is slightly shorter than in **8** (2.020(2) Å) [2] and in **9** (2.018(4) Å) [1]. As in

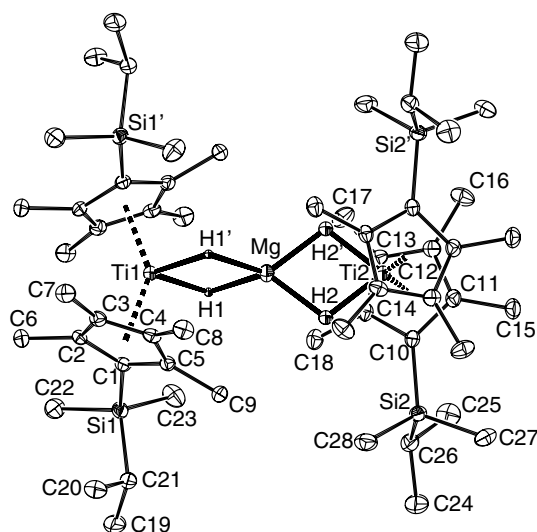


Fig. 4. The molecular structure of **3** (30% probability ellipsoids) with atom numbering scheme. All hydrogen atoms except those in intermetallic bridging positions are omitted for clarity. The prime-labeled and non-labeled atoms were generated by symmetry operation $(-x, y, 1/2 - z)$.

all other cases, the cyclopentadienyl ring is distorted by the acute ring angle at the silicon-bearing C(1) atom. Deviation of the silicon atom from the axis of this angle is largely smeared by high thermal parameters and the isopropyl group disorder.

2.3. Conclusions

As follows from crystallographic data the modification of the trimethylsilyl group by a more bulky and more electron donating isopropyl group resulted in a slight stabilization of low-valent titanocene compound **3** with respect to

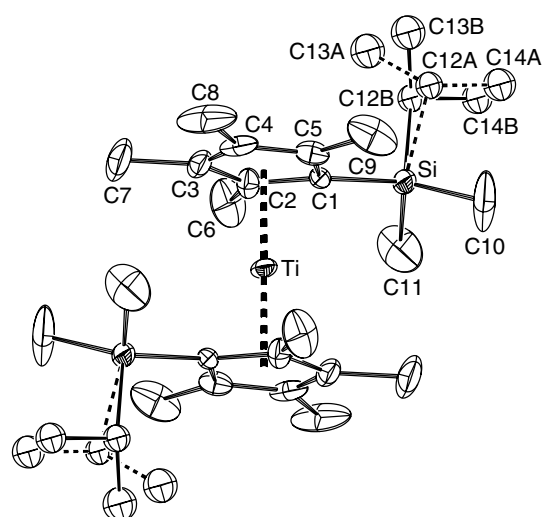


Fig. 5. The molecular structure of **7** (30% probability ellipsoids) with atom numbering scheme. Non-labeled cyclopentadienyl ligand was generated by the symmetry operation $(-x + 1, -y + 1, -z + 1)$. Disordered positions of isopropyl carbon atoms are denoted by dashed lines. For clarity, all hydrogen atoms are omitted.

the trifluoropropyldimethylsilyl derivative and titanocene **7** with respect to titanocene **8**. The reaction pathway to titanocene **7** through the thermolysis of its btmse complex in high vacuum affords practically clean product. The thermal stability of **7** is slightly higher than that of **8**.

3. Experimental

3.1. Methods

Syntheses of 5-(isopropyldimethylsilyl)-1,2,3,4-tetramethylcyclopenta-1,3-diene and titanocene dichloride

Table 2
Selected bond lengths (Å) and angles (°) for **3**

<i>Bond lengths</i>			
Ti(1)–Cg(1) ^a	2.080(2)	Ti(2)–Cg(2) ^a	2.076(2)
Ti(1)–H(1)	1.83(2)	Ti(2)–H(2)	1.82(2)
Mg–H(1)	1.83(2)	Mg–H(2)	1.85(2)
C–C(ring) _{av}	1.423(4)	C–C(Me) _{av}	1.508(4)
C(1)–Si(1)	1.865(3)	C(10)–Si(2)	1.868(3)
Ti(1)–Mg	2.8909(13)	Ti(2)–Mg	2.8880(13)
Ti(1)–Ti(2) ^b	5.779(2)		
<i>Bond angles</i>			
Cg(1)–Ti(1)–Cg(1') ^c	143.41(5)	Cg(2)–Ti(2)–Cg(2') ^c	144.61(5)
H(1)–Ti(1)–H(1') ^c	75.3(9)	H(2)–Ti(2)–H(2') ^c	77.1(10)
H(1)–Mg–H(1') ^c	75.4(9)	H(2)–Mg–H(2') ^c	75.4(9)
Ti(1)–H(1)–Mg	104.7(10)	Ti(2)–H(2)–Mg	103.7(10)
H(1)–Mg–H(2') ^c	124.8(7)	H(2)–Mg–H(1') ^c	134.54
H(1')–Mg–H(2') ^c	123.4(7)	Ti(1)–Mg–Ti(2) ^b	180 $\phi(1)$ ^d
τ^e	35.68(7)	$\phi(2)$ ^d	35.76(8)
	87.6(1.5)		

^a Cg1 denotes the centroid of the C(1–5) cyclopentadienyl ring atoms; Cg2 is the centroid of the C(10–14) cyclopentadienyl ring.

^b Nonbonding distance or angle.

^c Prime-labeled equivalent positions are generated by the symmetry operation $(-x, y, 1/2 - z)$.

^d Dihedral angle between the least-squares cyclopentadienyl planes ($\phi(1)$ at Ti(1), $\phi(2)$ at Ti(2) atoms).

^e Dihedral angle between the planes defined by the Mg, H(1), and H(1'), and Mg, H(2), and H(2') atoms.

Table 3
Selected bond lengths (Å) and angles (°) for **7**

Bond lengths			
Ti–Cg ^a	2.0135(16)	Ti–C(1)	2.310(3)
Ti–C(2)	2.334(3)	Ti–C(3)	2.380(4)
Ti–C(4)	2.370(3)	Ti–C(5)	2.330(4)
C–C(ring) _{av}	1.412(6)	C–C(Me) _{av}	1.507(7)
C(1)–Si	1.871(3)	C(10)–Si	1.857(6)
C(11)–Si	1.862(7)		
Bond angles			
Cg–Ti–Cg ^b	180	C(2)–C(1)–C(5)	104.9(3)
C(1)–C(2)–C(3)	109.4(3)	C(2)–C(3)–C(4)	107.9(3)
C(3)–C(4)–C(5)	108.5(3)	C(1)–C(5)–C(4)	109.3(3)
C(2)–C(1)–Si	126.4(2)	C(5)–C(1)–Si	127.3(2)
C(1)–C(2)–C(6)	125.7(4)	C(3)–C(2)–C(6)	124.8(4)
C(1)–C(5)–C(9)	126.3(4)	C(4)–C(5)–C(9)	124.4(4)
φ ^c	0		

^a Cg denotes the centroid of the C(1–5) cyclopentadienyl ring atoms.

^b Prime-labeled equivalent positions are generated by the symmetry operation $(-x + 1, -y + 1, -z + 1)$.

^c Dihedral angle between the least-squares cyclopentadienyl planes.

thereof were carried out under argon. All manipulations with Ti(III) and Ti(II) compounds were performed under vacuum on an all-glass high vacuum line using sealed glass devices equipped with breakable seals. ¹H (500 MHz) and ¹³C (125 MHz) NMR spectra were recorded on a Bruker DRX500 spectrometer in C₆D₆ solutions at 25 °C. The spectra of **7** were further investigated over the temperature range 20–60 °C. Chemical shifts (δ/ppm) are given relative to solvent signals (δ_H 7.15, δ_C 128.0). EI-MS spectra were obtained on a VG-7070E mass spectrometer at 70 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 Mn²⁺ standard at *g* = 1.9860 (*M*₁ = –1/2 line). A variable temperature unit STT-3 was used for measurements in the range –196 to +25 °C. UV-near IR spectra in the range of 280–2000 nm were measured on a Varian Cary 17 D spectrometer in all-sealed quartz cells (Hellma). IR spectra were taken in an air-protecting cuvette on a Nicolet Avatar FTIR spectrometer in the range 400–4000 cm^{–1}. KBr pellets were prepared in a glovebox Labmaster 130 (mBraun) under purified nitrogen. With the exception of air-stable titanocene dichloride **1**, all studied titanium compounds are extremely air- and moisture-sensitive, therefore the compounds were characterized by EI-MS spectra.

3.2. Chemicals

The solvents thf, hexane, and toluene were dried by refluxing over LiAlH₄ and stored as solutions of dimeric titanocene [(μ-η⁵:η⁵-C₅H₄C₅H₄){Ti(μ-H)(η⁵-C₅H₅)₂}] [23]. TiCl₄ (International Enzymes) was purified by refluxing over copper wire and distilled in vacuum. Butyllithium

(2.5 M in hexane, Aldrich), 1,2,3,4-tetramethylcyclopentadiene (mixture of isomers) and chlorodimethylisopropylsilane (Aldrich) were transferred via syringe under argon. Magnesium turnings (Aldrich, purum for Grignard reactions) were firstly used in a large excess for the preparation of [Ti(η²-btmse)(η⁵-C₅Me₅)₂] [7]. 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.

3.3. Synthesis of 5-(isopropylidimethylsilyl)-1,2,3,4-tetramethylcyclopenta-1,3-diene and bis{(isopropylidimethylsilyl)tetramethylcyclopentadienyl}dichlorotitanium (**1**)

1,2,3,4-Tetramethyl-cyclopenta-1,3-diene was obtained from 5-(dimethylisopropylsilyl)-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 chlorodimethylisopropylsilane (15.4 g, 0.113 mol) in thf. Yield 22.3.0 g (89%).

GC MS (*m/z*, relative intensity, %): 223 (17), 222 (M⁺; 79), 207 ([M–Me]⁺; 10), 180 (32), 179 ([M–Pr]⁺; 88), 121 (13), 120 ([M–HSiMe₂Pr]⁺; 44), 119 (19), 105 (28), 101 ([SiMe₂Pr]⁺; 73), 91 (18), 77 (11), 75 (46), 74 (24), 73 ([SiMe₃]⁺; 100), 60 (13), 59 ([SiMe₂H]⁺; 93). 58 (10), 45 (16), 43 (20). IR (neat, cm^{–1}): 2955 (vs), 2940 (vs), 2918 (s), 2863 (s), 2724 (vw), 1634 (w), 1462 (s), 1446 (m), 1381 (m), 1247 (s), 1219 (m), 1121 (w), 1110 (m), 1046 (m), 1024 (m), 997 (s), 982 (m), 951 (m), 920 (w), 881 (s), 830 (vs), 815 (vs), 793 (m), 769 (s), 762 (s), 726 (w), 692 (m), 664 (m), 590 (m), 487 (m), 420 (vw).

[TiCl₂{η⁵-C₅Me₄(SiMe₂Pr)₂}] (**1**) was prepared by reacting [TiCl₃(thf)₃] [generated in situ by adding LiBu in hexanes (22.5 ml of 1.6 M, 36.0 mmol) to TiCl₄ (4.0 ml, 36.0 mmol) in thf (50 ml)] with the cyclopentadienyl lithium obtained by addition of LiBu (30 mL of 2.5 M in hexanes, 75.0 mmol) to the above cyclopentadiene (16.2 g, 73.0 mmol) in thf (500 ml). After refluxing for 30 h and subsequent stirring with PbCl₂ (5.0 g, 18.0 mmol) at 40 °C for 1 h, the product was worked up as described for [TiCl₂{η⁵-C₅Me₄(SiMe₃)₂}] [9]. Yield of brown crystals of **1** was 7.6 g (38%).

EI MS (160 °C): *m/z* (relative abundance, %) (M⁺; 560) not observed, 547 (5), 545 ([M–Me]⁺; 5), 527 (14), 526 (14), 525 ([M–Cl]⁺; 26), 521 (10), 520 (14), 519 (30), 518 (19), 517 ([M–Pr]⁺; 36), 484 (8), 482 ([M–Pr–Cl]⁺; 8), 474 ([M–2 Pr]⁺; 7), 343 (19), 342 (20), 341 (72), 340 (34), 339 ([M–Cp]⁺; 100), 338 (13), 337 (11), 299 (9), 298 (19), 297 (22), 296 ([M–Cp–Pr]⁺; 30), 295 (26), 294 (18), 222 (20), 221 ([Cp]⁺; 85), 179 (43), 178 ([Cp–Pr]⁺; 43), 177 (20), 163 (24), 119 (19), 105 (10), 97 (10), 73 ([SiMe₃]⁺; 58), 59 ([SiMe₂H]⁺; 66). ¹H NMR (CDCl₃):

δ 0.37 (s, 12 H, SiMe₂); 0.79 (d, 12 H, CHMe₂, ²J_{HH} = 6.2 Hz); 1.26 (2H, CHMe₂); 2.03, 2.17 (2 × s 12H, C₅Me₄). ¹³C{¹H} NMR (CDCl₃): δ -2.0 (4C, SiMe₂); 12.9 (4C, CpMe); 15.1 (Prⁱ); 16.8 (Prⁱ); 18.2 (4C, CpMe); 129.3, 135.9, 137.4 (Cp). IR (KBr, cm⁻¹): 2954 (s), 2936 (s), 2916 (m), 2861 (s), 1478 (m), 1459 (m), 1407 (w), 1375 (m), 1362 (vw), 1340 (w), 1247 (s), 1123 (vw), 1023 (w), 998 (m), 881 (m), 834 (s), 825 (s), 811 (vs), 769 (s), 746 (vw), 679 (m), 669 (vw), 590 (m), 433 (m). Anal. Calc. for C₂₈H₅₀Cl₂Si₂Ti (M = 561.66): C, 59.88; H, 8.97. Found: C, 59.84; H, 8.92%.

3.4. Preparation of bis{(isopropyl dimethylsilyl) tetramethylcyclopentadienyl}chlorotitanium (2)

Compound **1** (0.56 g, 1.0 mmol) and Mg (0.012 g, 0.5 mmol) were degassed and thf (30 ml) was added by distillation in vacuum. This mixture was heated to 60 °C until all magnesium disappeared (ca. 2 h). The solvent was evaporated in vacuum, and the residue was extracted by 10 ml of hexane. A blue extract was concentrated to a volume of ca. 3 ml, and cooled in an ampule overnight to -18 °C. Blue crystalline [TiCl(η⁵-C₅Me₄(SiMe₂Prⁱ))] (2) was separated and dried in vacuum. Yield 0.41 g (78%).

M.p. 122 °C. EI MS (120 °C): *m/z* (relative abundance, %) 529 (9), 528 (21), 527 (54), 526 (51), 525 (M⁺; 100), 524 (16), 523 (12), 510 ([M-Me]⁺; 7), 485 (12), 484 (26), 483 (24), 482 ([M-Prⁱ]⁺; 48), 481 (7), 408 ([M-Me-SiMe₂-Prⁱ]⁺; 7) 387 (8), 386 (12), 385 (30), 384 (10), 383 (22), 382 (16), 381 ([M-Prⁱ-SiMe₂Prⁱ]⁺; 30), 380 (14), 345 (16), 344 (15), 343 (9), 302 (10), 301 (20), 300 (12), 299 (35), 284 (10), 277 (13), 276 (12), 275 (26), 263 (30), 262 (28), 261 ([M-Prⁱ-Cpⁱ]⁺; 80), 260 (40), 259 (38), 258 (23), 257 (19), 256 (24), 245 (12), 244 (18), 243 (33), 242 (12), 229 (15), 206 (12), 205 (9), 204 (22), 203 (10), 202 (10), 177 (15), 168 (31), 167 (13), 166 (21), 119 (13), 101 (24), 73 (93), 59 (88). IR (KBr, cm⁻¹): 2951 (vs), 2916 (s), 2861 (s), 1462 (m), 1412 (w), 1381 (m), 1331 (m), 1250 (s), 1178 (vw), 1126 (w), 1070 (vw), 1022 (m), 999 (m), 918 (vw), 881 (m), 834 (s), 810 (vs), 766 (m), 681 (m), 593 (w), 433 (m). EPR (22 °C, hexane): *g* = 1.959, ΔH = 14.0 G; (toluene, -140 °C): *g*₁ = 1.999, *g*₂ = 1.991, *g*₃ = 1.889, *g*_{av} = 1.959. UV-Vis (hexane, 22 °C): 562 > 665 (sh).

3.5. Preparation of bis{(isopropyl dimethylsilyl) tetramethylcyclopentadienyl}titanium hydride-magnesium hydride complex (3)

Compound **1** (1.12 g, 2.0 mmol) and Mg (0.24 g, 10 mmol) were degassed and btmse (2.2 g, 10 mmol) and thf (30 ml) were added by distillation in vacuum. This mixture was sealed out in an ampule and the content was stirred by a teflon-coated stirring bar at 60 °C in a water bath. The reduction to blue Ti(III) titanocene chloride occurred nearly instantly. After 2 h, the solution turned dark. It was separated from unreacted Mg, all volatiles evaporated,

and the residue was extensively extracted by hexane. A green solution was concentrated and cooled to -18 °C over 3 days. A separated turquoise crystalline material was washed by hexane, and dried in vacuum. Then it was dissolved in toluene, and the solution was investigated by ESR and UV-Vis spectra which revealed that it contains a mixture of the trinuclear Ti(III)-Mg-Ti(III) hydride complex Mg[Ti(μ-H)₂{η⁵-C₅Me₄(SiMe₂Prⁱ)₂}]₂ (**3**) and a dimeric complex containing the Cp₂Ti(μ-H)₂Mg moiety (**4**). Cooling of a concentrated toluene solution to -5 °C for 4 days afforded fine blue crystals which were separated and identified by X-ray single crystal diffraction to be compound **3**. Crystals from three experiments which showed ESR spectra of **4** as a minor component in solution were collected and subjected to X-ray investigation, however, they always diffracted as **3**. The structure of **4** therefore remains uncertain. The mother liquor after separation of **3** and **4** afforded a highly soluble in hexane amorphous solid **5** which did not crystallize. The structure of **5** is according to EI-MS, UV-Vis and ESR spectra an analogue of compound [Ti(η⁵-C₅Me₄SiMe₃){η⁵:η¹-C₅Me₄SiMe₂-(CH₂)}] (Chart 2, C) obtained under similar conditions from [TiCl₂(η⁵-C₅Me₄SiMe₃)₂] [19]. The nature of the bridging carbon atom in a Si-C-Ti bonding feature cannot be determined, however.

3: Yield 0.29 g (29%). M.p. 175 °C with decomposition (gas evolution). EPR (toluene, 23 °C): *g* = 1.990, ΔH = 14.5 G; (toluene, -140 °C): electronic triplet state, *g* = 1.990, *D* = 0.01166 cm⁻¹, *E* = 0. UV-Vis (23 °C, toluene): 355 >> 585 nm extending to 900 nm. EI MS (220 °C): *m/z* (relative abundance, %) (M⁺; 1008) not observed, 492 (15), 491 (38), 490 ([Cp₂Ti]⁺; 79), 489 ([Cp₂Ti-H]⁺; 93), 488 (71), 487 (54), 486 ([Cp₂Ti-4H]⁺; 61), 485 ([Cp₂Ti-5H]⁺; 100), 484 (34), 483 (48), 482 (15), 481 (19), 474 ([Cp₂Ti-H-Me]⁺; 8), 472 ([Cp₂Ti-3H-Me]⁺; 9), 446 ([Cp₂Ti-H-Prⁱ]⁺; 9), 73 ([SiMe₃]⁺; 25), 59 ([SiMe₂H]⁺; 20). IR (KBr, cm⁻¹): 2951 (vs), 2940 (s), 2914 (s), 2862 (vs), 2720 (vw), 1482 (w), 1461 (m), 1380 (m), 1351 (m), 1329 (s), 1247 (vs), 1200 (b,s), 1127 (m), 1069 (vw), 1021 (m), 998 (m), 917 (vw), 881 (m), 831 (s), 808 (vs), 761 (s), 677 (m), 594 (w), 431 (m). In addition, a broad absorption band (ca. 100 cm⁻¹) at ν 1230 cm⁻¹ can be attributed to a bridging Ti-H-Mg valence vibration [8,13–15].

4: EPR (23 °C, toluene): *g* = 1.991, *a*_H (1:2:1) = 7.3 G, ΔH = 3.6 G, *a*_{Ti} = 6.9 G; (toluene, -140 °C): *g*₁ = 2.000, *g*₂ = 1.990, *g*₃ = 1.982 (*a*₃(H) = 12 G).

5: Yield 0.37 g (38%). EI-MS (70 °C): *m/z* (relative abundance, %) 492 (8), 491 (24), 490 (48), 489 (M⁺; 88), 488 (44), 487 (62), 486 (62), 485 ([Cp₂Ti-4H]⁺; 100), 484 (45), 483 (62), 482 (20), 481 (26), 474 ([M-Me]⁺; 10), 472 ([Cp₂Ti-2H-Me]⁺; 12), 446 ([M-Prⁱ]⁺; 16), 390 (10), 388 (18), 73 ([SiMe₃]⁺; 35), 59 ([SiMe₂H]⁺; 27); (15 eV, 70 °C): *m/z* (relative abundance, %) 492 (10), 491 (27), 490 (50), 489 (M⁺; 100), 488 (21), 487 (24), 486 (9), 485 (14). IR (KBr, cm⁻¹): 2950 (vs), 2940 (sh), 2914 (s), 2860 (s), 1482 (w), 1461 (m), 1379 (m), 1329 (m), 1246 (s),

1129 (w), 1069 (vw), 1022 (m), 999 (m), 918 (vw), 880 (m), 833 (s), 811 (vs), 763 (s), 717 (vw), 681 (m), 593 (w), 576 (vw), 509 (vw), 480 (w), 430 (m). EPR (23 °C, hexane): $g = 1.958$, $\Delta H = 12.0$ G. UV–Vis (23 °C, hexane): 312(sh) \gg 455 > 592 nm.

3.6. Preparation of titanocene–btmse complex 6

Compound **1** (1.12 g, 2.0 mmol) and Mg (0.24 g, 10 mmol) were degassed and btmse (2.2 g, 10 mmol) and thf (30 ml) were added by distillation in vacuum. This mixture was sealed out in an ampule and heated to left to react at room temperature until its color changed to intense blue. Then, the ampule was cooled in a freezer to -18 °C with occasional shaking. The blue solution was slowly changing during several days to brownish yellow solution. This was separated from unreacted Mg, all volatiles evaporated, and the residue extracted by hexane (10 ml). A yellow hexane solution was concentrated to ca. 3 ml and cooled to -18 °C overnight. Yellow crystals were separated from mother liquor, washed with condensing hexane, and dried in vacuum. Yield of yellow crystals 0.95 g (72%).

6: M.p. 76 °C (no decomposition in sealed capillary under nitrogen). EI MS (90 °C): m/z (relative abundance, %) (M^+ ; 660) not observed, 493 (9), 492 (26), 491 (56), 490 ($[(Cp'_2Ti-H_2)^+]$; 84), 489 (37), 488 ($[(Cp'_2Ti-H_2)^+]$; 39), 487 (17), 486 (20), 485 (33), 484 (11), 483 (16), 385 (12), 383 (10), 381 (7), 346 (12), 170 ($[btmse]^+$; 29), 157 (26), 156 (57), 155 ($[btmse-Me]^+$; 100), 97 (20), 83 (18), 74 (9), 73 ($[SiMe_3]^+$; 86), 70 (15), 59 ($[SiMe_2H]^+$; 48). The spectrum was not constant: peaks due to btmse m/z 170, 157–155 were ceasing during evaporation. IR (KBr, cm^{-1}): 2950 (vs), 2919 (s), 2904 (s), 2861 (vs), 2720 (vw), 1634 (w), 1599 (s), 1562 (w), 1462 (s), 1379 (s), 1345 (w), 1326 (m), 1316 (m), 1248 (vs), 1129 (w), 1067 (vw), 1019 (m), 1001 (s), 918 (vw), 880 (s), 831 (vs,b), 815 (vs), 761 (s), 673 (m), 654 (m), 619 (vw), 594 (w), 445 (s), 426 (m). UV–near IR (hexane, 22 °C): 940 nm.

3.7. Preparation of titanocene 7

Bis{(isopropyl)dimethylsilyl}tetramethylcyclopentadienyl]-titanium **7** was obtained nearly pure by thermolysis of complex **6**. The yellow btmse complex **6** (0.68 g, 1.03 mmol) was loaded into an ampule as a solution in 5 ml of hexane. The ampule was sealed to another ampule which was evacuated to a high vacuum. After opening a breakable seal all the empty ampule was cooled by liquid nitrogen and a loaded ampule was slowly warmed to 75 °C and kept at this temperature for 2 h. Then, the ampules were sealed off, one containing hexane and btmse and the other nearly pure titanocene **7**. Crystallization from hexane afforded pure **7** as a somewhat less soluble fraction. Color of crystals was changing dependent on the angle of incident light from pale purple to pale green. The conversion of **6** to **7** is essentially quantitative, however, yield of recrystallized product was 0.33 g (67%).

M.p. 92 °C. EI MS (60 °C): m/z (relative abundance, %) 493 (9), 492 (24), 491 (52), 490 (M^+ ; 100), 489 (42), 488 ($[(Cp'_2Ti-H_2)^+]$; 51), 487 (17), 486 (20), 485 (33), 484 (11), 483 (16), 385 (12), 383 (10), 381 (7), 346 (10), 179 (9), 177 (9), 101 (8), 73 ($[SiMe_3]^+$; 81), 59 ($[SiMe_2H]^+$; 43). IR (KBr, cm^{-1}): 2953 (s), 2934 (s), 2912 (s), 2888 (sh), 2861 (vs), 2729 (vw), 1462 (m), 1381 (m), 1361 (vw), 1330 (m), 1316 (s), 1248 (vs), 1127 (w), 1071 (vw), 1021 (m), 998 (m), 917 (vw), 883 (m), 831 (s), 808 (vs), 762 (s), 679 (m), 590 (w), 442 (m), 435 (m), 428 (m). UV–Vis (hexane, 22 °C): 578 nm. 1H NMR (300 MHz, C_6D_6 , 298 K): 3.5 ($\Delta v_{1/2} \approx 90$ Hz, 6H, $SiMe_2$); 4.3 ($\Delta v_{1/2} \approx 75$ Hz, 1H, $CHMe_2$); 6.6 ($\Delta v_{1/2} \approx 40$ Hz, 6H, $CHMe_2$); 25.1 ($\Delta v_{1/2} \approx 150$ Hz, 6H, $CpMe_4-\beta$); 78.2 ($\Delta v_{1/2} \approx 320$ Hz, 6H, $CpMe_4-\alpha$).

Positions and half-widths of all observed signals are temperature dependent, with chemical shifts obeying the Curie law in the studied temperature range 293–333 K. The assignment of resonances is based on previous data for $[Ti\{\eta^5-C_5Me_4(SiMe_2Bu')\}_2]$ [**1**], $[Ti\{\eta^5-C_5Me_4(SiMe_3)\}_2]$ [**2,24**], $[Ti(\eta^5-C_5Me_4Bu')_2]$ [**5**], and $[Ti(\eta^5-C_5Me_5)_2]$ [**4a**]. The chemical shifts of resonances of two pairs of methyl groups in α - and β -position with respect to the $SiMe_2Pr^i$ substituent were tentatively assigned under the assumption that β -Me group that are surrounded by methyls only will be shielded similarly like Me groups in $[Ti(\eta^5-C_5Me_5)_2]$ where signals of Me protons appear at 22.6 ppm (at 34 °C) [**4a**].

3.8. X-ray crystallography

Crystals or crystal fragments of compounds **2**, **3**, **6**, and **7** were inserted into Lindemann glass capillaries in a glovebox and sealed by a wax. A red needle of compound **1** was mounted on a glass capillary with epoxy cement. Diffraction data were collected on a Nonius KappaCCD diffractometer. The structures were solved by direct methods (SIR-92, [**25**]) and refined by full-matrix least-squares on F^2 (SHELXL-97 [**26**]). Relevant crystallographic data are given in Table 4. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were fixed and refined in their theoretical positions except the bridging hydrides in **3** (H(1), H(2)). These were identified on difference electron density maps and refined with isotropic thermal motion parameters. The structure determination of compound **7** is hampered by vast disorder. The whole molecule is disordered along non-space group mirror going through Ti, Si, C1 atoms. Only atoms of isopropyl moiety and their “mirror” images differed sufficiently to be split into two positions and refined isotropically, for the rest of the molecule the disordered atoms are too close to each other to be distinguished and their disorder results in large displacement factor and consequently in low precision of structure determination. Neither change of space group symmetry or new measurement with another crystal at lower temperature afforded better results.

Table 4
Crystallographic data, data collection and structure refinement for compounds **1**, **2**, **3**, **6**, and **7**

Compound	1	2	3	6	7
Chemical formula	C ₂₈ H ₅₀ Cl ₂ Si ₂ Ti	C ₂₈ H ₅₀ ClSi ₂ Ti	C ₅₆ H ₁₀₄ MgSi ₄ Ti ₂	C ₃₆ H ₆₈ Si ₄ Ti	C ₂₈ H ₅₀ Si ₂ Ti
Molecular weight	561.66	526.21	1009.86	661.16	490.76
Temperature (K)	150(2)	150(2)	150(2)	293(2)	150(2)
Crystal description	red needle	turquoise bloc	blue prism	yellow bar	purple fragment
Crystal size (mm ³)	0.18 × 0.10 × 0.03	0.50 × 0.50 × 0.10	0.40 × 0.38 × 0.18	0.50 × 0.25 × 0.18	0.83 × 0.50 × 0.28
Crystal system	monoclinic	monoclinic	orthorhombic	monoclinic	monoclinic
Space group	<i>P</i> ₂ / <i>c</i>	<i>Cc</i>	<i>Pbcn</i> (No. 60)	<i>P</i> ₂ / <i>c</i>	<i>P</i> ₂ / <i>1</i> / <i>n</i>
<i>a</i> (Å)	8.1310(2)	32.8430(7)	10.3460(5)	18.7000(6)	12.8720(10)
<i>b</i> (Å)	17.0800(5)	8.8790(2)	29.2720 (7)	16.0610(7)	8.5060(4)
<i>c</i> (Å)	22.0430(5)	21.4310(4)	19.8770 (10)	13.7773(4)	13.8120(10)
α (°)	90	90	90	90	90
β (°)	92.6060(16)	105.8290(12)	90	96.751(2)	96.994(2)
γ (°)	90	90	90	90	90
<i>V</i> (Å ³)	3058.11(14)	6012.6(2)	6019.7(4)	4109.2(3)	1501.01(17)
<i>Z</i>	4	8	4	4	2
<i>D</i> _c (g cm ⁻³)	1.220	1.163	1.114	1.069	1.086
μ (Mo K α) (mm ⁻¹)	0.548	0.467	0.388	0.346	0.378
<i>F</i> (000)	1208	2280	2208	1448	536
θ Range (°)	3.02–27.47	2.98–27.49	3.16–24.63	3.71–27.50	2.82–32.04
Measured diffractions	27,464	27,826	40,779	36,987	11,412
Unique diffractions	6993	12,685	3828	9366	5139
Observed diffractions ^a	4655	10,688	2992	4938	3789
Parameters	314	611	310	392	145
<i>R</i> , <i>wR</i> obsd. diffractions	0.0445, 0.0936	0.0457, 0.0871	0.0404, 0.0895	0.0600, 0.1320	0.1011, 0.2598
<i>R</i> , <i>wR</i> all data	0.0872, 0.1084	0.0636, 0.0952	0.0577, 0.0981	0.1363, 0.1687	0.1284, 0.2833
Goodness of fit	1.032	1.004	1.054	1.019	1.030
$\Delta\rho$ (e Å ⁻³)	0.298, -0.364	0.115, -0.104	0.270, -0.215	0.262, -0.305	1.957, -0.504

^a Diffraction with $I_o > 2\sigma(I_o)$.

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Appendix A. Supplementary data

Crystallographic data, excluding structure factors, have been deposited at the Cambridge Crystallographic Data Centre (**1**: CCDC-278045, **2**: CCDC-278047, **3**: CCDC-278046, **6**: CCDC-278048, **7**: CCDC-278049). Copies of the data can be obtained free of charge upon application to CCDC (e-mail: deposit@ccdc.ac.uk). Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2005.10.018.

References

- [1] P.B. Hitchcock, F.M. Kerton, G.A. Lawless, *J. Am. Chem. Soc.* 120 (1998) 10264.
- [2] M. Horáček, V. Kupfer, U. Thewalt, P. Štěpnička, M. Polášek, K. Mach, *Organometallics* 18 (1999) 3572.
- [3] L. Lukešová, M. Horáček, P. Štěpnička, K. Fejfarová, R. Gyepes, I. Císařová, J. Kubišta, K. Mach, *J. Organomet. Chem.* 659 (2002) 186.
- [4] (a) J.E. Bercaw, R.H. Marvich, L.G. Bell, H.H. Brintzinger, *J. Am. Chem. Soc.* 94 (1972) 1219;
(b) J.E. Bercaw, *J. Am. Chem. Soc.* 96 (1974) 5087.
- [5] T.E. Hanna, E. Lobkovsky, P.J. Chirik, *J. Am. Chem. Soc.* 126 (2004) 14488.
- [6] R.D. Sanner, D.M. Duggan, T.C. McKenzie, R.E. Marsh, J.E. Bercaw, *J. Am. Chem. Soc.* 98 (1976) 8358.
- [7] V. Varga, K. Mach, M. Polášek, P. Sedmera, J. Hiller, U. Thewalt, S.I. Troyanov, *J. Organomet. Chem.* 506 (1996) 241.
- [8] L. Lukešová, M. Horáček, R. Gyepes, I. Císařová, P. Štěpnička, J. Kubišta, K. Mach, *Collect. Czech. Chem. Commun.* 70 (2005) 11.
- [9] M. Horáček, R. Gyepes, I. Císařová, M. Polášek, V. Varga, K. Mach, *Collect. Czech. Chem. Commun.* 61 (1996) 1307.
- [10] K. Mach, J.B. Raynor, *J. Chem. Soc., Dalton Trans.* (1992) 683.
- [11] W.W. Lukens, R.M. Smith III, R.A. Andersen, *J. Am. Chem. Soc.* 118 (1996) 1719.
- [12] U. Rosenthal, V.V. Burlakov, P. Arndt, W. Baumann, A. Spannenberg, *Organometallics* 22 (2003) 884.
- [13] S.I. Troyanov, V. Varga, K. Mach, *J. Chem. Soc., Chem. Commun.* (1993) 1174.
- [14] R. Gyepes, K. Mach, I. Císařová, J. Loub, J. Hiller, P. Šindelář, *J. Organomet. Chem.* 497 (1995) 33.
- [15] K. Mach, R. Gyepes, M. Horáček, L. Petrusová, J. Kubišta, *Collect. Czech. Chem. Commun.* 68 (2003) 1877.
- [16] H.H. Brintzinger, *J. Am. Chem. Soc.* 89 (1967) 6871.
- [17] J.G. Kenworthy, J. Myatt, M.C.R. Symons, *J. Chem. Soc. A* (1971) 1020.
- [18] (a) S.I. Troyanov, V. Varga, K. Mach, *J. Organomet. Chem.* 461 (1993) 85;
(b) M. Horáček, I. Císařová, J. Karban, L. Petrusová, K. Mach, *J. Organomet. Chem.* 577 (1999) 103.
- [19] M. Horáček, J. Hiller, U. Thewalt, M. Polášek, K. Mach, *Organometallics* 16 (1997) 4185.
- [20] V.V. Burlakov, A.V. Polyakov, A.I. Yanovsky, Yu.T. Struchkov, V.B. Shur, M.E. Vol'pin, U. Rosenthal, H. Görls, *J. Organomet. Chem.* 476 (1994) 197.
- [21] V. Kupfer, U. Thewalt, I. Tišlerová, P. Štěpnička, R. Gyepes, J. Kubišta, M. Horáček, K. Mach, *J. Organomet. Chem.* 620 (2001) 39.

- [22] V. Varga, J. Hiller, R. Gyepes, M. Polášek, P. Sedmera, U. Thewalt, K. Mach, *J. Organomet. Chem.* 538 (1997) 39.
- [23] H. Antropiusová, A. Dosedlová, V. Hanuš, K. Mach, *Transition Met. Chem. (London)* 6 (1981) 90.
- [24] The ^1H NMR spectrum of compound **8** was re-measured to low magnetic field (300 MHz, C_6D_6 , 298 K): 7.0 ($\Delta\nu_{1/2} \approx 80$ Hz, 9H, SiMe_3); 26.3 ($\Delta\nu_{1/2} \approx 130$ Hz, 6H, CpMe_4); 77.2 ($\Delta\nu_{1/2} \approx 270$ Hz, 6H, CpMe_4).
- [25] A. Altomare, M.C. Burla, M. Camalli, G. Cascarano, C. Giacovazzo, A. Guagliardi, G. Polidori, *J. Appl. Cryst.* 27 (1994) 435.
- [26] G.M. Sheldrick, *SHELXL97*. Program for Crystal Structure Refinement from Diffraction Data, University of Göttingen, Göttingen, 1997.