

Titanocene – 1,4,6-tris(trimethylsilyl)hex-3-ene-1,5-diyne-3-yl complexes – crystal structures and their retro reaction

Michal Horáček^a, Ivana Císařová^b, Jiří Kubišta^a, Anke Spannenberg^c, Kai Dallmann^c,
Uwe Rosenthal^{*,c,1}, Karel Mach^{a,*,1}

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

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

^c *Leibniz-Institut für Organische Katalyse an der Universität Rostock e.V., Buchbinderstrasse 5-6, D-18055 Rostock, Germany*

Received 26 April 2004; accepted 19 August 2004

Available online 25 September 2004

Abstract

Paramagnetic titanocene complexes containing the unsaturated carbyl group which consists of one and half molecule of 1,4-bis(trimethylsilyl)buta-1,3-diyne (BSD) are formed by the reduction of titanocene dichlorides with one molar equivalent of magnesium in the presence of 1.5 molar equivalent BSD in tetrahydrofuran (THF) for titanocene moieties $\text{Ti}(\eta^5\text{-C}_5\text{H}_5\text{-}_n\text{Me}_n)_2$ ($n = 5$ (**1**), **2**), and **3** (**3**)) and $\text{Ti}\{\text{Me}_2\text{Si}(\eta^5\text{-C}_5\text{Me}_4)_2\}$ (**4**). The non-methylated titanocene moiety affords under identical conditions known diamagnetic bis(η^5 -cyclopentadienyl)-2,4-bis(trimethylsilylethynyl)-3,5-bis(trimethylsilyl)titanacyclopenta-2,4-diene (**5**) as the major product. Crystal structures of **3** and **4** show the same bonding scheme for the 1,4,6-tris(trimethylsilyl)hex-3-ene-1,5-diyne-3-yl ligand as previously found for compound **1** [P.-M. Pellny, F.G. Kirchbauer, V.V. Burlakov, A. Spannenberg, K. Mach, U. Rosenthal, Chem. Commun. (1999) 2505]. Compound **1** is stable against weak proton donors like methanol or alk-1-yne even at 90 °C, however, it undergoes retroreaction when oxidized by PbCl_2 in THF, yielding nearly quantitatively BSD and $[\text{TiCl}_2(\eta^5\text{-C}_5\text{Me}_5)_2]$.

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Keywords: Titanium; Titanocene; 1,3-Butadiyne; Carbyl ligand; Bond cleavage; Electron spin resonance; X-ray crystallography

1. Introduction

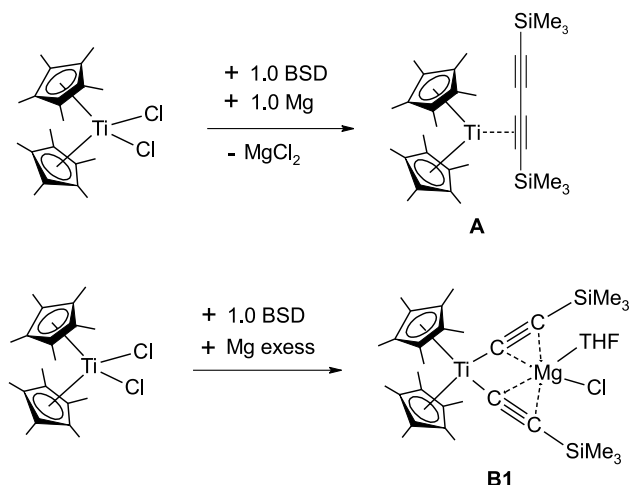
Recently, we have reported that the paramagnetic d^1 complex $[\text{Ti}(\eta^5\text{-C}_5\text{Me}_5)_2\{\eta^3\text{-Me}_3\text{SiC}_3\equiv\text{C}(\text{C}\equiv\text{CSiMe}_3)\text{-SiMe}_3\}]$ (**1**) can be obtained by the reduction of $[\text{TiCl}_2(\eta^5\text{-C}_5\text{Me}_5)_2]$ with one molar equivalent of magnesium in the presence of 1.5 equivalents of 1,4-bis(trimethylsilyl)buta-1,3-diyne (BSD) in tetrahydrofuran [1]. The formation of **1** requires essential keeping to the above

* Corresponding author. Tel.: +420266053735; fax: +420286582307.

E-mail address: mach@jh-inst.cas.cz (K. Mach).

¹ Both highly appreciate a smooth, long-time publishing cooperation with this journal.

mentioned stoichiometry: when the BSD:Ti ratio equals to 1.0 and the Mg/Ti ratio is also 1.0 a simple adduct with one coordinated triple bond (**A**) is obtained [2] whereas an excess of magnesium gives rise to tweezer complexes $[\text{Ti}(\eta^5\text{-C}_5\text{H}_5\text{-}_n\text{Me}_n)_2(\text{C}\equiv\text{CSiMe}_3)_2]^- [\text{Mg}(\text{THF})\text{Cl}]^+$ ($n = 5, 4$) (**B**₁, **B**₂) in a process involving the scission of BSD molecule [3] (Scheme 1). The non-methylated titanocene–bis(trimethylsilyl)ethyne (BTMSE) complex $[\text{Ti}(\eta^5\text{-C}_5\text{H}_5)_2(\eta^2\text{-Me}_3\text{SiC}\equiv\text{CSiMe}_3)]$ reacted with 2.0 equivalents of BSD to give the diamagnetic titanacyclopentadiene complex **5** [4], and with 0.5 equivalent of BSD the dimeric Ti(III) titanocene-acetylide (**C**) [5] (Scheme 2). Of the above mentioned products the tweezer complex **B**₁ was used as a catalyst for linear dimerization



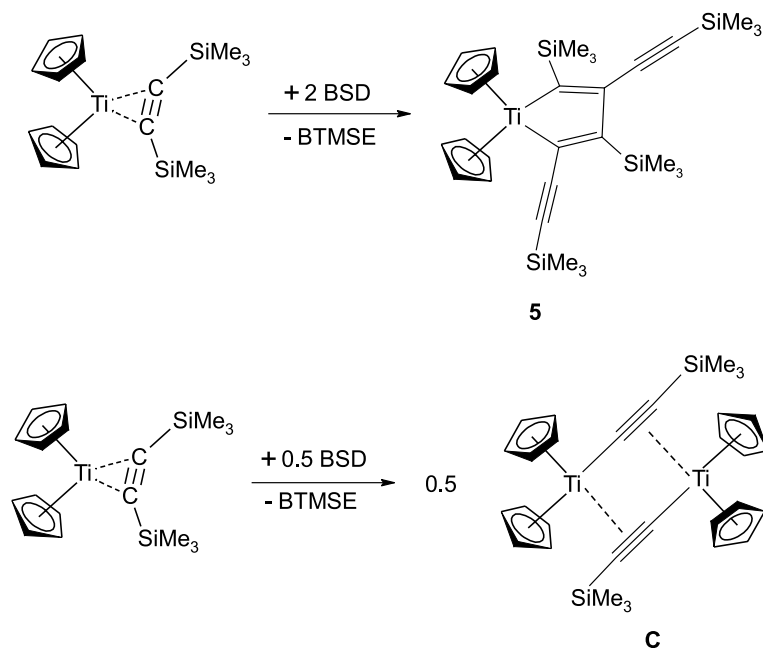
Scheme 1.

of alk-1-ynes [6] and compound **5** was explored for the synthesis of thiophene derivative, 2,4-bis(trimethylsilyl)thiophene [7]; the chemical reactivity of **1** has not been studied yet. The purpose of this work is to establish whether analogs of compound **1** are formed for the less methyl-substituted titanocene moieties $\text{Ti}(\eta^5\text{-C}_5\text{H}_{5-n}\text{Me}_n)_2$ ($n = 4, 3, \text{ or } 0$) and for the more opened *ansa*- $\text{Ti}\{\text{Me}_2\text{Si}(\eta^5\text{-C}_5\text{Me}_4)_2\}$ sandwich, and to establish the reactivity of compound **1** towards weak protonic acids and oxidation by PbCl_2 .

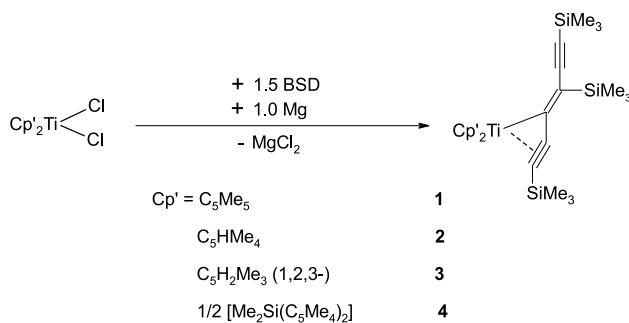
2. Results and discussion

The reduction of methyl-substituted titanocene dichlorides $[\text{TiCl}_2(\eta^5\text{-C}_5\text{H}_{5-n}\text{Me}_n)_2]$ ($n = 5, 4, \text{ and } 3$)

by magnesium in the presence of 1.5 molar equivalent of BSD in THF affords nearly quantitatively titanocene (Ti^{III}) complexes (**1**, **2**, and **3**, respectively) with 1,4,6-tris(trimethylsilyl)hex-3-ene-1,5-diyne-3-yl carbene ligand (L) whose C(1–2) triple bond is π -coordinated to the titanium atom (for **1** see [1]). Fully analogous product **4** was also obtained from *ansa*- $[\text{TiCl}_2\{\text{Me}_2\text{Si}(\eta^5\text{-C}_5\text{Me}_4)_2\}]$ upon the same treatment (Scheme 3). All the complexes display a similar EI-MS fragmentation, showing a low abundant molecular ion and $[\text{M} - \text{HL}]^+$ ion as a base peak. The characteristic fragments are also a highly abundant ion m/z 179 $[\text{C}_4(\text{SiMe}_3)_2\text{-Me}]^+$, its low-abundant precursor m/z 194 $[\text{C}_4(\text{SiMe}_3)_2]^+$, highly abundant m/z 73 $[\text{SiMe}_3]^+$ and moderately abundant m/z 97 $[\text{C}_2\text{SiMe}_3]^+$. The other spectroscopic data also showed that the structure of the coordinated hex-3-ene-1,5-diyne ligand did not vary remarkably with stereoelectronic changes in titanocene skeleton of **1–4**. A decreasing electron density on the metal with decreasing number of methyl substituents on cyclopentadienyl ligands in **1**, **2**, and **3** or a sterically more opened skeleton of **4** did not result in noticeable changes in IR $\nu(\text{C}\equiv\text{C})$ wavenumbers of the non-coordinated ($2098\text{--}2104 \text{ cm}^{-1}$) triple bonds which were accompanied by a weak satellite band occurring at wavenumbers higher by 42 (2) cm^{-1} . The double bond of the ligand weakly absorbs in the range of $1548\text{--}1568 \text{ cm}^{-1}$. The coordinated triple bonds were found absorbing in the range $1834\text{--}1859 \text{ cm}^{-1}$, however, the lowest value was found for **2** and the highest values for **1** and **4**. The absence of an expected decrease of $\nu(\text{C}\equiv\text{C})$ wavenumbers with increasing number of Me groups on the cyclopentadienyl ligands as demonstrated e.g., in $\text{Ti}(\eta^5\text{-C}_5\text{H}_{5-n}\text{Me}_n)_2(\eta^2\text{-BTMSE})$



Scheme 2.



Scheme 3.

($n = 0-5$) complexes [8] precludes to correlate the strength of coordination with electronic factors induced by cyclopentadienyls ligands in **1-3**. This is also true for evaluation of ESR spectra whose g_{iso} values spanned a narrow range 1.9913(3) for **1** and 1.9947(3) for **4**. These values, close to the values of η^3 -allyl titanocenes [9], and narrow linewidths of the ESR single line signal (ΔH 1.9–4.0 G) indicate that the unpaired electron density is residing largely on ligand L. A low electron density at the titanium atom was corroborated by finding of very low a_{Ti} coupling (2.7 G) observed in compound **1** which displayed the linewidth of 1.7 G only [1]. The ESR spectrum thus does not fit to the formula containing σ -bond between the titanium(III) atom and the C-3 carbon of the C₆ ligand (see Scheme 1) because such a structure should give a lower g -value and a larger linewidth of ESR signal (e.g., $\Delta H > 10$ G for alkyl [10a,10b] or acetylide [10c,10d]). The ESR spectra rather suggest an η^3 -bonded ligand as depicted in Chart 1 (values in Å for Ti–C and C–C bonds of **1** [1]). The crystallographic bond lengths for **1** [1], **3**, and **4** also corroborate the view of the bonding electron delocalized over C1–C3 carbon atoms of the carbyl ligand (vide infra). The electronic absorption spectra of all the compounds display one absorption band in the 500–600 nm region and a weaker band close to 1000 nm. The former one falls into the region where titanocene(Ti^{III}) compounds absorb [11], the latter coincides with the band occurring in the titanocene–BTMSE complexes where, however, a strong back donation interaction of Ti(II) with the triple bond

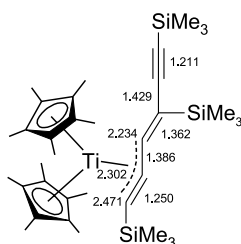


Chart 1.

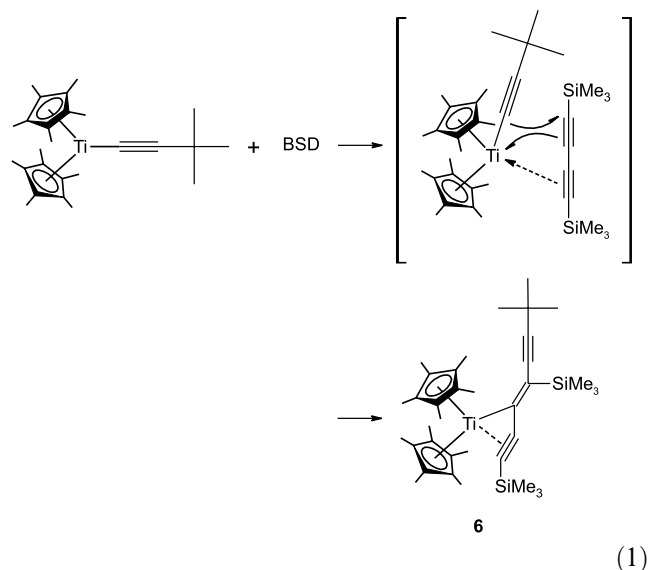
shifted $\nu(\text{C}\equiv\text{C})$ wavenumbers down to 1662–1598 cm^{-1} [8]. A much smaller shift of $\nu(\text{C}\equiv\text{C})$ of the coordinated triple bond in **1-4** reflects the fact that the Ti(III) atom in highly methyl-substituted titanocene moieties is a weak Lewis acid only. E.g., the $[\text{TiCl}(\eta^5\text{-C}_5\text{H}_{5-n}\text{Me}_n)_2]$ complexes for $n = 3$ and 4 coordinate THF only at low temperature while for $n = 5$ [12a] and the *ansa*- $[\text{Me}_2\text{Si}(\eta^5\text{-C}_5\text{Me}_4)_2\text{TiCl}]$ complex [12b] do not coordinate it at all.

The reduction of $[\text{TiCl}_2(\eta^5\text{-C}_5\text{H}_5)_2]$ under the same stoichiometry of all components as in the above experiments afforded diamagnetic compound **5** [4] as far the main isolated product in the yield of 65%. The identity of the compound was determined by single-crystal X-ray diffraction analysis, EI-MS and IR spectra. The mother liquor after crystallization of **5** contained a small amount of a paramagnetic product whose ESR data ($g_{\text{iso}} = 1.995$, $\Delta H = 2.5$ G, $a_{\text{Ti}} = 3.2$ G) could be compatible with the presence of $[\text{Ti}(\eta^3\text{-Me}_3\text{SiC}\equiv\text{C}-\text{C}(\text{C}\equiv\text{CSiMe}_3)=\text{CSiMe}_3)(\eta^5\text{-C}_5\text{H}_5)_2]$. The corresponding tweezer complex, if stable, should have likely a larger a_{Ti} coupling constant (cf. **B2**: $g_{\text{iso}} = 1.9935(3)$, $\Delta H = 2.5$ G, $a_{\text{Ti}} = 7.3$ G [2,13]). This overwhelming formation of **5** means that lowering of the number of methyl substituents on the cyclopentadienyl ligands to zero favours the double cycloaddition of BSD even when at least 1/4 of the titanocene compound has to be converted into another, unknown product(s).

2.1. On the mechanism of formation of the 1,4,6-tris(trimethylsilyl)hex-3-ene-1,5-diyne-3-yl carbyl ligand

Since the reacting system is heterogeneous the molar ratios of the components do change both in time and at the magnesium surface. Under such conditions both the products shown in Scheme 1 as well as the monomeric acetylide $[\text{Ti}(\text{III})(\text{C}\equiv\text{CSiMe}_3)(\eta^5\text{-C}_5\text{Me}_5)_2]$ (**D**) can be considered to be intermediates in the formation of **1-4**. Compound **D**, at variance with the non-substituted acetylide **C** (Scheme 2), does not dimerize because the electron-donating effect of methyl substituents makes the titanium less electropositive. The composition of **1-4** implies that an intermediate with cleaved BSD combines with BSD or with a compound containing uncleaved BSD or vice versa, and the nature of the primary intermediate is therefore the clue to the mechanism. To prove one of the possible ways and to differentiate between acetylide groups, $[\text{Ti}(\text{C}\equiv\text{CCMe}_3)(\eta^5\text{-C}_5\text{Me}_5)_2]$ [14] was reacted with one equivalent of BSD. Under very mild conditions the titanocene containing the 1,4-bis(trimethylsilyl)-6-*t*-butylhex-3-ene-1,5-diyne-3-yl carbyl ligand (**6**) was obtained as far the main product (Eq. (1)). Its composition and atom connectivity was proved by X-ray crystallography [15]. The structure of **6** was solved easily, however, the diffraction data were of low quality

due to an extensive disorder over the permethylcyclopentadienyl ligands and trimethylsilyl groups. The structure of **6** showed that the reaction pathway through an acetylide intermediate is feasible, however, its formation through the tweezer intermediate **B** (Scheme 1) cannot be excluded. Similar zirconocene(IV)-ate complex $\text{Li}[\text{Zr}(\text{C}\equiv\text{CPh})_3(\eta^5\text{-C}_5\text{H}_5)_2]$ was assumed by Negishi [16] as an intermediate in the reaction of $[\text{ZrCl}_2(\eta^5\text{-C}_5\text{H}_5)_2]$ with 3 equivalents of $\text{LiC}\equiv\text{CPh}$, however, Choukroun et al. [17] isolated from such a system a Zr(II) complex and determined its crystal structure as $\text{Li}[\text{Zr}(\eta^5\text{-C}_5\text{H}_5)_2(\text{C}\equiv\text{CPh})(\eta^2\text{-PhC}\equiv\text{CC}\equiv\text{Ph})]$. Such a complex in our (non-ionic) case represents an intermediate complex preceding the insertion of π -coordinated triple bond of BSD into the Ti–C bond of the acetylide (see Eq. (1)). The insertion reaction is apparently driven by a steric congestion of the intermediate complex and by a decrease of electronic energy. Reversely, stability of the above zirconium complex compared to the corresponding Ti intermediate in Eq. (1) is enhanced due to a higher electropositivity and larger covalent radius of Zr and a smaller size of non-substituted cyclopentadienyl ligands.



2.2. Reactivity of **1** toward weak protonic acids and PbCl_2

Compound **1** was further investigated for their reactivity toward terminal alkynes, methanol, and PbCl_2 . It appeared to be completely unreactive toward common terminal alkynes where no reaction was observed after heating to 90 °C for 10 h. After treating solid **1** in anhydrous methanol to 90 °C for 24 h only traces of a yellow-brown oil were found while compound **1** remained largely unreacted. On the other hand, the oxidation of **1** by one equivalent of PbCl_2 [18] in

THF resulted in nearly quantitative formation of the titanocene dichloride, and the only organic product of the reaction was BSD. This result indicates that a retro reaction proceeds with a high efficiency. Retro reactions proceed generally effectively for products of cycloaddition reactions, and in titanocene chemistry a recent example is known. The cyclizations of pendant alkenyl groups induced by the reduction of titanocene dichlorides to titanocenes yielding cyclopentadienyl ring-tethered titanacyclopentane derivatives undergo a retro reaction upon oxidation with PbCl_2 to give initial titanocene dichlorides with restored pendant alkenyl groups [19].

2.3. Crystal structures of complexes **3** and **4**

The crystal structures of compounds **3** and **4** are very similar to the structure of **1** [1] as it is seen from comparison of geometric parameters given in Table 1. The view of the compounds is represented by ORTEP drawing of molecule of **3** in Fig. 1. The bent titanocene moieties differ in the bite angle ϕ whose magnitude is determined by the steric congestion at the hinge position for **1** and **3** and by *ansa*- SiMe_2 bridge in **4**. The steric hindrance of methyl groups in the hinge position of staggered cyclopentadienyl rings of **1** makes the bite angle smaller than in **3** whose staggered cyclopentadienyl rings have only hydrogen atoms at the hinge positions ($\sim 41^\circ$ versus $49.4(2)^\circ$). The fixed eclipsed cyclopentadienyl rings due to the *ansa*- SiMe_2 bridge in **4** determine the largest bite angle of $53.0(1)^\circ$. The planar 1,4,6-tris(trimethylsilyl)hex-3-ene-1,5-diyne-3-yl ligand has virtually the same structure in all the compounds. The differences in bond lengths and valence angles given in Table 1 are smaller than threefold esd's except for the angles C14–C15–C16 ($171.8(2)^\circ$ for **4**, $175.3(3)^\circ$ for **3** and $173.2(4)^\circ$ for **1**). The π -coordinated triple bond C2–C3 is prolonged ($1.248(4)$ – $1.251(3)$ Å) compared to the non-coordinated one (C14–C15 $1.211(5)$ Å) and the double bond C1–C16 is longer ($1.353(4)$ – $1.362(5)$ Å) than the free double bond (1.33 Å). The C1–C2 bond $1.376(3)$ – $1.386(5)$ Å indicates a large contribution of sp^2 hybridization. Similar bond lengths were found in 1,4-substituted η^3 -butenyne ligands bonded to transition metals, e.g., Ru [20], Os [21], W [22] and Fe [23], and in zirconocene- η^3 -propargyl complexes [24].

2.4. Conclusions

Electronically “rich” methyl-substituted titanocene moieties $\text{Ti}(\eta^5\text{-C}_5\text{H}_5\text{-}_n\text{Me}_n)_2$ ($n = 5, 4,$ and 3) and $\text{Ti}\{\text{Me}_2\text{Si}(\eta^5\text{-C}_5\text{Me}_4)_2\}$ form Ti(III) complexes **1**–**4** with the 1,4,6-tris(trimethylsilyl)hex-3-ene-1,5-diyne-3-yl

Table 1
Selected bond lengths (Å) and angles (°) for complexes **3** and **4** and **1**

	3	4	1
<i>Bond distances</i>			
Ti–Cg1 ^a	2.073(2)	2.079(1)	2.112(5) ^c
Ti–Cg2 ^a	2.072(2)	2.082(1)	2.105(5) ^c
Ti–C1	2.220(3)	2.222(2)	2.234(4)
Ti–C2	2.294(3)	2.290(2)	2.302(4)
Ti–C3	2.417(3)	2.438(2)	2.471(4)
C1–C2	1.379(4)	1.376(3)	1.386(5)
C2–C3	1.248(4)	1.251(3)	1.250(5)
C1–C16	1.353(4)	1.356(3)	1.362(5)
C15–C16	1.430(4)	1.429(3)	1.429(5)
C14–C15	1.211(4)	1.211(3)	1.211(5)
Si1–C14	1.822(3)	1.826(2)	1.830(4)
Si2–C16	1.893(3)	1.884(2)	1.884(4)
Si3–C3	1.852(3)	1.855(2)	1.850(4)
<i>Bond angles</i>			
Cg1–Ti–Cg2	135.4(2)	135.2(1)	139.2(2) ^c
Si3–C3–C2	143.5(3)	142.7(2)	141.2(3)
C1–C2–C3	149.4(3)	150.9(2)	152.0(3)
C2–C1–C16	133.9(3)	133.1(2)	130.7(3)
C1–C16–C15	120.6(3)	122.3(2)	122.1(3)
C14–C15–C16	175.3(3)	171.8(2)	173.3(4)
Si1–C14–C15	179.2(3)	178.4(2)	177.3(4)
Si2–C16–C1	121.5(2)	124.4(2)	121.0(3)
C1–Ti–C3	66.1(1)	65.9(1)	65.6(1)
ϕ^b	49.4(2)	53.0(1)	$\sim 41^c$
$\psi 1^c$	25.1(2)	27.0(1)	–
$\psi 2^d$	24.5(2)	26.0(1)	–

^a Cg1 and Cg2 denote the centroids of the C(4–8) and C(9–13) cyclopentadienyl rings, respectively.

^b Dihedral angle subtended by the cyclopentadienyl least-squares planes.

^c Dihedral angle between the least-squares plane of the C(4–8) cyclopentadienyl ring and the least-squares plane of the Ti, C1, C2, C3 moiety.

^d Dihedral angle between the least-squares plane of the C(9–13) cyclopentadienyl ring and the least-squares plane of the Ti, C1, C2, C3 moiety.

^e Average values of disordered parameters of cyclopentadienyl rings.

ligand (L). The non-methylated titanocene moiety affords under identical conditions the known diamagnetic Ti(IV) complex bis(η^5 -cyclopentadienyl)-2,4-bis(trimethylsilylethynyl)-3,5-bis(trimethylsilyl)titanacyclopent-2,4-diene **5** as the major product. Compound **1** is stable against weak proton donors like methanol or alk-1-yne even at 90 °C, however, it undergoes retroreaction when oxidized by PbCl₂ in THF, yielding BSD and permethyl-titanocene dichloride. The ease of the retro-reaction and its high efficiency imply a relatively simple and straightforward reaction pathways including a scission of ligand L and recombination of (trimethylsilyl)ethynyl radicals to BSD. Intermediacy of Ti(III) (trimethylsilyl)ethynyl complexes, following from the synthesis of **6** from Ti(III)-*t*-butylethynyl complex and BSD corroborates the above opinion.

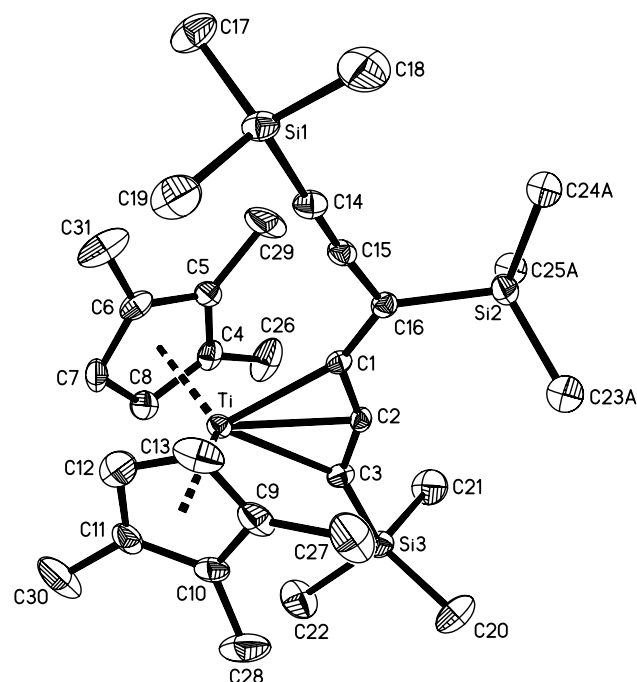


Fig. 1. Molecular structure of **3** (30% probability thermal motion ellipsoids) showing the atom numbering scheme. For clarity, the disordered positions of carbon atoms in the trimethylsilyl group (Si2) and all hydrogen atoms are omitted.

3. Experimental

3.1. General comments

Reductions of titanocene dichlorides by magnesium in the presence of 1,4-bis(trimethylsilyl)buta-1,3-diyne (BSD) in THF and all subsequent manipulations with solutions of the products were performed on a vacuum line in all-glass devices equipped with magnetically breakable seals. A combined device equipped with a pair of quartz cuvettes (10.0 and 1.0 mm, Hellma) and a Spectrosil quartz tube were used for UV–near IR and EPR measurements, respectively. Crystals for EI-MS measurements and melting point determinations were placed into glass capillaries and samples in KBr pellets for infrared measurement were prepared in a glovebox Labmaster 130 (mBraun) under purified nitrogen (concentrations of oxygen and water lower than 2.0 ppm). ESR spectra were registered on an ERS-220 spectrometer (Centre for Production of Scientific Instruments, Academy of Sciences of GDR, Berlin, Germany) equipped with a magnet controlling and data acquisition CU1 unit (Magnetech, Berlin, Germany) in the X-band. *g*-Values were determined using an Mn²⁺ (*M*₁ = –1/2 line) standard at *g* = 1.9860. An STT-3 variable temperature unit was used for the measurement in the range from –140 to +20 °C. UV–near IR measurements were performed on a Varian Cary 17 D spectrometer in the range 340–2000 nm. EI-MS spectra were obtained on

a VG-7070E double-focusing mass spectrometer at 70 eV. Crystalline samples in sealed capillaries were opened and inserted into the direct inlet under argon. The spectra are represented by the peaks of relative abundance higher than 6% and by important peaks of lower intensity. IR spectra were recorded in an air-protecting cuvette on a Nicolet Avatar FT IR spectrometer in the range of 400–4000 cm^{-1} .

3.2. Chemicals

Solvents THF, hexane, and toluene were dried by refluxing over LiAlH_4 and stored as solutions of dimeric titanocene $[(\mu-\eta^5:\eta^5\text{-C}_{10}\text{H}_8)(\mu\text{-H})_2\{\text{Ti}(\eta^5\text{-C}_5\text{H}_5)\}_2]$ [25] on a vacuum line. Magnesium turnings (Aldrich, purum for Grignard reactions) and BSD (Aldrich) were used as obtained. Titanocene dichlorides $\text{TiCl}_2(\eta^5\text{-C}_5\text{H}_5\text{-}_n\text{Me}_n)_2$ ($n = 5\text{--}3$) [26] and $\text{TiCl}_2\{\text{Me}_2\text{Si}(\eta^5\text{-C}_5\text{Me}_4)_2\}$ [27] were obtained by the literature procedures.

3.3. Preparation of complexes 1–4

All the complexes 1–4 were prepared by the general procedure using 2.0 mmol of the respective titanocene dichloride, 2 mmol of magnesium and 3.0 mmol of BSD in 15 ml of THF as reported for 1 in preliminary communication [1]. The mixture was stirred at 40 °C until all the magnesium disappeared; the reaction time depended on the length of induction period which was irreproducible even when using the same reagents. The procedure to obtain 2: $[\text{TiCl}_2(\eta^5\text{-C}_5\text{HMe}_4)_2]$ (0.722 g, 2.0 mmol), BSD 0.583 g, 3.0 mmol), and magnesium (0.0486 g, 2.0 mmol) were weighed into an ampoule equipped with a Teflon-coated magnetic stirrer and two breakable seals on a vacuum line, and after evacuation, 20 ml of THF was distilled in. The mixture was stirred at 40 °C until all metallic magnesium disappeared (after 21 h). The final dirty green solution was evaporated in vacuum and the residue was extracted by 20 ml of hexane. The solution was concentrated to ca. 5 ml and cooled to -18 °C for several days for crystallization. Dark green crystals were separated, washed with a cooled hexane and dried in vacuum. Yield of 2: 0.79 g (1.36 mmol, 68%). 2; m.p. 151 °C. MS (direct inlet, 140 °C; m/z (%)): 582 (3), 581 (M^+ ; 5), 292 (14), 291 (21), 290 (67), 289 ($[\text{M} - \text{HC}_6(\text{SiMe}_3)_3]^+$; 100), 288 (21), 287 (21), 285 (11), 278 (7), 277 (21), 180 (7), 179 ($[\text{C}_4(\text{SiMe}_3)_2\text{-Me}]^+$; 35), 168 (8), 167 (11), 166 (10), 165 (6), 164 (8), 155 (11), 97 (9), 73 ($[\text{SiMe}_3]^+$; 51). IR (KBr, cm^{-1}): 2947 (s), 2896 (s), 2854 (m), 2140 (vw), 2098 (s), 1836 (s), 1548 (w), 1480 (w), 1435 (m), 1371 (m), 1328 (vw), 1242 (vs), 1140 (s), 1100 (m), 1002 (s), 942 (vw), 830 (vs,b), 748 (s), 690 (m), 637 (m), 623 (w), 615 (vw), 529 (m), 460 (w). ESR (toluene): $g = 1.9935(3)$, $\Delta H = 2.1$ G; (toluene, -140 °C): $g_{\parallel} = 2.002$, $g_{\perp} = 1.992$, $g_{\text{av}} = 1.995$. UV–NIR (hexane,

23 °C): 305 > 330(sh) > 350(sh) \gg 550 > 1000(sh) nm. Calc. for $\text{C}_{33}\text{H}_{53}\text{Si}_3\text{Ti}$: C, 68.11; H, 9.18. Found: C, 67.97; H, 9.09%.

Compound 3 was obtained as brown crystals in yield 0.59 g (1.06 mmol, 53%); m.p. 103 °C. EI-MS (direct inlet, 120 °C; m/z (%)): 554 (4), 553 (M^+ ; 6), 480 ($[\text{M} - \text{SiMe}_3]^+$; 1), 277 (11), 263 (17), 262 (56), 261 ($[\text{M} - \text{HC}_6(\text{SiMe}_3)_3]^+$; 100), 260 (21), 259 (14), 190 (6), 179 ($[\text{C}_4(\text{SiMe}_3)_2\text{-Me}]^+$; 15), 155 (7), 154 (6), 73 ($[\text{SiMe}_3]^+$; 51). IR (KBr, cm^{-1}): 3067 (vw), 2947 (s), 2893 (s), 2854 (m), 2720 (vw), 2143 (vw), 2102 (s), 1840 (s), 1560 (w), 1478 (w), 1444 (m), 1398 (w), 1372 (m), 1302 (vw), 1242 (vs), 1442 (s), 1096 (m), 1020 (m), 1007 (s), 933 (vw), 834 (vs,b), 793 (sh), 772 (s), 751 (s), 690 (m), 634 (s), 618 (m), 525 (w), 475 (vw), 452 (w). ESR (hexane): $g = 1.9945(3)$, $\Delta H = 2.7$ G. UV–NIR (hexane, 23 °C): 305 \sim 330 > 350(sh) \gg 510(sh) > 1000 nm. Calc. for $\text{C}_{31}\text{H}_{49}\text{Si}_3\text{Ti}$: C, 67.22; H, 8.92. Found: C, 67.09; H, 9.00%.

Compound 4 was obtained in yield 0.99 g (1.55 mmol, 78%). *ansa*- $\text{Me}_2\text{Si}(\text{C}_5\text{Me}_4)_2\text{Ti}[\text{C}_6(\text{SiMe}_3)_3]$; m.p. 212 °C. EI-MS (temp. 170 °C; m/z relative abundance (%)): 638 (5), 637 (M^+ ; 8), 347 (18), 346 (42), 345 ($[\text{M} - \text{HC}_6(\text{SiMe}_3)_3]^+$; 100), 344 (14), 343 (10), 330 (5), 179 ($[\text{Me}_3\text{SiC}_4\text{SiMe}_2]^+$; 5), 73 ($[\text{SiMe}_3]^+$; 2). IR (KBr, cm^{-1}): 2955 (vs), 2899 (s), 2870 (m), 2146 (vw), 2104 (s), 1859 (m), 1568 (vw), 1452 (w), 1406 (vw), 1377 (w), 1350 (vw), 1316 (w), 1248 (vs), 1140 (m), 1008 (m), 841 (vs,b), 758 (s), 674 (m), 638 (m), 623 (vw), 526 (vw), 469 (m). EPR (toluene, 23 °C): $g = 1.9947(3)$, $\Delta H = 4.0$ G; (toluene, -140 °C): $g_{\parallel} = 2.002$, $g_{\perp} = 1.993$, $g_{\text{av}} = 1.996$. UV–NIR (hexane, 23 °C): 350(sh) \gg 600(sh) > 970(sh). Calc. for $\text{C}_{35}\text{H}_{57}\text{Si}_4\text{Ti}$: C, 65.88; H, 9.00. Found: C, 65.79; H, 8.94%.

Spectroscopic data for 1: m.p. 206 °C. EI-MS (direct inlet, 160 °C; m/z (%)): 609 (M^+ ; 6), 320 (10), 319 (30), 318 (88), 317 ($[\text{M} - \text{HC}_6(\text{SiMe}_3)_3]^+$; 100), 316 (27), 315 (14), 313 (7), 292 ($[\text{HC}_6(\text{SiMe}_3)_3]^+$; 16), 278 (9), 277 ($[\text{HC}_6(\text{SiMe}_3)_3\text{-Me}]^+$; 27), 182 (8), 181 (9), 180 (10), 179 ($[\text{C}_4(\text{SiMe}_3)_2\text{-Me}]^+$; 19), 178 (7), 155 (14), 119 (8), 97 ($[\text{C}_2\text{SiMe}_3]^+$; 10), 83 (7), 73 ($[\text{SiMe}_3]^+$; 51). IR (KBr, cm^{-1}): 2954 (vs), 2898 (vs), 2854 (m), 2715 (vw), 2146 (vw), 2104 (s), 1857 (s), 1547 (vw), 1493 (w), 1451 (m), 1432 (m), 1402 (w), 1377 (s), 1246 (vs), 1143 (s), 1106 (m), 1006 (s), 943 (vw), 840 (vs,b), 755 (s), 693 (m), 677 (w), 637 (s), 621 (w), 612 (vw), 526 (w), 455 (w). ESR (toluene): $g = 1.9913(3)$, $\Delta H = 1.7$ G, $a_{\text{Ti}} = 2.7$ G; (toluene, -140 °C): $g_{\parallel} = 2.002$, $g_{\perp} = 1.990$, $g_{\text{av}} = 1.994$. UV–NIR (hexane, 22 °C): 305 > 330(sh) > 350(sh) \gg 600(sh) > 1000(sh) nm.

3.4. Attempted synthesis of $[\text{Ti}\{\text{C}_6(\text{SiMe}_3)_3\}(\text{C}_5\text{H}_5)_2]$

Analogously to the above procedures $[\text{TiCl}_2(\eta^5\text{-C}_5\text{H}_5)_2]$ (0.498 g, 2.0 mmol), BSD 0.583 g, 3.0 mmol), and magnesium (0.0486 g, 2.0 mmol) were weighed into

an ampoule equipped with a Teflon-coated magnetic stirrer and two breakable seals on a vacuum line, and after evacuation, THF (20 ml) was distilled in. The mixture was stirred at 40 °C until all metallic magnesium disappeared (after 5 h). The final brown solution was evaporated in vacuum and the residue was extracted by 20 ml of hexane. The solution was concentrated to ca. 5 ml and cooled to –18 °C for several days for crystallization. Brown crystals were separated, washed with a cooled hexane and dried in vacuum. This product was diamagnetic, and the X-ray single crystal analysis proved the compound is identical with previously described complex $[(C_5H_5)_2Ti\{C_8(SiMe_3)_4\}]$ (**5**) [3]. Yield: 0.50 g (44%). No products in addition to **5** were isolated from this experiment. A small quantity of paramagnetic $[Ti\{C_6(SiMe_3)_3\}(C_5H_5)_2]$ was very probably contained in the mother liquor after crystallization of **5**. Its presence was indicated by ESR spectra only. ESR (hexane): $g = 1.995$, $\Delta H = 2.5$ G, $a_{Ti} = 3.2$ G; (toluene, –140 °C): $g_1 = 2.002$, $g_2 = 1.994$, $g_3 = 1.990$, $g_{av} = 1.995$.

3.5. Attempted reactions of **1** with terminal alkynes HCCR ($R = t\text{-Bu}$, $SiMe_3$) or methanol

Solid crystalline **1** (0.1 g, 0.16 mmol) was weighed into an ampoule in a glovebox, degassed on a vacuum line, and $HC\equiv CMe_3$ or $HC\equiv CSiMe_3$ or MeOH (2.0 ml each) were added by distillation on the line. The sealed ampoules were heated to 90 °C in a water bath for 5 h. Compound **1** was completely dissolved in the alkynes but only partly in MeOH. The solutions were dirty green colored. Then, the ampoules were attached to the vacuum line, the alkynes or methanol were distilled into a trap under vacuum, the residue was dissolved in hexane, and crystallized out by cooling. The alkynes were analyzed by GC–MS for the presence of dimers with negative results. Compound **1** was recovered unchanged in all cases as determined by IR spectra in KBr pellets and EI–MS analyses.

3.6. Reaction of $[Ti(CCCMe_3)(\eta^5-C_5Me_5)_2]$ with BSD

$[Ti(C\equiv CMe_3)(\eta^5-C_5Me_5)_2]$ (250 mg, 0.63 mmol) and BSD 122 mg, 0.63 mmol) were dissolved in 20 ml of hexane at room temperature and kept at this temperature overnight. The initial brown colour of the solution turned green. After evaporation of ca. 15 ml of hexane in vacuum and cooling the solution to –30 °C overnight black crystals of the adduct $[Ti\{\eta^3-Me_3SiC\equiv CC=C(C\equiv CMe_3)SiMe_3\}(\eta^5-C_5Me_5)_2]$ (**6**) were obtained. Yield: 0.357 g (0.60 mmol, 96%); m.p. 179–181 °C. Anal. Calc. C, 72.81; H, 9.67. Found: C, 72.26; H, 9.98%. Crystal structure of this compound suffered from extensive disorder, however, atom connectivity was safely established.

3.7. Oxidation of **1** with $PbCl_2$ in THF

Compound **1** (0.9 g, 1.5 mmol) was dissolved in THF (15 ml), and the solution was poured onto degassed $PbCl_2$ (0.28 g, 1.0 mmol). This mixture was stirred and heated to 70 °C for 6 h. The green solution turned reddish, and black lead precipitated at the bottom. The solution was poured away from lead, and concentrated in vacuum. Brown-red $[TiCl_2(\eta^5-C_5Me_5)_2]$ crystallized out from green mother liquor. Its identity was proved by infrared spectrum in KBr pellet and by EI–MS analysis. The mother liquor was evaporated in vacuum and the residue was extracted by hexane. A green solution was separated from another portion of low soluble $[TiCl_2(\eta^5-C_5Me_5)_2]$, and the hexane and all volatile products were distilled into a trap cooled by liquid nitrogen, finally from boiling water bath. The non-volatile residue was dissolved in a minimum of hexane and crystallized by cooling. The crystalline material was identified by IR and EI–MS measurements and by single-crystal X-ray diffraction analysis to be the initial compound **1**. The distillate was evaporated at room temperature to remove hexane. A white crystalline material was weighed and then identified by GC–MS analysis and by IR spectra to be pure BSD. Its yield was 0.268 g (1.38 mmol, 92% on $PbCl_2$).

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

Compound	3	4
Chemical formula	$C_{31}H_{49}Si_3Ti$	$C_{35}H_{57}Si_4Ti$
Molecular weight	553.87	638.07
Crystal system	Triclinic	Triclinic
Space group	$P\bar{1}$ (No. 2)	$P\bar{1}$ (No. 2)
T (K)	200(2)	150(2)
a (Å)	9.925(2)	9.4550(2)
b (Å)	11.187(2)	10.6780(2)
c (Å)	15.543(3)	19.9090(4)
α (°)	81.80(3)	78.1740(10)
β (°)	82.57(3)	88.8910(12)
γ (°)	89.99(3)	72.9500(11)
V (Å ³)	1693.5(6)	1879.11(7)
Z	2	2
Crystal size (mm ³)	$0.5 \times 0.5 \times 0.4$	$0.5 \times 0.2 \times 0.1$
D_{calc} (g cm ^{–3})	1.086	1.128
μ (Mo $K\alpha$) (mm ^{–1})	0.375	0.377
$F(000)$	598	690
θ Range (°)	1.84–24.17	3.09–27.56
h, k, l Range	–10/10, –12/12, 0/17	–12/12, –12/13, –25/25
Diffractions collected	5038	34658
Independent diffraction	5038	8537
Diffractions observed	3617	6843
Number of parameters	313	380
R, wR [$I > 2\sigma(I)$]	0.0456, 0.1132	0.0427, 0.0949
R, wR (all data)	0.0662, 0.1194	0.0601, 0.1033
S	0.978	1.021
$\Delta\rho_{max,min}$ (e Å ^{–3})	0.414, –0.319	0.320, –0.392

3.8. X-ray crystallography

Dark brown crystal fragments of **3** and **4** were inserted into a Lindemann glass capillaries and closed by a wax under purified nitrogen in a glovebox (mBraun), and the capillaries were then sealed by flame. Diffraction data of **3** were collected on a STOE-IPDS diffractometer using graphite-monochromated Mo K α radiation, and those of **4** on a Nonius KappaCCD diffractometer and analyzed by HKL program package [28]. The structure of **3** was solved by direct methods (SHELXS-86) [29] and refined by full-matrix least-squares techniques against F^2 (SHELXL-93) [30]. The structure of **4** was solved by direct methods (SIR-97 [31]), followed by consecutive Fourier syntheses and refined by full-matrix least-squares on F^2 (SHELX-97 [32]). In **3**, all non-hydrogen atoms except the carbon atoms of the disordered group were refined anisotropically. In **4**, all non-hydrogen atoms were refined anisotropically. In both the structures, hydrogen atoms were placed in ideal positions and refined as riding atoms. Relevant crystallographic data are given in Table 2.

4. Supplementary material

Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre (CCDC-236312 for **3**, CCDC-236703 for **4**). These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge, CB2 1EZ, UK; fax: +44 1223 336033; or deposit@ccdc.cam.ac.uk).

Acknowledgements

This investigation was supported by the Grant Agency of the Czech Republic (Project No. 203/02/0774). The Grant Agency of the Czech Republic also sponsored access to Cambridge Structure Database (Grant No. 203/02/0436).

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