

Bis[(η^8 -cyclooctatetraene)titanium] complex with perpendicularly bridging bis(trimethylsilyl)acetylene

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Abstract

The reduction of $[(\eta^8\text{-C}_8\text{H}_8)\text{Ti}(\text{THF})(\mu\text{-Cl})_2]$ by magnesium in the presence of bis(trimethylsilyl)acetylene (BTMSA) afforded the diamagnetic complex $[(\eta^8\text{-C}_8\text{H}_8)\text{Ti}]_2[\mu\text{-}\eta^2\text{-}\eta^2\text{-Me}_3\text{SiC}\equiv\text{CSiMe}_3]$ (**1**) in high yield. The crystal structure of **1** revealed that BTMSA is a four-electron ligand which binds two equivalent $(\eta^8\text{-C}_8\text{H}_8)\text{Ti}$ moieties under the angle of av. 69° . The average C–C distance of 1.51 Å in the acetylene ligand is close to that of sp^3 carbon atoms, however, a high thermal stability and enormously large down-field chemical shift of the acetylenic carbon atoms (δ 292.8 ppm) points to an unusually high contribution of π -back-bonding to the Ti–acetylene bond. An analogous reduction in the presence of diphenylacetylene afforded a tetraphenylcyclobutadiene complex $(\eta^8\text{-C}_8\text{H}_8)\text{Ti}(\eta^4\text{-C}_4\text{Ph}_4)$ and hexaphenylbenzene. © 1998 Elsevier Science S.A. All rights reserved.

Keywords: Titanium; Cyclooctatetraene dianion; Bis(trimethylsilyl)acetylene bridge; Crystal structure

1. Introduction

The titanocene-bis(trimethylsilyl)acetylene (BTMSA) complexes $(\text{C}_5\text{H}_5\text{-}_n\text{Me}_n)_2\text{Ti}[\eta^2\text{-Me}_3\text{SiC}\equiv\text{CSiMe}_3]$ ($n = 0\text{--}5$) form a class of well-defined Ti(II) complexes whose stability is enhanced by electron back-bonding interactions. They are easily obtained by the reduction of $(\text{C}_5\text{H}_5\text{-}_n\text{Me}_n)_2\text{TiCl}_2$ compounds by magnesium in THF in the presence of BTMSA [1,2]. They undergo easy substitution of BTMSA by other acetylenic ligands [1,3,4], rearrangements after thermally induced loss of BTMSA [2], or redox reactions with suitable ligands, e.g. with 2,2'-bipyridine [5,6] or 4,5-diazafluorene [5] to give $(\text{C}_5\text{H}_5\text{-}_n\text{Me}_n)_2\text{Ti(III)}$ complexes. The permethylated complex $(\text{C}_5\text{Me}_5)_2\text{Ti}[\eta^2\text{-Me}_3\text{SiC}\equiv\text{CSiMe}_3]$ is a superior catalyst for the head-to-tail dimerization of terminal acetylenes, whereas all other less methylated titanocene-BTMSA complexes ($n = 0\text{--}4$) are almost

inactive [7]. The Me substituents also influence the reactivity of the $(\text{C}_5\text{H}_5\text{-}_n\text{Me}_n)_2\text{Ti}[\eta^2\text{-Me}_3\text{SiC}\equiv\text{CSiMe}_3]$ ($n = 0\text{--}5$) complexes towards excess Mg: for $n = 0\text{--}2$ they yield binuclear Ti–Mg and trinuclear Ti–Mg–Mg complexes containing perpendicularly bridging BTMSA ligands between Ti and Mg atoms [8], while more methyl-substituted complexes are inert under the same conditions. Increasing number of Me groups in the $(\text{C}_5\text{H}_5\text{-}_n\text{Me}_n)_2\text{Zr}[\eta^2\text{-C}_2(\text{SiMe}_3)_2]$ ($n = 0\text{--}5$) complexes leads to a decreasing capability of the complexes to coordinate one molecule of THF solvent [9]. This is largely due to the electron donating effect of Me groups, however, steric hindrance may also contribute in highly methyl substituted compounds. In light of these results an attempt to prepare the $(\eta^8\text{-C}_8\text{H}_8)\text{Ti}[\eta^2\text{-Me}_3\text{SiC}\equiv\text{CSiMe}_3]$ complex, where no steric congestion is to be supposed, has been of interest.

Here we report the formation, properties and crystal structure of a novel BTMSA complex which arises by magnesium reduction of $(\eta^8\text{-C}_8\text{H}_8)\text{Ti}^{\text{III}}$ chloride.

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2. Experimental details

All manipulations, syntheses and most of spectroscopic measurements were carried out under vacuum using all-sealed glass devices equipped with breakable seals. The adjustment of single crystals into capillaries for X-ray analysis, preparation of KBr pellets and filling of IR KBr cuvettes were performed in a glovebox under atmosphere of nitrogen or argon.

2.1. Chemicals

The solvents THF, hexane, toluene and benzene- d_6 were purified by conventional methods, dried by refluxing over LiAlH_4 and stored as solutions of dimeric titanocene (C_{10}H_8)[$(\text{C}_5\text{H}_5)\text{Ti}(\mu\text{-H})_2$] [10]. Cyclooctatetraene (COT, Fluka) was degassed and distilled under vacuum onto solid dimeric titanocene. After standing overnight, it was distilled and distributed into ampoules on a vacuum line. Bis(trimethylsilyl)acetylene (BTMSA, Fluka) was degassed, stored as a solution of dimeric titanocene for 4 h and distilled into ampoules. TiCl_4 (Enzymes Intern.) was degassed, refluxed with copper wire for 2 h and distributed into ampoules by vacuum distillation. *n*-Butyllithium (BuLi) in hexane (1.6 M) (Chemetall, Frankfurt) was handled by syringe technique under argon. Potassium cyclooctatetraenide [11] was prepared from potassium (0.5 g, 13.0 mmol) and COT (0.7 ml, 6.4 mmol) in 40 ml of THF. The reaction mixture was shaken at 40°C until the potassium nearly completely disappeared to give a golden yellow solution of $\text{K}_2\text{C}_8\text{H}_8$. TiCl_3 was obtained by adding BuLi in hexane (1.6 M, 5.0 ml) to TiCl_4 (0.9 ml, 8.0 mmol) in 50 ml of THF under stirring. The mixture was refluxed for 30 min and the resulting brown precipitate was washed several times with THF and finally recrystallized from hot THF to give 2.4 g (6.5 mmol) of pale blue $\text{TiCl}_3 \cdot 3\text{THF}$. $[(\eta^8\text{-C}_8\text{H}_8)\text{TiCl} \cdot \text{THF}]_2$ was prepared by slow addition of $\text{K}_2\text{C}_8\text{H}_8$ in THF to a suspension of $\text{TiCl}_3 \cdot 3\text{THF}$ in THF as described elsewhere [12]. A bright green solution was poured away from a white solid of KCl containing a small amount of light blue crystals of $\text{TiCl}_3 \cdot 3\text{THF}$. Evaporation of the solution afforded large green crystals of $[(\text{C}_8\text{H}_8)\text{Ti}(\text{THF})(\mu\text{-Cl})_2]$. The compound was identified by its EI-MS and IR (KBr pellet) spectra, which agreed with the literature data [12]. Yield 1.0 g (1.9 mmol, 60%).

2.2. Methods

^1H -, ^{13}C - and ^{29}Si -NMR spectra were measured on a Varian UNITY Inova 400 spectrometer (399.95, 100.58 and 79.46 MHz, respectively) in C_6D_6 at 25°C. Chemical shifts (given in the δ scale) were referenced to the solvent signal (δ_{H} 7.15 ppm, δ_{C} 128.0 ppm) and to a solution of SiMe_4 in C_6D_6 as the external reference.

^{29}Si -NMR spectra were obtained using a standard DEPT pulse sequence. UV-vis spectra were measured in the range 270–2000 nm on a Varian Cary 17D spectrometer using all-sealed quartz cuvettes (Hellma). EI-MS spectra were measured on a VG-7070E double-focusing mass spectrometer (70 eV, 50 μA , 200°C). Samples in capillaries were opened and inserted into the direct inlet under argon. The spectra are represented by the peaks of relative abundance not < 5% and by important peaks of lower intensity. IR spectra were obtained on a Mattson Galaxy 2020 spectrometer. KBr pellets from estimated amounts of solid samples were prepared in a glovebox under purified nitrogen and were measured under nitrogen atmosphere in a closed cuvette.

2.3. Preparation of $[(\eta^8\text{-C}_8\text{H}_8)\text{Ti}]_2[\mu\text{-}\eta^2\text{-}\eta^2\text{-C}_2(\text{SiMe}_3)_2]$ (**1**)

Solid $[(\text{C}_8\text{H}_8)\text{TiCl} \cdot \text{THF}]_2$ (1.0 g, 1.9 mmol) was dissolved in 30 ml of THF and this solution was added to Mg turnings (0.24 g, 10 mmol) and BTMSA (2.0 ml, 9.0 mmol). The mixture was heated to 60°C for 8 h. The brown solution obtained was separated from excess magnesium and evaporated under vacuum. The dark residue was repeatedly extracted by 80 ml of hexane in a closed system to give a green solution. The residue obtained by evaporation of the extract was dissolved in hexane upon warming to 80°C and crystallized to give green elongated prisms. These did not melt up to 300°C under nitrogen in a sealed capillary. Yield of crystalline **1** was 0.68 g (76%). **1**: MS (210°C; m/z (%)): 474(M^+ ; 6.0), 401($[\text{M-SiMe}_3]^+$; 1.5), 304($[\text{M-BTMSA}]^+$; 100), 302(41), 276(6), 274(8), 224(9), 222(7), 170(6), 155(72), 152(21), 104(15), 103(11), 78(14), 77(8), 73(20). ^1H -NMR (C_6D_6): δ –0.15 (s, 18H, $2 \times \text{SiMe}_3$); 6.60 (s, 16H, COT). ^{13}C -NMR (C_6D_6): δ 2.8 (q, 6C, $2 \times \text{SiMe}_3$); 97.2 (d, 16C, COT); 292.8 (s, 2C, $\text{C}\equiv\text{C}$). ^{29}Si -NMR (C_6D_6): δ –26.9 (s, $2 \times \text{SiMe}_3$). UV-vis (λ_{max} , hexane): 350 $\gg$ 670 (br) nm. IR (KBr, cm^{-1}): 3042 w, 2949 m, 2890 w, 1875 vw, 1786 vw, 1640 vw, 1499 vw, 1433 w, 1391 w, 1317 w, 1235 s, 1146 m, 912 w, 850 vs, 826 s, 799 m, 762 m, 723 vs, 629 m, 432 w.

2.4. Reduction of $[(\text{C}_8\text{H}_8)\text{TiCl} \cdot \text{THF}]_2$ by Mg in the presence of diphenylacetylene

The reduction procedure followed in all respects the synthesis of **1** using diphenylacetylene (1.6 g, 9.0 mmol) instead of BTMSA. A green-brown reaction mixture was evaporated and the residue was extracted by hexane. The first fractions, which were brown, were removed and only the subsequent ones, which were green, were collected. The extraction continued until all green product was extracted. The residue contained MgCl_2 and hexaphenylbenzene. The collected extracts were

evaporated and fractionally extracted by hexane. The green, more soluble fraction contained $(\eta^8\text{-C}_8\text{H}_8)\text{Ti}(\eta^4\text{-C}_4\text{Ph}_4)$ (**2**), the less soluble part was colourless hexaphenylbenzene. Yield of **2** (containing ca. 1% of C_6Ph_6 according to ^{13}C -NMR spectrum) was 0.15 g (0.3 mmol, 15%). An estimated yield of C_6Ph_6 , largely in the residue after the first crude extraction, was 0.4 g (25%). **2**: MS (210–220°C; m/z (%)): 508(M^+ ; 100), 356(3), 254(M^{2+} ; 2), 224(3), 178(26), 152(95), 126(6), 124(7), 113(6), 98(3), 48(7). ^1H -NMR (C_6D_6): 6.22 (s, 8H, COT), 6.95–7.05 (m, 4H, Ph), 7.12–7.18 (m, 8H, Ph) and 7.43–7.48 (m, 8H, Ph). ^{13}C -NMR (C_6D_6) (all signals singlets): 98.9 (COT), 104.3 ($\eta^4\text{-C}_4\text{Ph}_4$); 124.7, 127.8 and 128.1 (CH, Ph), 138.1 (C_{ipso} , Ph). All spectral data are in good agreement with those reported in literature [13].

2.5. X-ray crystal structure analysis of **1**

A dark-green crystal fragment was mounted in a Lindemann glass capillary under purified nitrogen in a glovebox (mBraun Labmaster 130) and was sealed by wax. The X-ray measurements were carried out on a Philips PW 1100 four-circle diffractometer using graphite-monochromated Mo $\text{K}\alpha$ radiation (λ 0.71069 Å) at r.t. Crystal data were collected using $\omega - 2\theta$ scan. The structures were solved by Patterson method and developed by Fourier syntheses which yielded positions of all non-hydrogen atoms. Their coordinates and anisotropic thermal parameters were refined at first using the SHELX-76 program [14]. The final refinements were performed by full-matrix least-squares methods on all unique F_o^2 data using SHELXL-93 program [15]. Hydrogens were included in the theoretical positions. Crystallographic data for **1** are summarized in Table 1. The atomic positional parameters have been deposited at the Cambridge Crystallographic Data Centre under deposition number 101479.

3. Results and discussion

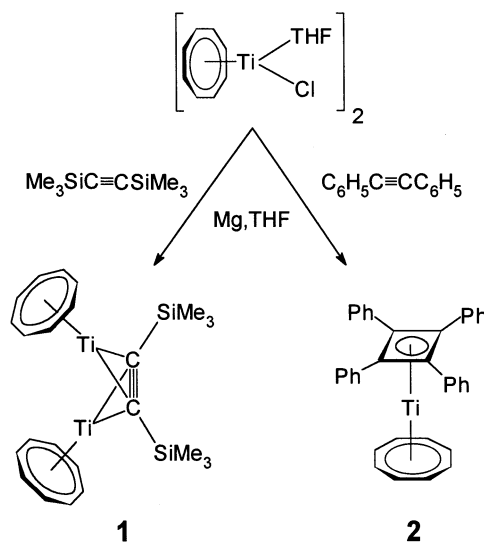
The Ti(III) complex $[(\eta^8\text{-C}_8\text{H}_8)\text{Ti}(\text{THF})(\mu\text{-Cl})_2]$ in THF is reduced by magnesium in the presence of excess BTMSA to give the dark green crystalline diamagnetic Ti(II) complex $[(\eta^8\text{-C}_8\text{H}_8)\text{Ti}]_2[\mu\text{-}\eta^2\text{:}\eta^2\text{-C}_2(\text{SiMe}_3)_2]$ (**1**) as the only isolated product. On the other hand, the analogous reaction in the presence of excess diphenylacetylene affords the known complex $(\eta^4\text{-C}_4\text{Ph}_4)(\eta^8\text{-C}_8\text{H}_8)\text{Ti}$ [**2**] and hexaphenylbenzene (Scheme 1). The difference in the reaction pathway is determined by the reactivity of the acetylenes; while BTMSA is reluctant to oligomerize [16], diphenylacetylene (DPA) easily cyclotrimerizes and cyclotetramerizes in the presence of various Ti-based catalytic systems [17]. Compound **2** is an intermediate or a byproduct in the DPA cyclotrimerization [13,18].

Table 1

Crystallographic data for **1**

Formula	$\text{C}_{24}\text{H}_{34}\text{Si}_2\text{Ti}_2$
Molecular weight	474.49
Crystal system	Monoclinic
Space group	$P2_1$ (No. 4)
Unit cell dimensions	
a (Å)	15.7109(14)
b (Å)	9.8031(6)
c (Å)	16.5190(12)
β (°)	92.807(9)
V (Å ³)	2541.1(3)
Z	4
D_{calc} (g cm ⁻³)	1.240
μ_{calc} (cm ⁻¹)	0.730
$F(000)$	1000
Crystal size (mm ³)	$0.6 \times 0.5 \times 0.4$
Data collection	
θ_{min} , θ_{max} (°)	3.23, 24.98
Range of hkl indices	–18 to 18, 0 to 11, 0 to 19
Reflections collected	4734
Independent reflections	4734
Data, restraints, parameters	4730, 0, 506
Goodness-of-fit on F^2	1.125
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.109$, $wR_2 = 0.288$
R indices (all data)	$R_1 = 0.121$, $wR_2 = 0.308$
Absolute structure parameter	0.18(11)
Min., max. residual electron density (e Å ⁻³)	–0.57, 1.09

The structural motif of **1** was inferred from its ^1H - and ^{13}C -NMR spectra which showed the presence of two equivalent C_8H_8 ligands affording single signals in both spectra and one BTMSA ligand exerting one



Scheme 1.

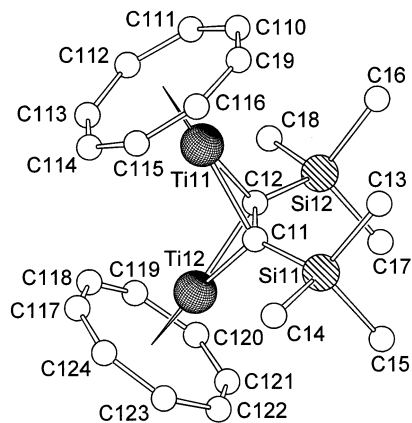


Fig. 1. PLUTON drawing of molecule 1 of $(\mu\text{-}\eta^2\text{-}\eta^2\text{-C}_8\text{H}_8\text{Ti}(\text{SiMe}_3)_2)[(\eta^8\text{-C}_8\text{H}_8)\text{Ti}]_2$ (**1**) with atom labelling scheme. The hydrogen atoms are omitted for clarity.

proton and one carbon signal corresponding to the SiMe_3 group and one carbon signal of the acetylenic carbon atoms. The COT-to-BTMSA ratio of 2:1 obtained from NMR measurements was further confirmed by electron impact mass spectrum which showed the molecular ion $[(\text{C}_8\text{H}_8\text{Ti})_2 \cdot \text{BTMSA}]^+$. The most abundant fragment ion m/z 304 arose through the loss of BTMSA. Less intense fragment ions corresponding to $(\text{M-SiMe}_3)^+$, $(\text{COTTi})^+$, $(\text{COT})^+$ and $(\text{SiMe}_3)^+$ also corroborated the molecular composition as outlined above. The IR spectrum is dominated by intense bands of the SiMe_3 group at 1235 cm^{-1} and 849 cm^{-1} . In contrast to titanocene-BTMSA complexes, no absorption band(s) attributable to the coordinated $\text{C}\equiv\text{C}$ bond is observed down to 1300 cm^{-1} . An intense absorption band non-assignable to the COT ligand is observed only at 1146 cm^{-1} .

The molecular structure of **1** becomes apparent from the X-ray crystal structure analysis. The PLUTON drawing (Fig. 1) shows that two $(\eta^8\text{-C}_8\text{H}_8)\text{Ti}$ moieties

are bound to one BTMSA ligand which is situated in a perpendicularly bridging position with respect to the metal atoms. Compound **1** contains two pairs of slightly inequivalent molecules in the unit cell. Molecule **1** is rather symmetrical, with approximately equal distance between the titanium atoms and carbon atoms of the acetylene (Fig. 2). In molecule **2**, each of the titanium atoms is closer to an opposite carbon atom of the acetylene by about 0.2 Å than to the other one. Simultaneously, a torsion angle of the silicon atoms with respect to the $\text{C}\equiv\text{C}$ bond is as large as 20° (Fig. 2). Important bond distances and valence angles for molecules (**1**) and (**2**) are listed in Table 2. Accuracy of the structure parameters suffers from a large thermal motion in both COT rings and trimethylsilyl groups. The cyclooctatetraenetitanium moieties have the least squares planes of their rings perpendicular to the Ti-CE (CE-centroid of the COT ring) vectors and the Ti-C distances (av. 2.31 Å) fall into the range of values found for $(\text{C}_8\text{H}_8)\text{Ti}(\text{C}_5\text{H}_5)$ (av. 2.32 Å) [19], $(\text{C}_8\text{H}_8)\text{Ti}(\text{C}_5\text{Me}_5)$ (av. 2.34 Å) [20], $(\text{C}_8\text{H}_8)_2\text{Ti}$ (av. 2.32 Å) [21] and $(\text{C}_8\text{H}_8)_3\text{Ti}_2$ (av. 2.35 Å) [22]. The average bond length of the Ti atoms to acetylenic carbon atoms is $2.06(2)\text{ Å}$ and this is close to the distances found in $(\text{C}_5\text{HMe}_4)_2\text{Ti} \cdot \text{BTMSA}$ ($2.106(3)\text{ Å}$) [2] and $(\text{C}_5\text{Me}_5)_2\text{Ti} \cdot \text{BTMSA}$ (av. $2.124(3)\text{ Å}$) [1] complexes. The angle between the planes defined by the Ti atoms and carbon atoms of the BTMSA ligand amounts to av. 69° . The least squares plane defined by the centroids of COT rings (CE) and titanium atoms [e.g. CE(1), CE(2), Ti(1) and Ti(2)] intersects the acetylenic bond in its centre (within the error of measurement). The angles defined by the silicon atoms and the two acetylene carbon atoms $136.5\text{--}138.7^\circ$ are also close to the values typical of the $(\text{C}_5\text{H}_5\text{--nMe}_n)_2\text{Ti} \cdot \text{BTMSA}$ complexes ($134.8\text{--}136.8^\circ$) [1,2]. At variance with the latter complexes, which have the acetylenic C-C bond lengths

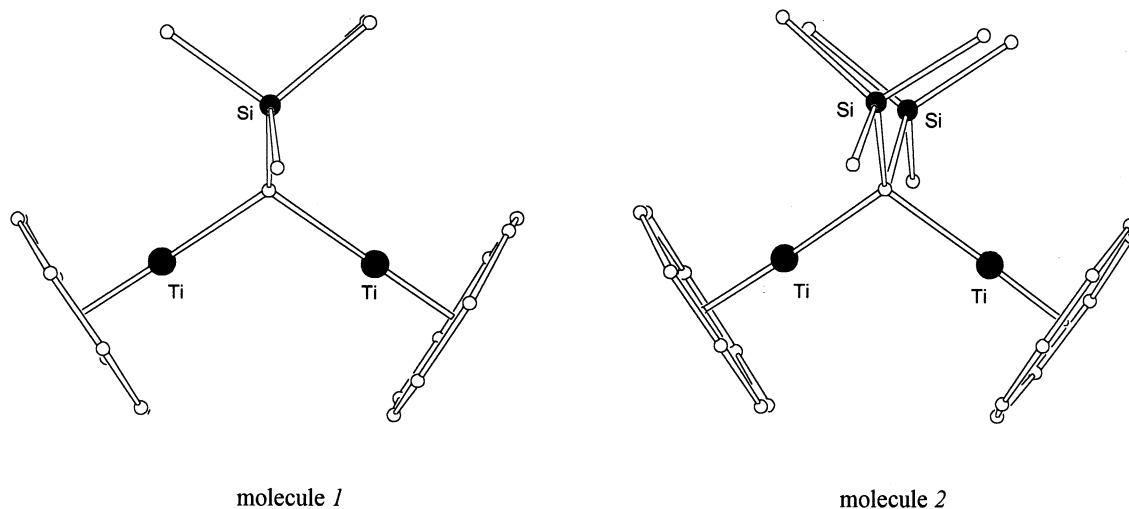
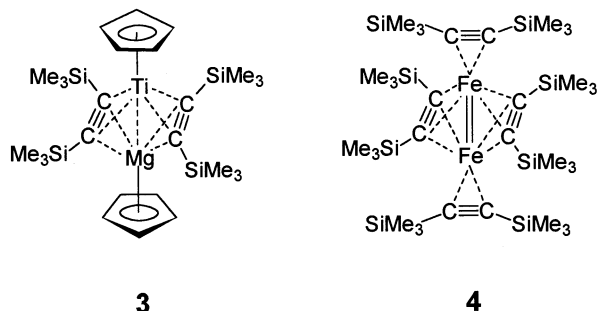


Fig. 2. View of molecule 1 and molecule 2 of compound **1** along the C-C bond of the acetylene.



Scheme 2.

1.303(5) Å and 1.309(4) Å, respectively, the average C–C bond length in **1** is as long as 1.51(2) Å.

This extraordinary long C–C distance, falling into the range of sp^3 carbon bonds, is compatible with the shift of $\nu(C\equiv C)$ vibration to 1146 cm^{-1} , close to the range of $\nu(C-C)$ vibrations. The extra large ^{13}C -NMR chemical shift δ_{C} 290.8 ppm of the acetylenic carbon atoms suggests an unusually strong π -back-bonding interaction of the titanium d^2 electrons with antibonding acetylene orbitals. The model of such an interaction in bimetallic complexes with perpendicularly bridging acetylene ligands has been based on extended Hückel MO calculations [23]. The exceptional bonding situation in **1** follows from the comparison of spectroscopic and geometric parameters in similar titanium-BTMSA complexes given in Table 3. In the titanocene·BTMSA complexes, the $d(C\equiv C)$ distance exhibits a low sensitivity to the number of methyl groups at the Cp ligands, however, δ_{C} ($C\equiv C$), δ_{Si} and $\nu(C\equiv C)$ clearly show that electron donation effect of methyl groups brings about a stronger coordination of BTMSA [2].

The spectroscopic parameters of the $[(\eta^5\text{-C}_5\text{H}_5)\text{Ti}][\mu\text{-}\eta^2\text{-}\eta^2\text{-Me}_3\text{SiC}\equiv\text{CSiMe}_3]_2[(\eta^5\text{-C}_5\text{H}_5)\text{Mg}]$ complex (**3**) [24], where two BTMSA ligands bind the Ti and Mg ions (Scheme 2), imply a considerably enhanced bonding involvement of BTMSA, however, the $C\equiv C$ distance is still close to that of a double bond. In **1**, the length of acetylenic C–C bond is close to the usual length between two sp^3 carbon atoms and the chemical shift of the carbon atoms shows on extremely low electron density seen by the carbon nuclei. Reasons for this shift cannot be sought in the valence strain at the carbon

Table 2

Selected bond distances (Å) and angles (°) for **1** (molecule 1 and molecule 2)

	Molecule 1		Molecule 2	
Bond distances (Å)				
Ti(11)–C(11)	2.061(14)	Ti(21)–C(21)	2.20(2)	
Ti(11)–C(12)	2.017(13)	Ti(21)–C(22)	1.97(2)	
Ti(11)–CE(11)	1.439(2)	Ti(21)–CE(21)	1.421(2)	
Ti(12)–C(11)	2.046(13)	Ti(22)–C(21)	1.882(14)	
Ti(12)–C(12)	2.050(14)	Ti(22)–C(22)	2.07(2)	
Ti(12)–CE(12)	1.412(2)	Ti(22)–CE(22)	1.435(2)	
Si(11)–C(11)	1.811(13)	Si(21)–C(21)	1.814(14)	
Si(11)–C _{Me} (av.)	1.83(3)	Si(21)–C _{Me} (av.)	1.88(3)	
Si(12)–C(12)	1.854(13)	Si(22)–C(22)	1.86(2)	
Si(12)–C _{Me} (av.)	1.87(3)	Si(22)–C _{Me} (av.)	1.88(3)	
C(11)–C(12)	1.53(2)	C(21)–C(22)	1.49(2)	
Ti(11)–Ti(12) ^a	3.127(4)	Ti(21)–Ti(22) ^a	3.133(4)	
Bond angles (°)				
CE(11)–Ti(11)–C(11)	156.4(12)	CE(21)–Ti(21)–C(21)	153.5(10)	
CE(11)–Ti(11)–C(12)	159.5(11)	CE(21)–Ti(21)–C(22)	164.9(13)	
CE(12)–Ti(12)–C(11)	159.4(17)	CE(22)–Ti(22)–C(22)	154.9(13)	
CE(12)–Ti(12)–C(12)	156.6(19)	CE(22)–Ti(22)–C(21)	160.7(19)	
C(12)–Ti(11)–C(11)	44.0(5)	C(22)–Ti(21)–C(21)	41.5(6)	
C(11)–Ti(12)–C(12)	43.8(5)	C(21)–Ti(22)–C(22)	44.2(7)	
C(12)–C(11)–Si(11)	136.5(10)	C(22)–C(21)–Si(21)	137.9(11)	
C(12)–C(11)–Ti(12)	68.2(7)	C(22)–C(21)–Ti(22)	74.5(8)	
Si(11)–C(11)–Ti(12)	129.0(8)	Si(21)–C(21)–Ti(22)	132.8(11)	
C(12)–C(11)–Ti(11)	66.5(7)	C(22)–C(21)–Ti(21)	60.9(8)	
Si(11)–C(11)–Ti(11)	130.3(7)	Si(21)–C(21)–Ti(21)	124.7(8)	
Ti(12)–C(11)–Ti(11)	99.2(5)	Ti(22)–C(21)–Ti(21)	99.8(6)	
C(11)–C(12)–Si(12)	138.7(9)	C(21)–C(22)–Si(22)	137.4(11)	
C(11)–C(12)–Ti(11)	69.5(7)	C(21)–C(22)–Ti(21)	77.7(9)	
Si(12)–C(12)–Ti(11)	128.6(8)	Si(22)–C(22)–Ti(21)	126.1(9)	
C(11)–C(12)–Ti(12)	67.9(7)	C(21)–C(22)–Ti(22)	61.3(8)	
Si(12)–C(12)–Ti(12)	128.0(7)	Si(22)–C(22)–Ti(22)	129.4(8)	
Ti(11)–C(12)–Ti(12)	100.5(5)	Ti(21)–C(22)–Ti(22)	101.7(7)	

^a Nonbonding distances.

atoms as in tris(*tert*-butyl)(trimethylsilyl)tetrahydronaphthalene $\text{C}_4(t\text{-Bu})_3(\text{SiMe}_3)$ the skeleton carbon atoms bearing *tert*-butyl groups exert δ_{C} 13.3 ppm and that one bearing the SiMe_3 group δ_{C} –23.0 ppm [26]. Only the actual loss of valence electrons leads to such a large deshielding effect in non-metallic systems. For instance, the pagodane dication $[\text{C}_{20}\text{H}_{20}]^{2+}$ with the charge delocalized over the cyclobutadiene ring gives chemical shift of these carbon atoms δ_{C} 251 ppm [27].

Table 3

^{13}C -NMR, ^{29}Si -NMR and IR data and structure parameters of the BTMSA ligand in **1** and related complexes

Complex	$\delta_{\text{C}}(C\equiv C)$ (ppm)	$\delta_{\text{Si}}(\text{SiMe}_3)$ (ppm)	$\nu(C\equiv C)$ (cm^{-1})	$d(C\equiv C)$ (Å)	$d(\text{Ti}-\text{C})$ (Å)	C–C–Si (°)	Ref.
1	292.8	–26.9	1146	av. 1.51	av. 2.06	av. 137	This work
3	269.1	–13.7	1510	av. 1.32	av. 2.04	av. 140	[24]
$\text{Me}_2\text{Si}(\text{C}_5\text{Me}_4)_2\text{Ti} \cdot \text{BTMSA}$	254.9	—	1580	1.297(5)	av. 2.099	av. 139	[25]
$(\text{C}_5\text{Me}_5)_2\text{Ti} \cdot \text{BTMSA}$	248.5	–17.3	1595	1.309(4)	av. 2.124	av. 136	[1]
$(\text{C}_5\text{H}_5)_2\text{Ti} \cdot \text{BTMSA}$	244.8	–14.4	1662	—	—	—	[2]

The redistribution of π -bonding electrons of BTMSA over two titanium atoms and probably of two pairs of d-electrons into antibonding orbitals of BTMSA generates surprisingly strong Ti–C bonds. Compound **1** is extremely thermally stable since it neither melts nor visually decomposes up to 300°C in a sealed capillary under dinitrogen. It does not react with trimethylsilylacetylene and pentamethylcyclopentadiene. When suspended in anhydrous methanol it slowly decomposes upon heating to 60°C. In THF solution, it is only slowly oxidized by excess PbCl_2 [28] to give grey lead. This high stability of **1** is remarkable also because the Ti–Ti distance of 3.13 Å precludes a direct bonding interaction between the titanium atoms (covalent radius of Ti 1.32 Å). This is at variance with a number of late transition metal binuclear complexes with bridging acetylenes, where the metal–metal distance below 3.0 Å anticipates a metal–metal bonding [29]. The acetylenic carbon atoms in such complexes are deshielded at maximum to δ 250 ppm. Among them, tetrakis-[bis(trimethylsilyl)acetylene]diiron (**4**) (Scheme 2) is structurally most relevant to **1**. The C≡C bond lengths of outer BTMSA ligands (1.288(3) Å) and bridging BTMSA ligands (1.314(3) Å) and the Fe–Fe distance of 2.465(1) Å indicate a usual involvement of the back-bonding mechanism and the participation of the metal–metal bonding [30]. ^{13}C -NMR spectrum of **4** was not measured due to its low solubility, however, the C–C bond lengths suggest chemical shifts in a usual region δ_{C} 200–250 ppm.

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