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Reactions of titanocene-bis(trimethylsilyl)ethyne complexes with diethynylsilane derivatives

Michal Horáček [a], Natalya Bazyakina [a,1], Petr Štepnička [b], Róbert Gyepes [b], Ivana Císařová [b], Stéphane Bredeau [c], Philippe Meunier [c], 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, Charles University, Prague, Czech Republic*
[c] *Laboratoire de Synthèse et d'Electrosynthèse Organométalliques associé au CNRS (LSEO UMR 5632), Université de Bourgogne, Faculté des Sciences Gabriel, Dijon, France*

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Abstract

Titanocene complexes $[Ti(\eta^5\text{-}C_5H_{5-n}Me_n)_2(\eta^2\text{-}Me_3SiC{\equiv}CSiMe_3)]$ ($n = 0$, 4 and 5) react uniformly with siladiynes $R^2_2Si(C{\equiv}CR^1)_2$, where $R^1 = Ph$, and $R^2 = Ph$ or Me, at elevated temperature in hydrocarbon solvents to give the corresponding silacyclobutene-annelated titanacyclobutene complexes, 3-bis(η^5-cyclopentadienyl)titana-6-diorganylsilabicyclo[2.2.0]hexa-1(2),4(5)-dienes, $[(\eta^5\text{-}C_5H_{5-n}Me_n)_2Ti\{R^1_2C_4(SiR^2_2)\}]$. Products arising from $[Ti(\eta^5\text{-}C_5H_{5-n}Me_n)_2(\eta^2\text{-}Me_3SiC{\equiv}CSiMe_3)]$ ($n = 0$, 2 (1,3-isomer), 4 and 5) and $Me_2Si(C{\equiv}CCMe_3)_2$ vary with n: the non-methylated titanocene complex affords a mixture of an analogous silacyclobutene-annelated titanacyclobutene and $[\{Ti(\eta^5\text{-}C_5H_5)_2\}_2\{\mu\text{-}\eta(3\text{–}5){:}\eta(4\text{–}6)\text{-}Me_3CC{=}CC{=}CCMe_3\}]$, the permethylated titanocene precursor gives mainly the allyldiene complex $[Ti(\eta^5\text{-}C_5Me_5)(\eta^3{:}\eta^4\text{-}C_5Me_3(CH_2)_2)]$ while no titanium-containing product could be isolated for $n = 4$. The reaction of $[Ti(\eta^5\text{-}1,3\text{-}C_5H_3Me_2)_2(\eta^2\text{-}Me_3SiC{\equiv}CSiMe_3)]$ with $Me_2Si(C{\equiv}CCMe_3)_2$, however, cleanly affords the expected silacyclobutene–titanacyclobutene complex. All complexes were studied by spectral methods and solid-state structure of two representatives, $[(\eta^5\text{-}C_5Me_5)_2Ti\{Ph_2C_4(SiMe_2)\}]$ and $[(\eta^5\text{-}1,3\text{-}C_5H_3Me_2)_2Ti\{(Me_3C)_2C_4(SiMe_2)\}]$ was determined by single-crystal X-ray diffraction. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Titanium; Titanocenes; Alkynes; Silanes; Oxidative addition; X-ray crystallography

1. Introduction

Highly unstable titanocenes and zirconocenes $[M(\eta^5\text{-}C_5H_{5-n}Me_n)_2]$ ($M = Ti$, Zr; $n = 0$ or 5) generated in situ from their complexes with bis(trimethylsilyl)ethyne (btmse), $[M(\eta^5\text{-}C_5H_{5-n}Me_n)_2(\eta^2\text{-}Me_3SiC{\equiv}CSiMe_3)]$ react with 1,4-disubstituted buta-1,3-diynes to give various products whose structure depends on the metallocene, the substituents of both the diynes and the η^5-cyclopentadienyl rings in the metallocene unit as well as on the metal-to-diyne ratio. Complex formation, coupling, and bond cleavage processes proceeding in these systems have been reviewed [1]. Nonconjugated diynes with a single atom spacer $(RC{\equiv}C)_2X$ ($X = CH_2$ or SiR_2) react with zirconocene precursors in different ways depending on the nature of the spacer X: diynes possesing a methylene group afford binuclear zirconacyclopentadiene complexes (Scheme 1, A; $R^1 = SiMe_3$) [2] whereas those with a bis(organyl)silylene bridge give rise to annelated zirconacyclobutene–silacyclobutene compounds (Scheme 2, B; $R^1 = Me$, Et, Ph; $R^2 = Ph$, *p*-tolyl) [3]. Diynes with polyatomic non-rigid spacers $(CH_2)_n$ ($n = 2$–5) afford, under similar conditions, mononuclear annelated metallacyclopentadienes (Scheme 1, C; $R^1 = Me$, Et, Bu; $M = Ti$ [4], $M = Zr$ [5]). Analogous zirconacyclopentadienes fused with heterocycles are also obtained for $X = CH_2OCH_2$, CH_2NRCH_2 [6] and $B(NR_2)CH_2B(NR_2)$ [7]. On the other hand, dialkynyl phosphanes $(PhC{\equiv}C)_2PX$ ($X =$ substituted aryl, CMe_3 and $N(i\text{Pr})_2$) react with zirconocene precursors to give zirconacyclopenta-

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[*] Corresponding author. Tel.: +420-2-8585367; fax: +420-2-8582307.

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

[1] On leave from G.A. Razuvaev Institute of Organometallic Chemistry, Russian Academy of Sciences, Nizhny Novgorod, Russia.

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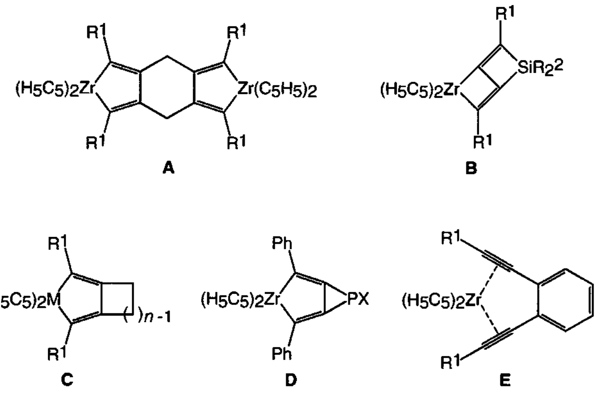


Scheme 1. Product arising from reactions of titanocene and zirconocene precursors with spaced diynes. For clarity, hapticity of the η^5-C_5H_5 ligands is omitted.

diene–phosphiranes (Scheme 1, D) [8]. In all cases, divalent zirconium of the zirconocene intermediate undergoes oxidative cycloaddition to Zr^{IV} complexes. Only the rigid two-carbon *ortho*-phenylene spacer allows the zirconium atom to remain divalent, π-coordinating both triple bonds (Scheme 1, E) [9].

As the reactions of titanocene precursors with spaced diynes have been studied in a lesser extent compared to the zirconium case (see also review [10]), we decided to investigate such systems. Here we report about the products arising from reactions of [Ti(η^5-$C_5H_{5-n}Me_n$)$_2$(η^2-btmse)] ($n = 0$–5) complexes with three diethynylsilane derivatives: $Ph_2Si(C{\equiv}CPh)_2$, $Me_2Si(C{\equiv}CPh)_2$, and $Me_2Si(C{\equiv}CCMe_3)_2$.

2. Results and discussion

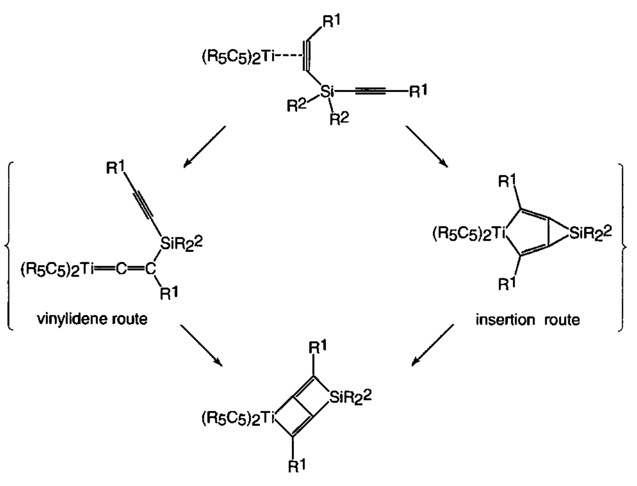
The [Ti(η^5-$C_5H_{5-n}Me_n$)$_2$(η^2-btmse)] ($n = 0$, 4, 5) complexes react cleanly with one equivalent of siladiynes $Ph_2Si(C{\equiv}CPh)_2$ or $Me_2Si(C{\equiv}CPh)_2$ in a uniform way giving silacyclobutene-annelated titanacyclobutene complexes **1**–**6** (Scheme 2). The reactions are completed within 2 h at 100°C in hexane. In all cases, a complete consumption of the parent titanocene–alkyne complexes was indicated by the disappearance of their absorption bands in UV–vis–NIR spectra (915–1025 nm) [11] and the liberated btmse was semi-quantitatively determined in the volatiles distilled from the reaction products in vacuum. Bright red compounds **1**–**6** were obtained by evaporation of the reaction mixture and crystallisation from hexane in yields varying between 67 and 83%. Their structures were determined from ^1H- and ^{13}C-NMR spectra. Furthermore, solid-state structure of complex **6** was confirmed by single-crystal X-ray diffraction.

Contrary to the above-mentioned diynes, $Me_2Si(C{\equiv}CCMe_3)_2$ reacts with the [Ti(η^5-$C_5H_{5-n}Me_n$)$_2$(η^2-btmse)] ($n = 0$, 4, 5) complexes either much less cleanly ($n = 0$), sluggishly ($n = 4$), or virtually does not react at all ($n = 5$). In the first case, compound **7** was formed easily at 100°C; however, ca. 30% of the titanocene precursor was converted into a so-called 'zigzag' complex [{Ti(η^5-C_5H_5)$_2$}$_2${μ-η(3–5):η(4–6)-$Me_3CC{=}CC{=}CCMe_3$}] (**9**) [12]. The [Ti(η^5-C_5HMe_4)$_2$(η^2-btmse)]-$Me_2Si(C{\equiv}CCMe_3)_2$ system required heating to 150°C for 13 h to achieve complete consumption of the starting alkyne complex, but unfortunately, no reaction product could be isolated from the reaction mixture. An analogous system with [Ti(η^5-C_5Me_5)$_2$(η^2-btmse)] as the titanocene component showed a complete disappearance of the parent alkyne complex after 8 h at 130°C. However, the only isolated compound was allyl-diene complex [Ti(η^5-C_5Me_5)(η^3:η^4-$C_5Me_3(CH_2)_2$)] as a product of twofold C–H bond activation in the titanocene intermediate [13]. Therefore, the [Ti(η^5-1,3-$C_5H_3Me_2$)$_2$(η^2-btmse)] complex was attempted to react with this siladiyne. It reacted smoothly at 80°C giving complex **8** as the only isolated product in 70% yield whose identity was proved by X-ray single-crystal analysis, mass and infrared spectra.

It is worth mentioning that the structure of compounds **1**–**8** is rather difficult to judge unless X-ray crystallographic data are available since the bands due to $\nu_{C=C}$ stretching in their IR spectra are shifted below

complex	C5R5	R1	R2
1	C5H5	Ph	Ph
2	C5HMe4	Ph	Ph
3	C5Me5	Ph	Ph
4	C5H5	Ph	Me
5	C5HMe4	Ph	Me
6	C5Me5	Ph	Me
7	C5H5	CMe3	Me
8	1,3-C5H3Me2	CMe3	Me

Scheme 2. Preparation of complexes **1**–**8** (hapticity of the η^5-C_5H_5 ligands is omitted).



Scheme 3. Vinylidene and insertion mechanism of silacyclobutene–titanacyclobutene complex formation (hapticity of the η^5-C_5H_5 ligands is omitted).

1500 cm^{-1} and cannot be identified. Moreover, the mass spectra display only very low-abundant molecular ions owing to dissociation of the complexes upon electron impact that affords titanocene cations $[Ti(C_5H_{5-n}Me_n)_2]^+$ as the most abundant fragment ions in the spectra. ^{13}C-NMR spectra of complexes **1**–**8** exhibit four resonances of the formerly triple-bond carbon atoms in a typical pattern which is only negligibly sensitive to the number of methyl groups on the cyclopentadienyl ligands. However, a complete assignment of these signals was not made because of lack of *direct* NMR evidence.

The formation of compounds **1**–**8** requires the replacement of the η^2-coordinated btmse ligand by a siladiyne molecule, followed by its oxidative addition across the titanium centre and a rearrangement mimicking the shift of one triple-bond substituent onto the silacyclobutene ring. The mechanism of the last two steps has been proposed by Takahashi et al. [3b] for the zirconocene reactions to proceed via vinylidene or insertion pathways (Scheme 3). The latter, leading to a zirconacyclopentadiene annelated with a silacyclopropene ring is more probable in view of the fact that the expected intermediate is a stable product of the reaction between the zirconocene source and a phosphadiyne (Scheme 1, D; [8]). The rearrangement step is initiated by scission of a weak Si–C bond in silacyclopropane that affords a stable final product. The metallacyclobutene–silacyclobutene skeleton is not a rare case since similar reactions of titanocene or zirconocene with tetraalkynylsilanes afford the products where the silicon atom is shared by two such moieties [14].

The processes resulting in the formation of complex **9** remain yet unclear since they require a formal elimination of the $SiMe_2$ group from $Me_2Si(C{\equiv}CCMe_3)_2$. However, no by-product indicating the presence of this group has been detected in the volatiles separated from the reaction mixture and its presence in mother liquor after crystallisation of **7** is difficult to prove because it should be present in only a low quantity. Nevertheless, as the structure of **9** comprises two fused titanacyclobutene moieties, it is likely that the $SiMe_2$ group is replaced by a titanocene species at the onset of its formation either during the rearrangement (from silacyclopropane intermediate, see Scheme 3, insertion route) or slowly from **7** during the heating. The formation of the zigzag complex exclusively in the system with $Me_2Si(C{\equiv}CCMe_3)_2$ may be connected with the fact that a titanacyclocumulene structure (the silacyclopropane structure in Scheme 3 can be imagined as if arising from an addition of dimethylsilylene to a titanacyclocumulene) is easily obtained from the reaction of 1,4-di-*t*-butyl-1,3-butadiyne with in situ generated titanocene $[Ti(\eta^5\text{-}C_5H_5)_2]$ [15] whereas it is not formed either from $[Ti(\eta^5\text{-}C_5Me_5)_2]$ intermediate [16] or when 1,4-diphenyl-1,3-butadiyne is the used diyne [17]. On the other hand, addition of vanadocene $[V(\eta^5\text{-}C_5H_5)_2]$ or $[Ni(PPh_3)_2]$ (L_nM) to such a titanacyclocumulene system seems to be well established in producing diyne-bridged complexes $[L_nM(\mu\text{-}\eta^2{:}\eta^4\text{-}R_2C_4)M'(\eta^5\text{-}C_5R_5)_2]$ (M′ = Ti and Zr) [18].

The titanocene zigzag complexes were so far obtained from titanocene species $[Ti(\eta^5\text{-}C_5H_5)_2]$ and diynes $R^1C{\equiv}CC{\equiv}CR^2$ ($R^1 = R^2 =$ Ph [19], CMe_3; $R^1 = SiMe_3$, $R^2 = CMe_3$ and Ph [12]), from titanocene acetylides $[Ti(\eta^5\text{-}C_5H_5)_2](\mu\text{-}C{\equiv}CPh)]$ [19,20] or $[Ti\{Me_2Si(\eta^5\text{-}C_5H_5)_2\}(\mu\text{-}C{\equiv}CPh)]$ [21] or from $[Ti(\eta^5\text{-}C_5H_4Me)_2(\eta^2\text{-btmse})]$ and $HC{\equiv}CCMe_3$ under action of sunlight [22]. Since no such product was detected in the present system containing titanocene with η^5-1,3-dimethylcyclopentadienyl ligands and no compounds of this type were yet reported for more methylated titanocenes, we suggest that stability of these complexes decreases with the number of methyl substituents and, hence, with increasing electron density on the titanium atom. The electronic and steric effects of *t*-butyl group in the siladiyne $Me_2Si(C{\equiv}CCMe_3)_2$ apparently lower its reactivity towards titanocene species or at least decrease the stability of the titanacyclobutene–silacyclobutene complexes formed thereof because both the $[Ti(\eta^5\text{-}C_5HMe_4)_2(\eta^2\text{-btmse})]$ and $[Ti(\eta^5\text{-}C_5Me_5)_2(\eta^2\text{-btmse})]$ complexes behave upon heating as if in the absence of the siladiyne [11].

*2.1. Crystal structures of **6** and **8***

The structures of **6** (Fig. 1) and **8** (Fig. 2) display structural features similar to an analogous zirconocene compound $[Zr(\eta^5\text{-}C_5H_5)_2\{Ph_2C_4(SiPh_2)\}]$ [3b]. In the sila-metalla-bicyclohexadiene part, metal–carbon σ-bonds [Ti–C(28) and Ti–C(30) in **6** and Ti–C(20) and Ti–C(22) in **8**] and carbon–carbon double bonds

[C(27)–C(28) and C(29)–C(30) in **6** and C(19)–C(20) and C(21)–C(22) in **8**] can clearly be distinguished. The bicyclic systems are planar and their planes bisect the Cg(1)–Ti–Cg(2) angles while the carbon atoms opposite to the titanium atom in the titanacyclobutene rings (C(29) or C(21)) are located in the planes defined by Cg(1), Ti and Cg(2), both within the precision of measurement. The structures of compounds **6** and **8** differ noticeably in the arrangement of the titanocene units: the Cg(1)–Ti–Cg(2) angle in **6** (139.2(5)°) is larger than in **8** (132.5(1)°) whereas the Ti–Cg distances in **6** (2.134(4) and 2.121(4) Å) are somewhat longer than in **8** (2.099(3) and 2.102(3) Å). These are common differences between the permethyl-substituted and non- or low methyl-substituted bent titanocene skeletons induced by the steric hindrance and an electron donating effect of the methyl substituents [23]. On the other hand, the C(28)–Ti–C(30) angle in **6** (75.3(4)°) is more acute compared to the corresponding angle in **8** (78.47(9)°). This can result from different stereoelectronic properties of phenyl and *t*-butyl substituents as well as from the above-mentioned difference in the Cg(1)–Ti–Cg(2) angle at the pseudotetrahedrally coordinated titanium atom. The distances from the Ti atom to the opposite carbon atom within the titanacyclobutene ring [Ti–C(29) 2.352(9) Å for **6** and Ti–C(21) 2.287(2) Å for **8**] are shorter than the Ti–C distances to cyclopentadienyl ring carbon atoms with range 2.425–2.477(4) in **6** and 2.383–2.445(3) Å in **8**, and therefore are at the π-bonding distance. The double-bond lengths involving these carbon atoms, which are shorter by ca. 0.02 Å compared to the double-bond lengths in the silacyclobutene rings, exclude a strong π-bonding interaction between the double bond and the titanium atom since it would result in their elongation [24]. An interesting feature of these metalla-sila-bicyclohexadiene complexes is an enormously long bonding distance between carbon atoms connecting the double bonds: 1.595(6) Å in [Zr(η^5-C$_5$H$_5$)$_2${Ph$_2$C$_4$(SiPh$_2$)}] [3b], 1.572(12) Å in **6** and 1.617(3) Å in **8**. This is the most striking difference between the titanacyclobutene moieties in these and zigzag complexes. For instance, this distance is only 1.508(5) Å in the zigzag complex [{Ti(η^5 - C$_5$H$_4$Me)$_2$}$_2${μ - η(3–5):η(4–6) - Me$_3$CC=CC=CCMe$_3$}] [21]. Similarly, the symmetrical 3,6-disilabicyclo[2.2.0]hexa-1(2),4(5)-diene, [Me$_2$C$_4${Si(CMe$_3$)$_2$}$_2$] [25] shows the bond length between the carbon atoms belonging to two different double bonds to be rather short, 1.485(6) Å, whereas the lengths of Si–C bonds in the silabutene cycle fall between the values found in **6** and **8** and the corresponding C–Si–C angle (75.1(1)°) is close to that of **6** and smaller by ca. 3° than that in **8** (see Tables 1 and 2).

Table 1
Selected bond lengths (Å) and bond angles (°) for complex **6** [a]

Bond lengths			
Ti–Cg(1)	2.134(4)	Ti–Cg(2)	2.121(4)
Ti–C(1)···C(5)	2.426–2.477(4)	Ti–C(6)···C(10)	2.425–2.455(4)
Ti–C(28)	1.967(8)	Ti–C(29)	2.352(9)
Ti–C(30)	2.190(4)	C(28)–C(29)	1.572(12)
C(29)–C(30)	1.330(10)	C(27)–C(28)	1.374(11)
C(26)–C(27)	1.484(9)	C(30)–C(31)	1.532(9)
Si–C(27)	1.866(9)	Si–C(29)	1.847(10)
Si–C(37)	1.883(6)	Si–C(38)	1.885(6)
(C_{Cp}–C_{Me})	1.491–1.505(6)	(C_{Cp}–C_{Cp})	1.404–1.425(6)
Bond and dihedral angles			
C(28)–Ti–C(30)	75.3(4)	C(29)–C(28)–Ti	82.5(5)
C(29)–C(30)–Ti	79.8(4)	C(28)–C(29)–C(30)	122.4(7)
C(27)–C(28)–C(29)	103.9(8)	C(27)–C(28)–Ti	173.6(8)
C(27)–Si–C(29)	77.5(4)	C(28)–C(27)–Si	91.9(6)
C(30)–C(29)–Si	151.0(6)	C(28)–C(29)–Si	86.6(6)
C(37)–Si–C(38)	106.7(2)		
Cg(1)–Ti–Cg(2)	139.2(5)	ϕ [b]	41.09(21)
ω_1 [c]	20.76(38)	ω_2 [c]	20.57(30)

[a] Cg(1) = centroid of C(1)–C(5) ring; Cg(2) = centroid of the C(6)–C(10) ring.

[b] ϕ — dihedral angle between the least-squares planes of the cyclopentadienyl rings.

[c] $\omega_1[\omega_2]$ — dihedral angle subtended by the least-squares cyclopentadienyl planes C(1)–C(5)[C(6)–C(10)] and a plane defined by Ti, C(28), C(29), and C(30) atoms.

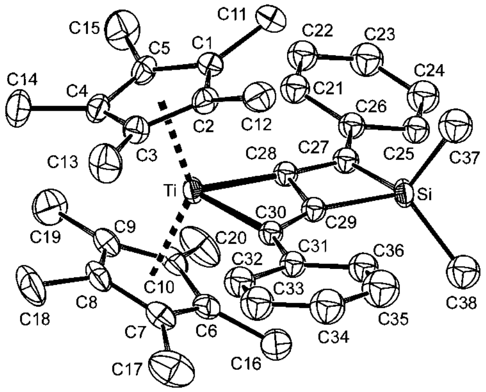


Fig. 1. Molecular structure of complex **6** with atom numbering scheme (drawn at 30% probability).

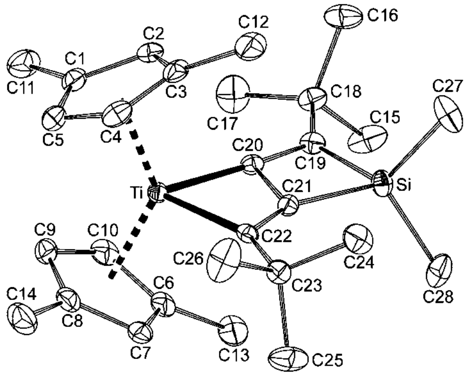


Fig. 2. Molecular structure of complex **8** with atom numbering scheme (drawn at 30% probability).

Table 2
Selected bond lengths (Å) and angles (°) for compound **8** [a]

Bond lengths			
Ti–Cg(1)	2.102(3)	Ti–Cg(2)	2.099(3)
Ti–C(1)···C(5)	2.400–2.429(3)	Ti–C(6)···C(10)	2.383–2.445(3)
Ti–C(20)	2.025(2)	Ti–C(21)	2.287(2)
Ti–C(22)	2.107(2)	C(20)–C(21)	1.617(3)
C(21)–C(22)	1.331(3)	C(19)–C(20)	1.351(3)
C(18)–C(19)	1.518(3)	C(22)–C(23)	1.519(3)
Si–C(19)	1.843(3)	Si–C(21)	1.881(2)
Si–C(27)	1.865(3)	Si–C(28)	1.870(3)
C_{Cp}–C_{Me}	1.491–1.499(4)	C_{Cp}–C_{Cp}	1.396–1.418(4)
Bond and dihedral angles			
C(20)–Ti–C(22)	78.47(9)	C(21)–C(20)–Ti	76.87(12)
C(21)–C(22)–Ti	79.92(14)	C(20)–C(21)–C(22)	124.7(2)
C(19)–C(20)–C(21)	105.8(2)	C(19)–C(20)–Ti	177.14(19)
C(19)–Si–C(21)	79.11(10)	C(20)–C(19)–Si	92.15(16)
C(22)–C(21)–Si	152.29(19)	C(20)–C(21)–Si	82.97(13)
C(27)–Si–C(28)	108.23(19)		
Cg(1)–Ti–Cg(2)	132.5(1)	ϕ [b]	49.79(13)
ω_1 [c]	24.49(14)	ω_2 [c]	25.32(13)

[a] Data for one orientation of the ligand generated from bis(phenylethynyl)diphenylsilane; Cg(1) = centroid of the C(1)–C(5) ring; Cg(2) = centroid of the C(6)–C(10) ring.

[b] ϕ — dihedral angle between the least-squares planes of the cyclopentadienyl rings.

[c] $\omega_1[\omega_2]$ — dihedral angle subtended by the least-squares cyclopentadienyl planes C(1)–C(5)[C(6)–C(10)] and a plane defined by Ti, C(20), C(21), and C(22) atoms.

3. Experimental

3.1. General comments and methods

All manipulations with titanium complexes were carried out on a high-vacuum argon line operated by means of non-greased glass-to-metal sealed valves (Hoke) in all-sealed glass devices equipped with breakable seals. Sealed NMR sample tubes were filled with C_6H_6-d_6 solutions using evacuated all-glass devices, and were sealed off by flame. The adjustment of single crystals into Lindemann glass capillaries for X-ray analyses, the inserting of crystals into capillaries for mass spectrometric measurements, and the preparations of KBr pellets for IR measurements were made in a glovebox under purified nitrogen (mBraun, O_2 and H_2O concentrations below 2.0 ppm). Infrared spectra of samples in KBr pellets were measured on a Specord IR-75 (Carl Zeiss, Jena, Germany) spectrometer in a closed cell under nitrogen. ^{1}H- (399.95 MHz) and ^{13}C- (100.58 MHz) NMR spectra were measured on a Varian UNITY Inova 400 spectrometer in C_6H_6-d_6 solutions at 298(1) K. Chemical shifts (δ ppm) are referenced to the solvent signal (δ_H 7.15, δ_C 128.0). Mass spectra were measured on a VG 7070E spectrometer at 70 eV using a direct inlet probe (crystalline samples in sealed capillaries were opened and inserted into the probe under argon). GC analyses were performed on a CHROM 5 gas chromatograph (Laboratory Instruments, Prague, Czech Republic) equipped by 10% SE-30 on a Chromaton N-AW-DMCS column. GC-MS analyses were carried out on a Hewlett Packard gas chromatograph (5890 series II; capillary column SPB-1 (Supelco)) interfaced to a mass spectrometric detector (5791 A). Melting points were determined for samples in N_2-filled sealed capillaries on a Kofler apparatus and are uncorrected.

3.2. Chemicals

Hexane, toluene, *m*-xylene and tetrahydrofuran (THF) were dried by refluxing over $LiAlH_4$ in an argon atmosphere, degassed and stored as solutions of green dimeric titanocene $[(\mu\text{-}\eta^5{:}\eta^5\text{-}C_{10}H_8)\{(\eta^5\text{-}C_5H_5)Ti(\mu\text{-}H)\}_2]$ [26] on a vacuum line. Likewise, C_6H_6-d_6 was degassed and stored as a solution of green dimeric titanocene on a vacuum line. Siladiynes $Ph_2Si(C{\equiv}CPh)_2$, $Me_2Si(C{\equiv}CPh)_2$ and $Me_2Si(C{\equiv}CCMe_3)_2$ were prepared by reacting the appropriate disubstituted dichlorosilane with two molar equivalents of magnesium or lithium acetylides [27]. All the diacetylenes were recrystallised from *n*-hexane, and their purity was checked by NMR, IR and MS spectra. Complexes $[Ti(\eta^5\text{-}C_5H_{5-n}Me_n)_2(\eta^2\text{-btmse})]$ ($n = 0$, 2, 4 and 5) were prepared by the reduction of the corresponding titanocene dichlorides with magnesium in the presence of excess btmse in THF [11].

3.3. Reactions of the $[Ti(\eta^5\text{-}C_5H_{5-n}Me_n)_2(\eta^2\text{-btmse})]$ complexes with the siladiynes

The parent titanocene complex $[Ti(\eta^5\text{-}C_5H_{5-n}Me_n)_2(\eta^2\text{-btmse})]$ (1.0 mmol) was mixed with the appropriate siladiyne (1.05 mmol) in a hydrocarbon solvent and the mixture was heated in an ampoule attached to a UV–NIR quartz cuvette ($d = 0.2$ cm). The conversion of the alkyne complex (or a η^2-diyne intermediate) was followed by UV–vis–NIR spectra of the reaction mixture in a temperature range 80–150°C (solvents hexane and *m*-xylene). When the absorption band of the starting complexes near 1000 nm had disappeared, all volatiles were distilled off in vacuum and the residue was extracted by hexane. All volatiles were analysed by GC-MS for the presence of btmse, its hydrogenated products ((*E*)- and (*Z*)-1,2-bis(trimethyl-silyl)ethene) and unreacted siladiyne. The solid products were purified by crystallisation from hexane.

*$[(\eta^5\text{-}C_5H_5)_2Ti\{Ph_2C_4(SiPh_2)\}]$ (**1**).* A solution of $[Ti(\eta^5\text{-}C_5H_5)_2(\eta^2\text{-btmse})]$ (0.488 g, 1.0 mmol) in hexane (4 ml) was added to degassed $Ph_2Si(C{\equiv}CPh)_2$ (0.403 g, 1.05 mmol) and the resulting mixture was heated to 80°C for 1 h. All volatiles were distilled off at 80°C in vacuum. GC-MS analysis revealed the presence of

btmse. The red-brown solid residue was extracted into hexane (10 ml) and the extract was cooled in a refrigerator overnight to give bright red crystalline **1** (0.41 g, 73%), m.p. 215°C. ^{1}H-NMR (C_6H_6-d_6): δ 5.32 (s, 10 H, C_5H_5), 7.05–8.05 (m, 20 H, *Ph*). $^{13}C\{^1H\}$-NMR (C_6H_6-d_6): δ 76.0 (C_{ipso}), 106.1 (C_5H_5); 127.3, 127.4 (2C), 128.1, 128.8 (2C), 128.8 (4C), 129.2 (2C), 130.4 (2C), 130.7 (2C), 135.6 (4C) (Ph, *C*H); 134.2 (2C), 140.6, 140.7 (Ph, C_{ipso}), 152.8 (C_{ipso}), 211.8, 265.1 (C_{ipso}). EI-MS (280°C; *m*/*z* (relative abundance, %)): 562 (M^+, 3), 385 (16), 384 ($[Ph_2C_4(SiPh_2)]^+$, 47), 383 (23), 308 (17), 307 (60), 306 (8), 305 (7), 206 (19), 205 (13), 204 (7), 181 (8), 180 (13), 179 (22), 178 ($[Ti(C_5H_5)_2]^+$, 100), 177 (12), 176 (12), 129 (36), 113 (19), 105 (13). IR (KBr, cm^{-1}): 3050 (m, b), 3005 (m), 1595 (s), 1566 (m), 1500 (w), 1480 (vs), 1440 (s), 1428 (vs), 1266 (s), 1186 (m), 1106 (vs), 1068 (m), 1014 (s), 960 (m), 900 (m), 807 (vs, b), 762 (vs), 740 (s), 707 (s), 694 (vs), 660 (m), 626 (m), 607 (m), 586 (s), 540 (s), 466 (m), 447 (s).

$[(\eta^5\text{-}C_5Me_4H)_2Ti\{Ph_2C_4(SiPh_2)\}]$ ***(2)***. An analogous reaction of $[Ti(\eta^5\text{-}C_5HMe_4)_2(\eta^2\text{-btmse})]$ (0.460 g, 1.0 mmol) with $Ph_2Si(C{\equiv}CPh)_2$ (0.403 g, 1.05 mmol) in hexane (4 ml) at 100°C for 1 h followed by an analogous workup afforded **2** as a light red crystalline material (0.56 g, 83%), m.p. 209°C. ^{1}H-NMR (C_6H_6-d_6): δ 1.34, 1.57, 1.94, 2.10 (4 × s, 6H, C_5Me_4H); 5.10 (s, 2H, C_5Me_4H), 7.05–8.05 (m, 20H, *Ph*). $^{13}C\{^1H\}$-NMR (C_6H_6-d_6): δ 12.4 (δ_H 1.34), 12.5 (δ_H 1.57), 14.3 (δ_H 1.94), 14.6 (δ_H 2.10) (C_5Me_4H); 89.7 (C_{ipso}), 106.3 (C_5Me_4H, *C*H), 114.1, 115.5, 118.6, 120.7 (C_5Me_4H, *C*Me); 127.0, 127.2, 127.7 (2C), 128.4 (6C), 128.8 (2C), 130.2 (2C), 130.6 (2C), 135.9 (4C) (Ph, *C*H); 137.6 (2C), 140.7, 140.9 (Ph, C_{ipso}); 151.1 (C_{ipso}), 212.8, 265.6 (C_{ipso}). EI-MS (305°C; *m*/*z* (relative abundance, %)): 674 (M^+; 1), 385 (16), 384 ($[Ph_2C_4(SiPh_2)]^+$; 38), 383 (18), 309 (23), 308 (17), 307 (65), 292 (15), 291 (30), 290 ($[Ti(C_5HMe_4)_2]^+$; 100), 289 (40), 288 (18), 287 (10), 284 (12), 283 (36), 281 (10), 278 (12), 207 (11), 206 (22), 205 (35), 204 (15), 202 (13), 188 (28), 187 (11), 186 (17), 183 (13), 182 (11), 181 (24), 180 (15), 179 (12), 178 (27), 168 (17), 167 (18), 166 (12), 164 (19), 155 (12), 153 (18), 152 (12), 150 (10), 130 (16), 129 (82), 121 (11), 119 (11), 105 (46), 103 (20), 93 (15), 91 (24), 79 (14), 78 (10), 77 (31), 69 (19), 65 (10), 57 (15), 55 (21), 53 (17), 51 (31), 50 (12), 44 (17), 43 (27), 41 (26), 39 (20). IR (KBr, cm^{-1}): 3053 (m), 3040 (m), 2970 (m), 2940 (m), 2887 (s), 2853 (sh), 1590 (s), 1567 (w), 1498 (m), 1482 (vs), 1463 (m), 1440 (s), 1430 (vs), 1380 (s), 1370 (m), 1262 (m), 1190 (m), 1105 (vs), 1070 (m), 1027 (s), 1000 (m), 967 (s), 833 (m), 763 (vs), 740 (s), 723 (s), 698 (vs), 664 (s), 627 (m), 606 (s), 591 (s), 540 (s), 466 (m), 446 (s).

$[(\eta^5\text{-}C_5Me_5)_2Ti\{Ph_2C_4(SiPh_2)\}]$ ***(3)***. Reaction of the $[Ti(\eta^5\text{-}C_5Me_5)_2(\eta^2\text{-btmse})]$ (0.488 g, 1.0 mmol) in hexane (10 ml) with $Ph_2Si(C{\equiv}CPh)_2$ (0.403 g, 1.05 mmol) gave after workup as given above bright red crystalline **3** (0.47 g, 67%), m.p. 241°C. ^{1}H-NMR (C_6H_6-d_6): δ 1.71 (s, 30H, C_5Me_5), 7.05–8.09 (m, 20H, *Ph*). ^{13}C-NMR (C_6H_6-d_6; only $^1J_{CH}$ are given): δ 12.6 (q, $^1J_{CH} = 126$ Hz, C_5Me_5), 88.2 (s, C_{ipso}), 116.4 (s, C_5Me_5), 126.8 (d), 127.1 (d), 128.3 (d, 2C), 128.4 (d, 6C), 128.7 (d, 2C), 130.1 (d, $^1J_{CH} = 159$ Hz, 2C), 130.8 (d, $^1J_{CH} = 156$ Hz, 2C), 135.8 (d, $^1J_{CH} = 158$ Hz, 4C) (Ph, *C*H); 138.2 (s, 2C), 141.0 (s), 141.2 (s) (Ph, C_{ipso}), 150.5 (s, C_{ipso}), 212.8, 266.5 (s, C_{ipso}). EI-MS (320°C; *m*/*z* (relative abundance, %)): 702 (M^+; 0.5), 384 ($[Ph_2C_4(SiPh_2)]^+$; 11), 383 (6), 318 (11), 319 (29), 318 ($[Ti(C_5Me_5)_2]^+$; 100), 317 (17), 316 (13), 307 (12), 181 (10), 129 (9). IR (KBr, cm^{-1}): 3055 (w), 3040 (w), 2978 (m), 3043 (m), 2892 (s), 2849 (m), 1585 (s), 1563 (w), 1493 (m), 1477 (s), 1426 (s, b), 1373 (s), 1245 (m), 1098 (vs), 1066 (w), 1020 (m), 962 (m), 894 (m), 759 (s), 735 (w), 719 (m), 695 (vs), 655 (w), 598 (m), 587 (w), 531 (m), 463 (s), 440 (s).

$[(\eta^5\text{-}C_5H_5)_2Ti\{Ph_2C_4(SiMe_2)\}]$ ***(4)***. Heating a mixture of $[Ti(\eta^5\text{-}C_5H_5)_2(\eta^2\text{-btmse})]$ (0.460 g, 1.0 mmol), $Me_2Si(C{\equiv}CPh)_2$ (0.273 g, 1.05 mmol) and hexane (10 ml) to 80°C for 2 h afforded yellow-red crystalline **4** (0.33 g, 76%). ^{1}H-NMR (C_6H_6-d_6): δ 0.41 (s, 6H, Me_2Si), 5.26 (s, 10H, C_5H_5), 7.17–7.91 (m, 10H, *Ph*). $^{13}C\{^1H\}$-NMR (C_6H_6-d_6): δ 0.0 (Me_2Si), 77.4 (C_{ipso}), 105.8 (C_5H_5), 127.1, 127.2 (2C), 127.8, 128.8 (2C), 129.1 (2C), 129.9 (2C) (Ph, *C*H); 140.9, 141.0 (Ph, C_{ipso}), 154.2 (C_{ipso}), 211.3 (C_{ipso}), 260.7 (C_{ipso}). EI-MS (230°C; *m*/*z* (relative abundance, %)): 438 (M^+; 3.0), 260 ($[Ph_2C_4(SiMe_2)]^+$; 19), 247 (6), 246 (22), 245 (87), 202 (7), 180 (7), 179 (19), 178 ($[Ti(C_5H_5)_2]^+$; 100), 177 (13), 176 (12), 153 (6), 129 (20), 113 (20), 43 (8). IR (KBr, cm^{-1}): 3053 (m), 3041 (m), 2947 (w, b) 1587 (s), 1565 (m), 1502 (m), 1477 (vs), 1439 (s), 1264 (m), 1240 (s), 1066 (m), 1014 (s), 962 (s), 898 (m), 835 (s), 800 (vs, b), 772 (s), 760 (sh), 716 (m), 686 (vs), 643 (m), 559 (m), 498 (m).

$[(\eta^5\text{-}C_5HMe_4)_2Ti\{Ph_2C_4(SiMe_2)\}]$ ***(5)***. Starting from $[Ti(\eta^5\text{-}C_5Me_4H)_2(\eta^2\text{-btmse})]$ complex (0.460 g, 1.0 mmol) and degassed $Me_2Si(C{\equiv}CPh)_2$ (0.273 g, 1.05 mmol) in hexane (4.0 ml), an analogous procedure (100°C, 2 h) gave complex **5** as bright red prismatic crystals (0.38 g, 69%). ^{1}H-NMR (C_6H_6-d_6): δ 0.65 (s, 6H, Me_2Si), 1.30, 1.50, 1.92, 2.08 (4 × s, 6H, C_5Me_4H); 5.07 (s, 2H, C_5Me_4H), 7.08–7.76 (m, 10H, *Ph*). $^{13}C\{^1H\}$-NMR (C_6H_6-d_6): δ 12.2, 12.3, 14.2, 14.6 (C_5Me_4H); 90.3 (C_{ipso}), 105.7 (C_5Me_4H, *C*H), 113.3, 114.8, 117.2, 119.8 (C_5Me_4H, *C*Me); 126.7, 126.9, 127.3 (2C), 128.4 (2C), 128.6 (2C), 130.3 (2C) (Ph, *C*H); 140.6, 140.8 (Ph, C_{ipso}); 153.7 (C_{ipso}), 211.4 (C_{ipso}), 261.3 (C_{ipso}). EI-MS (260°C; *m*/*z* (relative abundance, %)): 550 (M^+; 0.3), 292 (10), 291 (27), 290 ($[Ti(C_5HMe_4)_2]^+$; 100), 289 (19), 288 (22), 260 ($[Ph_2C_4(SiMe_2)]^+$; 16), 245 (81), 167 (7), 166 (7), 164 (6), 153 (5), 129 (13). IR (KBr, cm^{-1}): 3060 (sh), 3040 (w), 2960 (sh), 2927 (m), 2874 (s), 1586 (s), 1546 (m), 1494 (s), 1473 (vs), 1434 (s), 1375 (w), 1367 (m), 1247 (sh), 1237 (s), 1200 (w), 1146

(w), 1037 (m), 1020 (s), 961 (s), 898 (m), 830 (vs), 767 (sh), 754 (vs), 713 (m), 687 (vs), 641 (m), 600 (w), 560 (m), 500 (m).

*$[(\eta^5$-$C_5Me_5)_2Ti\{Ph_2C_4(SiMe_2)\}]$ (**6**).* A reaction of $[Ti(\eta^5$-$C_5Me_5)_2(\eta^2$-btmse)] and $Me_2Si(C{\equiv}CPh)_2$ performed as above gave compound **6** as a bright red crystalline solid (0.41 g, 71%), m.p. 131°C. ^{1}H-NMR (C_6H_6-d_6): δ 0.70 (s, 6H, Me_2Si), 1.70 (s, 30H, C_5Me_5), 7.09–7.77 (m, 10H, *Ph*). $^{13}C\{^1H\}$-NMR (C_6H_6-d_6): δ 2.7 (Me_2Si), 12.6 (C_5Me_5), 88.9 (C_{ipso}), 115.5 (C_5Me_5), 126.5, 126.7, 127.3 (2C), 128.4 (2C), 128.5 (2C), 130.5 (2C) (Ph, *C*H); 140.8, 141.1 (Ph, C_{ipso}), 153.1 (C_{ipso}), 211.4 (C_{ipso}), 262.3 (C_{ipso}). EI-MS (270°C; m/z (relative abundance, %)): 578 (M^+; 0.1), 320 (10), 319 (29), 318 ($[Ti(C_5Me_5)_2]^+$; 100), 317 (20), 316 (16), 260 ($[Ph_2C_4(SiMe_2)]^+$; 15), 246 (15), 245 (71), 202 (5), 181 (7), 178 (6), 129 (12). IR (KBr, cm^{-1}): 3050 (m, b), 2940 (s), 2887 (vs), 2854 (sh), 1586 (s), 1494 (s), 1480 (vs), 1460 (m), 1435 (s), 1373 (s), 1256 (m), 1240 (m), 1066 (m), 1024 (s), 964 (s), 834 (s), 770 (vs), 760 (vs), 717 (m), 696 (vs), 647 (m), 564 (m), 498 (m).

3.4. Reactions in the $[Ti(\eta^5$-$C_5Me_nH_{5-n})_2(\eta^2$-btmse)]/$Me_2Si(C{\equiv}CCMe_3)_2$ system

A solution of $[Ti(\eta^5$-$C_5H_5)_2(\eta^2$-btmse)] complex (0.348 g, 1.0 mmol) in hexane (10 ml) was mixed with a solution of $Me_2Si(C{\equiv}CCMe_3)_2$ in hexane (0.5025 M, 2.0 ml; 1.05 mmol) and the reaction mixture was heated to 100°C for 2 h (the absorption band of the starting complex at 1025 nm completely disappeared during this time). A greenish reaction solution was worked up as above; the volatiles showed the presence of only btmse and hexane. The solid residue was extracted by hexane to give the yellow crystalline product whose structure $[(\eta^5$-$C_5H_5)_2Ti\{(Me_3C)_2C_4(SiMe_2)\}]$ (**7**) was deduced from MS and NMR spectra. The remaining dark green powder was insoluble in hexane but moderately soluble in toluene. Its MS and NMR spectra corresponded to the known compound $[\{Ti(\eta^5$-$C_5H_5)_2\}_2\{\mu$-$\eta(3$–$5)$:$\eta(4$–$6)$-$Me_3CC{=}CC{=}CCMe_3\}]$ (**9**) [12].

Yield of **7**: 0.19 g (48%), m.p. 174°C (dec.). ^{1}H-NMR (C_6H_6-d_6): δ 0.26 (s, 6H, Me_2Si), 1.25, 1.33 (2 × s, 9H, CMe_3); 5.22 (s, 10H, C_5H_5Ti). $^{13}C\{^1H\}$-NMR (C_6H_6-d_6): δ 0.8 (Me_2Si), 30.8, 32.8 (CMe_3); 36.1, 39.0 (*C*Me_3); 71.8 (C_{ipso}), 105.0 (C_5H_5Ti), 164.3, 223.0, 257.3 (C_{ipso}). EI-MS (100°C; m/z (relative abundance, %)): 398 (M^+; 0.4), 220 ($[(Me_3C)_2C_4(SiMe_2)]^+$; 9), 206 (19), 205 (100), 179 (11), 178 ($[Ti(C_5H_5)_2]^+$; 57), 177 (7), 176 (7), 163 (20), 139 (8), 113 (20), 97 (17). IR (KBr, cm^{-1}): 3080 (w), 2934 (vs, b), 2880 (s), 2853 (m), 1580 (m), 1513 (m), 1450 (m), 1353 (s), 1254 (m), 1230 (s), 1060 (s), 1014 (s), 834 (s), 793 (vs), 767 (s), 698 (m), 620 (w), 464 (w). IR (KBr, cm^{-1}): 3110 (vw), 3084 (w), 2927 (vs, b), 2882 (s), 2846 (s), 1581 (m), 1516 (m), 1453 (s), 1440 (m), 1379 (w), 1351 (s), 1259 (m), 1233 (vs), 1060 (s), 1014 (s), 962 (m), 835 (s), 813 (sh), 790 (vs, b), 766 (s), 698 (s), 650 (m), 621 (m), 465 (m). UV–vis (nm, hexane, 22°C): 400 (sh).

Yield of **9**: 0.14 g (27% with respect to Ti). ^{1}H-NMR (C_6H_6-d_6): δ 1.22 (s, 9H, CMe_3), 5.32 (s, 10H, C_5H_5Ti). $^{13}C\{^1H\}$-NMR (C_6H_6-d_6): δ 32.6 (CMe_3), 42.1 (*C*Me_3), 106.3 (C_5H_5Ti), 124.5, 233.9 (C_{ipso}). EI-MS (155°C; m/z (relative abundance, %)): 518 (M^+; 3), 260 (12), 259 (M^{2+}; 46), 258 (6), 244 (8), 202 (6), 180 (9), 179 (21), 178 ($[Ti(C_5H_5)_2]^+$; 100), 177 (12), 176 (12), 113 (23). UV–vis (nm, toluene, 22°C): 380 (sh) > 685.

*$[(\eta^5$-1,3-$C_5H_3Me_2)_2Ti\{(Me_3C)_2C_4(SiMe_2)\}]$ (**8**).* A solution of the $[Ti(\eta^5$-1,3-$C_5H_3Me_2)_2(\eta^2$-btmse)] complex (0.10 g, 0.25 mmol) in hexane (4 ml) was mixed with a solution of $Me_2Si(C{\equiv}CCMe_3)_2$ in hexane (0.5025 M, 0.5 ml; 0.251 mmol) and the reaction mixture was heated to 80°C. The absorption band of the parent titanocene complex at 1000 nm disappeared after 1 h. The resulting brownish yellow solution was evaporated and the residue was crystallised from hexane to give yellow complex **8** (0.075 g, 66%). EI-MS (115°C; m/z (relative abundance, %)): 454 (M^+; 0.2), 236 (10), 235 (28), 234 ($[Ti(C_5H_3Me_2)_2]^+$; 100), 233 (49), 232 (27), 231 (20), 229 (9), 220 ($[(Me_3C)_2C_4(SiMe_2)]^+$; 7), 206 (16), 205 (83), 163 (17), 140 (19). IR (KBr, cm^{-1}): 3081 (w), 2940 (vs), 2910 (s), 2887 (m), 2853 (m), 1567 (m), 1508 (m), 1465 (sh), 1447 (s), 1367 (w), 1349 (s), 1253 (m), 1234 (s), 1056 (s), 1007 (m), 833 (vs), 793 (s), 762 (m), 691 (m), 642 (w), 605 (w), 460 (w). The structure of **8** was determined by single-crystal X-ray diffraction measurement.

The $[Ti(\eta^5$-$C_5HMe_4)_2(\eta^2$-btmse)]/$Me_2Si(C{\equiv}CCMe_3)_2$ system. A solution of the alkyne complex (0.460 g, 1.0 mmol) in hexane (4 ml) was mixed with a solution of $Me_2Si(C{\equiv}CCMe_3)_2$ in the same solvent (0.5025 M, 2.0 ml; 1.05 mmol) and the resulting solution was heated to 100°C for 8 h. As no decrease in the concentration of the btmse complex was detected by UV–vis–NIR spectra, hexane was replaced by *m*-xylene and the mixture was heated to 130°C for 8 h. However, the intensity of the absorption band at 920 nm did not decrease either. A portion (2 ml) of the reaction mixture was worked up. MS and IR spectra of the isolated solid identified only the initial alkyne complex. Prolonged heating (150°C, 8 h) followed by evaporation of all volatiles at 100°C in vacuum and extraction of a brown oily residue by hexane gave an intractable mixture of non-crystallising products.

The $[Ti(\eta^5$-$C_5Me_5)_2(\eta^2$-btmse)]-$Me_2Si(C{\equiv}CCMe_3)_2$ system. A solution of the appropriate alkyne complex (0.488 g, 1.0 mmol) in hexane (4 ml) was mixed with a solution of $Me_2Si(C{\equiv}CCMe_3)_2$ in hexane (0.5025 M, 2.0 ml, 1.05 mmol) and the reaction mixture was heated to 100°C for 8 h. Similarly to the above case, the absorption band of the btmse complex at 970 nm did not decrease in intensity. Hexane was distilled off in vac-

Table 3
Crystallographic data, data collection and structure refinement data for compounds **6** and **8** [a]

Compound	**6**	**8**
Empirical formula	$C_{38}H_{46}SiTi$	$C_{28}H_{42}SiTi$
Molecular weight	578.75	454.61
Crystal system	triclinic	monoclinic
Space group	$P\bar{1}$ (No. 2)	$P2_1/n$ (No. 14)
Unit cell dimensions		
a (Å)	9.695(2)	8.9130(2)
b (Å)	10.263(3)	22.2390(5)
c (Å)	16.617(6)	13.8790(4)
α (°)	86.17(3)	
β (°)	87.31(2)	105.864(1)
γ (°)	73.97(2)	
V (Å^3)	1584.9(8)	2646.3(1)
Z	2	4
D_{calc} (g cm^{-3})	1.204	1.141
μ(Mo Kα) (mm^{-1})	0.332	0.381
F(000)	612	984
Crystal size (mm)	$0.5\times0.3\times0.3$	$0.5\times0.3\times0.3$
Temperature (K)	150(2)	150(2)
θ Range (°)	1.2–25.0	3.1–25.0
Index ranges	$-10\leq h\leq 11$, $0\leq k\leq 12$, $-19\leq l\leq 19$	$0\leq h\leq 10$, $0\leq k\leq 26$, $-16\leq l\leq 15$
Diffractions collected	5567	4630
Parameters	272	439
R, wR [$I>2\sigma(I)$]	0.0784, 0.1936	0.0435, 0.1049
R, wR (all data)	0.1105, 0.2117	0.0592, 0.1189
S	1.101	1.138
Largest difference peak and hole (e Å^{-3})	0.791, −0.398	0.247, −0.339

[a] $R(F)=\Sigma||F_o|-|F_c||/\Sigma|F_o|$, $wR(F^2)=[\Sigma(w(F_o^2-F_c^2)^2)/\Sigma w(F_o^2)^2)]^{1/2}$, $S=[\Sigma(w(F_o^2-F_c^2)^2)/(N_{diffrs}-N_{params})]^{1/2}$.

uum and the residue was dissolved in *m*-xylene (4 ml) and the resulting solution was heated at subsequently increasing temperatures up to 130°C, where a slow decrease of the band intensity commenced. The band disappeared after 9 h at 130°C whereupon the mixture turned blue. The products were worked up as given above. Volatiles contained a mixture of (*E*)- and (*Z*)-1,2-bis(trimethylsilyl)ethene and only a trace of btmse. The only isolated titanocene complex (crystallised from hexane), a blue crystalline compound was identified by NMR and MS spectra to be Teuben's allyldiene compound [Ti(η^5-C_5Me_5)(η^3:η^4-$C_5Me_3(CH_2)_2$)] [13]. Yield was 0.18 g (0.57 mmol, 57%).

*3.5. Crystal structure analysis of **6** and **8***

A bright red platelet of compound **6** and a fragment of yellow platelet of **8** were mounted into Lindemann glass capillaries in a glovebox under purified nitrogen. Diffraction data for **6** were collected on an Enraf–Nonius CAD-4 MACH III diffractometer and those for **8** on a Nonius Kappa CCD diffractometer with CCD area detector at 150(2) K (graphite monochromated MoKα radiation). A Cryostream Cooler (Oxford Cryosystems) was used for cooling the samples. The structures were solved by direct methods (SIR-97) [28] and refined by a full-matrix least-squares procedure based on F^2 (SHELXL-97) [29]. In **6**, the ligand formed from $Me_2Si(C{\equiv}CPh)_2$ was disordered over two positions which could be mutually interconverted by rotation around a twofold axis passing through the titanium atom and an average position of the silicon atom. However, such a refinement over two positions was unstable because of overlapping atoms, and therefore all the ligand atoms were refined isotropically using geometric constraints to fit the phenyl groups to a regular hexagon. Hydrogen atoms of this ligand could not be distinguished on a difference electron density map because of disorder and were not refined. Non-hydrogen atoms of permethyltitanocene moiety were refined anisotropically without any restriction. Hydrogen atoms of methyl groups were located on a difference electron density map and this position was taken as an initial point for their geometrically restricted refinement. In **8**, all non-hydrogen atoms were refined anisotropically. The hydrogen atoms were localised on a difference Fourier map and refined isotropically. Crystallographic data, details on their collection, and the structure refinement are given in Table 3.

4. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC no. 153164 for compound **6** and CCDC no. 153163 for compound **8**. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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