Organometallics **2005,** *24,* 6094−6103

Nonclassical Bonding in Titanasilacyclohexadiene Compounds Resulting from Highly Methyl-Substituted Titanocene−Bis(trimethylsilyl)ethyne Complexes and Bis((trimethylsilyl)ethynyl)silanes

Michal Horáček,[†] Petr Štěpnička,[‡] Róbert Gyepes,[‡] Ivana Císařová,[‡]
Jiří Kubišta,[†] Lenka Lukešová,[†] Philippe Meunier,[§] and Karel Mach*,[†]

J. Heyrovský Institute of Physical Chemistry, Academy of Sciences of the Czech Republic, Dolejškova 3, 182 23 Prague 8, Czech Republic, Department of Inorganic Chemistry, Faculty of Science, Charles University, Prague, Czech Republic, and Laboratoire de Synthèse et d'Electrosynthèse Organométalliques associé au CNRS (LSEO UMR 5632), Université de Bourgogne, Faculté des Sciences Gabriel, Dijon, France

Received June 30, 2005

Reactions at elevated temperatures (150 °C) of titanocene−η^2-bis(trimethylsilyl)ethyne (btmse) complexes $[(\eta^5\text{-C}_5\text{H}_{5-n}\text{Me}_n)_2\text{Ti}(\eta^2\text{-btmse})]$ (n = 3−5; **1b**−**d**) with bis((trimethylsilyl)ethynyl)dimethylsilane (**2a**) afford the unusual 1,1-bis(η^5-cyclopentadienyl)-4,4-dimethyl-3,5-bis(trimethylsilyl)-1-titana-4-silacyclohexa-2,5-diene complexes $[(\eta^5\text{-C}_5\text{H}_{5-n}\text{Me}_n)_2\text{Ti}\{\text{C}{=}\text{C}(\text{SiMe}_3)\}_2\text{SiMe}_2]$ (**4b**−**d**), whereas the nonmethylated precursor $[(\eta^5\text{-C}_5\text{H}_5)_2\text{Ti}(\eta^2\text{-btmse})]$ (**1a**) gives under similar conditions the known dinuclear, acetylide-bridged complex $[\{(\eta^5\text{-C}_5\text{H}_5)_2\text{Ti}(\mu\text{-}\eta^1{:}\eta^2\text{-C}{\equiv}\text{CSiMe}_3)\}_2]$ (**3a**). In contrast, analogous reactions with bis((trimethylsilyl)ethynyl)diphenylsilane (**2b**) give the product of simple ligand exchange $[(\eta^5\text{-C}_5\text{Me}_5)_2\text{Ti}(\eta^2\text{-Me}_3\text{SiC}{\equiv}\text{CSiPh}_2\text{C}{\equiv}\text{CSiMe}_3)]$ (**6d**) from **1d** and mixtures containing the similar complex $[(\eta^5\text{-C}_5\text{HMe}_4)_2\text{Ti}(\eta^2\text{-Me}_3\text{SiC}{\equiv}\text{CSiPh}_2\text{C}{\equiv}\text{CSiMe}_3)]$ (**6c**) and the titanasilacyclohexadiene $[\text{Ti}(\eta^5\text{-C}_5\text{HMe}_4)_2\text{Ti}\{\text{C}{=}\text{C}(\text{SiMe}_3)\}_2\text{SiPh}_2]$ (**5c**) from **1c**. Hydrogenolysis of **5c** (1 bar/3 h) affords 1,4-bis(trimethylsilyl)-5,5-diphenyl-5-silacyclopenta-1,3-diene (**7**). Compounds **4** and **5** possess a surplus of two bonding electrons at the titanium-bonded carbon atoms (C^α) with paired spins, whose presence is reflected by extremely short Ti−C^α bond lengths (1.981(4)−1.998(3) Å) and C^α−C^α contacts (1.821(4)−1.933(2) Å), the latter excluding the presence of a 3-silacyclopenta-1,4-diene moiety simply bonded to titanium via two σ bonds. DFT calculations showed that the two singly occupied p orbitals at C^α interact with the titanocene 1a_1 orbital, giving rise to a three-center−two-electron, Δ-shaped bond.

Introduction

Titanocene− and zirconocene−bis(trimethylsilyl)ethyne (btmse) complexes, $[\text{M}(\eta^5\text{-C}_5\text{H}_{5-n}\text{Me}_n)_2(\eta^2\text{-btmse})]$ (M = Ti, Zr; n = 0, 5), are known to react with a variety of reagents by simple replacement of the btmse ligand. In this way, a number of organometallic products arising from reactions of otherwise highly unstable transient titanocenes or zirconocenes, $[\text{M}(\eta^5\text{-C}_5\text{H}_{5-n}\text{Me}_n)_2]$, were obtained under relatively mild conditions.[1] For the cases where the reagent contains an acetylenic moiety, the direct reduction of the metallocene dichlorides by magnesium in the presence of the acetylenic reagent can afford the same product as that arising from the btmse replacement. However, the latter method is less specific, because the active magnesium can activate other bonds which can thus participate in the reaction with the acetylenic reagent. Examples of such a behavior can be sought in the magnesium reduction of $[\text{MCl}_2(\eta^5\text{-C}_5\text{Me}_5)_2]$ (M = Ti, Zr) in the presence of 1,4-disubstituted buta-1,3-diynes where methyl groups at the pentamethylcyclopentadienyl ligands reacted with the diynes,[2a,b] yielding products differing from those obtained from the metallocene-btmse complexes.[2c]

Generally, the reaction pathway depends on the nature of the metallocene and 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.[1c] Nonconjugated diynes with single-atom spacers, $(\text{R}^1\text{C}{\equiv}\text{C})_2\text{X}$, where X = CH_2, SiR^2_2, PR^3, were shown to react with zirconocene precursors in different ways, depending on the nature of the spacer X: diynes possessing the methylene group afford binuclear zir-

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* To whom correspondence should be addressed. E-mail: mach@jh-inst.cas.cz.
[†] Academy of Sciences of the Czech Republic.
[‡] Charles University.
[§] Université de Bourgogne.

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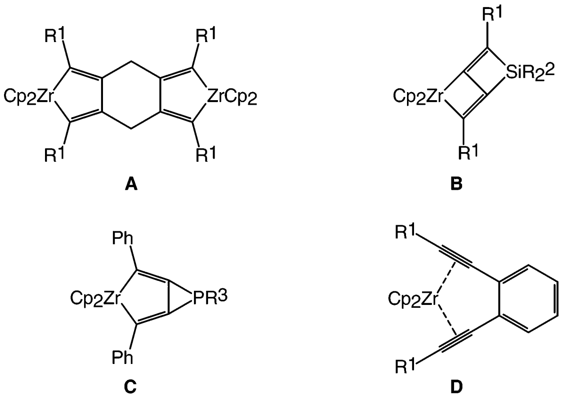
10.1021/om058038d CCC: \$30.25

Chart 1

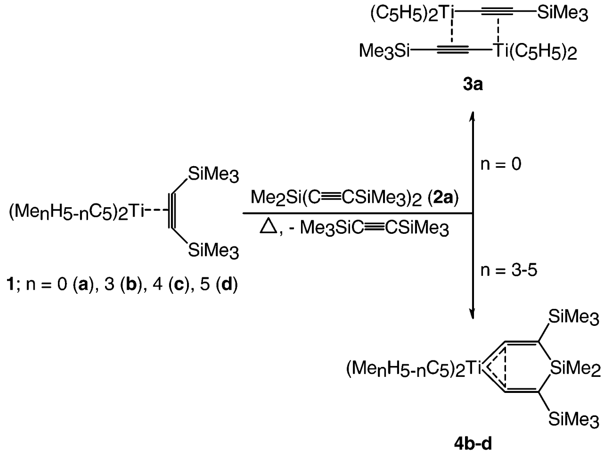


conacyclopentadiene complexes (Chart 1, **A**; $R^1 = SiMe_3$),[3] those with bis(organyl)silylene bridge give rise to annelated zirconacyclobutene−silacyclobutene compounds (Chart 1, **B**; R^1 = Me, Et, Ph; R^2 = Ph, *p*-tolyl),[4] and the dialkynylphosphanes $(PhC{\equiv}C)_2PR^3$ (R^3 = substituted aryl, CMe_3, $N(iPr)_2$) react to give zirconacyclopentadiene−phosphiranes (Chart 1, **C**).[5] In all cases, a divalent zirconium intermediate undergoes oxidative cycloaddition to provide Zr^{IV} complexes; only the rigid two-carbon *o*-phenylene spacer allows the zirconium atom to remain divalent, π-coordinating both triple bonds (Chart 1, **D**).[6]

Reactions between titanocene precursors and spaced diynes have been extensively studied by Rosenthal et al.[1c] It was shown that tetraalkynylsilanes react with titanocene− or zirconocene−btmse complexes to give dinuclear spirocyclic complexes in which the planar zirconacyclobutene−silacyclobutene moieties (type **B**) share a tetrahedral silicon atom.[7] We have found that compounds of type **B** (Chart 1) are accessible in high yields from $[Ti(\eta^2\text{-btmse})(\eta^5\text{-}C_5H_{5-n}Me_n)_2]$ (n = 0, 4, 5) and $R^2{}_2Si(C{\equiv}CR^1)_2$ for R^1/R^2 = Ph/Ph and Ph/Me, while for R^1/R^2 = *t*-Bu/Me the same reaction proceeds satisfactorily only with titanocene precursors having less sterically demanding cyclopentadienyl ligands such as C_5H_5 or 1,3-$C_5H_3Me_2$. The bulkier titanocene complex $[Ti(\eta^5\text{-}C_5HMe_4)_2(\eta^2\text{-btmse})]$ reacted sluggishly with $Me_2Si\{C{\equiv}C(t\text{-Bu})\}_2$ even at 150 °C/8 h, giving intractable product mixtures, whereas $[Ti(\eta^5\text{-}C_5Me_5)_2(\eta^2\text{-btmse})]$ underwent thermolysis at 130 °C to give the doubly tucked-in complex $[Ti(\eta^5\text{-}C_5Me_5)\{\eta^3{:}\eta^4\text{-}C_5Me_3(CH_2)_2\}]$.[8]

In this contribution, we report on the reactions of other bulky dialkynylsilanes, $(Me_3SiC{\equiv}C)_2SiMe_2$ and $(Me_3SiC{\equiv}C)_2SiPh_2$, with a series of titanocene−btmse complexes $[Ti(\eta^5\text{-}C_5H_{5-n}Me_n)_2(\eta^2\text{-btmse})]$ (n = 0, 3, 4, 5) and on the unprecedented bonding mode occurring in their products.

Scheme 1



Results and Discussion

The reaction of equimolar amounts of $[Ti(\eta^2\text{-}Me_3SiC{\equiv}CSiMe_3)(\eta^5\text{-}C_5H_{5-n}Me_n)_2]$ (**1**; n = 0 (**a**), 3 (**b**), 4 (**c**), 5 (**d**)) and $Me_2Si(C{\equiv}CSiMe_3)_2$ (**2a**) at 150 °C led to different products for n = 3−5 and for n = 0 (Scheme 1). For n = 0, the main reaction pathway was a scission of **2a**, affording the thermodynamically stable dimeric acetylide complex **3a**. The molecular structure of **3a** was virtually identical with those published by Wood et al.[9a] and by Rosenthal and Görls,[9b] although the unit cells differ crystallographically in all cases.[10] On the other hand, for n = 3−5, the above reaction yielded exclusively the highly unusual 1-titana-4,4-dimethyl-4-sila-3,5-bis(trimethylsilyl)cyclohexa-2,5-diene complexes **4b**−**d** (Scheme 1).

The molecular structures of **4b**−**d** have been established by X-ray single-crystal diffraction analysis (see below) and further corroborated by ^1H and ^{13}C NMR spectra. The spectra confirmed the presence of C_2- and/or mirror-symmetric $(\eta^5\text{-}C_5H_{5-n}Me_n)_2Ti$ units and two chemically different methylsilyl groups in the intensity ratio 2:1. In addition, the ^{13}C NMR spectra show very characteristic signals due to C^α and C^β at δ_C 335−338 and ca. 133, respectively. The proton-coupled ^{13}C NMR spectra clearly exclude the presence of hydrogen atoms at C^α and C^β, showing the expected $^1J_{CH}$ coupling constants for the rest of the molecules.

IR spectra of complexes **4b**−**d** and **5c** showed a strong and broad absorption band attributable to a $\nu(C_\alpha{=}C_\beta)$ stretching vibration, whose position shifts from 1544 cm^{-1} for **4b** to 1528 cm^{-1} for **4d**, following the increasing electron density at the titanium atom. In EI-MS spectra, the compounds displayed only low-intensity peaks for the molecular ions, whose intensities were lower as the temperature of evaporation became higher. In addition, the spectra displayed titanocene ions as the base peaks, ions of the diynes, and fragments of the latter.

In subsequent work, the diyne component was modified at the bridging silicon atom by replacing the methyls with phenyl groups. However, this change

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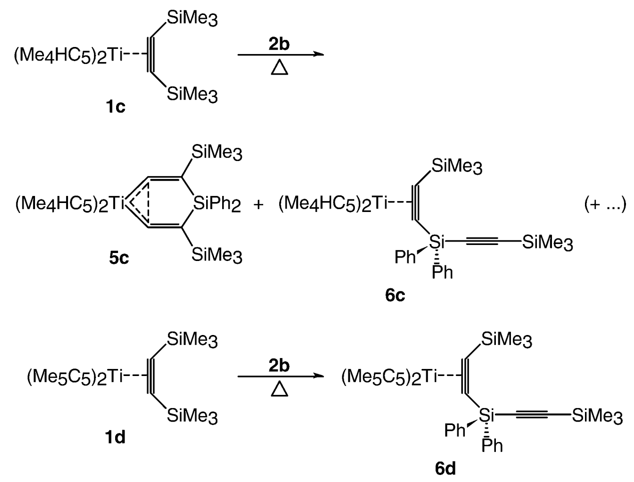
[10] Crystallographic data for $C_{30}H_{38}Si_2Ti_2$: monoclinic crystal system, space group $P2_1/n$ (No. 14), a = 11.3200(4) Å, b = 14.9700(5) Å, c = 16.6930 Å; β = 96.216(2)°; V = 2812.17(15) Å^3, Z = 4, ρ = 1.300 g cm^{-3}, CCDC deposition number CCDC-275739.

Scheme 2



resulted in a remarkable change of the diyne reactivity: the decamethyltitanocene complex **1d** reacted with bis((trimethylsilyl)ethynyl)diphenylsilane (**2b**) with ligand exchange to give $[(\eta^5\text{-}C_5Me_5)_2Ti(\eta^2\text{-}Me_3SiC{\equiv}CSiPh_2\text{-}C{\equiv}CSiMe_3)]$ (**6d**), while the less electron-saturated and less sterically congested titanocene–btmse complex **1c** afforded under identical conditions a mixture of $[(\eta^5\text{-}C_5HMe_4)_2Ti(\eta^2\text{-}Me_3SiC{\equiv}CSiMe_2C{\equiv}CSiPh_3)]$ (**6c**) and 1,1-bis(η^5-tetramethylcyclopentadienyl)-4,4-diphenyl-3,5-bis(trimethylsilyl)-1-titana-4-silacyclohexa-2,5-diene (**5c**) (Scheme 2). Neither prolonged heating of the **1d**–**2b** mixture to 130 °C nor heating to a higher temperature led to a titanasilacyclohexadiene complex. Instead, compound **6d** dissociated at 150 °C with a concurrent hydrogen transfer from two vicinal methyl groups of one cyclopentadienyl ligand onto the leaving silyldiyne to give the allyl–diene derivative $[Ti(\eta^5\text{-}C_5Me_5)\{\eta^3{:}\eta^4\text{-}C_5Me_3(CH_2)_2\}]$.[11] It is noteworthy that this compound results directly from thermolysis of **1d** (at 130 °C).[12] The reaction of **2b** with **1a** gave an intractable material, though the NMR signals at δ_C 234.3 and 248.5 clearly indicate the presence of a **6**-type product; attempts to isolate pure product, however, failed. The molecular structures of **6d** and **5c** were established by X-ray diffraction analysis and NMR and IR spectra.

Attempts to prepare the titanocene complexes with η^2-coordinated **2b** by reduction of the appropriate titanocene dichlorides with magnesium in the presence of 1 molar equiv of the diyne met with no success except for $[TiCl_2(\eta^5\text{-}C_5Me_5)_2]$, which afforded **6d** in a high yield. The analogous products **6a** and **6c** are likely formed as well, but the reluctance of the crude reaction mixtures to crystallize did not allow for isolation of pure products.

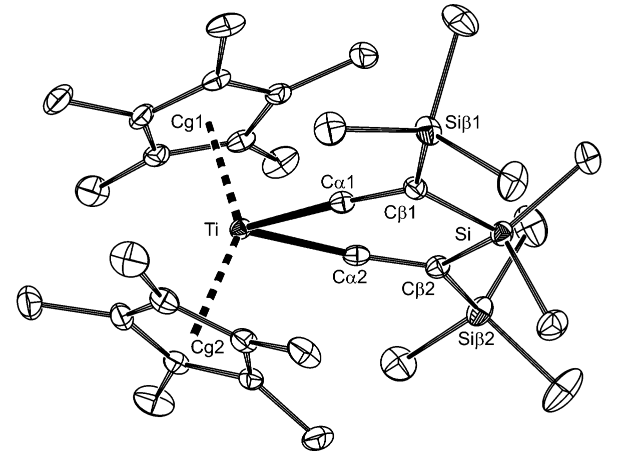
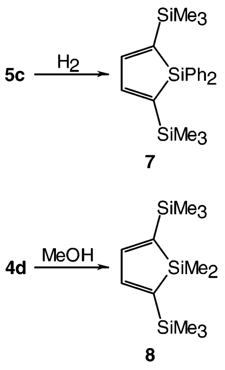


Figure 1. View of molecule 1 of compound **4d**. Thermal ellipsoids are drawn at the 30% probability level; hydrogen atoms are omitted for clarity.

Scheme 3



To support the formulation and bonding (see below) of **4** and **5** type complexes, we attempted hydrogenolysis or methanolysis of each representative type. Thus, exposure of hexane solution of **5c** to hydrogen (1 bar/3 h) resulted in liberation of 1,4-bis(trimethylsilyl)-5,5-diphenyl-5-silacyclopenta-1,3-diene (**7**; Scheme 3), which was identified by means ^1H and ^{13}C NMR and EI-MS spectra. Likewise, heating of a hexane solution of **4d** with excess methanol to 90 °C for 3 h afforded 1,4-bis(trimethylsilyl)-5,5-dimethyl-5-silacyclopenta-1,3-diene (**8**; Scheme 3), according to GC-MS analysis. Other products of the methanolysis were pentamethylcyclopentadiene (IR spectrum) and $[(\eta^5\text{-}C_5Me_5)Ti(OMe)(\mu\text{-}OMe)]_2$,[13] identified by its IR spectrum and X-ray crystal structure analysis.

Structural Data. The molecular structures of complexes **4b**–**d** and **5c** combine titanocene moieties with the unprecedented titanasilacyclohexadiene moieties, whose geometric parameters provide essential information for the discussion of the bonding situation. Molecular structures of complexes **4d** and **5c** as determined by single-crystal X-ray diffraction are presented in Figures 1 and 2, respectively, and the selected geometric parameters for **4b**–**d** and **5c** are listed in Table 1.

The arrangement of the bent-titanocene moiety is known to vary with the number of the ring methyl substituents.[14] In the compounds studied, the cyclopentadienyl ligands are staggered, and when they contain at least one hydrogen substituent on each cyclopentadienyl ligand, these protons occupy the hinge positions. In the permethylated complex **4d**, the sterically strained methyl groups in the hinge positions are responsible for a remarkably smaller dihedral angle between the cyclopentadienyl ring least-squares planes (38.3(2) vs 45.3(1)° for **4c**).

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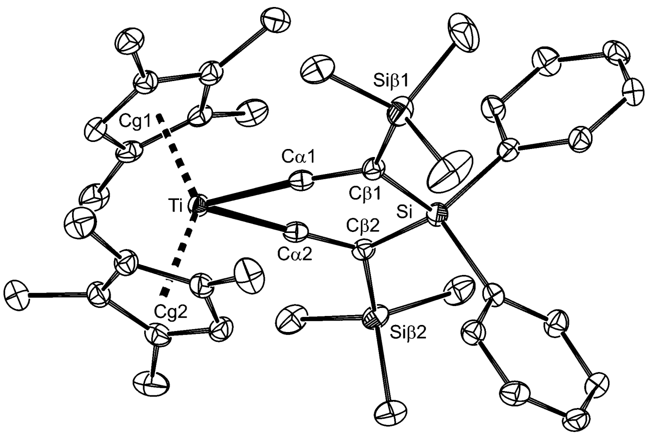


Figure 2. Perspective view of the molecular structure of **5c**, showing the atom-labeling scheme (30% probability).

Table 1. Selected Bond Lengths (Å) and Bond Angles (deg) for 4b−d and 5c

	4b	**4c**	**4d**	**5c**
		Bond Lengths		
Ti−Cg(1)[a]	2.068(1)	2.0717(7)	2.099(2)	2.0722(17)
Ti−Cg(2)[a]	2.067(1)	2.0764(7)	2.099(2)	2.0837(17)
Ti−C(α1)	1.996(2)	1.9894(14)	1.981(4)	1.998(3)
Ti−C(α2)	1.985(2)	1.9916(15)	1.996(4)	1.992(3)
C(α1)−C(β1)	1.326(3)	1.326(2)	1.333(6)	1.348(4)
C(α2)−C(β2)	1.324(3)	1.328(2)	1.338(6)	1.333(4)
Si−C(β1)	1.882(2)	1.8780(15)	1.878(5)	1.870(3)
Si−C(β2)	1.882(2)	1.8791(15)	1.881(4)	1.869(3)
C(β1)−Si(β1)	1.870(2)	1.8665(15)	1.862(4)	1.869(3)
C(β2)−Si(β2)	1.871(2)	1.8691(15)	1.859(4)	1.858(3)
C(α1)−C(α2)[b]	1.924(3)	1.933(2)	1.902(6)	1.821(4)
		Bond Angles		
Cg(1)−Ti−Cg(2)[a]	137.98(4)	139.12(3)	142.81(9)	140.13(7)
Cg(1)−Ti−C(α1)	107.38(7)	107.96(5)	105.86(14)	107.87(11)
Cg(1)−Ti−C(α2)	107.14(7)	108.25(5)	106.01(14)	107.54(11)
Cg(2)−Ti−C(α1)	109.44(7)	107.65(5)	106.51(14)	107.93(11)
Cg(2)−Ti−C(α2)	109.20(7)	107.24(5)	106.66(14)	107.29(11)
C(α1)−Ti−C(α2)	57.81(9)	58.09(6)	57.16(17)	54.32(13)
Ti−C(α1)−C(β1)	171.05(18)	171.3(1)	173.0(4)	174.4(3)
Ti−C(α2)−C(β2)	172.18(18)	171.0(1)	171.2(3)	174.8(3)
Si−C(β1)−C(α1)	110.13(16)	110.3(1)	109.6(3)	108.4(2)
Si−C(β2)−C(α2)	109.89(16)	110.4(1)	110.0(3)	108.8(2)
C(β1)−Si−C(β2)	98.65(10)	98.62(6)	98.5(2)	98.45(14)
Si(β1)−C(β1)-C(α1)	123.51(17)	123.97(11)	124.3(4)	123.2(2)
Si(β2)−C(β2)-C(α2)	122.89(17)	124.75(11)	124.4(3)	122.1(3)
φ[c]	48.18(10)	45.3(1)	38.3(2)	41.49(15)
τ[d]	23.33(14)	23.0(1)	19.3(2)	23.20(21)
τ[e]	24.85(14)	22.3(1)	19.0(2)	18.29(25)

[a] Cg(1) and Cg(2) are centroids of the cyclopentadienyl rings denoted by lower and higher numbers of carbon atoms, respectively. [b] Nonbonding distance. [c] φ is the dihedral angle between the least-squares cyclopentadienyl planes. [d] τ is the dihedral angle between the least-squares plane defined by Ti, C(α1), C(β1), C(α2), C(β2), and Si and the least-squares plane of the cyclopentadienyl ring of Cg(1). [e] τ is the dihedral angle between the least-squares plane defined by Ti, C(α1), C(β1), C(α2), C(β2), and Si and the least-squares plane of the cyclopentadienyl ring of Cg(2).

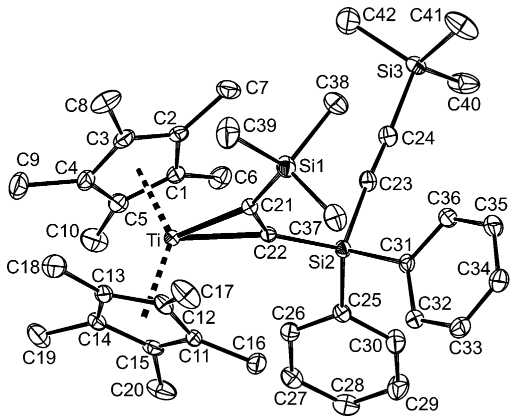


Figure 3. Perspective view of the molecular structure of **6d** with the atom-labeling scheme (30% probability).

Table 2. Selected Bond Lengths (Å) and Bond Angles (deg) for 6d

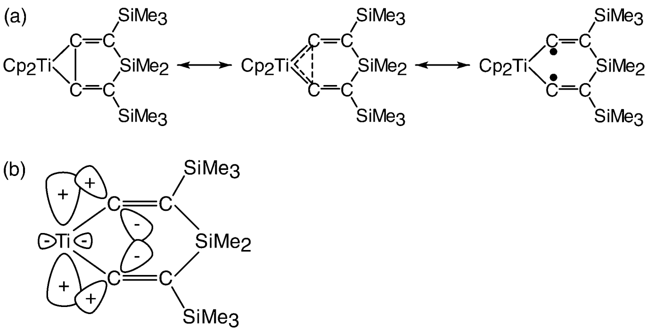
Ti−Cg(1)[a]	2.1174(12)	Ti−Cg(2)[a]	2.1235(12)
Ti−C(21)	2.130(2)	Ti−C(22)	2.128(2)
C(21)−C(22)	1.313(3)	C(23)−C(24)	1.210(3)
C(21)−Si(1)	1.868(2)	C(22)−Si(2)	1.846(2)
Si(2)−C(23)	1.839(3)	Si(3)−C(24)	1.847(3)
Si(2)−C(25)	1.877(2)	Si(2)−C(31)	1.883(2)
Cg(1)-Ti−Cg(2)[a]	138.69(5)	Cg(1)-Ti−C(21)	108.99(8)
Cg(1)-Ti−C(22)	109.43(7)	Cg(2)-Ti−C(21)	109.55(7)
Cg(2)-Ti−C(22)	110.37(7)	C(21)−Ti−C(22)	35.93(9)
Ti−C(21)−C(22)	71.97(14)	Ti−C(22)−C(21)	72.10(14)
Si(1)−C(21)−C(22)	136.27(19)	Si(2)−C(22)−C(21)	135.15(19)
C(22)−Si(2)−C(23)	109.44(11)	Si(2)−C(23)−C(24)	175.3(2)
Si(3)−C(24)−C(23)	176.8(2)	φ[b]	40.84(7)
τ[c]	21.35(12)	τ[d]	19.66(12)

[a] Cg(1) and Cg(2) are centroids of the C(1−5) and C(11−15) cyclopentadienyl rings, respectively. [b] φ is the dihedral angle between the least-squares cyclopentadienyl planes. [c] τ is the dihedral angle between the plane defined by Ti, C(21), and C(22) and the least-squares plane of the cyclopentadienyl plane of Cg(1). [d] τ is the dihedral angle between the plane defined by Ti, C(21), and C(22) and the least-squares plane of the cyclopentadienyl plane of Cg(2).

In all the structures, the 1-titana-4-silacyclohexa-2,5-diene moiety is planar, with both terminal trimethylsilyl groups attached to C^{β} carbon atoms with respect to the titanium center. This is at variance with structure **B** (Chart 1), where the shift of only one terminal silyl group allows for cross-linking via carbon atoms with the formation of a fused titanacyclobutene−silacyclobutene system.[8] There is no doubt about the position of the double bonds; their lengths range from 1.326(2) to 1.348(4) Å. The Ti−C_{α} bonds (1.985(2)−1.998(3) Å) are shorter by ca. 0.2 Å than in the corresponding derivatives possessing **B**-type structures,[8] and the distances between the C_{α} carbon atoms attached to titanium are within 1.821(4) Å (**5c**) and 1.933(2) Å (**4c**). The C−Si bonds within the rings (average 1.879(2) Å) are slightly longer than the C−Si bonds to outer trimethylsilyl groups (average 1.868(2) Å). The in-ring angles at the silicon atoms are much larger (average 98.65(7)°) than the analogous angles at the titanium atoms (average 58.05(6)°) and, correspondingly, the angles at the double bonds to Ti (average 171.2(1)°) are much larger than to ring Si atoms (110.2(1)°). Accordingly, the angles at the double bonds involving the outer Si atoms are larger than expected for the ideal sp^2 hybridization (average 124.3(1)°). The structure of **5c** with a bridging diphenylsilyl group differed from the **4b**−**d** structures in a considerably shorter C_{α}−C_{α} distance of 1.821(4) Å, a smaller C_{α}−Ti−C_{α} angle at the Ti atom (54.3(1)°), and a more linear arrangement of Ti−C_{α}−C_{β} bonds (average Ti−C_{α}−C_{β} = 174.6(3)°) (see Table 1).

In compound **6d**, the permethyltitanocene moiety binds one triple bond in a π-bonding mode, as in the parent complex **1d** (Figure 3). The molecular geometry of the titanocene−acetylenic moiety (Table 2) is very close to that of **1d** (n.b.: the triple bond is substituted by similar silyl groups).[1b,15] The angles at the coordinated triple bond, Si1−C21−C22 = 136.3(2)° and Si2−C22−C21 = 135.2(2)°, and at the free triple bond, Si2−

Scheme 4



C23−C24 = 175.3(2)° and Si3−C24−C23 = 176.8(2)°, differ negligibly in the pairs, and the bond lengths C21−C22 = 1.313(3) Å and C23−C24 = 1.210(3) Å fall into the range of distances known thus far.[1c] The angle subtended by the cyclopentadienyl least-squares planes, 40.8(1)°, is nearly regularly bisected by the Ti,C21,C22 plane (21.3(1) and 19.6(1)°). A similar permethyltitanocene−1,4-bis(trimethylsilyl)buta-1,3-diyne π-coordinated by one triple bond showed a remarkable difference between the angles of the coordinated triple bond with the $SiMe_3$ group (130.0(2)°) and with the carbon atom of the noncoordinated triple bond (141.9(3)°).[2a]

Ab Initio Study. A $C^{\alpha}-C^{\alpha}$ distance larger than 1.82 Å is not compatible with a σ bond, as drawn in a silacyclopentadiene−titanacyclopropane representation of compounds **4** and **5**. Simultaneously, the diamagnetism of these compounds corroborates that that the compounds are not true biradicals (Scheme 4a). On the other hand, the shortness of the Ti−C^{α} bonds can be accounted for by the contribution of multiple bonding (see discussion of the crystal structures above). Since there is no pairing electron available at the titanium atom, whose valency cannot be formally higher than 4, one has to assume that one valence electron resides predominantly on each of the C^{α} carbon atoms, resulting not only in an increase of the Ti−C bond order but also leading to some $C^{\alpha}-C^{\alpha}$ interactions that are reflected in contacts significantly shorter than the sum of van der Waals radii.

For a proper understanding of the rather peculiar bonding scheme, the molecule of **4c** has been subjected to DFT studies. In agreement with chemical intuition, calculational results confirmed the presence of σ bonds between C^{α} carbon atoms and the central titanium atom. These σ bonds are the result of the Cp_2Ti fragment b_2 frontier orbital[16] interacting with the appropriately oriented carbon p orbitals. As further expected, the second set of p orbitals generates the π bonds between C^{α} and C^{β} atoms.

Examination of the highest occupied molecular orbital (HOMO) revealed the nature of the seemingly missing $C^{\alpha}-C^{\alpha}$ bond. The spatial shape of the HOMO indicates that C^{α} carbon atoms undergo a bonding interaction, despite their large interatomic distance, and this interaction is extended even to the metallic center. The respective molecular orbital is generated from the empty a_1 orbital at the titanium atom, which being in proper orientation for good overlap with the singly occupied carbon p orbitals (Scheme 4b), causes the carbon p lobes to become more elongated and generate a long-range $C^{\alpha}-C^{\alpha}$ bond (Figure 4). Although this bond is formally of σ type (the wave function having no node in the $C^{\alpha}-C^{\alpha}$ interconnection), it can be described more properly as a three-center−two-electron (3c−2e) C−Ti−C bond both for its shape and for the involvement of the metallic center. To justify the correctness of the 3c−2e bond formalism, a natural bonding analysis (NBA) was carried out against several possible Lewis representations and the best fit to the molecular wave function was obtained under the assumption of a 3c−2e bonding interaction while retaining the "regular" Ti−C^{α} σ bonds. In our further discussion, this 3c−2e bond will be referred to as a Δ bond because of its unique shape.

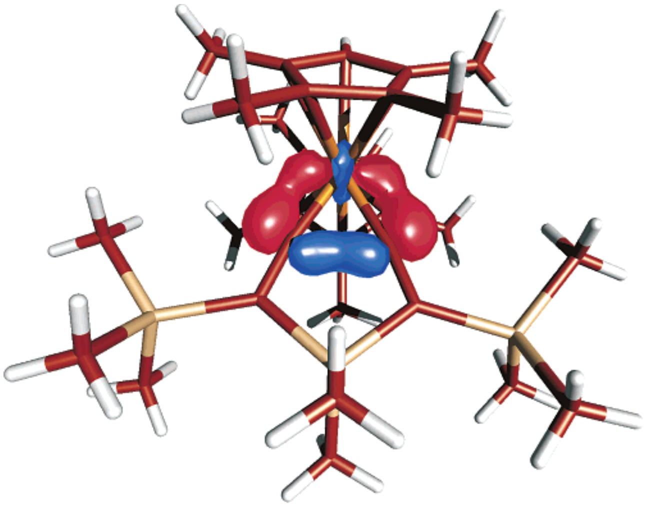


Figure 4. Graphical representation of the $\Psi 1$ molecular orbital (Δ bond).

The above molecular wave function was also utilized to obtain the NMR shifts for individual atoms in **4c**. The excellent correlation between GIAO parameters and observed ^{13}C NMR shifts confirmed the correctness of the wave function.

The genesis of the Δ bond is similar to that of other 3c−2e bonds. Its best theoretical description lies in the extension of the MO LCAO scheme to three interacting atoms, producing three MO's (one bonding, one practically nonbonding, and one antibonding) from three AO's. It is important to realize at this point that any potential ligand orbital going into interaction with the titanocene a_1 orbital must transform according to the same irreducible representation. In our case, however, neither of the carbon p orbitals obeys this criterion. Nevertheless, the hybrid orbital resulting from the linear combination $\varphi 1 + \varphi 2$ meets this requirement (Scheme 5). Interaction of this hybrid orbital with the metallic a_1 orbital gives rise to one bonding (Ψ_1, the Δ bond) and one nonbonding MO (Ψ_2). The third MO (Ψ_3), resulting from the antibonding interaction $\varphi 1 - \varphi 2$, has b_2 symmetry and will have an interaction with the appropriate frontier titanocene orbital.

Comments on the Tentative Reaction Mechanism. As for the formation of zirconocene **B**-type

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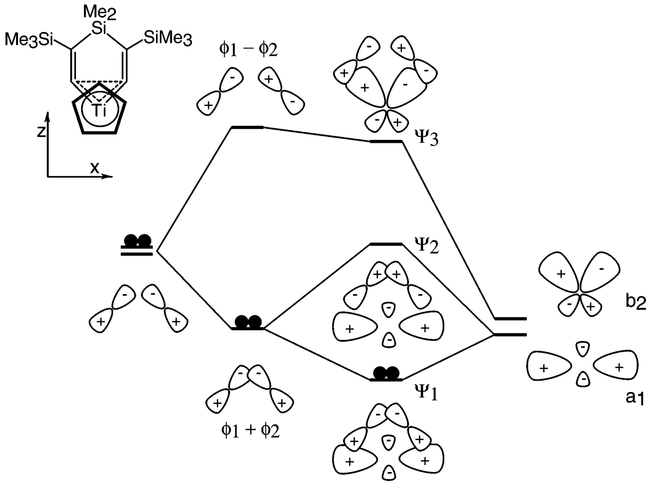
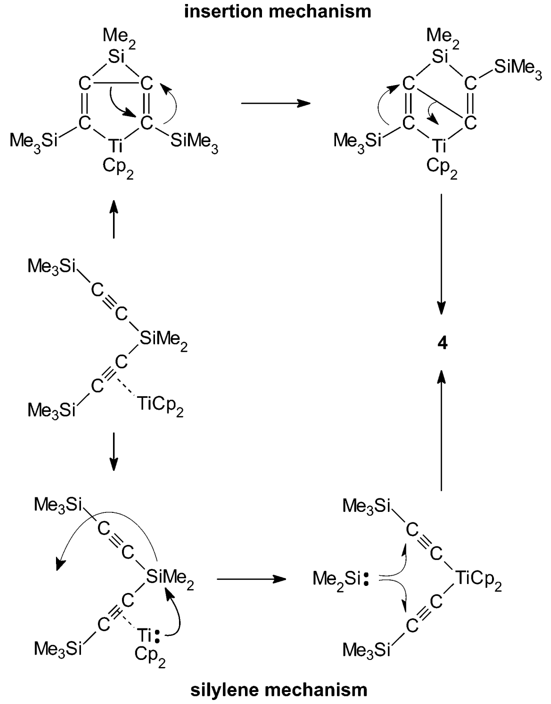
(15) Burlakov, V. V.; Rosenthal, U.; Beckhaus, R.; Struchkov, Yu. T.; Oehme, G.; Shur, V. B.; Vol'pin, M. E. *Organomet. Chem. USSR* **1990**, *3*, 237−238. (b) Burlakov, V. V.; Polyakov, A. V.; Yanovsky, A. I.; Struchkov, Yu. T.; Shur, V. B.; Vol'pin, M. E.; Rosenthal, U.; Görls, H. *J. Organomet. Chem.* **1994**, *476*, 197−206.

(16) Orbitals are labeled according to: Lauher, J. W.; Hoffmann, R. *J. Am. Chem. Soc.* **1976**, *98*, 1729−1741.

Scheme 5



Scheme 6



complexes, a vinylidene mechanism and an insertion mechanism were considered, both suggesting the initial coordination of the dialkynylsilane by one triple bond to the titanium atom (Scheme 6).[4b] The vinylidene mechanism should plausibly give the **B**-type product; however, the titanocene–vinylidene species are known to be highly unstable,[17] and their presence is not considered to take part in catalytic conversions mediated by early-transition-metal complexes.[18] On the other hand, the insertion mechanism required the transient formation of a fused zirconacyclopentadiene–silirane intermediate.[4b] The rearrangement of the latter to the **B**-type complex was recently explained by Negishi to proceed via formation of zirconate–carbocationic dipoles.[19]

The formation of thermodynamically stable compounds **4** and **5**, different from those of type **B**, is apparently controlled by electronic and steric effects of terminal trimethylsilyl groups. These are in "allylic" positions with respect to the bridging dimethylsilylene group, which leads to the induction of a positive charge on all silicon atoms and, hence, to their mutual destabilization. This effect has recently been demonstrated for the first stable vinyl cation stabilized by the presence of two silyl groups in positions β to the carbocation.[20] The same effect is apparently responsible for an easy scission of 1,4-bis(trimethylsilyl)buta-1,3-diyne at low-valent titanocene species, affording dimeric titanocene(III) acetylides,[21a] methyl-substituted titanocene(III) diacetylide tweezer complexes,[21b] or butenyne derivatives,[22] as well as for an easy silicon migration over cyclopentadiene systems.[23]

When the above-mentioned insertion mechanism[4b,20] (Scheme 6) is considered, the silicon β-effect of bridging silylene could also facilitate the 1,2-shift of $\mathrm{SiMe_3}$ groups following the subsequent scission of the silirane and silacyclobutene rings. In the particular case of dialkynylsilanes **2a**,**b**, however, the two terminal trimethylsilyl groups in β-positions should also facilitate the liberation of silylene. Since compounds **4** and **5** are formed at temperatures where the titanocene–btmse complexes lose btmse while generating titanocene intermediates,[12] one can expect the Ti d^2 atom to compete with the silylene to give titanocene diacetylide, which is subsequently stabilized by addition of the evolved silylene to give thermodynamically stable structures **4** or **5** (Scheme 6). The process, for simplicity depicted as a concerted one, is apparently a complex sequence of steps which may contain, e.g., an oxidative addition of the $\mathrm{{\equiv}C{-}SiMe_2C{\equiv}}$ bond to Ti(II) followed by liberation of $\mathrm{SiMe_2}$, which brings about the formation of **3a** in case of more acidic and less sterically shielded $[\mathrm{Ti}(\eta^5\text{-}\mathrm{C_5H_5})_2]$ species.[24] For highly methyl-substituted titanocenes the homolysis of the $\mathrm{Ti{-}SiMe_2(C_2SiMe_3)}$ bond should lead to the intermediate depicted in Scheme 6. In the absence of direct experimental evidence, however, no preference can be given to either mechanism. A somewhat similar process resulting in a formal shift of phenyl groups was observed during coupling of phenylacetylide groups in zirconocene diacetylide induced by vanadocene.[25]

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[24] Oxidative addition of $\mathrm{Me_3SnC{\equiv}CSnMe_3}$ to $\{(\eta^5\text{-}\mathrm{C_5H_{5-\mathit{n}}Me_\mathit{n}})_2\mathrm{Ti}\}$ species afforded analogues of **3a,** $[\{(\eta^5\text{-}\mathrm{C_5H_{5-\mathit{n}}Me_\mathit{n}})_2\mathrm{Ti}(\mu\text{-}\eta^2{:}\eta^1\text{-}\mathrm{C{\equiv}CSnMe_3})\}_2]$ ($n = 0, 2$), and hexamethyldisilane under mild conditions: Varga, V.; Mach, K.; Hiller, J.; Thewalt, U.; Sedmera, P.; Polášek, M. *Organometallics* **1995**, *14*, 1410–1416.

Conclusions

The interaction of siladiyne **2a** with the highly methylated titanocene equivalents **1b**,**c** results in complete isomerization of the siladiyne, yielding the uprecedented titanasilacyclohexadiene complexes **4b**−**d**. In contrast, the nonmethylated titanocene precursor **1a** gives under similar conditions the known complex **3a**, whereas siladiyne **2b** reacts to give the η^2 complexes **6c**,**d** and titanasilacyclohexadiene **5c**, depending on the titanocene component. As indicated by theoretical calculations, the titanasilacyclohexadiene complexes feature unusual triangular 2e−3c bonds involving the titanium and both C^{α} atoms. The reasons for the 2-fold migration of the trimethylsilyl groups in diynes **2** can be sought in their steric interactions with the bulky methyl-substituted cyclopentadienyl ligands and their electronic interaction with the silylene group. In consideration of the reaction course, one has to bear in mind that the reaction requires temperatures around 150 °C to proceed, which allows the products to acquire the thermodynamically most stable structure.

Experimental Section

General Considerations. Reactions of titanocene−btmse complexes with **2a**,**b** were carried out under vacuum conditions in sealed glass ampules equipped with breakable glass seals. Sample tubes for NMR measurements were also sealed to glass devices at the vacuum line, filled with C_6D_6 solutions under vacuum, and sealed off. Crystalline samples for EI-MS and IR spectra, melting points, and X-ray diffraction measurements were handled in a Labmaster 130 glovebox (mBraun) under purified nitrogen.

NMR spectra were recorded on a Varian UNITY Inova 400 spectrometer (^{1}H, 399.95 MHz; ^{13}C, 100.58 MHz) in C_6D_6 solutions at 25 °C. Chemical shifts (δ/ppm) are referenced to the residual solvent signal (δ_H 7.15) and to the solvent resonance (δ_C 128.0). EI-MS spectra were measured on a VG-7070E mass spectrometer at 70 eV. The crystalline samples in sealed capillaries were opened and inserted into a direct inlet probe under argon. IR spectra were measured in an air-protecting cuvette on a Nicolet Avatar FT IR spectrometer in the range 400−4000 cm^{-1}. KBr pellets were prepared in the glovebox.

Chemicals. The solvents THF, hexane, and toluene were dried by refluxing over $LiAlH_4$ and stored as solutions of dimeric titanocene $[(\mu\text{-}\eta^5{:}\eta^5\text{-}C_5H_4C_5H_4)(\mu\text{-}H)_2\{Ti(\eta^5\text{-}C_5H_5)\}_2]$.[26] Butyllithium in hexanes, dimethyldichlorosilane, diphenyldichlorosilane, and (trimethylsilyl)ethyne (all Aldrich) were transferred by syringe under argon. Bis((trimethylsilyl)ethynyl)dimethylsilane and bis((trimethylsilyl)ethynyl)diphenylsilane were synthesized as reported.[27] Complexes **1a**−**e** were obtained in nearly quantitative yields from the reduction of the respective bis(η^5-cyclopentadienyl)dichlorotitanium(IV) complexes with magnesium in THF in the presence of excess btmse, as reported earlier.[12]

Preparation of Bis((trimethylsilyl)ethynyl)dimethylsilane $[(Me_3SiC{\equiv}C)_2SiMe_2]$ (2a). LiBu (2.5 M in hexanes, 46.0 mL, 0.115 mol) was added to a stirred solution of (trimethylsilyl)ethyne (17.0 mL, 0.120 mmol) in hexane (50 mL). After the mixture was stirred for 2 h, about half of the solvent was distilled off under vacuum. The residue was cooled to dry-ice temperature, dichlorodimethylsilane (6.0 mL, 50 mmol) was added dropwise, and the mixture was warmed to ambient temperature with stirring and then refluxed for 6 h. Subsequently, most of the volatiles were distilled off, and the residue was purified by chromatography on alumina using hexane as the eluent. The pure product was obtained as a colorless oil, which crystallized in a refrigerator. Yield: 10.3 g (68% on $Me_3SiC{\equiv}CH$).

^{1}H NMR (C_6D_6): δ 0.08 (s, 9 H, Si*Me*$_3$), 0.34 (s, 3 H, Si*Me*$_2$). ^{13}C{^{1}H} NMR (C_6D_6): δ −0.4 (Si*Me*$_3$), 0.5 (Si*Me*$_2$), 110.2 and 115.6 (*C*≡*C*). IR (neat, cm^{-1}): 2948 (s), 2895 (m), 2850 (sh, w), 2780 (vw), 2100 (w), 1940 (vw), 1863 (vw), 1450 (w), 1405 (m), 1315 (w), 1248 (s), 1116 (w), 1040 (w, b), 832 (vs, b), 753 (s), 697 (m), 664 (w), 625 (vw), 614 (vw), 440 (w).

Preparation of Bis((trimethylsilyl)ethynyl)diphenylsilane $[(Me_3SiC{\equiv}C)_2SiPh_2]$ (2b). The above procedure for obtaining **2a** was followed using the same molar ratios of LiBu, $HC{\equiv}CSiMe_3$, and $SiCl_2Ph_2$. Column chromatography as above afforded pure crystalline **2b**. Yield: 17.5 g, 83%.

^{1}H NMR (C_6D_6): δ 0.00 (s, 9 H, Si*Me*$_3$), 7.04−7.98 (m, 5 H, Ph). ^{13}C{^{1}H} NMR (C_6D_6): δ −0.5 (Si*Me*$_3$), 107.2, 119.1 (*C*≡*C*), 128.4, 130.5, 133.1, and 135.2 (Ph). EI-MS (50 °C; *m/z* (relative abundance, %)): 378 (12), 377 (25), 376 ($M^{\bullet+}$; 57), 375 (23), 362 (16), 361 ($[M - Me]^+$; 37), 336 (12), 303 ($[M - SiMe_3]^+$; 22), 281 (12), 280 (27), 279 ($[M - C_2SiMe_3]^+$; 84), 226 (13), 221 (27), 217 (20), 202 ($[M - C_2SiMe_3 - Ph]^+$; 16), 197 (19), 173 (21), 159 (36), 145 (17), 136 (15), 135 (87), 129 (21), 105 (40), 73 ($[SiMe_3]^+$; 100). IR (KBr; cm^{-1}): 3068 (m), 3051 (m), 3023 (w), 2961 (s), 2107 (w), 1589 (w), 1570 (vw), 1484 (w), 1429 (m), 1251 (s), 1188 (w), 1114 (s), 1029 (vw), 998 (vw), 847 (vs, b), 768 (vs, b), 741 (m), 711 (m), 698 (s), 501 (s).

Preparation of $[\{(\eta^5\text{-}C_5H_5)_2Ti(\mu\text{-}\eta^1{:}\eta^2\text{-}C{\equiv}CSiMe_3)\}_2]$ (3a). A mixture of **1a** (0.35 g, 1.0 mmol) and **2a** (0.25 g, 1.0 mmol) in toluene (10 mL) was heated to 150 °C for 5 h in a sealed ampule. After the mixture was cooled, all volatiles were removed under vacuum, and the residue was extracted with hexane. Cooling of a concentrated solution in the refrigerator gave orange-red crystals, which were identified by X-ray single-crystal analysis to be another crystallographic modification of **3a**.[8,9] Yield: 0.18 g (65%). (Note: NMR analysis of the crude reaction mixture revealed minor signals attributable to a titanasilahexadiyne product, particularly the signal at δ_C 343.2.)

EI-MS (direct inlet, 70 eV, 160 °C; *m/z* (relative abundance) 550 ($M^{\bullet+}$; 7), 276 (11), 275 ($[M/2]^+$; 36), 274 (7), 260 (9), 202 (8), 180 (10), 179 (21), 178 ($[(C_5H_5)_2Ti]^+$; 100), 177 (12), 176 (12), 113 (14), 83 (12), 71 (11), 69 (9), 57 (18), 55 (11), 43 (17). IR (KBr; cm^{-1}): 3090 (w, b), 2945 (s), 2889 (m), 2847 (w), 1788 (s), 1560 (m), 1503 (w), 1443 (m), 1404 (m), 1365 (w), 1297 (vw), 1246 (s), 1128 (vw), 1066 (w), 1016 (s), 905 (m), 835 (vs, b), 753 (s), 723 (m), 687 (s), 640 (m), 593 (m), 506 (vw), 482 (w), 442 (w). UV−vis (hexane; nm): 370 (sh) > 450 ≫ 830 > 1050 (sh).

Preparation of 4,4-Dimethyl-3,5-bis(trimethylsilyl)-1-titana-4-silacyclohexa-2,5-dienes (4). Solutions of the $[Ti(\eta^5\text{-}C_5H_{5-n}Me_n)_2(\eta^2\text{-}Me_3SiC{\equiv}CSiMe_3)]$ complexes (**1b**−**d**; 2.0 mmol) in *m*-xylene (10 mL) were mixed with **2a** (0.6 mL, 2.3 mmol), and the mixture was heated to 150 °C for 8 h (**1b**,**c**) or 5 h (**1d**) in an ampule with attached quartz cell ($d = 0.2$ cm). The conversion of the btmse complexes to titanasilacyclohexadiene compounds was followed by diminution of absorption band intensity due to the starting btmse complex (**1b** at 915 nm, **1c** at 920 nm, and **1d** at 915 nm). When the reaction was complete, the ampule was cooled to ambient temperature and all volatiles were distilled off under vacuum at 100 °C. The residue was extracted with hexane. Concentrated solutions were cooled by dry ice for crystallization. The crystals were recrystallized from a minimum amount of hexane in a freezer (−18 °C).

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cyclo-[(η^5-1,2,3-$C_5H_2Me_3$)$_2$Ti{C=C($SiMe_3$)}$_2$$SiMe_2$] (4b). Red crystals. Yield: 0.71 g (69%). Mp: 95 °C. ^{1}H NMR (C_6D_6): δ 0.19 (s, 9 H, Si*Me*$_3$), 0.47 (s, 3 H, Si*Me*$_2$), 1.73 (s, 3 H, C_5*Me*), 1.78 (s, 6 H, C_5*Me*$_2$), 5.00 (s, 2 H, C_5*H*$_2$). ^{13}C{^{1}H} NMR (C_6D_6): δ 1.5 (Si*Me*$_3$), 3.4 (Si*Me*$_2$), 12.3 and 14.8 (2 C) (C_5*Me*$_3$), 101.0 (*C*H of $C_5Me_3H_2$), 115.6 (2 C), 116.3 (*C*Me of $C_5Me_3H_2$); 133.4 (s, *C*$_{ipso}$), 338.0 (s, C$_{ipso}$). EI-MS (110 °C; *m/z* (relative abundance, %)): 515 (10), 514 (M$^{•+}$; 16), 264 (9), 263 (25), 262 ([Cp′$_2$Ti]$^+$; 100), 261 (19), 260 (15), 252 ([**2a**]$^+$; 16), 238 (10), 237 ([**2a** − Me]$^+$; 35), 155 ([Cp′Ti]$^+$; 7), 141 (9), 73 ([SiMe$_3$]$^+$; 59). IR (KBr; cm^{-1}): 3083 (vw), 2949 (vs), 2905 (s), 2854 (m), 1544 (vs), 1445 (vw), 1430 (vw), 1392 (w), 1377 (m), 1245 (vs), 1010 (m), 899 (s), 852 (vs), 836 (vs), 801 (s), 766 (s), 684 (m), 635 (vw, 611 (w), 588 (vw), 487 (m), 431 (m). Anal. Calcd for $C_{28}H_{46}Si_3Ti$ (514.81): C, 65.33; H, 9.01. Found: C, 65.38; H, 8.97.

cyclo-[(η^5-C_5HMe_4)$_2$Ti{C=C($SiMe_3$)}$_2$$SiMe_2$] (4c). Orange-brown crystals. Yield: 0.91 g (84%). Mp: 160 °C. ^{1}H NMR (C_6D_6): δ 0.21 (s, 9 H, Si*Me*$_3$), 0.49 (s, 3 H, Si*Me*$_2$), 1.73 and 1.75 (2 × s, 6 H, C_5*Me*$_4$H), 5.01 (s, 1 H, C_5Me_4*H*). ^{13}C NMR (C_6D_6): δ 1.8 (q, $^1J_{CH}$ = 118 Hz, Si*Me*$_3$), 3.4 (q, $^1J_{CH}$ = 119 Hz, Si*Me*$_2$), 12.9 and 14.0 (2 × q, $^1J_{CH}$ = 126 Hz, C_5*Me*$_4$H), 105.2 (d, $^1J_{CH}$ = 167 Hz, C_5Me_4H, *C*H), 111.6 and 116.1 (s, C_5Me_4H, *C*Me), 132.8 (s, C$_{ipso}$), 337.6 (s, C$_{ipso}$). EI-MS (130 °C; *m/z* (relative abundance, %)): 542 (M$^{•+}$; 0.4), 292 (10), 291 (28), 290 ([(C_5HMe_4)$_2$Ti]$^+$; (100), 289 (17), 288 (15), 252 ([**2a**]$^+$; 5), 238 (7), 237 ([**2a** − Me]$^+$; 24), 111 (5), 73 ([SiMe$_3$]$^+$; 11). IR (KBr; cm^{-1}): 3060 (vw), 2949 (s), 2906 (s), 2856 (m), 1541 (vs, b), 1434 (w), 1380 (m), 1368 (m), 1245 (s), 1149 (vw), 1022 (w, b), 897 (s), 850 (vs), 835 (vs), 766 (m), 683 (m), 644 (vw), 613 (w), 486 (w), 435 (m). Anal. Calcd for $C_{30}H_{50}Si_3Ti$ (542.87): C, 66.37; H, 9.28. Found: C, 66.39; H, 9.26.

cyclo-[(η^5-C_5Me_5)$_2$Ti{C=C($SiMe_3$)}$_2$$SiMe_2$] (4d). Orange-brown crystals. Yield: 0.89 g (78%). Mp: 219 °C. ^{1}H NMR (C_6D_6): δ 0.25 (s, 3 H, Si*Me*$_3$), 0.53 (s, 1 H, Si*Me*$_2$), 1.73 (s, 5 H, C_5*Me*$_5$). ^{13}C NMR (C_6D_6; only $^1J_{CH}$ are given): δ 1.9 (q, $^1J_{CH}$ = 118 Hz, Si*Me*$_3$), 3.6 (q, $^1J_{CH}$ = 119 Hz, Si*Me*$_2$), 12.3 (q, $^1J_{CH}$ = 126 Hz, C_5*Me*$_5$), 113.1 (s, *C*$_5$Me$_5$), 132.0 (s, *C*$_{ipso}$), 335.5 (s, C$_{ipso}$). EI-MS (180 °C; *m/z* (relative abundance, %)): 570 (M$^{•+}$; 1), 320 (18), 319 (46), 318 ([Cp$^*_2$Ti]$^+$; 100), 317 (26), 316 (22), 252 ([**2a**]$^+$; 3), 237 ([**2a** − Me]$^+$; 8), 181 ([(C_5Me_5)Ti − 2H]$^+$; 6), 178 (4), 159 (11), 73 ([SiMe$_3$]$^+$; 6). IR (KBr; cm^{-1}): 2978 (sh), 2953 (vs), 2903 (vs), 2867 (sh), 1528 (s, b), 1435 (m), 1375 (s), 1253 (sh), 1246 (vs), 1021 (m), 902 (s), 844 (vs), 835 (vs), 769 (m), 684 (m), 643 (vw), 615 (w), 485 (m), 432 (m). Anal. Calcd for $C_{32}H_{54}Si_3Ti$ (570.92): C, 67.32; H, 9.53. Found: C, 67.37; H, 9.49.

Reaction of 1c with 2b. A reaction as above of **1c** with **2b** in toluene at 150 °C for 8 h gave a mixture of the η^2-alkyne complex **6c**, the titanasilahexadiene complex **5c**, and an unknown titanocene compound. Whereas pure **5c** partly crystallized from the mixture, **6c** and the unknown component could not be separated due to similar solubilities. Nevertheless, data for **6d** allowed us to analyze NMR data for the mixture (**5c**, δ_C 336.32 (C$_{ipso}$); unknown byproduct, δ_C 179.1 (CH) and 246.8 (C$_{ipso}$)).

Data for **5c** are as follows. Mp: 175 °C. EI-MS (direct inlet, 70 eV, 220 °C; *m/z* (relative abundance)): 666 (M$^{•+}$; 1), 376 ([**2b**]$^+$; 19), 361 ([**2b** − Me]$^+$; 9), 292 (15), 291 (38), 290 ([Cp′$_2$Ti]$^+$; 100), 289 (29), 288 (23), 135 (32), 91 (9), 73 (29). IR (KBr; cm^{-1}): 3083 (vw), 3067 (w), 3045 (vw), 2949 (s), 2903 (s), 2861 (sh), 1514 (s, b), 1429 (m), 1379 (w), 1328 (vw), 1240 (s), 1181 (vw), 1101 (m, b), 1021 (w), 908 (m), 835 (vs), 756 (m), 736 (m), 701 (s), 648 (vw), 614 (vw), 523 (m), 504 (m), 455 (w).

Data for **6c** are as follows. ^{1}H NMR (C_6D_6): δ −0.02 and 0.23 (2 × s, 9 H, SiMe$_3$), 1.36, 1.56, 1.97, and 2.04 (4 × s, 6 H, C_5H*Me*$_4$), 5.85 (s, 2 H, C_5*H*Me$_4$), 7.06−7.47 (m, 10 H, Ph). ^{13}C{^{1}H} NMR (C_6D_6): δ −0.13 and 3.13 (SiMe$_3$), 13.19, 13.27, 13.60, and 14.30 (Me of C_5HMe_4), 113.64 (CH of C_5HMe_5), 114.31 and 117.47 (C≡C), 122.65, 123.16, 124.74, and 125.52 (C$_{ipso}$ of C_5HMe_5), 127.64, 129.36, and 135.84 (3 × CH of Ph), 137.38 (C$_{ipso}$ of Ph), 227.21 and 254.78 (η^2-C≡C). UV−vis (hexane; nm): 920.

Preparation of [Ti(η^5-C_5Me_5)$_2$(η^2-$Me_3SiC{\equiv}CSiPh_2$-$C{\equiv}CSiMe_3$)] (6d). A solution of [Ti(η^5-C_5Me_5)$_2$(η^2-$Me_3SiC{\equiv}CSiMe_3$)] in toluene (2.0 mmol in 10 mL) was mixed with solid **2b** (0.752 g, 2.0 mmol), and the mixture was heated to 130 °C for 8 h. After the mixture was cooled, all volatiles were evaporated under vacuum at 100 °C, and the dark solid was extracted by hexane. Slow cooling of the concentrated solution in a freezer induced crystallization of blue crystals of [Ti(η^5-C_5Me_5){η^3:η^4-$C_5Me_3(CH_2)_2$}].[11] These were removed, and the yellow solution was further cooled to −18 °C for crystallization. Yellow crystals were obtained from the mother liquor after 3 days. The mother liquor afforded an additional crop of crystals. Total yield of **6d**: 1.08 g (78%).

Mp: 182 °C. ^{1}H NMR (C_6D_6): δ 0.06 and 0.22 (2 × s, 9 H, SiMe$_3$), 1.80 (s, 30 H, C_5Me_5), 7.08−7.37 (m, 10 H, Ph). ^{13}C{^{1}H} NMR (C_6D_6): δ −0.19 and 4.42 (SiMe$_3$), 13.14 (Me of C_5Me_5), 115.26 and 117.60 (C≡C), 122.94 (C$_{ipso}$of C_5Me_5), 127.50 (CH of Ph), 129.35 (CH of Ph), 136.35 (CH of Ph), 137.63 (C$_{ipso}$ of Ph), 228.52 and 255.09 (η^2-C≡C). EI-MS (direct inlet, 70 eV, 230 °C; *m/z* (relative abundance)): 694 (M$^{•+}$; not observed), 377 (16), 376 ([**2b**]$^+$; 41), 375 (15), 362 (9), 361 ([**2b** − Me]$^+$; 24), 320 (12), 319 (29), 318 ([Cp$^*_2$Ti]$^+$; 100), 317 (23), 316 (18), 303 ([**2b** − SiMe$_3$]$^+$; 16), 299 ([**2b** − Ph]$^+$; 7), 279 ([**2b** − C_2SiMe$_3$]$^+$; 10), 221 ([**2b** − Ph − HPh]$^+$; 17), 217 (13), 202 (11), 181 (10), 178 (10), 173 (43), 159 (24), 135 (43), 105 (16), 73 (31). IR (KBr; cm^{-1}): 3068 (w), 3051 (w), 2957 (m), 2900 (s), 2859 (m), 1613 (w), 1556 (m), 1485 (w), 1445 (m), 1428 (s), 1377 (m), 1250 (s), 1241 (s), 1192 (vw), 1107 (m), 1022 (w), 847 (vs, b), 796 (m), 764 (vs), 739 (s), 702 (s), 651 (w), 586 (w), 517 (vs), 479 (w), 438 (m). UV−vis (hexane; nm): 900. Anal. Calcd for $C_{42}H_{58}Si_3Ti$ (695.06): C, 72.58; H, 8.41. Found: C, 72.61; H, 8.38.

Alternative Preparations of 6d. (A) A mixture of **1d** (0.49 g, 1.0 mmol) and **2b** (0.38 g, 1.0 mmol) in toluene (10 mL) was heated to 150 °C for 5 h in a sealed ampule. After workup as above pure crystalline yellow **6d** (0.30 g, 43%) and blue [Ti(η^5-C_5Me_5){η^3:η^4-$C_5Me_3(CH_2)_2$}] (0.066 g, 21%) were separated.

(B) [$TiCl_2$(η^5-C_5Me_5)$_2$] (0.388 g, 1.0 mmol), magnesium (0.12 g, 5 mmol), and **2b** (0.376 g, 1.0 mmol) were degassed, and THF (20 mL) was added. This mixture was heated to 60 °C in a sealed ampule until its color changed to yellow (5 h). Then, all volatiles were evaporated under vacuum, and the residue was extracted with hexane. Cooling to −18 °C of the concentrated hexane solution afforded yellow crystals of **6d**: 0.60 g (86%).

Hydrogenolysis of 5c. A solution of **5c** (ca. 0.2 g) in hexane (8 mL) was exposed to hydrogen (1 bar) for 3 h while being stirred with a magnetic stirrer. The volatiles were evaporated under vacuum, the residue was dissolved in C_6D_6, and the solution was analyzed by NMR spectra. Then, the tube was opened to air and the solution purified by chromatography on a silica gel column using diethyl ether−hexane (1:5) as the eluent. The first band was collected and evaporated to give a yellowish oily residue, which was analyzed by NMR spectroscopy. The spectra recorded for the crude and purified samples were practically identical, showing 1,4-bis(trimethylsilyl)-5,5-diphenyl-5-silacyclopenta-1,3-diene (**7**) as the major component. The yield was not determined.

^{1}H NMR (C_6D_6): δ 0.04 (s, 9 H, SiMe$_3$), 7.12−7.82 (m, 5 H, SiPh), 7.33 (s, 1 H, =CH). ^{13}C NMR (C_6D_6): δ −0.13 (q, $^1J_{CH}$ = 118 Hz, SiMe$_3$), 130.17 (dt, $^1J_{CH}$ =160 Hz, CH of Ph), 132.62 (br s, C$_{ipso}$ of Ph), 135.88 (d of m, $^1J_{CH}$ ca. 160 Hz, CH of Ph), 149.15 (s, =CSiMe$_3$), 156.33 (dd, $^1J_{CH}$ = 157, $^2J_{CH}$ = 8.5 Hz, =CH); one CH resonance of the phenyl group is probably obscured by the solvent signal. GC-MS (*m/z* (relative abundance)): 380 (12), 379 (29), 378 (M$^{•+}$; 71), 364 (19), 363 ([M − Me]$^+$; 46), 306 (21), 305 ([M − SiMe$_3$]$^+$; 69), 291 (13), 290 ([M − Me − SiMe$_3$]$^+$; 40), 283 (19), 245 (12), 244 (13), 243 (51), 228 (16), 227 (11), 197 (26), 145 (20), 135 (100), 105 ([PhSi]$^+$;

Table 3. Crystallographic Data and Data Collection and Structure Refinement Details for Compounds 4b–d, 5c, and 6d[a]

	4b	**4c**	**4d**	**5c**	**6d**
formula	$C_{28}H_{46}Si_3Ti$	$C_{30}H_{50}Si_3Ti$	$C_{32}H_{54}Si_3Ti$	$C_{40}H_{54}Si_3Ti$	$C_{42}H_{58}Si_3Ti$
mol wt	514.82	542.87	570.92	667.00	695.05
cryst syst	monoclinic	triclinic	monoclinic	monoclinic	monoclinic
space group	$P2_1/n$ (No. 14)	$P\bar{1}$ (No. 2)	$C2/c$ (No. 15)	$P2_1/c$ (No. 14)	$P2_1/c$ (No.14)
a (Å)	9.9510(2)	9.9650(1)	35.9376(3)	10.0360(3)	15.1670(4)
b (Å)	17.5260(3)	18.2720(2)	20.8789(2)	17.3500(9)	11.3270(2)
c (Å)	16.9310(3)	18.8890(3)	36.4854(3)	23.2160(11)	23.4860(6)
α (deg)	90	106.5850(7)	90	90	90
β (deg)	91.4700(10)	104.7610(7)	96.6974(4)	111.992(3)	95.5150(10)
γ (deg)	90	90.6820(8)	90	90	90
V (Å^3)	2951.82(9)	3174.13(7)	27189.5(4)	3748.3(3)	4016.14(16)
T (K)	150(2)	150(2)	150(2)	150(2)	150(2)
Z	4	4	32	4	4
D_{calcd} (g cm^{-3})	1.158	1.136	1.116	1.182	1.150
μ (mm^{-1})	0.426	0.399	0.376	0.350	0.330
cryst color	red	red	deep red	red	orange
cryst size (mm^3)	0.6 × 0.45 × 0.35	0.7 × 0.45 × 0.45	0.5 × 0.42 × 0.25	0.28 × 0.18 × 0.10	0.40 × 0.15 × 0.10
θ_{max} (deg)	27.47	27.55	25.04	25.01	25.05
no. of rflns collected	6747	14 247	23 910	6575	7097
no. og unique rflns	5629	12 188	18 254	3891	5327
no. of params	303	645	1369	411	431
R; R_w (all data)[a]	5.56; 10.41	4.34; 8.95	11.91; 16.08	11.86; 11.43	6.75; 10.56
R (obsd data)[b]	4.35	3.39	8.47	5.23	4.20
$\Delta\rho$ (e Å^{-3})	0.64; −0.41	0.31;−0.32	0.68; −0.41	0.24; −0.25	0.28; −0.29

[a] Definitions: $R(F) = \sum||F_o| - |F_c||/\sum|F_o|$, $R_w(F^2) = [\sum(w(F_o^2 - F_c^2)^2)/(\sum w(F_o^2)^2)]^{1/2}$. [b] Reflections with $I > 2\sigma(I)$.

26), 73 ($[Me_3Si]^+$; 49). HR-MS: calcd for $C_{22}H_{30}Si_3$, 378.1655; found, 378.1663.

Methanolysis of 4d. Compound **4d** (0.32 g, 0.56 mmol) in hexane (3 mL) was reacted with anhydrous MeOH (0.5 mL, 12 mmol) at 80 °C for 5 h, whereupon the color changed from intense brown-red to brown. All volatiles were distilled under high vacuum into a trap cooled by liquid nitrogen, and the residue was dissolved in a minimum amount of hexane and crystallized by cooling to −18 °C. The volatiles were separated by column chromatography on silica gel. Elution with hexane gave the first fraction, containing 1,4-bis(trimethylsilyl)-5,5-dimethyl-5-silacyclopenta-1,3-diene (**8**) according to GC-MS analysis. The following band eluted with hexane gave, after evaporation, an oily residue whose IR spectrum indicated an overwhelming presence of pentamethylcyclopentadiene. Brown crystals obtained from the solid residue exhibited unit cell parameters identical with those of $[(\eta^5\text{-}C_5Me_5)Ti(OMe)(\mu\text{-}OMe)]_2$.[13]

Data for **8** are as follows. GC-MS: 255 (25), 254 ($M^{\bullet+}$; 58), 241 (17), 240 (42), 239 ($[M - Me]^+$; 91), 238 (13), 182 (28), 181 ($[M - SiMe_3]^+$; 77), 180 (11), 166 ($[M - Me - SiMe_3]^+$; 17), 141 ($[M - C_3H_4 - SiMe_3]^+$; 20), 83 (13), 73 ($[SiMe_3]^+$; (100).

X-ray Crystallography. The diffraction data for complexes **4b**–**d**, **5c**, and **6d** were collected on a Nonius KappaCCD image plate diffractometer (Mo Kα radiation, $\lambda = 0.710\ 73$ Å) and analyzed by the HKL program package.[28] In all cases, the structures were solved by direct methods (SIR97),[29] followed by consecutive Fourier syntheses and refined by full-matrix least squares on F^2 (SHELX97).[30] All non-hydrogen atoms were refined anisotropically; hydrogen atoms were included in ideal positions and refined isotropically using the riding model.

Compound **4d** crystallizes in monoclinic space group $C2/c$ in an extremely large unit cell containing four symmetrically independent molecules in the asymmetric unit. Although the unit cell parameters were determined with precision comparable to that for **4c** (see Table 3) the precision in determination of molecular parameters for molecules of **4d** is considerably lower.

Computational Details. DFT calculations, including NBA and GIAO analyses, have been performed at the Supercomputer Centre of Charles University using Gaussian 98, Revision A.7.[31] The applied density functional combined the Becke exchange[32] and the Perdew-Wang 91 correlation functional.[33] The 6-311G(2d) basis set was employed for all atoms. The input geometry was that obtained from X-ray diffraction data for **4c** at ambient temperature using the coordinates of one of the two symmetrically independent molecules. Due to the size of the problem, no geometry optimization was carried out.

Although the molecule should apparently possess a C_{2v} symmetry in solution, symmetrization of the solid-state structure was not carried out, as this would have led to some rather significant changes in atomic positions. For this reason, DFT calculations were performed in point group C_1; however, irreducible representations for orbitals are given assuming C_{2v} symmetry.

Natural bonding analysis was performed by the NBO 3.1[34] program integrated in Gaussian as link 607; contours of the Δ bond appearing in Figure 4 were obtained using Molden.[35]

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Acknowledgment. This research was supported by the Grant Agency of the Czech Republic (Grant No. 104/05/0474). The suggestions of Prof. U. Rosenthal (Universität Rostock) on the reaction mechanism are highly appreciated.

Supporting Information Available: CIF files for the structures of **4b**–**d**, **5c**, and **6d**, Platon drawings of structures **4b**–**d**, **5c**, and **6d** at the 30% probability level, Lewis representations of examined bonding modes in **4c**, and GIAO parameters and their correlation with experimental ^{13}C NMR shifts. This material is available free of charge via the Internet at http://pubs.acs.org.

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