

CRYSTAL STRUCTURES OF UNUSUAL TITANOCENE BY-PRODUCTS FROM ATTEMPTED DIMERIZATION OF TERMINAL ALKYNES

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Received March 14, 2000

Accepted June 16, 2000

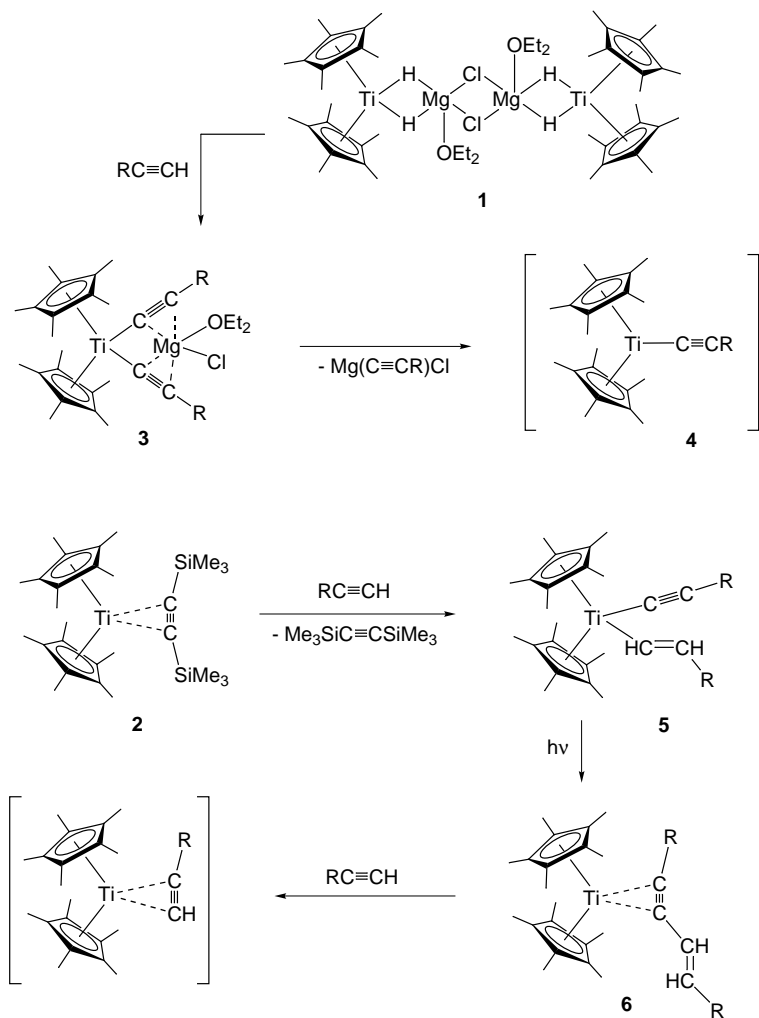
Dedicated to Professor Josef Loub on the occasion of his 70th birthday.

Structures of unusual organometallic products μ -[(1,2,3,3a,7a- η):-(3a,4,5,6,7,7a- η)-4,7-bis(trimethylsilyl)indenyl]-di- μ -hydridobis(η^5 -cyclopentadienyl)titanium($\text{Ti}^{\text{III}}/\text{Ti}^{\text{II}}$) (**9**) and μ -[(3,4,5- η):-(4,5,6- η)-(E,E)-2,2,7,7-tetramethylocta-3,5-diene]bis[bis(η^5 -methylcyclopentadienyl)titanium] (**10a**) were determined by X-ray diffraction analysis. Compounds **9** and **10a** arose as by-products in very low yields in the $\text{Ti}(\text{C}_5\text{H}_5)_2(\eta^2\text{-Me}_3\text{SiC}\equiv\text{CSiMe}_3)\text{-HC}\equiv\text{CSiMe}_3$ and $\text{Ti}(\text{C}_5\text{H}_4\text{Me})_2(\eta^2\text{-Me}_3\text{SiC}\equiv\text{CSiMe}_3)\text{-HC}\equiv\text{CCMe}_3$ systems, respectively, when exposed to sunlight. Mechanisms of their formation were tentatively discussed.

Key words: Titanium; Titanocenes; Metallocenes; Alkynes; Oligomerization; Indenyl bridge; Hydride bridge; Butadiene bridge; X-Ray diffraction.

Terminal acetylenes not bearing electron-donor atoms are extremely selectively dimerized by the action of permethyltitanocene(Ti^{III}) hydride complex $[\{\text{Ti}(\text{C}_5\text{Me}_5)_2(\mu\text{-H})_2\text{Mg}(\text{OEt}_2)(\mu\text{-Cl})\}_2]$ (**1**) (ref.¹) or by the permethyltitanocene(Ti^{II})-bis(trimethylsilyl)ethyne complex $[\text{Ti}(\text{C}_5\text{Me}_5)_2(\eta^2\text{-Me}_3\text{SiC}\equiv\text{CSiMe}_3)]$ (**2**) (ref.²) to give exclusively head-to-tail dimers. This applies to all the 1-alkynes except *tert*-butylethyne (TBUE) which, however, was shown to dimerize exclusively to head-to-tail dimer with a very high activity (turnover of TBUE close to 10^4 molecules per one Ti atom) under the catalysis by the bis(tetramethylcyclopentadienyl)titanium(III) hydride complex $[\{\text{Ti}(\text{C}_5\text{HMe}_4)_2(\mu\text{-H})_2\text{Mg}(\text{OEt}_2)(\mu\text{-Cl})\}_2]$ (ref.³). This dramatic change in the catalytic activity and selectivity has been accounted for by meeting steric

requirements of the 1-alkyne substituents and a free coordination space at the titanium atom delimited by the $\eta^5\text{-C}_5\text{Me}_5$ or $\eta^5\text{-C}_5\text{HMe}_4$ groups. It has been shown that complex **1** reacts with 1-alkynes $\text{HC}\equiv\text{CR}$ to give Ti(III) tweezer complexes⁴ $[\text{Ti}(\text{C}_5\text{Me}_5)_2(\text{C}\equiv\text{CR})_2]^-[\text{Mg}(\text{OEt}_2)\text{Cl}]^+$ (**3**). However, the carriers of the catalytic activity were proposed to be monomeric titanocene acetylides $[\text{Ti}(\text{C}_5\text{Me}_5)_2(\text{C}\equiv\text{CR})]$ (**4**) (Scheme 1)^{1b}; although, unequivocal evidence that compounds **4** are catalytic centres is missing.



SCHEME 1

Dimerizations catalyzed by complex **2** were shown to be photoassisted by sunlight^{2b}. The smooth oxidative addition of 2 molecules of 1-alkyne afforded catalytically inactive $[\text{Ti}(\text{C}_5\text{Me}_5)_2(\text{C}\equiv\text{CR})(\text{E}-\text{HC}=\text{CHR})]$ compounds (**5**); these were activated by sunlight to give a head-to-head dimer π -coordinated by its triple bond to titanium in compounds $[\text{Ti}(\text{C}_5\text{Me}_5)_2(\eta^2\text{-RC}\equiv\text{C}-\text{CH}=\text{CHR})]$ (**6**). These complexes then entered the catalytic cycle producing exclusively head-to-tail dimers, presumably *via* exchange of the dimer with 1-alkyne (see Scheme 1). Thus, the same catalytic properties were observed in the two systems containing Ti(III) and Ti(II) catalytic centres, and this enigma is tempting to solve.

The dimerization to head-to-tail dimers proceeds neither on the hydride complexes $[\{\text{Ti}(\text{C}_5\text{H}_{5-n}\text{Me}_n)_2(\mu\text{-H})_2\text{Mg}(\text{OEt}_2)(\mu\text{-Cl})\}_2]$ nor on the $[\text{Ti}(\text{C}_5\text{H}_{5-n}\text{Me}_n)_2(\eta^2\text{-Me}_3\text{SiC}\equiv\text{CSiMe}_3)]$ complexes if they contain less methyl substituted cyclopentadienyl ligands $\text{C}_5\text{H}_{5-n}\text{Me}_n$ ($n = 0-3$). These systems produce largely cyclic trimers (1,3,5- and 1,2,4-trisubstituted benzenes). For $n = 0$ and 1, these trimers were accompanied by minor amounts of disubstituted benzenes^{1b,2a}. In these early experiments with the $\text{Me}_3\text{SiC}\equiv\text{CSiMe}_3$ complexes, attention was not paid to the above-mentioned effect of daylight, and this caused poor reproducibility of the results and one order lower conversions of acetylenes for $n = 4$ and 5 compared with those obtained in sunlight^{2b}.

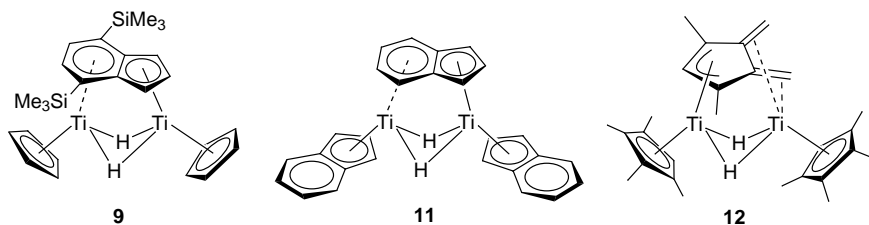
Here we report the crystal structures of the only isolated very minor organometallic products obtained in the $[\text{Ti}(\text{C}_5\text{H}_5)_2(\eta^2\text{-Me}_3\text{SiC}\equiv\text{CSiMe}_3)]\text{-HC}\equiv\text{CSiMe}_3$ and $[\text{Ti}(\text{C}_5\text{H}_4\text{Me})_2(\eta^2\text{-Me}_3\text{SiC}\equiv\text{CSiMe}_3)\text{-HC}\equiv\text{CCMe}_3$ systems when they were exposed to sunlight.

RESULTS AND DISCUSSION

Unsubstituted and monomethyl substituted bis(cyclopentadienyl)titanium complexes with π -coordinated bis(trimethylsilyl)ethyne $[\text{Ti}(\text{C}_5\text{H}_5)_2(\eta^2\text{-Me}_3\text{SiC}\equiv\text{CSiMe}_3)]$ (**7**) and $[\text{Ti}(\text{C}_5\text{H}_4\text{Me})_2(\eta^2\text{-Me}_3\text{SiC}\equiv\text{CSiMe}_3)]$ (**8**) react with (trimethylsilyl)ethyne (TMSE) and *tert*-butylethyne (TBUE), respectively, in a non-specific way converting *ca* 10 molar equivalents of the 1-alkynes into a mixture of oligomers whose volatile parts mainly consist (by GC-MS analysis) of a mixture of 1,3,5- and 1,2,4-substituted benzenes with few per cent of disubstituted benzenes^{2a}. When the reaction mixtures are exposed to sunlight for 5 days, the above-mentioned volatile products are strongly enriched by dimers containing two hydrogen atoms in excess. The non-volatile products form a brown waxy solid rapidly hardening in air, apparently due to oxidation. This behaviour as well as the expected

irregular composition of the oligomers arising from proton and substituent transfers discouraged us to attempt isolation of some product components. The anticipated products of interaction of **7** with TMSE and **8** with TBUE, compounds of type **5** for the reaction in the dark or compounds of type **6** for the reaction in sunlight (Scheme 1), are highly soluble in aliphatic hydrocarbons and they do not crystallize from viscous reaction mixtures^{2b}. Surprisingly, several blue crystals of **9** grew up in the **7**-TMSE system and a few dark turquoise crystals of **10a** in the **8**-TBUE system when the volatiles (largely hexane) were slowly distilled off *in vacuo*. The crystals were carefully isolated in *ca* 5 mg quantities and their molecular structures were determined by X-ray diffraction measurements.

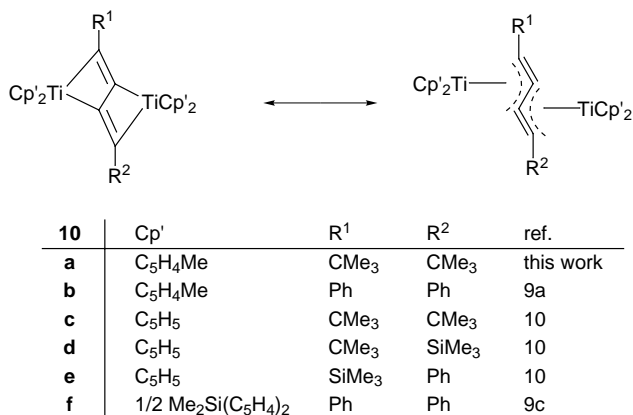
The crystal structure analysis revealed the molecular structure of **9** as μ -[(1,2,3,3a,7a- η):(3a,4,5,6,7,7a- η)-4,7-bis(trimethylsilyl)indenyl]di- μ -hydridobis(η^5 -cyclopentadienyl)titanium containing Ti^{III} bonded to the cyclopentadienyl ring and Ti^{II} to the benzene ring of the indenyl ligand. The Ti^{III}/Ti^{II} valency of titanium atoms follows from the C-C bond lengths in



the indenyl rings, the Ti-C bond lengths and bonding capability of all ligands (*vide infra*). Moreover, the presence of only one Ti^{III} atom is corroborated by the ESR spectrum of **9** showing the triplet splitting arising from the interaction of one d electron with two equivalent hydrogen atoms ($a_{\text{H}} = 5.5$ G). In the case of two d¹ electrons, the coupling to hydrogen atoms would not be observed in solution; instead, coupling of d electrons would give an electronic triplet state in the solid state⁵. Similar dititanium compounds having one μ -organyl and two μ -H bridges, μ -[(1,2,3,3a,7a- η):(3a,4,5,6,7,7a- η)-indenyl]di- μ -hydridobis[(η^5 -indenyl)titanium] (**11**) and (μ -[(1,2,3- η):(4,5-di(η^2 -methylidene)-1,3-dimethylcyclopentenyl)]di- μ -hydridobis(η^5 -tetramethylcyclopentadienyl)titanium (**12**) arose from the interaction of bis(indenyl)dimethyltitanium with phenylsilane⁶ and from the [Ti(C₅HMe₄)₂Cl₂]-LiAlH₄ system in boiling mesitylene⁷, respectively. The triplet superhyperfine splitting observed in their ESR spectra ($g = 1.9887$, $a_{\text{H}} = 0.48$ mT for **11** and $g = 1.9871$, $a_{\text{H}} = 0.43$ mT for **12**) was assigned to the

presence of Ti^{III}/Ti^{II} pairs in the both compounds. The electronic absorption spectrum of **9** in hexane solution displays a distinct absorption band at 595 nm which has been observed close to this value in a number of complexes containing $(C_5H_{5-n}Me_n)_2Ti^{III}(\mu-H)_2$ ($n = 0-5$) moieties^{5,8}.

The X-ray diffraction analysis revealed **10a** to be μ -[(3,4,5- η):(4,5,6- η)-(*E,E*)-2,2,7,7-tetramethylocta-3,5-diene}bis{bis(η^5 -methylcyclopentadienyl)-titanium} (*vide infra*). Compound **10a** is diamagnetic as all known complexes of this structural type **10b–10f** (Scheme 2). They were prepared by the rearrangement of $\{[Ti(C_5H_4Me)_2(\mu-C\equiv CPh)]_2\}$ (**10b**) (refs^{9a,9b}) or $\{[Ti[Me_2Si(C_5H_4)_2](\mu-C\equiv CPh)]_2\}$ (**10f**) (ref.^{9c}), from *in situ* formed titanocene $[Ti(C_5H_4Me)_2]$ and 1,4-diphenylbuta-1,3-diyne (**10b**) (ref.^{9a}) or by the reaction of **7** with appropriate 1,4-disubstituted buta-1,3-diyne (**10c**, **10d**, and **10e**) (ref.¹⁰). The dark turquoise colour of **10a** agrees with the reported colour of **10b–10e**.



SCHEME 2

Crystal Structures of **9** and **10a**

The molecular structure of **9** (Fig. 1) is crystallographically unsymmetrical. The two titanium atoms Ti1 and Ti2 are bridged by two Ti–H–Ti electron-deficient bonds and by a common 4,7-bis(trimethylsilyl)indenyl ligand. The Ti–H distances range from 1.72 to 1.85 Å and the bridging hydride bonds are bent (Table I) so that the angle between planes defined by the Ti1, H51, and H52 atoms and Ti2, H51, and H52 atoms amounts to 43(1)°. The geometry of the hydride bridge is close to analogous hydride bridges in dimeric titanocene, μ -(η^5 : η^5 -fulvalenediyl)di- μ -hydridobis-[(η^5 -cyclopentadienyl)titanium(III)] (ref.¹¹), compound **11** (ref.⁶), and **12**

(ref.⁷). The planes of the two cyclopentadienyl rings are perpendicular to the Ti-CE (CE – centroid of the ring) vectors within the precision of the measurement. The six-membered ring of the indenyl ligand is folded at the interconnection of C11 and C14 atoms that bear the trimethylsilyl groups. The folding angle between the planes defined by the C11, C12, C13, and C14 atoms and the C11, C14, C15, and C19 atoms is 20.5(1)°. The distances of annelated carbon atoms of the indenyl ligand C15 and C19 are somewhat longer to Ti1 (2.441(3) and 2.446(3) Å) than to Ti2 (2.427(3) and 2.421(3) Å), the distances of all other carbon atoms range the between values 2.264(3) and 2.318(3) Å. The shortest C–C distances in the indenyl ligand are those of C12–C13, C16–C17, and C17–C18 that are below 1.400 Å, the other distances being in the range 1.425(4)–1.475(4) Å (Table I). Particularly long Ti–C and C–C distances involve the annelated C15 and C19 atoms, and this may indicate a contribution of the μ -[η^3 : η^4 -4,7-bis-(trimethylsilyl)indenyl] bonding mode. The silicon atoms do not deviate from the least-squares plane of the folded six-membered ring more than the ring-carbon atoms; this is in line with the both μ -(η^5 : η^6) and μ -(η^3 : η^4) bonding modes of the indenyl ligand. The geometry of the μ -indenyl is described in detail for the first time in a dititanium compound as the folding of the C₆ ring and the geometry of the μ -indenyl system were not determined in the crystal structure of **11** due to the disorder in the placement of the bridging indenyl ligand and *syn* and *anti* arrangement of terminal

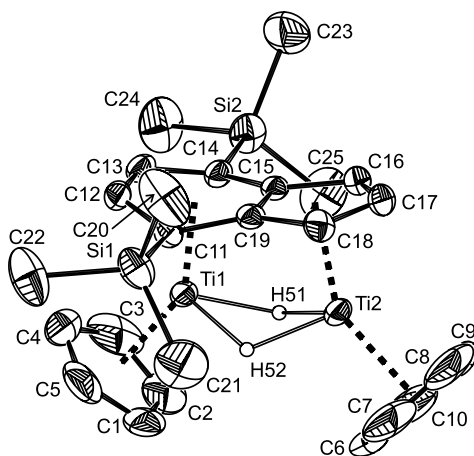


FIG. 1

ORTEP drawing of compound **9** at the 30% probability level with atom labelling scheme. All hydrogen atoms attached to carbon atoms are omitted

TABLE I
Selected bond lengths (Å) and angles (°) for $\{[\text{Ti}(\text{C}_5\text{H}_5)_2(\mu\text{-H})_2\{\text{C}_9\text{H}_5(\text{SiMe}_3)_2\}]\}$ (9)

Atoms	Lengths	Atoms	Lengths
Ti1-CE1 ^a	2.032(6)	Ti2-CE2 ^b	2.016(8)
Ti1-H51	1.85(2)	Ti1-H52	1.79(3)
Ti2-H51	1.83(2)	Ti2-H52	1.72(3)
Ti1-CE4 ^d	1.852(3)	Ti2-CE3 ^c	2.024(3)
Ti1-C11	2.264(3)	Ti2-C12	2.309(3)
Ti1-C13	2.300(3)	Ti1-C14	2.259(3)
Ti1-C15	2.441(3)	Ti-C19	2.446(3)
Ti2-C15	2.427(3)	Ti2-C16	2.318(3)
Ti2-C17	2.300(3)	Ti2-C18	2.300(3)
Ti2-C19	2.421(3)	C11-C12	1.431(4)
C12-C13	1.376(5)	C13-C14	1.430(4)
C14-C15	1.475(4)	C15-C19	1.426(4)
C11-C19	1.472(4)	C15-C16	1.432(4)
C16-C17	1.396(4)	C17-C18	1.383(4)
C18-C19	1.425(4)	C11-Si1	1.853(3)
C14-Si2	1.854(3)	Ti1-Ti2	2.778(7)
Atoms	Angles	Atoms	Angles
Ti1-H51-Ti2	98.1(11)	Ti1-H52-Ti2	104.5(18)
H51-Ti1-H52	66.6(13)	H51-Ti2-H52	68.4(13)
CE1 ^a -Ti1-CE4 ^d	148.0(2)	CE2 ^b -Ti2-CE3 ^c	144.5(2)
C11-C12-C13	123.5(3)	C12-C13-C14	124.2(3)
C13-C14-C15	111.6(3)	C14-C15-C19	121.6(2)
C15-C19-C11	121.5(2)	C19-C11-C12	112.0(3)
C12-C11-Si1	122.7(2)	C19-C11-Si1	122.1(2)
C13-C14-Si2	122.6(2)	C15-C14-Si2	122.4(2)

^a CE1, centroid of the C1-C5 atoms. ^b CE2, centroid of the C6-C10 atoms. ^c CE3, centroid of the C15-C19 atoms. ^d CE4, centroid of the C11-C15 and C19 atoms.

indenyl ligands⁶. Such a folding was not found in $\{[\mu-(\eta^5:\eta^6\text{-indenyl})\text{V}]_2\}$ where V–C and C–C bond lengths fall into the 2.165–2.278 and 1.402–1.455 Å ranges, respectively, and the V–V distance of 2.349 Å indicates an intermetallic bond¹².

The molecular structure of **10a** is shown in Fig. 2 and important bond distances and angles are listed in Table II. The molecule consists of two bis(η^5 -methylcyclopentadienyl)titanium units bonded *via* the central 1,3-butadiene system, and is centrosymmetric. The titanocene units have their methyl groups placed on opposite sides of staggered cyclopentadienyl rings. The central bridging C_4 skeleton is planar: the deviation of the C1 atom from the plane defined by Ti, C2, and C2' (a symmetry-generated C2) atoms is close to the precision of the measurement and the C3 atom of the *tert*-butyl group is deviated less than 0.10 Å from this plane. This plane and the planes defined by CE1, Ti, and CE2 are nearly perpendicular ($88.2(1)^\circ$). This structure is very close to the known structures **10b** (ref.^{9a}), **10c**, and **10d** (ref.¹⁰) (see Scheme 2). The distances between the Ti and C2 and C1' atoms (2.085(3) and 2.159(3) Å) are shorter than that between Ti and C1 (2.325(2) Å) and also the C1–C1' distance is longer (1.508(5) Å) than that of the C1–C2 bond (1.322(3) Å). These distances together with the zig-zag structure of the C_4 chain are consistent with the *s-trans* butadiene structure and σ -bonds Ti–C2 and Ti–C1' as it is depicted in Scheme 2, left. However, the Ti–C1 distance is short enough to exert a considerable π -bonding interaction, the Ti–C2–C1 and Ti–C1'–C1 bonding angles are too acute to exert a

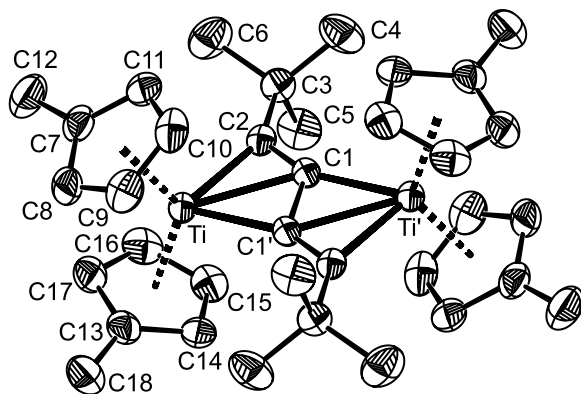


FIG. 2

ORTEP drawing of compound **10a** at the 30% probability level with atom labelling scheme. For clarity, all hydrogen atoms are omitted

strong σ -Ti-C bond, and the dark turquoise colour may indicate the presence of a Ti d electron. In addition, recent quantum chemical calculations corroborated the earlier view^{9,10,13} that energy of compounds of type **10** is close to that of dimeric alkynyltitanocenes $[\{\text{Ti}(\text{C}_5\text{H}_5)_2(\mu\text{-C}\equiv\text{CR})\}]_2$ with titanium π -bound to the triple bond of the other molecule¹⁴. Thus, one can consider the σ -bound Ti^{IV} and the η^3 -allenyl bound Ti^{III} structures (Scheme 2) as the extreme descriptions of bonding in compounds of type **10**. The above-mentioned dimeric alkynyltitanocenes are diamagnetic due to pairing of d-electron spins¹⁵⁻¹⁷ and the same behaviour can be anticipated for the allenyltitanocene structure in **10**.

Formation of **9** and **10a**

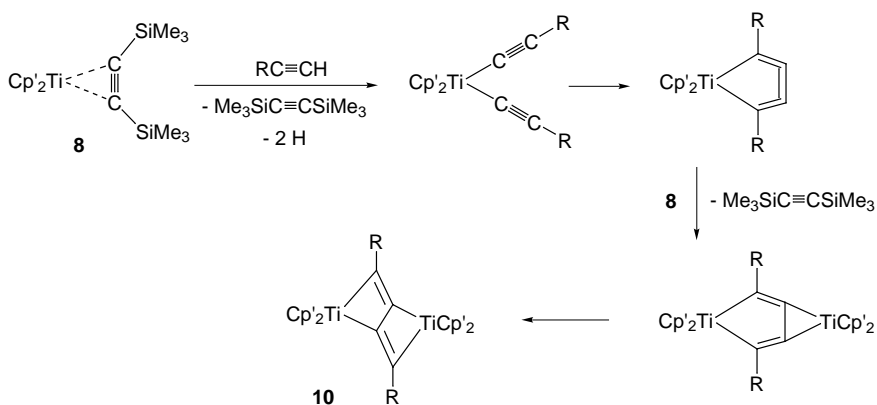
Owing to the negligible yields of **9** and **10a**, it is impossible to relate their formation to any reaction of the 1-alkyne oligomerization; although, the presence of partially hydrogenated dimer is in line with the elimination of

TABLE II
Selected bond lengths (Å) and angles (°) for $[\{\text{Ti}(\text{C}_5\text{H}_4\text{Me})_2\}_2\{\mu\text{-}\{\text{C}_8\text{Me}_4\}\}]$ (**10a**)

Atoms	Lengths	Atoms	Lengths
Ti1-CE1 ^a	2.098(2)	Ti1-CE2 ^b	2.112(2)
Ti1-C1	2.325(2)	Ti1-C1'	2.159(3)
Ti1-C2	2.085(3)	C1-C1'	1.508(5)
C1-C2	1.322(3)	C2-C3	1.524(3)
C3-C4	1.522(4)	C3-C5	1.535(4)
C3-C6	1.531(4)		
Atoms	Angles	Atoms	Angles
CE1-Ti1-CE2	131.0(1)	C1-Ti-C2	34.35(9)
C1-Ti-C1'	39.07(11)	C2-Ti-C1'	73.42(9)
Ti-C1'-C1	76.4(1)	Ti-C2-C1	82.79(16)
C1-C2-C3	130.2(2)	C2-C1-C1'	127.4(3)

^a Centroid of the C7-C11 atoms. ^b Centroid of the C13-C17 atoms. ^c Symmetry transformation (-x, -y, -z + 1) used to generate equivalent atoms C1', etc.

hydrogen which is required for obtaining **10a** (Scheme 3). Common step in the interaction of both **7** and **8** with the respective 1-alkynes is the replacement of $\text{Me}_3\text{SiC}\equiv\text{CSiMe}_3$ with 1-alkyne and its oxidative addition giving $[\text{TiCp}'_2(\text{H})(\text{C}\equiv\text{CR})]$. This may eliminate molecular hydrogen to give transient $[\text{TiCp}'_2(\text{C}\equiv\text{CR})]$ (ref.¹⁸) which then dimerizes through the formation of the coordinated diyne system, as it was shown for **10b** (ref.^{9a}). Alternatively, addition of another molecule of $\text{HC}\equiv\text{CR}$ to $[\text{TiCp}'_2(\text{H})(\text{C}\equiv\text{CR})]$ affords compound **5** (Scheme 1), and this may transfer two protons to a suitable acceptor, *e.g.* dimers of TBUE, in a photoassisted process. The obtained diacetylide can rearrange to a cumulene intermediate, and this can react with compound **8** to give **10a**. This reaction pathway was proposed and partly proved by Rosenthal *et al.* (ref.¹³).



SCHEME 3

Compound **9** has been obtained from **7** in a more complex way whose mechanism is not clear. It is apparent that compound **7** after fast replacement of $\text{Me}_3\text{SiC}\equiv\text{CSiMe}_3$ with TMSE loses one cyclopentadienyl ligand and that cycloaddition of two molecules of TMSE to cyclopentadienyl generates the bridging 4,7-bis(trimethylsilyl)indenyl ligand found in **9**. All that is to be accompanied by a hydrogen transfer to form the hydride bridges between titanium atoms. Such hydrogen transfers proceed in the formation of dimeric titanocene¹⁹ and compounds **11** (ref.⁶) and **12** (ref.⁷). A possible intermediate, a highly reactive and sufficiently thermally stable compound of the overall composition $[\text{Ti}_2(\text{C}_5\text{H}_5)_3]$, with one bridging cyclopentadienyl ligand, is also known²⁰. On the other hand, the formation of a dihydroindenyl ligand from internal alkynes on a titanocene species is also known: cycloaddition of two molecules of internal alkynes gives rise to a titan-

acyclopentadiene intermediate which then undergoes a cycloaddition to one of the cyclopentadienyl ligands²¹. In the present case, we can imagine a photoinduced addition of the head-to-tail dimer in compound **6** (Scheme 1) to a cyclopentadienyl ligand of a neighbouring titanocene species accompanied by elimination of one of the cyclopentadienyl ligands as a radical, and a transfer of two hydrogen atoms from the formed dihydroindenyl ligand into the intermetallic bridge. The sequence of these steps is uncertain, however.

EXPERIMENTAL

Chemicals

Solvents hexane or toluene were dried by reflux with LiAlH₄ and finally were stored as solutions of dimeric titanocene. 1-Alkynes HC≡CSiMe₃ (TMSE) and HC≡CCMe₃ (TBUE) (Aldrich) were degassed, distilled onto dimeric titanocene^{19a} and after another 2 h, into a storage ampoule on a vacuum line. Complexes [Ti(C₅H₅)₂(η²-Me₃SiC≡CSiMe₃)] (**7**) and [Ti(C₅H₄Me)₂(η²-Me₃SiC≡CSiMe₃)] (**8**) were prepared as described elsewhere²², and were used as 1.0 M hexane solutions.

Complexes **9** and **10a**

Reactions of **7** with TMSE and **8** with TBUE were performed under vacuum conditions used for a similar reaction with dimeric titanocene²³. Compounds **7** and **8** (1.0 mmol) in hexane solution (2.0 ml) were mixed with TMSE (1.4 ml, 10.0 mmol) and TBUE (1.2 ml, 3.5 mmol), respectively, and the mixtures in sealed glass (Simax) ampoules were exposed to sunlight for 5 days. Then the solution was poured into one arm of the ampoule while the other arm was slightly cooled with wet cotton to slowly distil the solvent and to concentrate the solution. After two days several blue crystals of **9** grew in the first system and several turquoise crystals of **10a** in the second. Brown mother liquors were poured into the second arm and the crystals were washed by condensing vapours of hexane, dried and sealed off in a breakable seal (estimated yields *ca* 5 mg). Crystals suitable for X-ray diffraction analysis were adjusted in Lindemann glass capillaries in a glovebox under purified nitrogen. A few crystals were also dissolved in hexane (**9**) or toluene (**10a**) for UV-VIS and ESR spectroscopic measurements. Two crystals of **10a** were used for mass spectra analysis (inserted under argon into direct inlet of a VG 7070E spectrometer).

Complex 9: ESR (hexane, 22 °C): $g = 1.991$, triplet 1 : 2 : 1, $a_{\text{H}} = 5.5$ G, $a_{\text{Ti}} = 6.5$ G. UV-VIS (hexane): 390 sh, 595 nm.

Complex 10a: MS (direct inlet, 170 °C), m/z (%): 574 (M⁺, 0.3), 287 (5), 207 (11), 206 (38), 205 (100), 204 (22), 203 (20), 202 (6), 201 (6), 191 (6), 128 (5), 127 (20), 126 (29), 125 (11), 124 (7), 113 (7), 48 (10). ESR silent. UV-VIS (hexane): 380 sh, 685 nm.

The composition and structure of **9** and **10a** were determined by X-ray diffraction analysis. Attempts to increase the yields of **9** or **10a** by increasing excess of 1-alkyne failed and the absence of sunlight appeared to be counterproductive.

Investigation of the Reaction Systems

The reaction mixtures **7**-TMSE and **8**-TBUE prepared as above were transferred into a glass device having attached a quartz cuvette (Hellma, $d = 0.2$ cm) and an ESR sample tube. The mixture turned red while the absorption bands at 1 060 and 990 nm indicated a large decrease in the concentration of **7** and **8**, respectively. At the same time, a number of ESR sig-

TABLE III
Crystal and structure refinement data for **9** and **10a**

Parameter	9	10a
Empirical formula	$C_{25}H_{35}Si_2Ti_2$	$C_{36}H_{46}Ti_2$
Formula weight	487.51	574.52
Crystal system	monoclinic	monoclinic
Space group	$P2_1/n$ (No. 14)	$P2_1/n$ (No. 14)
a , Å	7.7362(10)	11.375(5)
b , Å	19.6087(17)	8.446(5)
c , Å	17.3998(18)	15.567(5)
β , °	92.959(9)	101.874(5)
V , Å ³	2 636.0(5)	1 463.6(12)
Z	4	2
Calculated density, g cm ⁻³	1.228	1.304
μ (MoK α), mm ⁻¹	0.706	0.569
$F(000)$, e	1 028	612
Crystal size, mm ³	0.50 × 0.35 × 0.27	0.50 × 0.25 × 0.55
θ_{\min} , θ_{\max} , °	1.57, 24.97	2.03, 24.98
Range of hkl	0→9, 0→23, -20→20	0→13, 0→10, -18→18
Reflections collected	4 623	2 687
Independent reflections	4 619	2 560
Data/restraints/parameters	4 619/0/297	2 560/0/172
Goodness-of-fit on F^2	1.005	1.119
$R1$, $wR2$ (all data)	0.0805, 0.1088	0.0740, 0.0941
$R1$, $wR2$ [$I > 2\sigma(I)$]	0.0387, 0.0941	0.0361, 0.0852
Maximal and minimal residual density, e Å ⁻³	0.308, -0.336	0.285, -0.210

nals appeared, dominated by that at $g = 1.990$ showing probably a doublet splitting $a_H = 6.5$ G. After 5 days in daylight nearly all free 1-alkynes disappeared, as indicated by the diminution of their absorption bands at 1 560 nm for TMSE and 1 540 nm for TBUE (refs^{2a,3}), while the ESR spectra showed yet weaker signals. Electronic absorption spectra showed a continuous absorption increasing in intensity from 1 200 nm to shorter wavelengths. All volatiles were distilled from the reaction mixture at 100 °C under vacuum of a rotary pump into an ampoule cooled by liquid nitrogen. GC-MS analysis²³ of collected volatiles from the 7-TMSE system revealed the presence of unreacted TMSE (m/z 98), BTMSE (m/z 170), (TMSE + H)₂ (m/z 198), and (TMSE)₃ (m/z 294) of comparable intensities and a lower amount of [(TMSA)₃ - (CH₂=SiMe₂)] (m/z 222). The volatiles from the 8-TBUE system gave a similar composition of oligomers. Other products formed a waxy mass which rapidly oxidized in air giving a glassy yellow resin, and were not further investigated.

Crystal Structure Analysis of **9** and **10a**

A fragment of a blue crystal of **9** and a prism of turquoise **10a** were mounted into Lindemann glass capillaries in a glovebox under purified nitrogen. Diffraction data were collected on an Enraf-Nonius CAD-4 MACH III diffractometer at room temperature using graphite monochromated MoK α radiation (λ 0.71069 Å). The structures were solved by direct methods (SIR-92 (ref.²⁴)). All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were included in calculated positions. The bridging hydrogen atoms of **9** were found on difference Fourier electron density map and refined isotropically. Calculations were performed using the SHELXL97 program²⁵. Crystallographic data, details of their collection, and the structure refinement are given in Table III. Crystallographic data for structures **9** and **10a** reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication numbers CCDC-141318 (for **9**) and CCDC-141317 (for **10a**). Copies of the data can be obtained free of charge on application to CCDC, e-mail: deposit@ccdc.cam.ac.uk.

This investigation was supported by the Grant Agency of the Czech Republic (grant No. 203/99/0846) which also sponsored access to Cambridge Structure Database (grant No. 203/99/0067).

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