

SYNTHESIS AND CRYSTAL STRUCTURE OF (TRIMETHYLSILYL)ACETYLIDE-BRIDGED DIMERIC TITANOCENE

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Dimeric titanocene $[(\mu-\eta^5:\eta^5-C_{10}H_8)\{(\mu-H)(\eta^5-C_5H_5)Ti\}_2]$ (**1**) reacts with one equivalent of (trimethylsilyl)acetylene (TMSA) to give a mixture of diamagnetic (trimethylsilyl)acetylide-bridged compounds $[(\mu-\eta^5:\eta^5-C_{10}H_8)(\mu-H)(\mu-\eta^1:\eta^2-C\equiv CSiMe_3)\{(\eta^5-C_5H_5)Ti\}_2]$ (**2**) and $[(\mu-\eta^5:\eta^5-C_{10}H_8)\{(\mu-\eta^1:\eta^2-C\equiv CSiMe_3)(\eta^5-C_5H_5)Ti\}_2]$ (**3**), and some oligomers of TMSA. Compound **2** crystallizes from hexane in the triclinic space group $P\bar{1}$ (No. 2; $a = 9.385(4)$ Å, $b = 14.487(6)$ Å, $c = 18.085(6)$ Å, $\alpha = 110.34(2)^\circ$, $\beta = 101.56(2)^\circ$, $\gamma = 96.65(3)^\circ$, $V = 2212(2)$ Å³, $Z = 2$). A highly soluble compound **3** could not be isolated from a mixture with oligomers of TMSA.

Key words: Sandwich complexes; Metallocenes; Titanocenes; Titanium; (Trimethylsilyl)acetylene oligomerization; Dimeric titanocene; (Trimethylsilyl)acetylide-bridged complex; Crystal structure.

Bright green dimeric titanocene $[(\mu-\eta^5:\eta^5-C_{10}H_8)\{(\mu-H)(\eta^5-C_5H_5)Ti\}_2]$ (**1**) has been frequently observed as a thermodynamically stable product of various reductions of titanocene dichloride under conditions where the reduction to monomeric titanocene $(C_5H_5)_2Ti(II)$ was assumed¹⁻⁵. The molecular structure of **1** was the subject of many investigations based on chemical as well as spectroscopic evidence⁶⁻¹³ until 1992 when its X-ray structure was determined¹⁴. In spite of preparative accessibility¹⁵, compound **1** has not attracted much attention in organometallic synthesis^{7,16}, the dichloro-bridged compound $[(\mu-\eta^5:\eta^5-C_{10}H_8)\{(\mu-Cl)(\eta^5-C_5H_5)Ti\}_2]$ being frequently used instead¹⁶⁻¹⁸. In organic synthesis, compound **1** replaces halogen in alkyl and aryl halides by hydrogen¹⁸. Furthermore, it is a relatively poor catalyst for some olefin hydrogenations

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and isomerizations under mild conditions¹⁹. At elevated temperatures, it catalyzes disproportionation of ethene into ethane and butadiene, albeit with a low efficiency²⁰. At temperatures above 140 °C, it is an excellent catalyst of *E/Z* isomerizations and double bond shifts, intramolecular cyclizations and intermolecular hydrogen transfers^{21–25}.

In this work, we report on the products of reaction of **1** with (trimethylsilyl)acetylene and the crystal structure of dimeric titanocene containing one bridging (trimethylsilyl)acetylidyl group.

EXPERIMENTAL

General Data and Methods

All manipulations with reagents, syntheses and most of spectroscopic measurements were carried out under vacuum using all-sealed glass devices equipped with breakable seals. Electron impact mass spectra were measured on a VG-7070E mass spectrometer at 70 eV (only important ionic species and peaks of relative abundance above 5% are reported). Samples in capillaries were opened and inserted into the direct inlet probe under argon. Single crystals of compound **2** were adjusted into capillaries for the X-ray measurement and KBr pellets of **2** and **3** were prepared in a glovebox Labmaster 130 (mBraun) under purified nitrogen. The IR spectra of the pellets were recorded in an air-protecting cuvette on a Specord 75 IR (Zeiss, Jena, Germany) spectrometer. ¹H, ¹³C and ²⁹Si NMR spectra of **2** and **3** were measured on a Varian Unity INOVA 400 (¹H 399.95 MHz, ¹³C 100.58 MHz, ²⁹Si 79.46 MHz) as C₆D₆ solutions. ²⁹Si NMR spectra were measured using the DEPT technique. Chemical shifts (δ) were referenced to the solvent signal (δ_H 7.15 ppm, δ_C 128.0 ppm) or to external Me₄Si in C₆D₆. UV-VIS spectra were measured in the range 280–2 400 nm on a Varian Cary 17D spectrometer using all-sealed quartz cuvettes (Hellma; *d* = 0.1 and 1.0 cm). GC-MS analyses were carried out on a Hewlett–Packard gas chromatograph (5890 series II) equipped with a capillary column SPB-1 (length 30 m; Supelco) and a mass spectrometric detector (5971 A).

Chemicals

The solvents hexane, toluene and C₆D₆ were purified by conventional methods, dried by refluxing over LiAlH₄ and stored as solutions of dimeric titanocene. Dimeric titanocene (**1**) was obtained from (C₅H₅)₂TiCl₂ and LiAlH₄ as described elsewhere¹⁵. (Trimethylsilyl)acetylene (TMSA) (Aldrich) was degassed, stored as a 1% solution of dimeric titanocene for 4 h and vacuum-distilled into glass ampoules on a vacuum line.

Reaction of **1** with Equimolar Amount of TMSA

The benzene solvate **1**·1.5 C₆H₆ (0.95 g, 2 mmol) was dissolved in benzene (50 ml) and TMSA (0.28 ml, 2 mmol) was added under stirring at room temperature. The mixture was warmed to 60 °C for 2 h in a sealed ampoule. Then, the volatiles were evaporated and the brown residue was repeatedly extracted with hexane leaving a green, sparingly soluble solid. This was dissolved in toluene to give a bright green solution. UV-VIS spectrum of the solution was identical to that of the starting compound **1** (recovered **1**: 0.28 g, 30%). The green-brown extract was concentrated and cooled to 0 °C overnight. A crop of brown crystals of **2** separated and the mother liquor was again concentrated and cooled until the crystals appeared no longer. Recrystallization from hexane afforded **2** as brown crystals suitable for X-ray analysis. Total yield of pure **2** was 0.32 g (35%). The remaining khaki-green

solution was evaporated to give a waxy solid, which contained **3** as the main product according to MS. GC-MS analysis revealed the absence of oligomers (TMSA)_x for $x = 1-3$ in the volatile part; however, NMR spectra inferred the presence of higher oligomers of TMSA.

(μ - η^5 : η^5 -Fulvalenediyl)-di(μ -hydrido)-bis[η^5 -cyclopentadienyl]titanium(III)] (**1**). EI-MS (direct inlet, 75 eV, 110–130 °C) in agreement with reported data⁶. UV-VIS (toluene) 430 << 825 nm (*cf.* ref.¹²).

(μ - η^5 : η^5 -Fulvalenediyl)-(μ -hydrido)-[μ - η^1 : η^2 -(trimethylsilyl)ethynyl]-bis[η^5 -cyclopentadienyl]-titanium(III)] (**2**). ¹H NMR (C₆D₆): δ -0.21 s, 9 H (Me₃Si); 4.89 bs, 4 H (fulvalenediyl CH); 5.61 s, 5 H (Cp); 5.94 unresolved dt, 4 H (fulvalenediyl CH). ¹³C NMR (C₆D₆): δ 1.0 s (Me₃Si); 102.8 s, (Cp); 97.7 s (fulvalenediyl CH); 105.2 s (fulvalenediyl CH); 105.3 s (fulvalenediyl CH); 133.2 (fulvalenediyl C_{ipso}); 133.6 (fulvalenediyl C_{ipso}); 154.3 (TiC \equiv C); 250.3 (TiC \equiv C). ²⁹Si NMR (C₆D₆): δ -18.1 s (Me₃Si). EI-MS [direct inlet, 170–180 °C; *m/z* (relative abundance)]: 452 (M⁺, 82), 386 (18), 384 (22), 382 (19), 380 (12), 354 (54), 353 (44), 352 (100), 351 (36), 350 (45), 348 (19), 288 (18), 287 (12), 286 (12), 178 (22), 177.5 (25), 177 (75), 176.5 (20), 176 (31), 113 (18). IR (KBr; ν , cm⁻¹): 2 015 (w), 1 438 (m), 1 360 (w), 1 240 (m), 1 030 (m,b), 1 012 (s), 850 (sh), 833 (sh), 793 (vs), 752 (s), 690 (s), 627 (vs,b), 565 (vs,b). UV-VIS (hexane): 425 > 820 nm.

(μ - η^5 : η^5 -Fulvalenediyl)-bis[μ - η^1 : η^2 -(trimethylsilyl)ethynyl]-bis[η^5 -cyclopentadienyl]titanium(III)] (**3**). The presence of **3** as the dominant component was evidenced by its molecular ion in EI-MS spectra (*m/z* 548, M⁺). However, fragment ions of **3** coincide with those of **2** which was also present as an impurity. Another minor impurity in the mass spectrum is a compound with ions *m/z* 550. UV-VIS (hexane): 425 \approx 745 nm. Unfortunately, an admixture of oligomers (TMSA)_x ($x > 3$) and **2** prevented NMR spectra to be evaluated unequivocally.

Reaction of **1** with Excess TMSA

Benzene solvate 1.1.5 C₆H₆ (0.46 g, 1 mmol) was dissolved in 50 ml of hexane and TMSA (1.4 ml, 10 mmol) was added under stirring at room temperature. The mixture was warmed to 60 °C for 10 h in a sealed ampoule. A brown solution was exposed to air and worked up by chromatography on a silica gel column (diameter 3 cm, length 30 cm). Elution with hexane gave yellow fractions with gradually increasing molecular weights according to mass spectra. GC-MS of the first fraction revealed the presence of dimer, trimer, tetramer and pentamer which were accompanied by compounds richer in hydrogen (M + H₂ and M + 2 H₂) and poorer in Me₃Si groups [M - n 72] ($n = 1, 2$). The abundance of these accompanying compounds was comparable with that of oligomers. The infrared spectra of all fractions show very intense bands at 1 246 (s), 860 (sh), 833 (vs), 750 (m), 690 (m), 648 (w) and 620 (w) cm⁻¹ which belong to trimethylsilyl groups. Further attempts to isolate individual oligomers were abandoned.

Crystal Structure Analysis of **2**

A brown prismatic crystal of **2** was mounted into a Lindenmann glass capillary in a glovebox under purified nitrogen. Intensities were collected on a Philips PW1100 four-circle diffractometer at 20 °C. The structure was solved by direct methods (Multan-80) and refined by full-matrix least-squares on *F*² applying variance-based weighting scheme in the form $w = [\sigma^2(F_o^2) + (0.0342 P)^2 + 1.41 P]^{-1}$, where $P = [\max(F_o^2) + 2 F_c^2]/3$ (SHELXL93, ref.²⁶). All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were localized on the difference Fourier map and refined isotropically except for H94, which could not be refined freely and was thus kept in its theoretical position. Details of the data collection and refinement are given in Table I. Selected bond distances and bond angles are listed in Table II. Relevant crystallographic data for **2** have been deposited at the Cambridge Crystallographic Data Centre.

RESULTS AND DISCUSSION

Reaction of TMSA with **1** is complicated by a rapid oligomerization of TMSA yielding oily products. These preclude the isolation of titanium-containing products and hence their formation is to be minimized. At an equimolar ratio of TMSA and **1**, a mixture of titanium-containing products and oligomers of TMSA is obtained (Scheme 1). The titanium complexes are easily separated on the basis of different solubilities in hexane. Bright green compound **1** is the least soluble; brown compound **2** is moderately soluble and is well separated from the khaki-green mother liquor which contains compound **3** and oligomers of TMSA. Attempts to separate **3** from the oligomers were unsuccessful.

TABLE I
Crystal and structure refinement data for **2**

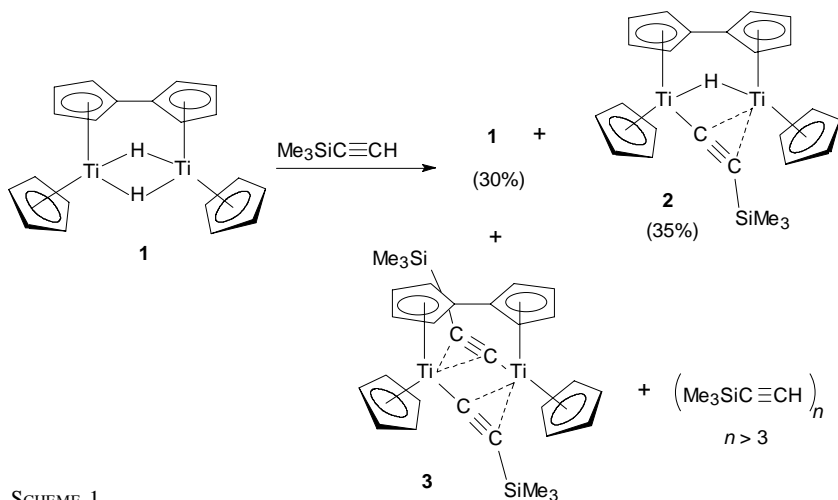
Empirical formula	C ₂₅ H ₂₈ SiTi ₂
Formula weight	452.36
Crystal system	triclinic
Space group	$P\bar{1}$ (No. 2)
a , Å	9.385(4)
α , °	110.34(2)
b , Å	14.487(6)
β , °	101.56(2)
c , Å	18.085(6)
γ , °	96.65(3)
V , Å ³	2 212(2)
Z	2
d_{calc} , g cm ⁻³	1.358
$\mu(\text{MoK}\alpha)$, mm ⁻¹	0.784
$F(000)$, e	944
θ_{min} , θ_{max} , °	3.04, 23.02
Range of hkl indices	-10→9, -15→14, 0→19
Reflections collected	6 117
Independent reflections	6 117
Data /restraints/parameters	6 116/0/727
Goodness-of-fit on F^2	1.015
$R1$, $wR2$ (all data)	0.0880, 0.0937
$R1$, $wR2$ [$I > 2\sigma(I)$]	0.0363, 0.0788
Maximal and minimal residual density, e Å ⁻³	0.386; -0.281

The use of the TMSA/Ti ratio equal to 2 results in a larger consumption of **1**; however, the yield of **2** is much lower. The TMSA oligomers were obtained and isolated at a larger TMSA excess. At the TMSA/**1** ratio equal to 10, a viscous brown solution is obtained which, after work-up in air, affords a yellow wax. This contains a very complex mixture of oligomers and their partially hydrogenated and/or desilylated analogues. This shows that the oligomerization though catalytic is nonspecific and is of poor synthetic potential.

TABLE II
Selected interatomic distances (in Å) and angles (in °) for **2**

Atoms	Distances	Atoms	Distances	Atoms	Angles
Molecule 1					
Ti1-CE1	2.065(6)	Ti1-CE2	2.076(7)	CE1-Ti1-CE2	133.3(2)
Ti2-CE3	2.039(6)	Ti2-CE4	2.061(8)	C2-C1-Ti2	163.7(3)
Ti1-H1	1.82(3)	Ti2-H1	1.87(3)	C1-Ti1-C2	31.77(12)
C1-C2	1.260(5)	Ti1-C1	2.287(4)	Ti2-C1-Ti1	89.56(13)
Ti1-C2	2.313(4)	Ti2-C1	2.044(4)	C1-C2-Si1	150.4(3)
Ti1-C10	2.342(4)	Ti1-C11	2.406(4)	CE3-Ti2-CE4	136.8(3)
Ti1-C12	2.427(5)	Ti1-C13	2.397(5)	C2-C1-Ti1	75.2(2)
Ti1-C14	2.345(4)	Ti2-C30	2.329(4)	C1-Ti2-Ti1	48.46(10)
Ti2-C31	2.338(5)	Ti2-C32	2.385(5)	C1-C2-Ti1	73.0(2)
Ti2-C33	2.389(5)	Ti2-C34	2.365(5)	Ti1-H1-Ti2	111.6(18)
Si1-C2	1.837(4)	Ti1-Ti2	3.056(1)		
Molecule 2					
Ti3-CE6	2.058(8)	Ti3-CE7	2.078(8)	CE6-Ti3-CE7	132.7(3)
Ti-CE8	2.036(8)	Ti4-CE9	2.052(13)	C52-C51-Ti4	164.5(4)
Ti3-H2	1.85(3)	Ti4-H2	1.89(3)	C51-Ti3-C52	31.41(14)
C51-C52	1.247(5)	Ti3-C51	2.290(4)	Ti4-C51-Ti3	90.0(2)
Ti3-C52	2.317(5)	Ti4-C51	2.041(5)	C51-C52-Si2	146.4(4)
Ti3-C60	2.345(4)	Ti3-C61	2.394(5)	CE8-Ti4-CE9	136.8(4)
Ti3-C62	2.400(5)	Ti3-C63	2.405(6)	C52-C51-Ti3	75.5(3)
Ti3-C64	2.342(6)	Ti4-C80	2.329(4)	C51-Ti4-Ti3	48.32(12)
Ti4-C81	2.335(5)	Ti4-C82	2.383(6)	C51-C52-Ti3	73.1(3)
Ti4-C83	2.384(6)	Ti4-C84	2.365(5)	Ti3-H2-Ti4	109.9(17)
Si2-C52	1.838(5)	Ti3-Ti4	3.066(2)		

Structures of **2** and **3** were inferred from electron impact mass spectra and ^1H , ^{13}C , ^{29}Si NMR and infrared spectra. The mass spectra of **2** showed an intense molecular ion peak (m/z 452, 82%) and a low-intensity peak due to the loss of C_5H_6 (cyclopentadiene) accompanied by peaks with loss of 2 H, 4 H and 6 H. Such a loss of hydrogen is typical of the fragmentation of **1** (ref.⁶) and of its chloro-hydrido analogue¹¹. The loss of the acetylide group is demonstrated by a group of peaks m/z 354 (54%)–348 (19%) flanking the basic peak m/z 352 ($\text{M}^{+\bullet} - \text{TMSA} - \text{H}_2$). ^1H and ^{13}C and ^{29}Si NMR spectra gave clear evidence of the presence of all the ligands except the bridging hydride. This is not observed in pure dimeric titanocene either²⁷. The bridging hydrogen was, however, unequivocally located in the X-ray crystal structure analysis (*vide infra*). Compound **3** is tentatively identified in EI-MS spectra of samples containing TMSA oligomers. The



SCHEME 1

molecular ion m/z 548 proves that **3** is the main component in the sample where **2** and a compound characterized by m/z 550 are impurities. ^1H , ^{13}C and ^{29}Si NMR spectra are not informative since they contain a great number of signals belonging probably to various oligomers derived from TMSA.

X-Ray Crystal Structure of **2**

Compound **2** crystallizes in triclinic space group ($\bar{P}1$) and the unit cell contains two pairs of centrosymmetrically placed molecules. The crystallographically different molecules are denoted as molecule *1* and molecule *2*. The PLATON representation of molecule *1* with an atom numbering scheme is shown in Fig. 1. Molecule *2* differs only slightly from molecule *1*; its numbering scheme is analogous, with number 5 added to the first digit of each number of C and CE in molecule *1*. Selected bond lengths and

angles for molecules **1** and **2** are listed in Table II. The overall structure of **2** as well as the bonding distance of Ti atoms from the fulvalenediyl and cyclopentadienyl carbon atoms do not differ noticeably from those observed for other doubly bridged fulvalenediyl dititanium(III) complexes (*cf.* ref.¹⁴). In comparison with the structure parameters of **1**, the introduction of a σ -bonded and π -bonded ligand leads to a marginal lengthening of all Ti–C bonds in the dimeric titanocene skeleton, close to the values of estimated standard deviations. Interestingly, the bonds involving Ti2, σ -bonded to the acetylide, are noticeably shorter (by *ca.* 0.02 Å) than the bonds involving Ti1, which is π -coordinated to the triple bond. The Ti–H bonds in **2** are by *ca.* 0.1 Å longer than in **1**. The binding mode of the bridging (trimethylsilyl)acetylide group is well known from dimeric titanocene acetylides [$\{\text{Cp}_2\text{Ti}(\text{C}\equiv\text{CSiMe}_3)_2\}$] (refs.^{28,29}) or [$\{\text{Cp}_2\text{Ti}(\text{C}\equiv\text{CSnMe}_3)_2\}$] (ref.³⁰) and also its geometry is analogous. The acetylide C1 carbon atom is σ -bonded to the Ti2 atom and both C1 and C2 atoms are π -bonded to the Ti1 atom. The bonding distance of the former atom is by *ca.* 0.02 Å shorter than that of the latter, both of them being shorter than any Ti–C distance to π -bonded cyclopentadienyl or fulvalenediyl

TABLE III

Distances (d , Å) in bridging acetylide groups (Ti–C $_{\alpha}$ ≡C $_{\beta}$) and ¹³C NMR chemical shifts of acetylide carbon atoms (δ , ppm) in **2** and dimeric titanocene acetylides [$(\eta^5\text{-C}_5\text{H}_5)_2\text{Ti}(\mu\text{-}\eta^1\text{-}\eta^2\text{-C}\equiv\text{CSiMe}_3)_2$] (A) and [$(\eta^5\text{-C}_5\text{H}_5)_2\text{Ti}(\mu\text{-}\eta^1\text{-}\eta^2\text{-C}\equiv\text{CSnMe}_3)_2$] (B)

Compound <i>d</i>	$d(\text{C}_{\alpha}\text{-C}_{\beta})$	$d(\sigma\text{-Ti-C}_{\alpha})$	$d(\sigma\text{-Ti-C}_{\omega})$	$d(\sigma\text{-Ti-C}_{\omega})$	$d(\text{Ti-Ti})$	δC_{α}	δC_{β}
2 ^a	1.253(5)	2.042(5)	2.288(5)	2.315(5)	3.061(2)	250.3	154.3
A ^b	1.253(15)	2.056(11)	2.395(7)	2.312(8)	3.550(3)	237.5	142.8
B ^c	1.242(7)	2.065(5)	2.413(5)	2.273(5)	3.573(1)	236.1	139.7

^a Data for molecule **1**. ^b Data from ref.²⁸. ^c Data from ref.³⁰.

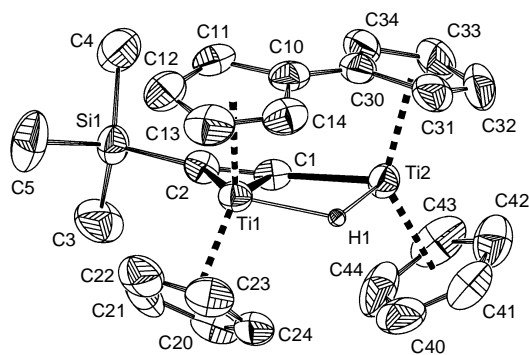


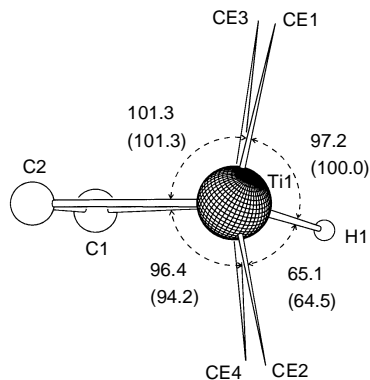
FIG. 1
ORTEP drawing of **2** (molecule **1**) at the 30% probability level with atom-labelling scheme

ligands. The acetylenic $C\equiv C$ bond length of average $1.253(5)$ Å is between the typical bond lengths of sp - and sp^2 -hybridized carbon atoms.

Replacement of one bridging hydrogen atom by a (trimethylsilyl)acetylide group removes all the molecular symmetry of **1** (ref.¹⁴). A schematic view of molecule **1** along the Ti1–Ti2 direction (Fig. 2) illustrates the least-squares planes which are defined as follows: PL1 (CE1, CE3, Ti1 and Ti2), PL2 (CE2, CE4, Ti1 and Ti2) and PL3 (C1, C2, Ti1 and Ti2) and the plane PL4 defined by (H1, Ti1 and Ti2). The dihedral angles between the planes are given in appropriate sectors; those for molecule **2** are given in parentheses. The (trimethylsilyl)acetylide group gains more space by declining the fulvalenediyl and both cyclopentadienyl ligands so that the angle between PL1 and PL2 is 162.3° (164.5°). The bridging hydrogen atom and the acetylide group incline to the side of the cyclopentadienyl ligands, the angle between planes PL3 and PL4 being 161.5° (158.7°). The fulvalenediyl ligand is bent. The dihedral angle between the planes of its cyclopentadienyl rings is 18.6° (18.5°). This bending occurs in all known doubly bridged fulvalenediyl dititanium(III) complexes; the larger is the dihedral angle the shorter is the distance between the titanium atoms¹⁴. In **2**, this angle is marginally larger than in **1** (18.5° vs 17.7°) although the distance between the Ti atoms is slightly longer (average $3.061(2)$ Å vs $2.989(1)$ Å). This is apparently caused by a slightly different orientation of Ti1–Ti2 and CE1–CE3 connecting lines (see Fig. 2) induced by a non-symmetric position of the acetylide ligand.

FIG. 2

View of molecule **1** of **2** in the direction Ti1–Ti2 illustrating the least-squares planes containing the Ti1 and Ti2 atoms and CE1 and CE3 (PL1), CE2 and CE4 (PL2), C1 and C2 (PL3) and the plane containing H1 (PL4). Dihedral angles between the planes are given in appropriate sectors (values for molecule **2** in parentheses)



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