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Sunlight photolysis of cyclopentadienyl-tethered titanium(iv) permethyltitanocene chlorides



Jiří Pinkas^a, Jiří Kubišta^a, Karel Mach^a, Róbert Gyepes^{a,b}, Michal Horáček^{a,*}

^a J. Heyrovský Institute of Physical Chemistry, Czech Academy of Sciences, Dolejškova 3, 182 23 Prague 8, Czech Republic ^b Department of Inorganic Chemistry, Faculty of Science, Charles University, Hlavova 2030, 128 43 Prague 2, Czech Republic

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ABSTRACT

Solutions of permethylcyclopentadienyl-tethered titanium(IV) chlorides incorporating one double bond in their tethers were exposed in glass vessels to sunlight, which triggered their photolytical reactions providing mixtures of products. Although the formation of several different products was apparent from ¹H NMR spectra, only a single product could be identified in the crude reaction mixtures. This product was dicyclopentadiene [$C_{10}Me_{10}$], which arose from the recombination of the generally photodissociated C_5Me_5 radical. Amongst products that contained titanium, three complexes (**3a**, **3b** and **4a**) could be isolated after employing fractional crystallization and these complexes were characterized. The mechanism of **3a** formation involves photodissociation of one $\eta^5-C_5Me_5$ ligand from the parent complex, complemented by chlorine abstraction from another reactant molecule. Complexes **3b** and **4a** become formed via tether rearrangement, which starts with dissociating the tether Ti–C bond and is followed by rotating the tether, reattaching it subsequently through its available radical terminus.

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1. Introduction

Sunlight photolysis belongs to the family of methods used to run chemistry in sustainable development mode [1]. Especially in the field of organic chemistry, a considerable number of large-scale syntheses has been driven by photolysis [2,3]. The contemporary goal for utilizing artificial photosynthesis lies in catalytic water oxidation [4,5] and in the electrolysis of carbon dioxide using photovoltaic electricity [6]. The cost-effective utilization of hydrogen as a "green" fuel has turned attention to transition metal hydrides and their photochemical behaviour with the aim to obtain recoverable hydrogen storing systems [7]. Unfortunately, thermally stable titanocene(TiIII) hydrides [8] are low on their bonded hydrogen content and are additionally inert towards visible light. Amongst other titanocene compounds, great attention has been devoted to the photolytic behaviour of titanocene dichloride [Cp₂TiCl₂] (Cp = η^{5} - C_5H_5), which is the raw material for the synthesis of other titanocene derivatives and parent compound in titanium-based ethylene polymerization catalysts [9]. Early photolytic studies indicated the decomposition of $[Cp_2TiCl_2]$ to Cp radical and $(CpTiCl_2)$, where the products were characterized by EPR spectra of their adducts with spin traps [10]a,b and by the photolysis of [Cp₂TiCl₂] in

* Corresponding author. E-mail address: michal.horacek@jh-inst.cas.cz (M. Horáček). chlorinated solvents affording [CpTiCl₃] as the sole product containing titanium [10]c. While this photodecomposition was later found to proceed analogously for the titanocene difluoride and dibromide analogues, the photolysis of Cp₂TiI₂ resulted only in the elimination of I₂ [11]a. This behaviour was due to its increased halogenide \rightarrow Ti LM-CT transition energy with respect to the lighter halides, which results in swapping the frontier orbitals for Cp₂TiI₂ [11]b-d. Nevertheless, the substitution of both Cp ligands in Cp₂TiI₂ for their more electron donating analogues η^5 -C₅Me₅ (Cp^{*}) decreased the $Cp^* \rightarrow$ Ti transition energy, which was demonstrated experimentally by the elimination of the C₅Me₅ radical detected by spin trapping it with nitrosodurene and also by the formation of Cp*Til₃ upon performing the photolysis in iodoform [11]c. Similarly, the photolysis of [Cp₂TiMe₂] resulted mostly in methane elimination and yielded only some poorly soluble "polytitanocene" of decreased hydrogen content [12].

Further research of photoassisted water dissociation was until recently hampered by the observation, that the photolysis of permethyltitanocene dihydroxide $Cp*_2Ti(OH)_2$ by visible light provides the C_5Me_5 radical instead of the desired OH radical [13]a. However, since properties of titanocene complexes are often altered substantially upon introducing suitable functional groups on their cyclic ligand(s) [14], the linking of cyclopentadienyl ligands with a diatomic ansa-bridge enhanced the photolytic stability of the permethyltitanocene moiety significantly [13]b,c. For the sake of example, ansa-bis(dimethylsilylene)(C_5Me_4)₂Ti(OH)₂ exhibited selec-



Scheme 1. Preparation of permethylcyclopentadienyl-tethered titanocene (Ti(IV)) derivatives 1a-1g according to ref. [16]).



Scheme 2. Preparation of permethylcyclopentadienyl-tethered titanocene (Ti(IV)) derivatives 2a and 2b (according to ref. [16]).

tive OH radical elimination upon its photolysis using wavelengths over 420 nm [13]d, while ansa-titanocene(III/IV) triflate complexes exhibited properties that made them capable of acting in a closed catalytic cycle for overall water splitting [13]e.

Herein we report the results of an exploratory research on sunlight photolysis of permethyltitanocene-tethered (TiIV) monochlorides, which were obtained by inserting various internal acetylenes into the titanium-methylene bond of the singly tucked-in titanocene [Cp*Ti(η^5 : η^1 -C₅Me₄CH₂)] [15] and the Ti(III) products formed were subsequently chlorinated with PbCl₂ in tetrahydrofuran (Scheme1 and Scheme2) [16]. All photolytic reactions were carried out in C₆H₆ and C₆D₆.

The progress of sunlight photolysis for **1a-1g**, **2a** and **2b** in their C_6D_6 solutions was followed by ¹H NMR and exposure to sunlight was terminated after reaching the consumption of reactant around 90%. Amongst the generated products, only those that could be isolated by fractional crystallization were investigated further and were identified. The reaction mechanisms of the photolytical processes were studied by means of Density Functional Theory (DFT) computations.

2. Results and discussion

Compounds **1a-1g**, **2a** and **2b** dissolved in C_6H_6 or C_6D_6 turned their colour after exposing their solutions in NMR sample tubes to sunlight for up to four days commonly from red to brownish-yellow. ¹H NMR measurements were used to follow the photolytic decay of reagents, needed for indicating the time necessary to terminate the photolytic experiments on a larger scale. No assignment for the newly formed products could be drawn from these spectral data, only the signals at δ_H 1.14, 1.66 and

1.76 ppm in intensity ratio 1:2:2 were indicating the presence of bis-(1,2,3,4,5-pentamethylcyclopenta-2,4-diene-1-yl) [$C_{10}Me_{10}$], which arose from recombination of the C_5Me_5 radicals (see Figure A.1 in Supplementary material). Since the measurements were conducted in C_6D_6 , the above ¹H chemical shifts are shifted downfield with respect to the values reported by Jutzi and Hielscher [17] for [$C_{10}Me_{10}$] in CDCl₃. The chemical shifts and linewidths exhibited slight variation also due to the presence of varying amounts of paramagnetic Ti(III) intermediates and products, which were indicated by their EPR spectra showing mostly singlet signals in the range $g_{iso} \sim 1.96 - 1.99$ and exhibiting varying intensities during the photolytical process.

The sunlight photolysis of **1a-g** (Scheme 1) and **2a** and **2b** (Scheme 2) resulted always in complex product mixtures. Pure products could successfully be obtained from these mixtures only in three cases upon using repeated fractional crystallization from hexane. Amongst all the photolyzed compounds, only products from **1a**, **1b**, and **2a** could be isolated in crystalline form from scaled-up photolytic experiments carried out in benzene. These isolated products (**3a**, **3b**, and **4a**, respectively) were characterized by EI-MS, ¹H and ¹³C NMR, IR spectra and by X-ray single-crystal diffraction and the mechanism of their formation was elucidated by DFT computations.

2.1. Photolysis of **1a** to give **3a**

The sunlight photolysis of **1a** dissolved in C_6H_6 lasting 12 h in a rotated ampule afforded **3a** in 28% isolated yield. This means that after photodissociation of the Cp* ligand, the resulting Ti(III) intermediate had to acquire a further chloride ligand from an external source, presumably from another molecule of **1a** (Scheme 3).



Scheme 3. Photolysis of 1a yielding 3a.



Fig. 1. Solid-state model of **3a** with thermal ellipsoids drawn at 30% probability level. Atom C(5) is the cyclopentadienyl carbon atom residing between C(1) and C(4). Hydrogen atoms are drawn with rods without reflecting the values of their thermal parameters.

Table 1

Selected bond lengths (Å), bond angles (°) and torsion angles (°) for 3a .						
)						
)						
)						
8)						
4)						
7)						

 ${}^{a}Cg(1)$ denotes the centre of gravity of the cyclopentadienyl ring C(1)–C(5).

The EI-MS spectra of **3a** showed the molecular ion (m/z 388) of moderate abundance, which fragmentated by HCl elimination to the base peak m/z 352 or by the tether L₁ (L₁ = head-to-tail dimer of 1-pentyne [18]) elimination affording m/z 252 ([$M - L_1$]⁺; 48). The ¹H NMR and ¹³C NMR spectra were fully assigned to the tethered permethylcyclopentadienyl ligand containing one exomethylene double bond and one double bond vicinal to titanium, which were detected also in the solid-state structure of **3a** (Fig. 1 and Table 1). Both double bonds were detected also in the IR (KBr) spectra of **3a** — the double bond vicinal to titanium at 1553 cm⁻¹ and the exo-methylene double bond at 1603 cm⁻¹. This assignment agrees with the corresponding double bond distances established from the solid-state model.

2.2. Photolysis of 1b to give 3b

Exposing benzene solution of **1b** to sunlight for 24 h resulted in the initial red colour turning to dark yellow. Crystallization from hexane afforded a pale red crystalline solid product **3b**, obtained in 36% yield after recrystallization (Scheme 4).

Although EI-MS spectra of **3b** displayed the molecular ion m/z548 that could be ascribed also to 1b, the fragmentation of both compounds followed completely different pathways. No molecular ion was observed for 1b [16] since it underwent an abundant loss of its whole tether L_2 ($L_2 = h$ -t-t dimer of HC=CSiMe_3) [18], whereas no $[M - L_2]^+$ ion was observed for **3b**. The common feature for both compounds was the presence of base peak m/z 218 $[M - C_5Me_4CH_2 - L_2]^+$. The tether isomerization in **1b**, indicated by EI-MS spectra of 3b has become evident after complete assignment of ¹H and ¹³C NMR spectra of **3b** based on APT, ²⁹Si INEPT, 1DNOESY, gCOSY, gHMBC, and NOESY experiments. The arrangement around the two double bonds of 3b has been derived from 1DNOESY experiments. These showed a strong interaction of the =CHSiMe₃ (5.26 ppm) proton with one proton of the CH_2 group (2.94 ppm) and with protons of SiMe₃ group (0.241 ppm) in one case and the interaction of the TiCH= proton (8.16 ppm) with the protons of the other SiMe₃ group (0.247 ppm) and the Cp* protons (1.76 ppm) in the other case. The IR (KBr) spectrum of **3b** exhibited a broadened band of medium intensity at 1593 cm⁻¹ that could be attributed to both double bonds. The stretching C-H vibrations of double bonds should be overlapped with the strong C-H valence vibrations of the methyl groups. The X-ray single-crystal diffraction experiment yielded a structure model of 3b in agreement with spectral data (Fig. 2, Table 2). The asymmetric part of the unit cell incorporates two molecules that are differing mostly in the orientation of their tether arms. (Fig. 3).

The sunlight-induced tether isomerization is to be initiated by dissociating the tether Ti–C bond, which is followed by rotation of the π -isomerized dienyl tether around the CH₂–C_{quaternary} bond, allowing the most distal tether sp² carbon atom to restore a regular Ti–C overlap (Scheme 5).

A similar isomerization mechanism, albeit induced by adding dihydrogen has been recently observed for the permethyltitanocene tethered complexes bearing a methyl substituent on the tether carbon attached to the cyclopentadienyl methylene [19].

DFT studies suggested the energy required to generate a singletstate excited molecule of 1b to be 474 nm via vertical excitation. Taking into consideration the possibility of intersystem crossing (which cannot be ruled out entirely due to the presence of the metal and the prolonged exposition times), the first vertical excitation energy to the electronic triplet-state molecule decreases to 564 nm. In both cases, the excitation of 1b occurs within the visible region of light, and irrespective of the actual excited-state multiplicity, the photolytical process follows the same pathway. Both excited-state geometry optimizations arrived to molecular geometries having their tether dissociated from the metal (hereafter denoted as **1b**^{*}; Fig. 4). The tether arm becomes subsequently free to rotate around the σ bond between the tether carbon and its neighbouring atom bonded to the cyclopentadienyl skeleton. After rotation to a sterically less congested position and bringing the distal methylene group to the vicinity of the metal, the tether becomes reattached to the metal. The isomerization process is driven by enthalpy, as the total energy of 1b and 3b differs by 49.49 kJ/mol in favour of the latter.

2.3. Photolytic conversion of 2a to 4a

Another example of photolysis that is capable to yield an isolable isomerization product with a surprisingly high selectivity occurred with **2a** (Scheme 6). The isolated yield of 63% after pho-



Scheme 4. The photolytically induced rearrangement of 1b to 3b.

Table 2

Selected bond lengths (Å), angles (°) and torsion angles (°) for the solid-state structure of **3b**. The left part of the table includes data for the first molecule depicted in Fig. 2, the right part the corresponding quantity for the second molecule.

Bond lengths			
Ti(1)-Cl(1)	2.362(3)	Ti(2)-Cl(2)	2.361(3)
Ti(1)-C(27)	2.140(10)	Ti(2)-C(57)	2.138(10)
C(1)-C(6)	1.518(14)	C(31)-C(36)	1.493(14)
Ti(1)-Cg(1)*	2.103(5)	Ti(2)-Cg(3)	2.104(5)
Ti(1)-Cg(2)**	2.114(5)	Ti(2)-Cg(4)	2.113(5)
Bond angles			
Cg(1)-Ti(1)-Cg(2)	139.1(2)	Cg(3)-Ti(2)-Cg(4)	139.3(2)
Cg(1)-Ti(1)-Cl(1)	104.66(18)	Cg(2)-Ti(2)-Cl(2)	104.01(19)
Cg(2)-Ti(1)-Cl(1)	106.57(19)	Cg(3)-Ti(2)-Cl(2)	105.7(2)
Cg(1)-Ti(1)-C(27)	102.3(3)	Cg(3)–Ti(2)–C(57)	103.4(3)
Cg(2)-Ti(1)-C(27)	102.9(3)	Cg(4)-Ti(2)-C(57)	103.8(3)
Cl(1)-Ti(1)-C(27)	90.9(3)	Cl(2)-Ti(2)-C(57)	90.1(3)
Ti(1)C(27)C(26)	141.8(8)	Ti(2)-C(57)-C(56)	141.2(8)
Torsion angles			
C(1)-C(6)-C(21)-C(26)	-57.3(11)	C(31)-C(36)-C(51)-C(56)	-56.3(13)
Ti(1)-C(27)-C(26)-C(21)	3.5(16)	Ti(2)-C(57)-C(56)-C(51)	1.7(18)

* Cg(1) denotes the centre of gravity of the cyclopentadienyl ring C(1)–C(5).

** Cg(2) denotes the centre of gravity of the cyclopentadienyl ring C(11)-C(15).





Fig. 2. Solid-state structure of **3b** with thermal ellipsoids drawn at 30% probability level and with the atom labelling scheme. Only one of the two symmetrically independent molecules is drawn. Hydrogen atoms are drawn with rods without reflecting the values of their thermal parameters. The skeleton of the upper cyclopentadienyl ligand is constructed from atoms C(1)–C(5). Atom C(1) is the ring atom bonded to the tether C(6).





Scheme 5. Proposal for the isomerization of 1b to 3b.



Fig. 4. Perspective view of optimized 1b (1b*) after singlet excitation. Colour legend: Ti – yellow, Cl – green, C – dark grey, Si – brown, H – light grey.



Scheme 6. Photolytically induced rearrangement of 2a to 4a.

tolyzing **2a** for 12 h showed the formation of **4a** to be the overwhelming process in the system.

The EI-MS spectra of **4a** displayed the molecular ion (m/z 572)and the $[M - C_5Me_5]^+$ ion of low intensity and the base peak arising from the loss of the permethylcyclopentadienyl tether [M - $C_5Me_4CH_2 - L_3]^+$ ($L_3 = Me_2Si(C \equiv Ct-Bu)_2$) differing for **2a** [16] only slightly in intensities. The ¹H NMR spectrum of 4a preserved most features of the tether from 2a and contained a doublet which had to be assigned to a methylene group residing on the titanium. The chemical shifts of its protons differed strongly according to the extent of their interaction with the titanium ligand field electron density. The proton residing close to the titanocene pseudoequatorial plane with high electron density was shifted upfield (-0.84 ppm), while the other was found at 3.40 ppm. Compared with the ¹³C NMR resonance at 240.69 ppm of **2a**, due to the presence of a quaternary carbon of the silacycle residing on the titanium atom [16] the quaternal carbon directly connected to C_5Me_4 ring in 4a was shifted strongly highfield to 153.2 ppm. Similarly, the highfield shift could be observed for remaining carbon atom signals of silacycle in **4a** compared to **2a**. The signal of C=C-Si was found at 159.7 ppm in 4a (compared to 170.4 ppm in 2a) and the signal of C-C-Si was localized at 135.8 ppm in 4a (compared to 149.1 ppm in 2a). Indeed, a formal displacement of methylene group from cyclopentadienyl ring to titanium atom led to its ¹³C NMR signal downfield shift (from 28.5 ppm in 2a to 79.9 ppm in 4a). The ²⁹Si NMR signal at 3.72 ppm for 4a that appeared shifted downfield from that of 2a at -6.89 ppm [16] was also compatible with the separation of the silacycle from titanium by the methylene group. In IR spectra, the two very weak absorption bands in ν (C=C) region at 1592 cm⁻¹ and 1558 cm⁻¹ for **2a** were replaced by a medium intensity band at 1615 cm^{-1} for **4a**, which could be assigned to the both double bonds with only marginally differing surroundings. The above spectral assignments are in good agree-



Fig. 5. The solid-state structure of **4a** with thermal ellipsoids drawn at 30% probability level. Hydrogen atoms are omitted for clarity. Only one of the two symmetrically independent molecules is drawn.



Fig. 6. Superposition of the two molecules residing in the asymmetric part of unit cell of **4a**. The tether arms are orientated towards the reader. The two molecules are differentiated by using different colours for all atoms of each molecule. Hydrogen atoms are omitted.

ment with the solid-state model of **4a** (Fig. 5). Selected bond angles and distances are provided in Table 3.

The asymmetric part of the unit cell includes two molecules that are two rotamers of **4a**. The most important difference between the two molecules lies in the orientation of their tether arms (Fig. 6). Although this difference is modest, it is manifested well by the torsion angles on the tether arm (Table 3).

The molecular geometry of both **2a** and **4a** was optimized by DFT, yielding the total energy of **4a** lower by 3.69 kJ/mol and the Gibbs energy at 298.15 K by 19.97 kJ/mol. This difference is to be accounted for a steric relief at the central atom, suggested by a notable decrease of internuclear repulsion energy of 152.42 hartrees in favour of **4a**.

Table 3

Selected bond lengths (Å), angles (°) and torsion angles (°) for the solid-state structure of **4a**. The left part of the table includes data for the first molecule depicted in Fig. 5, the right part the corresponding quantity for the second molecule.

Bond lengths			
Ti(1)-Cl(1)	2.338(3)	Ti(2)-Cl(2)	2.347(4)
Ti(1)-C(20)	2.260(11)	Ti(2)-C(54)	2.268(12)
C(1)-C(10)	1.473(13)	C(35)-C(44)	1.472(14)
Ti(1)-Cg(1)*	2.111(5)	Ti(2)-Cg(3)	2.102(5)
Ti(1)-Cg(2)**	2.153(5)	Ti(2)-Cg(4)	2.156(5)
Bond angles			
Cg(1)-Ti(1)-Cg(2)	136.8(2)	Cg(3)-Ti(2)-Cg(4)	136.7(2)
Cg(1)-Ti(1)-Cl(1)	106.79(16)	Cg(3)-Ti(2)-Cl(2)	106.75(17)
Cg(2)-Ti(1)-Cl(1)	104.05(17)	Cg(4)-Ti(2)-Cl(2)	105.69(18)
Cg(1)-Ti(1)-C(20)	104.2(3)	Cg(3)-Ti(2)-C(54)	104.4(3)
Cg(2)-Ti(1)-C(20)	105.0(3)	Cg(4)-Ti(2)-C(54)	104.1(3)
Cl(1)-Ti(1)-C(20)	90.8(3)	Cl(2)-Ti(2)-C(54)	89.1(3)
Ti(1)-C(20)-C(19)	125.5(7)	Ti(2)-C(54)-C(53)	129.0(7)
Torsion angles			
C(1)-C(10)-C(12)-C(13)	-10(2)	C(35)-C(44)-C(46)-C(47)	-8(2)
C(1)-C(10)-C(11)-C(19)	22(2)	C(35)-C(44)-C(45)-C(53)	13(2)
Ti(1)-C(20)-C(19)-C(11)	-56(1)	Ti(2)-C(54)-C(53)-C(45)	-50(1)

 $c_{\rm Cg(1)}$ denotes the centre of gravity of the cyclopentadienyl ring C(1)–C(5).

* Cg(2) denotes the centre of gravity of the cyclopentadienyl ring C(25)-C(29).



Fig. 7. Perspective view of optimized $2a^*$ in singlet excitation. Colour legend: Ti – yellow, Cl – green, C – dark grey, Si – brown, H – light grey.

DFT computations allowed for a deeper insight into the mechanism by identifying the first excited-state molecular geometry. The singlet excitation energy for 2a was computed to be 446.99 nm with the excitation occurring from the orbital incorporating mostly the Ti–C_{silacycle} σ -overlap. As a result, the first excited-state molecule of 2a (denoted hereafter 2a*; Fig. 7) showed after geometry optimization its Ti-Csilacycle bond becoming prolonged from 2.170 Å to 2.541 Å with the concurrent decrease of the respective Mayer Bond Order (MBO) value to 0.212, indicating a substantial release of the silacycle from the metal. Simultaneously, the silacycle carbon established a bonding overlap with the closest cyclopentadienyl carbon atom (interatomic distance 1.631 Å; MBO 0.798) after its release from the titanium to 2.515 Å and decreasing the respective MBO to 0.081. This carbon atom becomes formally pentacoordinated [20], having its methyl substituent deviated considerably from the cyclopentadienyl least square plane orientated outwards from the titanium.

After converting the multiplicity of this excited-state molecule to a triplet leads to a decrease in its total energy and the silacyclopentadienyl ligand becomes completely detached from the metal (acquiring the Ti–C distance 2.990 Å). We assume the next step to be the scission of the tether methylene group from the cyclopentadienyl ring, in conjunction with methyl migration to this liberated position on the cyclopentadienyl. Such a mechanism arranges all the necessary changes on the cyclopentadienyl ligand needed for the formation of **4a** (Scheme 7). Unfortunately, this suggested mechanism could not be verified by DFT, as the computational demands necessary to locate a proper transition state of an excited-state molecule incorporating a transition metal were prohibitive.

The importance of steric and electronic effects exerted by the seemingly uninvolved and innocent substituents (t-Bu and SiMe₃) was demonstrated by the unsuccessful attempts at obtaining any crystalline product from the analogous photolysis of **2b** containing bis(trimethylsilylethinyl)dimethylsilane.

2.4. Conclusions

Exploratory results obtained for the sunlight photolysis of permethylcyclopentadienyl-tethered titanium(IV) chlorides 1a-1g and 2a and 2b indicate that both their Ti-Cp* and Ti-C(tether) moieties become activated upon photoexcitation. Photolysis of the former moiety resulted always in the C₅Me₅ radical elimination in various abundance, as indicated by ¹H NMR evidence for [C₁₀Me₁₀] in all solutions photolyzed. The complementary titanium-containing product 3a could be obtained only from the photolysis of 1a. The structure of 3a indicates the transiently formed Ti(III) intermediate abstracting a chlorine from another molecule of 1a as its only source in the system, while the tether undergoes no change. Products requiring the Ti-C_(tether) bond to photodissociate were obtained from 1b and 2a. The tether radical rotating at the CH₂ group of **1b** allowed to restore the Ti-C overlap by involving the most distal sp² carbon and the reaction yielded 3b. The analogous photodissociation of the Ti-C bond in 2a is a necessary prerequisite for tether rearrangement to yield 4a; however, the overall mechanism is less straightforward than for 3b. DFT studies suggested 2a to undergo a significant weakening of two of its Ti-C bonds upon excitation - the carbon of the silacycle and its closest neighbour on the cyclopentadienyl ring. These two carbons become bonded mutually, while the cyclopentadienyl carbon achieves transient pentacoordination. To reach 4a, the cyclopentadienyl methyl migrates to the neighbouring atom what destabilizes that atom's bond to the tether. The tether CH₂



Scheme 7. Proposal for the rearrangement mechanism of 2a to 4a.

group then links to the titanium and the methyl group becomes attached to the liberated position on the cyclopentadienyl ring.

3. Experimental

3.1. Methods

Synthesis, treatment, and subsequent reactions of low-valent titanium compounds were carried out on a vacuum line in sealed all-glass devices equipped with magnetically breakable seals. ¹H (300 MHz), ¹³C (75 MHz) and ²⁹Si (59.6 MHz) NMR spectra were recorded on a Varian Mercury 300 spectrometer in C₆D₆ at 25 °C, unless stated otherwise. Chemical shifts (δ /ppm) are given relative to the residual solvent signal $\delta_{\rm H}$ 7.15 ppm and to the solvent resonance $\delta_{\rm C}$ 128.0 ppm. ²⁹Si NMR spectra were referenced to an external signal of SiMe₄ ($\delta_{Si} = 0.0$ ppm). EI-MS spectra were obtained on a VG-7070E mass spectrometer at 70 eV. Crystalline samples in sealed capillaries were opened and inserted into the direct inlet under argon. The spectra are represented by peaks of relative abundance higher than 7% and by important peaks of lower intensity. EPR spectra were recorded on a MiniScope MS400 (Magnettech GmbH, Berlin, Germany) equipped with a microwave frequency counter FC 400 and a temperature controller H03. Crystalline samples for EI-MS measurements and melting point determinations were placed in glass capillaries in a glovebox Labmaster 130 (mBraun) under purified nitrogen (concentrations of oxygen and water were lower than 2.0 ppm) and sealed with flame. KBr pellets of solid samples were prepared in the glovebox and measured in an air-protected pellet holder on a Nicolet Avatar FT IR spectrometer in the range 400-4000 cm⁻¹. Melting points were measured on a Koffler block in sealed glass capillaries under nitrogen, and are uncorrected.

Photolysis of benzene solutions of 1a-1 g and 3a and 3b in NMR sample tubes (C_6D_6) and ampules (0.1 M in 20 mL of C_6H_6) were performed in summer (Prague, 50.08° N, 14.42° E) with direct sunlight that passed through 2 \times 4.0 mm glass windows and 2.0 mm Pyrex glass of the ampule. The photolysis was terminated when a contemporaneously photolyzed sample in an NMR tube showed no more than 10% of the initial compound signal intensity. The products in ampules were processed under diffuse daylight. Benzene was removed by evaporating it under vacuum, the residues were then dissolved in 4.0 mL of dry, vacuum-distilled hexane and this solution was transferred into an ampoule with 3 arms equipped with breakable seals. The ampule was placed into a refrigerator by one arm close to a cooling side for slow solvent condensation. After the formation of crystalline solid, the mother liquor and washings were collected in the cooled arm. Hexane was distilled back to dissolve the crystalline product and the arm was sealed off. The crystallization was repeated using the other arm, and finally the pure crystalline product was collected in the third arm, dried in vacuum, sealed off, and transferred to the glovebox where it was weighed and handled further for analytical methods.

3.2. Chemicals

The solvents benzene, toluene, hexane, and tetrahydrofuran (THF) were dried by refluxing over LiAlH₄ and stored as solutions

of green dimeric titanocene [$(\mu - \eta^5: \eta^5 - C_5H_4C_5H_4)(\mu - H)_2$ {Ti $(\eta^5 - C_5H_4C_5H_4)(\mu - H)_2$ $(C_5H_5)_2$ [21]. Benzene- d_6 (99.6% D) (C_6D_6) or toluene- d_8 (C_7D_8) (both Sigma Aldrich) was degassed, distilled under vacuum onto singly tucked-in permethyltitanocene [Ti(C₅Me₅)(C₅Me₄CH₂)] [15] and stored as its solution on a vacuum line. Solutions of compounds $1a\mathchar`1g$ and 2a and 2b in C_6D_6 were identical with those described in ref. [16]. Compounds 1a and 1b were obtained newly from 2.0 mmol of [Ti(C5Me5)(C5Me4CH2)] and excess of head-to-tail dimer of 1-pentyne and (trimethylsilyl)ethyne (RC=CC(R)=CH₂; R = Pr, SiMe₃), respectively, compound **2a** by reacting $[Ti(C_5Me_5)(C_5Me_4CH_2)]$ with ditert.butylethinyldimethylsilane and compound 2b by reacting it with bis(trimethylsilylethinyl)dimethylsilane. The obtained Ti(III) tethered products were chlorinated with PbCl₂ (see Scheme 1 and Scheme 2) [16]. The above acetylene dimers were obtained from terminal alkynes using Ti catalysts [18].

3.3. Photolysis of 1a to 3a

A solution of **1a** in benzene (0.1 M, 20 mL) was exposed to sunlight for 12 h, turning its red colour to dark yellow. Crystallization from hexane afforded orange needles of **3a**.

3a: Yield 0.22 g, 28%. Mp. 108-110 °C. EI-MS (160 °C): m/z (relative abundance) 392 (10), 391 (12), 390 (29), 389 (17), 388 (M⁺; 38), 387 (9), 386 (8), 356 (9), 355 (15), 354 (45), 353 (36), 352 ([M - HCl]⁺; 100), 351 (22), 350 (31), 349 (8), 348 (11), 347 (11), 346 (8), 345 (13), 338 (10), 337 ([M - HCl - Me]⁺; 17), 336 (10), 335 (9), 325 (10), 324 (12), 323 (13), 321 (9), 317 (11), 316 ([M - 2 HCl]+; 23), 256 (12), 255 (11), 254 (36), 253 (17), 252 ([M - L₁]+; 48), 236 (13), 218 (15), 219 (8), 218 (15), 217 (11), 216 ([M $-L_1 - HCl]^+$; 18), 215 (9), 214 (8), 213 (11), 134 (15), 119 (17), 105 (9), 91 (15), 79 (12), 69 (13). $^1{\rm H}$ NMR (C_6D_6): 0.85 (t, $^3\!J_{\rm HH}=$ 7.5 Hz, 3H, =CCH₂CH₂Me); 0.96 (t, ${}^{3}J_{HH}$ = 7.2 Hz, 3H, C(=CH₂)CH₂CH₂Me); 1.31–1.46 (m, 2H, =CCH₂CH₂); 1.46–1.62 (m, 2H, C(=CH₂)CH₂CH₂); 1.77 (pseudo t, 2H, =CCH₂); 1.93, 2.02 (2 \times s, 2 \times 6H, C₅Me₄); 2.17-2.29 (m, 2H, C(=CH₂)CH₂); 3.09 (s, 2H C₅Me₄CH₂); 5.27 (dd, ${}^{2}J_{\text{HH}} = 3.6$ Hz, ${}^{4}J_{\text{HH}} = 1.8$ Hz, 1H, =CH₂); 5.40 (dd, ${}^{2}J_{\text{HH}} = 3.6$ Hz, ${}^{4}J_{\text{HH}} = 1.8 \text{ Hz}, 1\text{H}, =CH_{2}$). ${}^{13}\text{C} \{{}^{1}\text{H}\}(C_{6}D_{6})$: 12.9, 13.2 ($C_{5}Me_{4}$); 14.3 $(2 \times CH_2CH_2Me)$; 20.8, 22.4 $(2 \times CH_2CH_2Me)$; 34.1 $(C_5Me_4CH_2)$; 35.4, 37.3 (2 \times CH₂CH₂Me); 115.8 (=CH₂); 136.0, 138.8 (C₅Me₄); 150.2 (C=CH₂); 167.3 (Ti-C=C); 234.7 (Ti-C=C); (C_{ipso}, C₅Me₄) not detected. IR (KBr, cm⁻¹): 3071 (w), 2957 (vs), 2929 (m), 2905 (m), 2869 (m), 2835 (w), 2726 (vw), 1603 (m), 1553 (s), 1493 (w,b), 1463 (m), 1452 (w), 1432 (m), 1416 (w), 1379 (m), 1310 (w), 1257 (w), 1218 (vw), 1082 (vw), 1025 (w), 987 (w), 914 (w), 889 (m), 872 (w), 755 (s), 513 (m), 464 (s), 409 (vs).

3.4. Photolysis of 1b to give 3b

Compound **1b** (0.62 g, 1.13 mmol) in 12 mL of benzene was exposed to sunlight for 24 h turning its red colour to dark yellow. Crystallization from hexane afforded dark yellow needles of **3b**.

3b: Yield 0.23 g, 36%. Mp. 215 °C. EI-MS (160 °C): m/z (relative abundance) 550 (3), 549 (3), 548 (M^{++} ; 7), 533 ([M - Me]⁺; 4), 512 ([M - HCl]⁺; 4), 475 ([$M - SiMe_3$]⁺; 2), 413 ([$M - C_5Me_5$]⁺; 2), 398 ([$M - C_5Me_5 - Me$]⁺; 3), 222 (12), 221 (20), 220 (89),

219 (74), 218 ($[M - C_5Me_4CH_2 - L_2]^+$; 100), 217 (57), 216 (55), 215 (16), 214 (12), 213 (21), 203 ([M - C₅Me₄CH₂ - L₂ - Me]⁺; 17), 182 (10), 181 (12), 180 (11), 178 (14), 135 (11), 119 (18), 105 (10), 91 (12), 74 (19), 73 ($[SiMe_3]^+$; 96). ¹H NMR (C_6D_6): 0.25, 0.26 (2 \times s, 2 \times 9H, SiMe₃); 1.52, 1.69 (2 \times s, 2 \times 3H, C_5Me_4 ; 1.77 (s, 15H, C_5Me_5); 1.86, 2.14 (2 × s, 2 × 3H, C_5Me_4); 2.95 (d, ${}^{2}J_{HH} = 16.2$ Hz, 1H, CH₂); 3.13 (dd, ${}^{2}J_{HH} = 16.2$ Hz, ⁴J_{HH} = 1.8 Hz, 1H, CH₂); 5.27 (br s, 1H, =CHSiMe₃); 8.17 (s, 1H, Ti=CH). ¹³C {¹H}(C₆D₆): 0.7, 1.6 (SiMe₃); 10.7, 11.2 (C₅Me₄); 12.8 (C₅Me₅); 13.5, 14.0 (C₅Me₄); 43.0 (CH₂); 117.0, 118.8 (C₅Me₄); 122.9 (=CHSiMe₃); 123.7 (C₅Me₅); 127.5, 129.3 (C₅Me₄); 142.1 (C=CHSiMe₃); 161.4 (Ti-CH=C); 220.2 (Ti-CH=C). The 5-th signal of (C_5Me_4) is overlapped by C_6D_6 signal. ²⁹Si {¹H} (C_6D_6) : -11.1, -10.3 (SiMe₃). 1DNOESY (C₆D₆, selected): ¹H_{irr}/¹H_{res}: 2.94/1.51, 3.12, 5.26 $(CH_2/C_5Me_4, CH_2, =CHSiMe_3); 3.12/2.13 (CH_2/C_5Me_4); 5.26/0.24,$ 1.51, 2.94 (=CHSiMe₃/SiMe₃, C₅Me₄, CH₂); 8.16/0.25, 1.76 (Ti=CH/ SiMe₃, C₅Me₅). IR (KBr, cm⁻¹): 2985 (m,sh), 2952 (m), 2900 (s), 2720 (vw), 1593 (m), 1485 (w), 1433 (w,b), 1377 (m), 1331 (vw), 1245 (s), 1209 (w), 1079 (vw), 1064 (vw), 1022 (w), 940 (w), 929 (w), 870 (m), 851 (s), 837 (vs), 749 (w), 687 (w), 648 (vw), 625 (vw), 520 (vw), 486 (vw), 415 (m).

3.5. Photolysis of 2a to give 4a

Compound **2a** (0.52 g, 0.91 mmol) in 10 mL of benzene was exposed to sunlight for 12 h turning its red colour to dark yellow. Crystallization from hexane afforded yellow-brown plates of **4a**.

4a: Yield 0.33 g, 63%. M.p. 204 °C. EI-MS (200 °C): m/z (relative abundance) 574 (11), 573 (12), 572 (M^{.+}; 19), 539 (6), 538 (5), 537 ($[M - Cl]^+$; 9), 522 ($[M - Cl - Me]^+$; 2), 439 (7), 438 (6), 437 ($[M - C_5Me_5]^+$; 13), 422 ($[M - C_5Me_5 - Me]^+$; 3), 380 $([M - C_5Me_5 - Bu]^+; 2), 365 ([M - C_5Me_5 - Bu - Me]^+; 2), 323$ $([M - C_5Me_5 - 2 Bu]^+; 2), 221 (8), 220 (39), 219 (22), 218 ([M - C_5Me_5 - 2 Bu]^+; 2))$ C₅Me₄CH₂ - L₃]⁺; 100), 217 (13), 216 (15), 73 ([SiMe₃]⁺; 21), 59 (11), 57 (14); $(L_3 = Me_2Si(C \equiv CtBu)_2)$. ¹H NMR (C_6D_6) : -0.83 (d, $^{2}J_{\text{HH}} = 11.1$ Hz, 1H, TiCH₂); 0.53, 0.63 (2 × s, 2 × 3H, SiMe₂); 1.15, 1.25 (2 \times s, 2 \times 9H, CMe₃); 1.40 (2 \times s, 2 \times 3H, C₅Me₄); 1.77 (s, 3H, C₅Me₄); 1.83 (s, 15H, C₅Me₅); 2.34 (s, 3H, C₅Me₄); 3.41 (d, $^{2}J_{\text{HH}} = 11.1$ Hz, 1H, TiCH₂). ^{13}C {¹H}(C₆D₆): 1.6, 1.8 (SiMe₂); 10.5 (C₅Me₄); 12.5 (C₅Me₅); 12.8, 15.9 (C₅Me₄); 30.7, 31.0 (CMe₃); 35.6, 39.5 (CMe₃); 79.9 (TiCH₂); 115.4, 116.2 (C₅Me₄); 123.7 (C₅Me₅); 124.1, 133.0, 134.2 (C₅Me₄); 135.8 (TiCH₂C=C); 153.2 (C₅Me₄C=); 158.6 (TiCH₂C=C); 159.7 (C₅Me₄C=C). ²⁹Si {¹H}(C₆D₆): 3.7 (SiMe₂). IR (KBr, cm⁻¹): 2955 (vs), 2899 (s), 2862 (m), 2719 (vw), 1615 (m), 1548 (vw), 1477 (m), 1460 (m), 1432 (m), 1379 (s), 1356 (m), 1275 (vw), 1243 (s), 1202 (w), 1196 (w), 1158 (vw), 1120 (vw), 1089 (vw), 1047 (w), 1018 (w), 1007 (vw), 845 (vs), 828 (m), 775 (s), 711 (w), 691 (m), 636 (vw), 560 (vw).

3.6. Solid-state structure determination

Single crystals of **3a**, **3b**, and **4a** were mounted into Lindemann glass capillaries in a Labmaster 130 glovebox (mBraun) under purified nitrogen atmosphere. Diffraction data were collected on a Nonius KappaCCD diffractometer equipped with a Bruker APEX II detector (MoK_{α} radiation, $\lambda = 0.71073$ Å) at 150 K by using an Oxford Cryostream cooler. Collected data were processed by the diffractometer software. The phase problem was solved by intrinsic phasing and structure models were refined by full matrix least squares on F² using the SHELX program suite [22]. All non-hydrogen atoms were refined anisotropically. Any hydrogen atoms were placed in idealized positions and were refined isotropically. Molecular graphics was generated using PLATON [23] and Raster3D [24]. Relevant crystallographic data are gathered in the Supplementary material.

The crystal lattice of **3b** was suffering from twinning and the two lattices could not be separated properly during data collection

due to hardware limits. Their partial separation was done during postprocessing, but since the twinning occurred under a low angle (about 3.5°), this caused many diffraction spots to overlap generating numerous symmetry equivalent violations. These inconsistent reflections were discarded from the final data set, which decreased the data completeness.

The asymmetric part of the unit cell contains two symmetrically independent molecules, which both have the same chemical composition. One of these molecules has its SiMe₃ group disordered, where its methyl groups become rotated by about 45° These two positions have been refined by setting the occupancy factors atoms of all methyl group atoms to 0.5. The carbon atoms could be refined only isotropically.

Similarly, the crystal lattice of **4a** was struck by twinning, which could be accounted for after data reduction. The asymmetric part of the unit cell again incorporated two independent molecules. Both molecules have been refined using anisotropic thermal parameters for their non-hydrogen atoms.

3.7. Computational methods

Computational studies were carried out using Gaussian 16, Revision C.01 [25]. All computations used the M11 functional [26] and the 6–31G(d,p) basis set on all atoms. The wavefunctions of ground-state molecules were always checked for stability. The optimized molecules of **2a** and **4a** in their ground states were additionally checked for the presence of no imaginary vibrations. The optimization of excited-state **2a** was done using time-dependant DFT computing simultaneously the five lowest-lying excitations and optimizing the geometry on the first root. Convergence difficulties during SCF were managed by employing quadratic convergence when needed.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could influence the work reported in this paper.

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Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2020. 121536.

Appendix A. Supplementary Data

Deposition Number 1,970,667–1,970,669 contain supplementary crystallographic data for **3a**, **3b** and **4a**. These data are provided free of charge by the joint Cambridge Crystallographic Data Centre and Fachinformationszentrum Karlsruhe Access Structures service www.ccdc.cam.ac.uk/structures.

Table of crystallographic data, data collection and structure refinement data for **3a**, **3b**, and **4a**. ¹H NMR records of photolysis of **1a**; ¹H NMR, ¹³C NMR and ²⁹Si NMR spectra of **3a**, **3b**, and **4a**. Cartesian coordinates of optimized **1b**, **1b***, **2a**, **2a*** and **4a**.

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