

# Dimerization of titanacyclocumulenes to titanium substituted radialenes: synthesis, stability and reactions of five-membered titanacyclocumulenes with a coupling of two 1,4-diphenyl-1,3-butadiyne between two titanocene molecules to radialene-like fused titanacyclopentadiene compounds

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Received 24 July 1998

## Abstract

The reactions of the excellent titanocene source  $\text{Cp}_2\text{Ti}(\eta^2\text{-Me}_3\text{SiC}_2\text{SiMe}_3)$  with different 1,4-substituted 1,3-butadiynes  $\text{RC}\equiv\text{C}-\text{C}\equiv\text{CR}$  give, by substitution of the acetylene in a one to one complexation of titanocene and the diyne, different five-membered titanacyclocumulenes  $\text{Cp}_2\text{Ti}[\eta^4\text{-(1-2-3-4)-RC}_4\text{R}]$ . While these complexes are very stable for  $\text{R} = \text{tBu}$ , the metallacyclocumulene with  $\text{R} = \text{Ph}$  is unstable in solution and stabilizes by dimerization to dinuclear isomers: a fused titanacyclopentadiene-titanacyclopentene complex **1** and a compound **2** consisting of two fused titanacyclopentadiene ring systems and thus possessing a titanium substituted radialene structure. With the monomethyl-cyclopentadienyl complex  $(\text{H}_4\text{MeC}_5)_2\text{Ti}(\eta^2\text{-Me}_3\text{SiC}_2\text{SiMe}_3)$  in the reaction with  $\text{PhC}\equiv\text{C}-\text{C}\equiv\text{CPh}$  the titanium substituted radialene **7** was isolated in a low yield among some other as yet unidentified complexes. Complexes **2** and **7** were investigated by an X-ray crystal structure analysis. © 1999 Elsevier Science S.A. All rights reserved.

**Keywords:** Titanocene; Alkyne; Butadiyne; Cyclocumulene; Radialene; C–C-coupling

## 1. Introduction

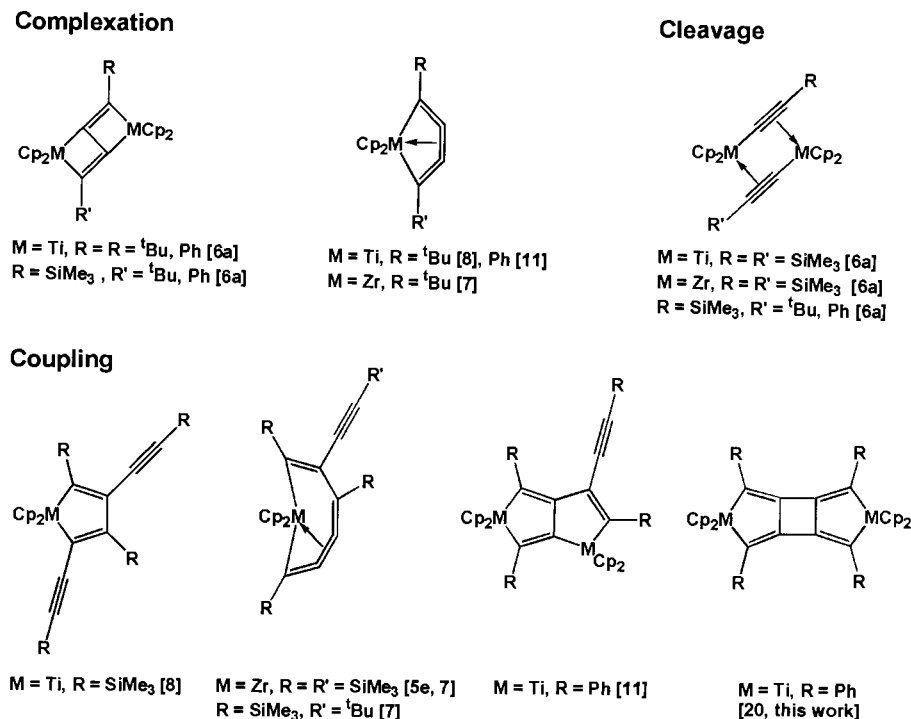
In modern acetylene chemistry [1] synthesis of carbon rich compounds is an intensively researched area, which is also directed toward organometallic polymers with conjugated  $\pi$  systems [2]. Such compounds form the basis for high-grade materials in the field of material science [3]. For the synthesis of various carbon networks [4] it is interesting to understand the principles of

the coupling of polyynes  $\text{R}(\text{C}\equiv\text{C})_n\text{R}$ . Since these polyalkyne compounds are difficult to investigate, butadiynes  $\text{R}(\text{C}\equiv\text{C})_2\text{R}$  as the smaller homologues were first used as model compounds in reactions with titanocene and zirconocene [5]. In this series of investigations we could often illustrate unexpected results of different complexations, C–C-single bond cleavage and different types of coupling reactions (Scheme 1) [6].

The resulting products strongly depend on the substituents R, the metals and the employed stoichiometry [6]. The bis(trimethylsilyl)acetylene titanocene and zirconocene complexes generate the unstable metallocenes, 'Cp<sub>2</sub>M' (M = Ti, Zr) [6] under mild conditions, which

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Scheme 1.

react with  $\text{}^t\text{BuC}\equiv\text{C}-\text{C}\equiv\text{C}^t\text{Bu}$  to give five-membered metallacyclocumulenes [7,8]. The X-ray diffraction studies of these complexes have shown the ring system to be planar and containing three  $\text{C}=\text{C}$  double bonds from which the central bond is internally coordinated to the metal center. Later on, an alternative bonding description, a diyne–metallocene complex without a central double bond, was preferred [9]. In the reaction of  $\text{Ni}(0)$  complexed 1,4-diphenyl-1,3-butadiyne with titanocene and zirconocene sources, we observed an external complexation of the central bond of the five-membered cyclocumulenes resulting in heterobimetallic systems [10]. We could show by detailed investigations that the metallacyclocumulenes are the key intermediates in the complexation leading to dinuclear complexes, in the  $\text{C}-\text{C}$ -single bond cleavage reaction as well as in the four different types of coupling reactions (Scheme 1) [8,10,11]. Therefore it is valuable to study the factors which influence the stability and reactivity of metallacyclocumulenes.

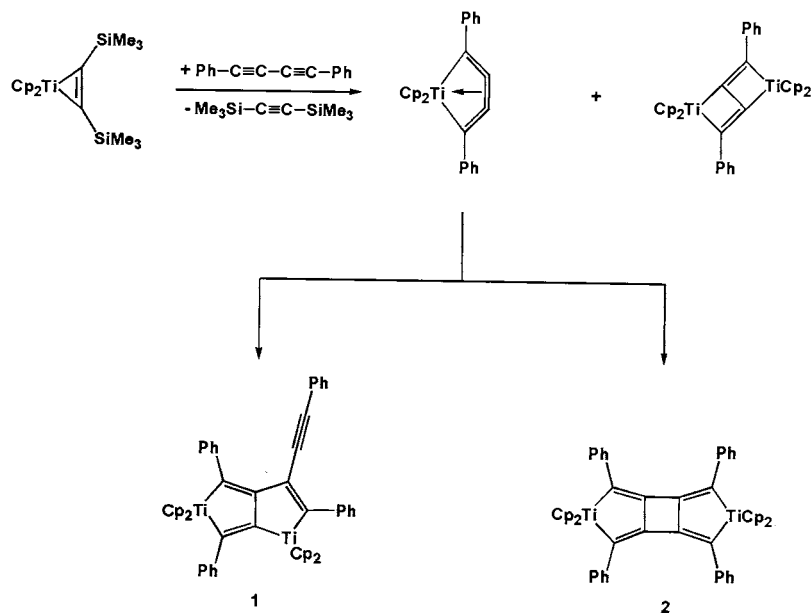
Herein we report about the reaction of the phenyl-substituted five-membered titanacyclocumulene to compound **2** which consists of two fused titanacyclopentadiene ring systems, having an unprecedented [5e,f,g] radialene-like structure, and about attempts to prepare analogous methylsubstituted compounds.

## 2. Results and discussion

Recently published results concerning the reaction of  $\text{Cp}_2\text{Ti}(\eta^2\text{-Me}_3\text{SiC}_2\text{SiMe}_3)$  [6b] with an equimolar amount of  $\text{PhC}\equiv\text{C}-\text{C}\equiv\text{CPh}$  in *n*-hexane at room temperature (r.t.) describe an air and moisture sensitive orange–brown material of the phenylsubstituted titanacyclocumulene soiled with small amounts of green and red–brown crystals (Scheme 2) [11].

After standing 3 days in toluene solution green crystals of the dinuclear complex **1** (46%) together with a small amount of a red–brown by-product **2** (18%), both with an identical elemental composition, were observed (Scheme 2). Complex **1** was characterized by NMR and X-ray structural analysis [11], while the structure of complex **2** has not been solved satisfactorily and was a subject of investigation described in this work.

The dimerization of 1,2,3-trienes to 4-radialenes is not unusual [13]. The thermal [13] as well as the  $\text{Ni}(0)$  catalyzed dimerization of cyclohepta-1,2,3-triene to a tricyclic [4]radialene, whose structure was confirmed by X-ray diffraction, was described [14]. Due to the low temperature and the presence of titanocene we suggest a titanium catalyzed dimerization for the formation of **2**. The molecular structure of **2** [12] was also characterized by X-ray crystal structure analysis. The results



Scheme 2.

provide strong evidence for a dinuclear complex which contains two fused titanacyclopentadiene ring systems. The titanacyclopentadienes are phenylsubstituted in the  $\alpha$  and  $\alpha'$  position and annelated at the  $\beta$  and  $\beta'$  carbon atoms. However, the poor quality of the determination made it impossible to discuss bond lengths and angles in detail. Nevertheless, connectivity has been established.

Due to complex **2** being completely insoluble in all solvents which do not degrade the complex solid-state NMR spectra were recorded. The findings are consistent with the radialene description. The resonances of the cyclopentadienyl ligands and the titanium-bound olefinic carbon atoms appear doubled. Hence, the environment of the metal atoms must modestly deviate from ideal  $C_{2v}$  symmetry. This is also found in the analogous complex **7** (see below) with slightly different titanium–carbon distances within the metallacyclic subunits.

Acidolysis of complex **2** by hydrogen chloride in dioxane does not lead to the metal-free radialene. The organic product is the *cis*-3,4-dibenzylidene-1,6-diphenyl-1-hexene-5-yne **3a**, exclusively, probably formed by a typical acidolytic reaction of the titanacyclopentadiene **2** to the unstable radialene and a subsequent H shift with a ring opening reaction (Scheme 3). Compound **3a** was characterized by GC, MS, NMR and elemental analysis.

In the analogous reaction of complex **1** with hydrogen chloride in dioxane only the *trans*-3,4-dibenzylidene-1,6-diphenyl-1-hexene-5-yne **3b** was formed, also characterized by GC, MS, NMR and elemental analysis (Scheme 4). The different configurations of the prod-

ucts of protolysis are evident from the coupling constant  $^3J(\text{H,H})$  across the double bonds (**3a**, *cis*: 12 Hz; **3b**, *trans*: 16 Hz), as confirmed by  $^1\text{H-NOE}$  measurements. The formation of the *cis*-product **3a** starting from **2** on the one hand and of the *trans*-compound **3b** as resulting from **1** on the other hand supports the different structures of **2** and **1**.

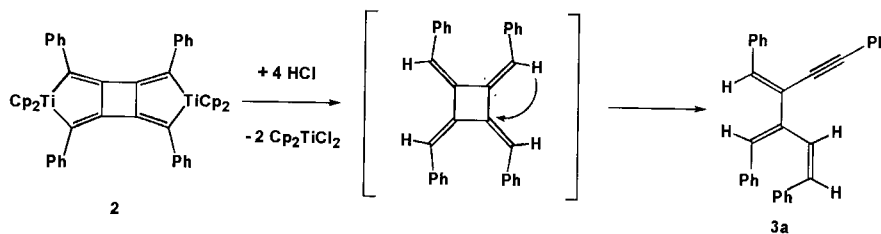
To study the influence of different substituents R of the butadiynes  $\text{RC}\equiv\text{C}-\text{C}\equiv\text{CR}$  and of substituted Cp-ligands on the possibility of obtaining stable metallacyclocumulenes, we conducted the experiments described hereafter. In this series we also tried to obtain better crystals for crystal structure analysis of a titanium substituted radialene.

In the reaction of  $\text{Cp}_2\text{Ti}(\eta^2\text{-Me}_3\text{SiC}_2\text{SiMe}_3)$  with  $\text{MeC}\equiv\text{C}-\text{C}\equiv\text{CMe}$  we were not able to isolate or to detect a methylsubstituted titanacyclocumulene. Only a mixture of the dinuclear complex  $[\text{Cp}_2\text{Ti}]_2[\mu\text{-}\eta^2\text{-(1-3)-}\eta^2\text{-(2-4)-trans,trans-(MeC}_4\text{Me)}]$  **4** and the fused titanacyclopentadiene–titanacyclopentene complex **5**, being analogous to **1**, were isolated. The mononuclear titanacyclopentadiene complex **6** was obtained as a by-product (Scheme 5). No radialene-like compound, analogous to **2**, was found.

Employing a different stoichiometry pure complex **4** was obtained as the sole product (Scheme 6).

When using the corresponding monomethyl–cyclopentadienyl complex  $(\text{H}_4\text{MeC}_5)_2\text{Ti}(\eta^2\text{-Me}_3\text{SiC}_2\text{SiMe}_3)$  [15] instead of  $\text{Cp}_2\text{Ti}(\eta^2\text{-Me}_3\text{SiC}_2\text{SiMe}_3)$  in the reaction with  $\text{PhC}\equiv\text{C}-\text{C}\equiv\text{CPh}$  the radialene **7** could be isolated in a very low yield among some other yet unidentified complexes (Scheme 7).

The molecular structure of **7** [16] was also characterized by X-ray crystal structure analysis. The results



Scheme 3.

confirm, as found for **2**, a dinuclear complex which contains two fused titanacyclopentadiene ring systems. The titanacyclopentadienes are phenylsubstituted in the  $\alpha$  and  $\alpha'$  position and annellated at the  $\beta$  and  $\beta'$  carbon atoms (Fig. 1).

The obtained data for the central radialene unit of complex **7** [C15–C16 1.528(4), C15–C16a 1.525(4), C1–C16 1.344(4), C8–C15 1.336(4) Å, C15–C16–C15a 89.8(2), C16–C15–C16a 90.2(2), C15a–C16–C1 142.6(3), C15–C16–C1 127.6(3), C8–C15–C16 127.5(3), C8–C15–C16a 142.3(3)°] are comparable to those in the cyclobutane ring of the [4]radialene mentioned above [14] (e.g. single bonds of 1.484(2) (little ring) and 1.492(2) Å (large ring); double bonds 1.326(2), 1.326(1) Å; angles in the ring 90.01(7), 89.99(7)°, angles at the double bonds in the fused rings 132.93(9), 133.07(8)°, the others 136.90(8), 136.91(8)°). The four-membered cyclobutane ring C15, C15a, C16, C16a is planar and coplanar with the two fused titanacyclopentadiene ring systems (deviations Ti –0.0201, C1 0.0205, C8 0.0202, C15 –0.0049, C16 –0.0056; T1a +0.0201, C1a –0.0205, C8a –0.0202, C15a +0.0049, C16a +0.0056 Å). The planes of the phenyl groups bonded to one titanacyclopentadiene ring are twisted to each other (19.6°) and show angles of 47.6 and 60.9° to the plane of the central four-membered ring.

The permethyltitanocene analogue  $(\text{Me}_5\text{C}_5)_2\text{Ti}(\eta^2\text{-Me}_3\text{SiC}_2\text{SiMe}_3)$  [6b] did not react with  $\text{PhC}\equiv\text{C}-\text{C}\equiv\text{CPh}$  and  $\text{Me}_3\text{SiC}\equiv\text{C}-\text{C}\equiv\text{CSiMe}_3$  in a reaction time of 5 days at room temperature. Similarly in the reaction of the corresponding permethylzirconocene complex  $(\text{Me}_5\text{C}_5)_2\text{Zr}(\eta^2\text{-Me}_3\text{SiC}_2\text{SiMe}_3)$  [17] with  $\text{PhC}\equiv\text{C}-\text{C}\equiv\text{CPh}$  no substitution of the acetylene for the diyne

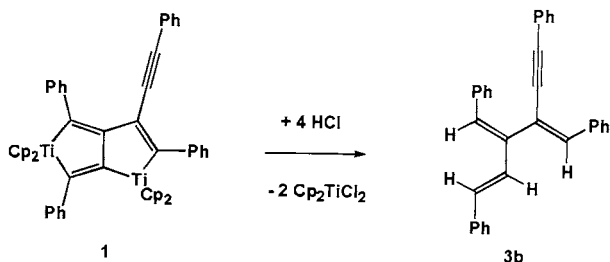
was indicated after 4 days at r.t. In the reaction of  $(\text{Me}_5\text{C}_5)_2\text{Zr}(\eta^2\text{-Me}_3\text{SiC}_2\text{SiMe}_3)$  with  $\text{MeC}\equiv\text{C}-\text{C}\equiv\text{CMe}$  four yet unidentified complexes were indicated after 24 h at 60°C, next to 80% of the starting material. An explanation for this behaviour is suggested by the substitution of silylacetylene in  $\text{Cp}_2\text{Zr}(\text{THF})(\eta^2\text{-Me}_3\text{SiC}_2\text{SiMe}_3)$  for ethylene in an associative mechanism [18] (commencing addition of ethylene and subsequent elimination of silylacetylene). It is assumed that the steric restrictions resulting from the bulky permethylcyclopentadienyl ligands prevent similar reactions with the diynes. Nevertheless, using a different reaction path and starting with  $(\text{Me}_5\text{C}_5)_2\text{ZrCl}_2$  and magnesium in the presence of  $\text{PhC}\equiv\text{C}-\text{C}\equiv\text{CPh}$  the five-membered zirconacyclocumulene  $(\text{Me}_5\text{C}_5)_2\text{Zr}[\eta^4\text{-(1-2-3-4)-PhC}_4\text{Ph}]$  [19] was prepared. In contrast to the titanocene complex  $\text{Cp}_2\text{Ti}[\eta^4\text{-(1-2-3-4)-PhC}_4\text{Ph}]$ , which is unstable in solution and dimerizes to complexes **1** and **2**, the permethylzirconocene complex is very stable both as a solid and in solution.

### 3. Conclusion

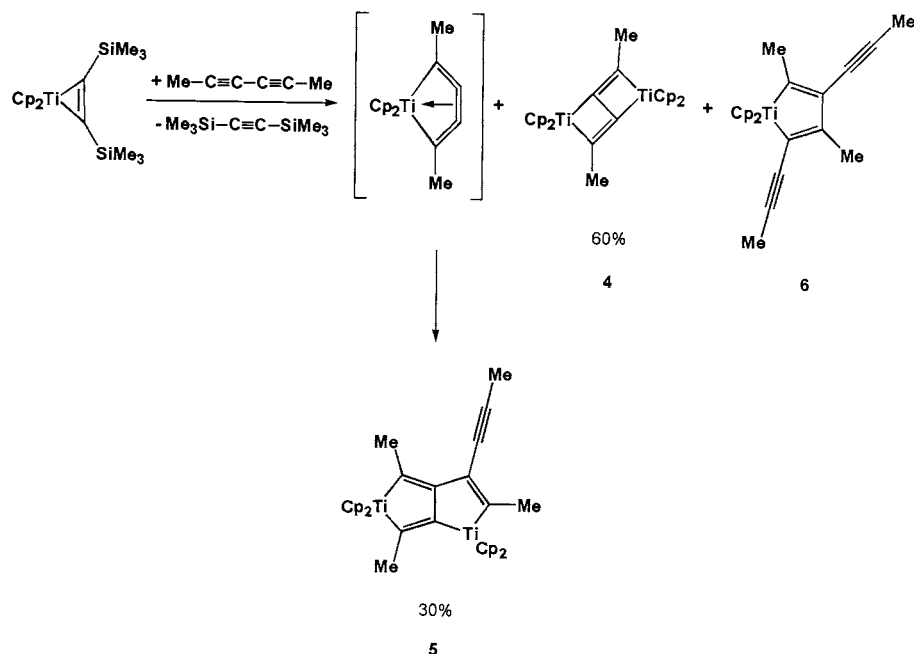
In the reactions of titanocene fragments with 1,4-disubstituted 1,3-butadiynes  $\text{RC}\equiv\text{C}-\text{C}\equiv\text{CR}$  the stability and reactivity of the obtained five-membered titanacyclocumulenes strongly depend on the substituents employed. With  $\text{R} = \text{SiMe}_3$  the cyclocumulene is unstable and a C–C-bond cleavage is favored. With  $\text{R} = \text{tBu}$  the cyclocumulene is very stable and unreactive toward e.g. carbon dioxide, water, acetone etc. For  $\text{R} = \text{Ph}$  the titanacyclocumulene is stable as a solid, but not in solution. In solution it can react like a cyclocumulene, like an alkyne complex or simultaneously as a cyclocumulene and an alkyne complex [11].

Three reaction pathways (i–iii) seem possible leading to the titanium substituted radialene **2**: the titanacyclocumulene can react like organic cyclocumulenes do, e.g. coupling with another cyclocumulene (i) (Scheme 8).

This pathway includes the formation of a substituted metallacyclopentane by an oxidative coupling of two central double bonds of two different cyclocumulenes with a metal complex as assumed also in the metal catalyzed dimerization of cyclohepta-1,2,3-triene to the



Scheme 4.



Scheme 5.

tricyclic [4]radialene [14]. According to this idea the bond description for the starting metallacyclocumulenes as a diyne-metalocene complex without a central double bond [9] does not appear realistic.

Alternatively, the dimerization to the radialene could also start from two alkyne complexes (ii) (Scheme 8). A hint of the possibility of such an intermediate is given by the existence of a similar nickel(0) complex with two bridging butadiynes ( $\text{LNi})_2(\mu-\eta^2, \eta^2-\text{Me}_3\text{SiC}\equiv\text{C}-\text{C}\equiv\text{CSiMe}_3)_2$ , L = 2,6-dimethylpyridine, which was isolated and characterized by X-ray crystal structure analysis [20].

A third possibility is to start with a substituted titanacyclopentadiene which can react with a further titanocene moiety to yield the titanium substituted radialene **2** (iii) (Scheme 8). A similar reaction path was proposed for the reaction of  $\text{Me}_3\text{SiC}\equiv\text{C}-\text{CH}_2-\text{C}\equiv\text{CSiMe}_3$  with zirconocene [5g]. The pathway (i) leads to a product with the former butadiyne entity being bonded to one titanium atom, while (ii) and (iii) result in a bonding to two titanium atoms.

Further experiments using two differently substituted butadiynes can provide an answer to the question of the actual reaction pathway.

The dimerization processes lead to carbon rich metal complexes from which the examples of radialene-like molecules such as **2** and **7** were unknown so far.

## 4. Experimental

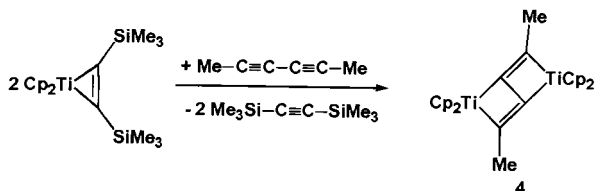
### 4.1. General

All operations were carried out in an inert atmosphere (argon) with standard Schlenk techniques. Solvents were freshly distilled from sodium tetraethylaluminate under argon prior to use. Deuterated solvents were treated with sodium or sodium tetraethylaluminate, distilled and stored under argon. The following spectrometers were used: NMR, Bruker ARX 400 (liquids) and Bruker MSL 300 (solids); IR, Nicolet Magna 550 (Nujol mulls using KBr plates); MS, AMD 402. Melting points were measured in sealed capillaries on a Büchi 535 apparatus.

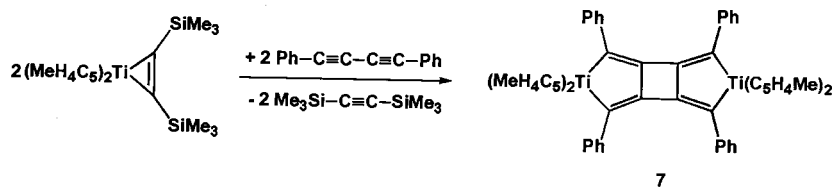
### 4.2. Synthesis of compounds

#### 4.2.1. Preparation of **2**

A sample of 0.442 g (2.18 mmol) of  $\text{PhC}\equiv\text{C}-\text{C}\equiv\text{CPh}$  was dissolved in 10 ml of THF. The solution was added to 0.746 g (2.14 mmol) of  $\text{Cp}_2\text{Ti}(\text{Me}_3\text{SiC}_2\text{SiMe}_3)$ . After 5 h the solution was filtered from a green precipitate and placed at r.t. After 14 days red-brown crystals formed in the green solution. They were separated, washed with THF and dried in vacuum to give 0.220 g (27%) of complex **2**, m.p. 259–261°C. Calc. for



Scheme 6.



Scheme 7.

$\text{C}_{52}\text{H}_{40}\text{Ti}_2$  (760.65) C: 82.11, H: 5.30; Found C: 81.52, H: 5.38.

$^{13}\text{C}$ -NMR (solid state, CP/MAS technique, chemical shifts referenced against external adamantane,  $\delta$  38.4):  $\delta$ /ppm 181.3 and 179.7 (C–Ti), 147.6, 144.6 (quart. C, *ipso*-Ph or four-membered ring), 128.0, 126.4, 123.8 (CH Ph), 113.0 and 111.9 (Cp).

#### 4.2.2. Acidolysis of **2**

To 0.382 g (0.50 mmol) of complex **2** under argon, 7–8 ml of THF and 1 ml of a 4 M solution of HCl in 1,4-dioxane were added. The resulting suspension (complex **2** is totally insoluble in THF, benzene, diethylether, *n*-hexane) was stirred, and after 5 min the dark precipitate of **2** dissolved and fine red crystals of  $\text{Cp}_2\text{TiCl}_2$  formed. After 30 min the solvent was evaporated and the residue was extracted with 15 ml ( $3 \times 5$  ml) diethylether. The red precipitate was washed with *n*-hexane and dried in vacuum to give 0.242 g (97%) of  $\text{Cp}_2\text{TiCl}_2$ . The filtrate was evaporated to dryness in vacuum to give 0.201 g (93%) of a light-yellow oil, which during 1 day, transformed into a yellow solid of *cis*-**3a**. M.p. 98–100°C (after recrystallization from *n*-hexane). Calc. for  $\text{C}_{32}\text{H}_{24}$  (408.54) C: 94.08, H: 5.92; Found C: 93.84, H: 5.84.

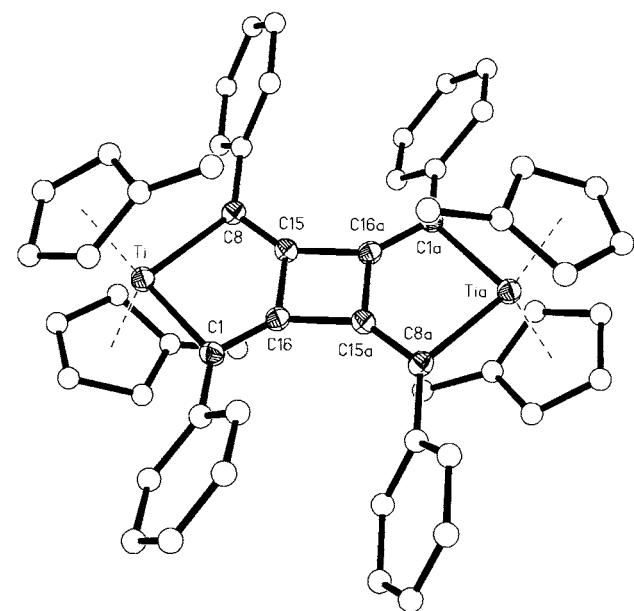


Fig. 1.

$^1\text{H}$ -NMR (THF- $d_8$ ):  $\delta$ /ppm 6.85 (d,  $J = 12.3$  Hz, 1H, 1-H), 6.48 (dd,  $J = 12.3$  and 1.8 Hz, 1H; 2-H), 7.48 (br s, 1H; 3-CH), 7.17 (1H; 4-CH), 7.42, 7.17, 7.09 (*o, m, p* 1-Ph), 7.61, 7.26, 7.17 (*o, m, p* 3-Ph), 7.81, 7.30, 7.21 (*o, m, p* 4-Ph), 7.59 (*o* 6-Ph), 7.39 (*m, p* 6-Ph).  $^{13}\text{C}$ -NMR (THF- $d_8$ ):  $\delta$ /ppm 135.0 (C1), 127.2 (C2), 138.3 (C3), 131.9 (3-CH), 122.0 (C4), 136.5 (4-CH), 88.2 (C5), 98.3 (C6), 137.7, 129.2, 128.8, 128.2 (*i, o, m, p* 1-Ph), 138.2, 130.2, 128.7, 127.9 (*i, o, m, p* 3-Ph), 137.7, 130.0, 128.7, 128.8 (*i, o, m, p* 4-Ph), 124.2, 132.2, 129.2, 129.2 (*i, o, m, p* 6-Ph).

MS (70 eV): 408 [ $M$ ] $^+$ .

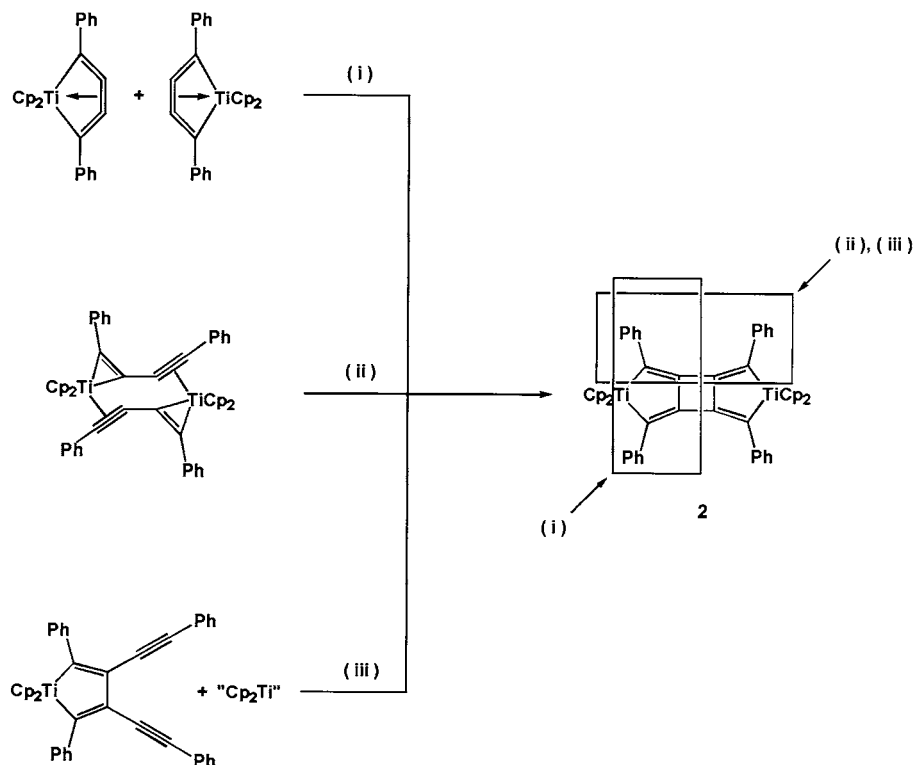
#### 4.2.3. Acidolysis of **1**

A total of 0.369 g (0.49 mmol) of complex **1** was dissolved in 20 ml of THF under argon and the green solution was filtered. To this solution 1 ml of a 4 M solution of HCl in 1,4-dioxane was added and the resulting mixture was stirred. The color of the solution rapidly changed to red. After 10 min the solvent was evaporated in vacuum and the residue was extracted with 15 ml ( $3 \times 5$  ml) of diethylether. The red precipitate was washed with *n*-hexane and dried in vacuum to give 0.225 g (93%) of  $\text{Cp}_2\text{TiCl}_2$ . The filtrate was evaporated by an argon stream and the resulting yellow crystals were dried in vacuum to give 0.192 g (97%) of light-yellow needles of *trans*-**3b**, m.p. 142–147°C (after recrystallization from *n*-hexane). Calc. for  $\text{C}_{32}\text{H}_{24}$  (408.54) C: 94.08, H: 5.92; Found C: 93.74, H: 5.64.

$^1\text{H}$ -NMR (THF- $d_8$ ):  $\delta$ /ppm 7.01 (d,  $J = 16.4$  Hz, 1H, 1-H), 7.26 (d,  $J = 16.4$  Hz, 1H, 2-H), 7.02 (s, 1H, 3-CH), 7.12 (s, 1H, 4-CH), 7.46, 7.29, 7.20 (*o, m, p* 1-Ph), 7.46, 7.37, 7.26 (*o, m, p* 3-Ph), 8.06, 7.41, 7.31 (*o, m, p* 4-Ph), 7.45, 7.32, 7.31 (*o, m, p* 6-Ph).  $^{13}\text{C}$ -NMR (THF- $d_8$ ):  $\delta$ /ppm 135.4 (C1), 125.5 (C2), 141.2 (C3), 131.5 (3-CH), 123.6 (C4), 138.4 (4-CH), 89.7 (C5), 97.8 (C6), 138.4, 127.3, 129.3, 128.4 (*i, o, m, p* 1-Ph), 137.6 $^\#$ , 130.6, 128.9, 128.0 (*i, o, m, p* 3-Ph), 138.3 $^\#$ , 129.9, 128.9, 129.1 (*i, o, m, p* 4-Ph), 124.3, 132.0, 129.2, 129.1 (*i, o, m, p* 6-Ph);  $^\#$  assignment may be interchanged. MS (70 eV): 408 [ $M$ ] $^+$ .

#### 4.2.4. Preparation of **4**

A total of 0.784 g (2.25 mmol) of  $\text{Cp}_2\text{Ti}(\text{Me}_3\text{SiC}_2\text{SiMe}_3)$  was dissolved in 10 ml of THF under argon, and a solution of 0.090 g (1.15 mmol) of  $\text{MeC}\equiv\text{C-C}\equiv\text{CMe}$  in 5 ml of THF was added. The color



Scheme 8.

of the mixture quickly changed from yellow to green. After 1 day the solution was filtered, evaporated in vacuum to 10 ml, treated with 10 ml of *n*-hexane and cooled to  $-30^\circ\text{C}$ . After 1 day green crystals formed, the solution was decanted, the crystals were washed with *n*-hexane and dried in vacuum to give 0.251 g (56%) of complex **4**; m.p.  $253\text{--}254^\circ\text{C}$  (dec. under argon). Calc. for  $\text{C}_{26}\text{H}_{26}\text{Ti}_2$  (434.25) C: 71.91, H: 6.03; Found C: 71.44, H: 6.24.

$^1\text{H-NMR}$  ( $\text{C}_6\text{D}_6$ ):  $\delta/\text{ppm}$  2.43 (s, 6H, Me), 5.26 (s, 10H, Cp).  $^{13}\text{C-NMR}$  ( $\text{C}_6\text{D}_6$ ):  $\delta/\text{ppm}$  25.5 (Me), 105.6 (Cp), 126.9 (C=CMe), 218.2 (C=CMe). MS (70 eV): 434  $[M]^+$ , 217  $[M/2]^+$ , 178  $[\text{Cp}_2\text{Ti}]^+$ .

#### 4.2.5. Preparation of **5**

A total of 0.235 g (3.01 mmol) of  $\text{MeC}\equiv\text{C}-\text{C}\equiv\text{CMe}$  in 10 ml of *n*-hexane was added to a solution of 0.986 g (2.83 mmol) of  $\text{Cp}_2\text{Ti}(\text{Me}_3\text{SiC}_2\text{SiMe}_3)$  in 5 ml of *n*-hexane. The color of the mixture changed from yellow to green and a precipitate formed. After 30 min the solution was filtered from a green solid which contained 60% of complex **4** (determined by NMR). The solution was allowed to stand under argon at r.t. After 1 day green crystals deposited which were washed with *n*-hexane and dried in vacuum to give 0.217 g (30%) of complex **5** (dec. =  $140^\circ\text{C}$ ). Calc. for  $\text{C}_{32}\text{H}_{32}\text{Ti}_2$  (512.37) C: 75.02, H: 6.30; Found C: 75.23, H: 6.15.

$^1\text{H-NMR}$  ( $\text{THF-d}_8$ ):  $\delta/\text{ppm}$  0.54 (s, 3H, 5-Me), 1.06 (s, 3H, 1-Me), 1.72 (s, 3H, 22-Me), 1.77 (s, 3H, 2-Me), 5.93, 6.28 (2 s, 10H each, Cp).  $^{13}\text{C-NMR}$  ( $\text{THF-d}_8$ ):  $\delta/\text{ppm}$  4.1 (2-Me), 20.7 (5-Me), 21.5 (1-Me), 22.5 (22-Me), 82.0, 85.4 (C $\equiv$ C), 111.7, 115.3 (Cp), 121.4 (C2), 126.8 (C3), 172.2 (C4), 188.5 (C22), 196.0 (C5), 215.1 (C1); see Ref. [11] for the numbering scheme. MS (70 eV): 512  $[M]^+$ ; IR (Nujol mull):  $2188\text{ cm}^{-1}$  ( $\nu\text{C}\equiv\text{C}$ ).

#### 4.2.6. Preparation of **7**

A total of 0.221 g (1.09 mmol) of  $\text{PhC}\equiv\text{C}-\text{C}\equiv\text{CPh}$  was dissolved in 10 ml of THF. The solution was added to 0.376 g (1.00 mmol) of  $(\text{H}_4\text{MeC}_5)_2\text{Ti}(\eta^2\text{-Me}_3\text{SiC}_2\text{SiMe}_3)$  [15]. After 5 h the solution was filtered and allowed to stand at r.t. After 30 days dark-brown crystals formed which were separated, washed with THF and dried in vacuum to give 0.040 g (10%) of complex **7**, m.p.  $230\text{--}234^\circ\text{C}$ . Calc. for  $\text{C}_{56}\text{H}_{48}\text{Ti}_2$  (816.76) C: 82.35, H: 5.92; Found C: 81.70, H: 5.40.

$^1\text{H-NMR}$  ( $\text{THF-d}_8$ ):  $\delta/\text{ppm}$  1.83 (s, 12H, Me), 5.61 ( $t'$ , 8H,  $\text{H}_4\text{MeC}_5$ ), 6.05 ( $t'$ , 8H,  $\text{H}_4\text{MeC}_5$ ), 6.60 (m, 8H, *o* Ph), 6.72 (m, 12H, *m*, *p* Ph).

#### Acknowledgements

This research was supported by the Max-Planck-Gesellschaft, the Fonds der Chemischen Industrie and

the Stiftung Volkswagenwerk (spectrometer grant, MSL 300). We thank Professor H. Günther, Siegen, for helpful discussions.

## References

- [1] (a) F. Diederich, *Oligoacetylenes*, in: P.J. Stang, F. Diederich (Eds.), *Modern Acetylene Chemistry*, VCH, Weinheim 1995, S. 443. (b) F. Diederich, Y. Rubin, *Angew. Chem.* 104 (1992) 1123; *Angew. Chem. Int. Ed. Engl.* 31 (1992) 1101. (c) R. Gleiter, D. Kratz, *Angew. Chem.* 105 (1993) 884; *Angew. Chem. Int. Ed. Engl.* 32 (1993) 842.
- [2] (a) W. Beck, B. Niemer, M. Wieser, *Angew. Chem.* 105 (1993) 969; *Angew. Chem. Int. Ed. Engl.* 32 (1993) 923. (b) U. Bunz, *Angew. Chem.* 108 (1996) 1047; *Angew. Chem. Int. Ed. Engl.* 35 (1996) 969. (c) H. Lang, *Angew. Chem.* 106 (1994) 569; *Angew. Chem. Int. Ed. Engl.* 33 (1994) 547. (d) N. Pirio, D. Touchard, P.H. Dixneuf, M. Fettouhi, L. Ouahab, *Angew. Chem.* 104 (1992) 664; *Angew. Chem. Int. Ed. Engl.* 31 (1992) 651. (e) W. Weng, T. Bartik, M. Brady, B. Bartik, A.M.A. Ramsden, J.A. Gladysz, *J. Am. Chem. Soc.* 117 (1995) 7129. (f) H. Werner, *Nachr. Chem. Tech. Lab.* 140 (1992) 435.
- [3] T.A. Skotheim, *Handbook of Conductive Polymers*. Vols. 1, 2, Marcel Dekker, New York, 1986.
- [4] U. Bunz, *Angew. Chem.* 106 (1994) 1127; *Angew. Chem. Int. Ed. Engl.* 33 (1994) 1073.
- [5] (a) W.A. Nugent, D.F. Taber, *J. Am. Chem. Soc.* 111 (1989) 6435, and references cited therein. (b) S.S.H. Mao, T.D. Tilley, *J. Am. Chem. Soc.* 117 (1995) 5365. (c) S.S.H. Mao, T.D. Tilley, *J. Am. Chem. Soc.* 117 (1995) 7031. (d) S.S.H. Mao, F.-Q. Liu, T.D. Tilley, *J. Am. Chem. Soc.* 120 (1998) 1193. (e) D.P. Hsu, W.M. Davis, S.L. Buchwald, *J. Am. Chem. Soc.* 115 (1993) 10394. (f) B.P. Warner, W.M. Davis, S.L. Buchwald, *J. Am. Chem. Soc.* 116 (1994) 5471. (g) B. Du, M.F. Faron, D.B. McConville, W.J. Youngs, *Tetrahedron* 51 (1995) 4359. (h) T. Takahashi, K. Aoyagi, V. Denisov, N. Suzuki, D. Choueiry, E. Negishi, *E. Tetrahedron Lett.* 34 (1993) 8301. (i) T. Takahashi, K. Kasai, Z. Xi, V. Denisov, *Chem. Lett.* (1995) 347. (j) T. Takahashi, Z. Xi, Y. Obora, N. Suzuki, *J. Am. Chem. Soc.* 117 (1995) 2665. (k) F.-Q. Liu, G. Harder, T.D. Tilley, *J. Am. Chem. Soc.* 120 (1998) 3271.
- [6] (a) A. Ohff, S. Pulst, N. Peulecke, P. Arndt, V.V. Burlakov, U. Rosenthal, *Synlett* (1996) 111, and references therein. (b) V.V. Burlakov, A.V. Polyakov, A.I. Yanovsky, Yu.T. Struchkov, V.B. Shur, M.E. Vol'pin, U. Rosenthal, H. Görls, *J. Organomet. Chem.* 476 (1994) 197, and references therein. (c) U. Rosenthal, A. Ohff, M. Michalik, H. Görls, V.V. Burlakov, V.B. Shur, *Angew. Chem.* 105 (1993) 1228; *Angew. Chem. Int. Ed. Engl.* 32 (1993) 1193.
- [7] U. Rosenthal, A. Ohff, W. Baumann, R. Kempe, A. Tillack, V.V. Burlakov, *Angew. Chem.* 106 (1994) 1678; *Angew. Chem. Int. Ed. Engl.* 33 (1994) 1605.
- [8] V.V. Burlakov, A. Ohff, C. Lefeber, A. Tillack, W. Baumann, R. Kempe, U. Rosenthal, *Chem. Ber.* 128 (1995) 967.
- [9] B. Temme, G. Erker, R. Fröhlich, M. Grehl, *Angew. Chem.* 106 (1994) 1570; *Angew. Chem. Int. Ed. Engl.* 33 (1994) 1480.
- [10] S. Pulst, P. Arndt, B. Heller, W. Baumann, R. Kempe, U. Rosenthal, *Angew. Chem.* 108 (1996) 1175; *Angew. Chem. Int. Ed. Engl.* 35 (1996) 1112.
- [11] V.V. Burlakov, N. Peulecke, W. Baumann, A. Spannenberg, R. Kempe, U. Rosenthal, *J. Organomet. Chem.* 536–537 (1997) 293.
- [12] Crystal data for **2** (crystals were obtained from a solution of *n*-hexane/THF):  $a = 11.513(2)$ ,  $b = 7.681(2)$ ,  $c = 21.130(3)$  Å,  $\alpha = 90$ ,  $\beta = 95.41(1)$ ,  $\gamma = 90^\circ$ ,  $R = 0.184$ ,  $wR_2 = 0.497$ .
- [13] (a) E. Lee-Ruff, *Carbocyclic three- and four-membered ring compounds*, in: A. de Meijere (Ed.), *Houben-Weyl*, Vol. E17/e, Georg Thieme Verlag Stuttgart, New York, 1997, p. 104. (b) R.P. Johnson, *Chem. Rev.* 89 (1989) 1111. (c) H. Hopf, G. Maas, *Angew. Chem.* 104 (1992) 953; *Angew. Chem. Int. Ed. Engl.* 31 (1992) 931.
- [14] S. Hashmi, K. Polborn, G. Szeimies, *Chem. Ber.* 122 (1989) 2399.
- [15] V. Varga, K. Mach, M. Polasek, P. Sedmera, J. Hiller, U. Thewalt, S.I. Troyanov, *J. Organomet. Chem.* 506 (1996) 241.
- [16] Crystal data for **7** (crystals were obtained from a solution of *n*-hexane/THF):  $0.2 \times 0.1 \times 0.1$  mm, brown prisms, space group  $P\bar{1}$ , triclinic,  $a = 9.097(2)$ ,  $b = 10.439(2)$ ,  $c = 11.820(2)$  Å,  $\alpha = 64.47(3)$ ,  $\beta = 86.86(3)$ ,  $\gamma = 86.09(3)^\circ$ ,  $V = 1010.1(3)$  Å<sup>3</sup>,  $Z = 1$ ,  $\rho_{\text{calc.}} = 1.343$  g cm<sup>-3</sup>, 5468 measured, 3034 were independent of symmetry, of which 2114 were observed ( $I \geq 2\sigma(I)$ ) reflections,  $R = 0.045$ ,  $wR_2$  (all data) = 0.118, 256 parameters. STOE-IPDS diffractometer, graphite monochromatized Mo-K $\alpha$  radiation,  $\lambda = 0.71069$  Å, structure solved by direct methods (SHELXS-86: G.M. Sheldrick, *Acta Crystallogr. Sect. A* 46 (1990) 467) and refined with the full-matrix least-squares method against  $F^2$  (SHELXL-93: G.M. Sheldrick, still unpublished), structural representation: XP (Siemens). Further details of the crystal structure investigation are available upon request from the Director of the Cambridge Crystallographic Data Centre, 12 Union Road, GB-Cambridge CB21EZ (UK), on quoting the full journal citation.
- [17] J. Hiller, U. Thewalt, M. Polasek, L. Petrusova, V. Varga, P. Sedmera, K. Mach, *Organometallics* 15 (1996) 3752.
- [18] S. Mansel, D. Thomas, C. Lefeber, D. Heller, R. Kempe, W. Baumann, U. Rosenthal, *Organometallics* 16 (1997) 2886.
- [19] V.V. Burlakov, U. Rosenthal (unpublished results).
- [20] U. Rosenthal, S. Pulst, R. Kempe, K.-R. Pörschke, R. Goddard, B. Proft, *Tetrahedron* 54 (1998) 1277.