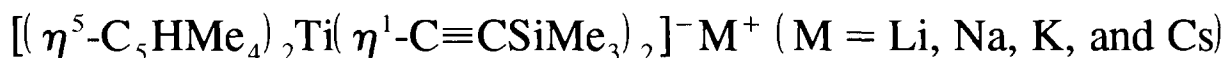


## Synthesis and structure of titanium(III) tweezer complexes with embedded alkali metal ions:



Vojtech Varga<sup>a</sup>, Jörg Hiller<sup>b</sup>, Miroslav Polášek<sup>a</sup>, Ulf Thewalt<sup>b</sup>, Karel Mach<sup>a,\*</sup>

<sup>a</sup> J. Heyrovský Institute of Physical Chemistry, Academy of Sciences of the Czech Republic, Dolejškova 3, 182 23 Prague 8, Czech Republic  
<sup>b</sup> Sektion für Röntgen- und Elektronenbeugung, Universität Ulm, Ulm D-89069, Germany

Received 18 September 1995

### Abstract

Complexes  $[(\eta^5\text{-C}_5\text{HMe}_4)_2\text{Ti}(\eta^1\text{-C}\equiv\text{CSiMe}_3)_2]^- \text{M}^+$  (M = Li (2), Na (3), K (4), and Cs (5)) were prepared by the redox reaction of  $(\eta^5\text{-C}_5\text{HMe}_4)_2\text{Ti}(\eta^1\text{-C}\equiv\text{CSiMe}_3)_2$  (1) with the alkali metals in toluene. The X-ray crystal analysis of 4 (monoclinic,  $P2_1/c$ ,  $a = 10.888(3)$  Å,  $b = 18.047(8)$  Å,  $c = 16.562(3)$  Å,  $\beta = 104.10(2)^\circ$ ,  $Z = 4$ ) revealed a tweezer structure with the potassium cation embedded between the trimethylsilylacetylide tweezer arms in a position which is slightly closer to the inner acetylide carbon atoms (2.946(4) Å and 2.949(4) Å) than to the outer ones (3.021(4) Å and 2.961(4) Å). The  $\text{K}^+$  ion simultaneously binds a  $\text{C}_5\text{HMe}_4$  ligand of the adjacent molecule at the K-centroid distance of 3.186(5) Å, thus forming a polymer chain arrangement of molecular units. The complexes 2–5 afford characteristic EPR spectra ( $g = 1.9924\text{--}1.9935$ ,  $\Delta H = 2.0\text{--}2.4$  G,  $a_{\text{Ti}} = 7.8\text{--}8.4$  G), infrared ( $\nu(\text{C}\equiv\text{C})$  at 1935–1948  $\text{cm}^{-1}$ ) and UV–vis spectra (two CT bands in the region 355–390 nm). The molecular ions of 2–5 were observed in EI mass spectra.

**Keywords:** Titanium(III); Titanium tweezer; X-ray structure; Alkali metals; Octamethyltitanocene; Trimethylsilylethynyl arms

### 1. Introduction

The first titanocene Ti(III) tweezer complex  $[(\eta^5\text{-C}_5\text{HMe}_4)_2\text{Ti}(\eta^1\text{-C}\equiv\text{CSiMe}_3)_2]^- [\text{Mg}(\text{THF})\text{Cl}]^+$  has been obtained by a cleavage of 1,4-bis(trimethylsilyl)buta-1,3-diyne in the  $(\text{C}_5\text{HMe}_4)_2\text{TiCl}_2\text{-Mg-THF}$  system [1]. The permethylated titanocene–magnesium tweezer complexes of this type were found to be the catalyst intermediates in the well-known head-to-tail dimerization of 1-alkynes [2]. Recently, the first alkali metal Ti(III) tweezer complex  $[(\eta^5\text{-C}_5\text{HMe}_4)_2\text{Ti}(\eta^1\text{-C}\equiv\text{CC}\equiv\text{SiMe}_3)_2]^- [\text{Li}(\text{THF})_2]^+$  has been synthesized from  $(\text{C}_5\text{HMe}_4)_2\text{TiCl}$  by adding two equivalents of  $\text{LiC}\equiv\text{CC}\equiv\text{CSiMe}_3$  in tetrahydrofuran (THF) solution [3]. The  $\text{Li}^+$  ion coordinating two molecules of THF was situated close to the inner carbon atoms of the inner pair of triple bonds. The alkali metal tweezer complexes of this structural type have so far been described for permethylmetallocene derivatives of lanthanide ele-

ments Y [4], Sm, Nd and Ce [5]. It has to be mentioned that amongst a large number of titanocene Ti(IV) tweezer complexes no alkali metal complexes have so far been reported [6] although the complexes with embedded Group 1B metals Cu [7,8] and Ag [9] are known.

Here we report the synthesis of alkali metal Ti(III) tweezer complexes  $[(\eta^5\text{-C}_5\text{HMe}_4)_2\text{Ti}(\eta^1\text{-C}\equiv\text{CSiMe}_3)_2]^- \text{M}^+$  (M = Li, Na, K, and Cs) from the Ti(IV) diacetylide  $(\eta^5\text{-C}_5\text{HMe}_4)_2\text{Ti}(\eta^1\text{-C}\equiv\text{CSiMe}_3)_2$  (1) and alkali metals in toluene or THF, and the crystal structure of the potassium-containing complex.

### 2. Experimental details

All manipulations with reagents, the synthesis, and most of spectroscopic measurements were carried out under vacuum using all-sealed glass devices equipped with breakable seals. The adjustment of single crystals into capillaries for X-ray analysis, preparation of KBr pellets and filling of infrared cuvettes were performed in an atmosphere of purified nitrogen or argon.

\* Corresponding author.

## 2.1. Chemicals

The solvents toluene, hexane, THF and 2-methyltetrahydrofuran (MTHF) were purified by conventional methods, dried by refluxing over  $\text{LiAlH}_4$  and stored as solutions of the dimeric titanocene  $(\text{C}_{10}\text{H}_8)[(\text{C}_5\text{H}_5)_2\text{Ti}(\mu\text{-H})_2]$  [10]. Butyllithium (BuLi) in hexane (1.6 M) was obtained from Aldrich.  $(\text{C}_5\text{HMe}_4)_2\text{TiCl}$  was prepared from  $(\text{C}_5\text{HMe}_4)_2\text{TiCl}_2$  in toluene by adding one equivalent of BuLi. Trimethylsilylethyne (Aldrich) was degassed and distilled onto a small amount of dimeric titanocene. After standing overnight, the solution was degassed and trimethylsilylethyne was distilled into a storage ampoule under metal valve.

## 2.2. Methods

EPR spectra were recorded on an ERS-220 spectrometer (Centre for Production of Scientific Instruments, Academy of Sciences, Berlin, Germany) in the X-band.  $g$ -Values were determined using an  $\text{Mn}^{2+}$  ( $M_1 = -1/2$  line) standard at  $g = 1.9860$  and a proton magnetometer MJ-110 R (Radiopan, Poznan, Poland). Concentrations of the paramagnetic compounds were estimated from integrated first derivation spectra. A variable temperature unit STT-3 was used for the measurement in the range from  $-140$  to  $+20$  °C. Samples were measured as solutions in hexane, THF, toluene and MTHF. The toluene and MTHF solutions were used for the measurement of anisotropic spectra in frozen organic glasses. UV-vis spectra in the range 280–2000 nm were obtained on a Varian Cary 17D spectrometer using all-sealed quartz cuvettes (Hellma). Mass spectra were measured on a JEOL D-100 spectrometer at 70 eV (only important mass peaks and peaks of intensity equal to or greater than 5% are reported). Samples in capillaries were opened and inserted into the direct inlet under argon. Infrared spectra were recorded on a UR-75 (Zeiss,

Jena, Germany). Hexane or toluene solutions were filled into KBr cuvettes under argon; regions  $2800\text{--}3000$   $\text{cm}^{-1}$  and  $1400\text{--}1550$   $\text{cm}^{-1}$  were overlaid by strong absorption bands of the solvents.  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were measured on a Varian VXR-400 spectrometer (400 and 100 MHz respectively) in  $\text{C}_6\text{D}_6$  at 25 °C. Samples were referenced to residual benzene as internal standard,  $\delta_{\text{H}}$  7.15 and  $\delta_{\text{C}}$  128.00 ppm respectively.

## 2.3. Preparation of $(\eta^5\text{-C}_5\text{HMe}_4)_2\text{Ti}(\eta^1\text{-C}\equiv\text{CSiMe}_3)_2$ (1)

Trimethylsilylethyne (0.6 ml, 4 mmol) and toluene (60 ml) were distilled into the reaction vessel and BuLi (1.6 M, 2.5 ml) in hexane was added. After stirring overnight the obtained solution of  $\text{LiC}\equiv\text{CSiMe}_3$  [11] was mixed with the solution of  $(\text{C}_5\text{HMe}_4)_2\text{TiCl}_2$  (0.65 g, 2 mmol) in 30 ml of toluene and stirred for 2 h. Then the reaction mixture was evaporated in vacuum and the residue was extracted with hexane. The orange-yellow solution was separated from a white sediment of LiCl. The solution was kept at  $-18$  °C for 2 days and then a clear intense yellow solution was carefully separated from an additional sediment. The hexane was evaporated in vacuum to leave an orange-yellow waxy solid of **1**. Yield 0.71 g (82%). WARNING: **1** and its solutions were kept in the dark as it decomposes in daylight.

$^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ ):  $\delta$  0.198 (18 H, s,  $\text{SiMe}_3$ ), 1.761 (12 H, s,  $4 \times \text{Me}$ ), 2.269 (12 H, s,  $4 \times \text{Me}$ ), 4.991 (2 H, s,  $\text{H}(\text{Cp})$ ).  $^{13}\text{C}$  NMR ( $\text{C}_6\text{D}_6$ ):  $\delta$  0.78 (q, 6 C), 14.51 (q, 4 C), 15.16 (q, 4 C), 109.90 (d, 2 C), 122.03 (s, 2 C), 122.06 (s, 2 C), 129.14 (s, 2 C), 181.15 (s, 2 C). MS (direct inlet, 80 °C, 75 eV):  $m/e$  (intensity) 484 (0.6,  $\text{M}^+$ ), 387 (7.5), 386 (19.1), 292 (10.4), 291 (27.1), 290 (100), 289 (25.1), 288 (16.2), 287 (8.0), 179 (6.6), 168 (9.8), 167 (8.4), 166 (11.9), 164 (6.2), 83 (6.3), 73 (14.7). Elemental analysis: 179.0715, error  $-0.3 \times 10^{-3}$  for  $\text{C}_9\text{H}_{15}\text{Si}_2$ . IR (hexane):  $\nu(\text{C}\equiv\text{C})$  2017  $\text{cm}^{-1}$ .

Table 1  
EPR and electronic absorption spectra of **2–5** in toluene and MTHF<sup>a</sup>

Complex	Solvent	$g_{\text{iso}}$	$a_{\text{Ti}}$ (G)	$g_1$	$g_2$	$g_3$	$g_{\text{av}}$	$\lambda_1$ (nm)	$\lambda_2^b$ (nm)
<b>2</b>	toluene	1.9935	7.8	2.0008	1.9913	1.9866	1.9929	340	363
	MTHF	1.9928	7.9	1.9986	1.9910	1.9880	1.9925	355	385
<b>3</b>	toluene	1.9927	8.3	2.0016	1.9926	1.9869	1.9937	335sh	375
	MTHF	1.9924	8.3	1.9993	1.9911	1.9872	1.9925	360sh	380
<b>4</b>	toluene	1.9927	8.3	2.0011	1.9922	1.9869	1.9934	365sh	380
	MTHF	1.9923	8.4	1.9996	1.9920	1.9874	1.9930	360	380
<b>5</b>	toluene	1.9933	8.3 <sup>c</sup>	2.0011	1.9927	1.9927	1.9955	370sh	390
	MTHF	1.9927	8.3 <sup>d</sup>	2.0014	1.9936	1.9866	1.9938	360	390

<sup>a</sup> Values of  $g_{\text{iso}}$  were determined with an accuracy  $\pm 0.0003$ , those of the  $g$ -tensor components  $\pm 0.0005$ . The linewidths  $\Delta H_{\text{pp}}$  of solution EPR signals  $\Delta H_{\text{pp}}$  ranged from 2.0–2.4 G. Positions of absorption bands are given within an error of  $\pm 2$  nm. <sup>b</sup> In addition to  $\lambda_1$  and  $\lambda_2$ , whose  $\epsilon$  is estimated to be  $(3\text{--}6) \times 10^3$   $\text{cm}^2 \text{mmol}^{-1}$ , the absorption spectra showed a shoulder of about the same intensity at 310–320 nm. The other data are given in the text. <sup>c</sup>  $\Delta H_{\text{pp}}$  of the central signal implied the coupling to  $^{133}\text{Cs}$  ( $I = 7/2$ , 100% abundance). <sup>d</sup> Coupling  $a_{\text{Cs}} = 2.0$  G.

#### 2.4. Preparation of $[(\eta^5\text{-C}_5\text{HMe}_4)_2\text{Ti}(\eta^1\text{-C}\equiv\text{CSiMe}_3)_2]^- \text{M}^+$ ( $M = \text{Li, Na, K, and Cs}$ ) (2–5) from **1** and alkali metals in toluene

The solution of **1** in toluene (1 mmol in 25 ml) was added to excess alkali metals (freshly cut pieces of Li–K or fine drops of Cs) in vacuum. The mixture was gently stirred by glass-coated magnetic stirrer bar. The reaction time ranged from 1 h for Cs to 2 weeks for Li. The true reaction times were usually shorter than those given below for particular complexes because the reaction mixtures were worked up only after it was certain that all **1** had been consumed. The absence of **1** in the reaction mixture was checked by IR spectra (the absence of a band at  $2017\text{ cm}^{-1}$ ). The isolation procedures for particular complexes and their characteristics are described below. The EPR data and UV–vis spectra are collected in Table 1. The  $g$ - and  $a_{\text{Tl}}$  values for the hexane and toluene and THF and MTHF solutions were identical within the accuracy of the determination.

##### 2.4.1. $[(\eta^5\text{-C}_5\text{HMe}_4)_2\text{Ti}(\eta^1\text{-C}\equiv\text{CSiMe}_3)_2]^- [\text{Li}]^+$ (**2**)

After a reaction time of 2 weeks a brown reaction solution was separated from the pieces of Li metal and was evaporated in vacuo. The residue was extracted by hexane to give an orange-brown solution. The saturated solution yielded a crop of brown crystals. The crystallization was repeated with partly evaporated mother liquor and the combined crops were recrystallized from hexane. The first crop was used for the characterization and spectroscopic measurements. Total yield of brown crystalline **2** was 0.42 g (86%).

MS ( $120\text{ }^\circ\text{C}$ ;  $m/e$ , (%)): 491( $\text{M}^+$ ; 3), 393(0.5), 386(19), 371(2), 290(100), 179(6), 168(11), 167(9), 166(13), 165(5), 164(6), 83(11), 73(4), 7( $\text{Li}^+$ ; 3). Elemental analysis: 491.2591, error  $+3 \times 10^{-3}$  for  $\text{C}_{28}\text{H}_{44}\text{LiSi}_2\text{Ti}$ ; 386.1907, error  $+0.2 \times 10^{-3}$  for  $\text{C}_{23}\text{H}_{34}\text{SiTi}$ . IR (toluene)( $\text{cm}^{-1}$ ): 1948 (vs); 1937 (vs); 1916 (w, sh); 1257 (m, sh); 1244 (s); 1148 (w); 1020 (m,  $\text{C}_5\text{HMe}_4$ ); 975 (w); 848 (vs); 757 (s); 616 (w). EDX ( $\text{K}\alpha$ ): approximate ratio Ti:Li = 1.

##### 2.4.2. $[(\eta^5\text{-C}_5\text{HMe}_4)_2\text{Ti}(\eta^1\text{-C}\equiv\text{CSiMe}_3)_2]^- [\text{Na}]^+$ (**3**)

After a reaction time of 5 days the solution was separated from the remainder of sodium metal and was evaporated in vacuo. The residue was extracted with repeatedly used 20 ml of hexane to give a brown solid of **3** and a saturated solution. The solid was dissolved in toluene to give a brown solution. Crystalline **3** was obtained from saturated toluene solution by cooling. Yield of brown crystalline product was 0.47 g (93%). Recrystallization from 50 ml of hexane afforded metallic blue crystals. They were soluble both in hexane or in toluene to give brown solutions.

MS ( $130\text{ }^\circ\text{C}$ ;  $m/e$ , (%)): 507( $\text{M}^+$ ; 4.5), 386(21), 371(2), 290(100), 179(8), 168(11), 167(10), 166(13),

165(6), 164(7), 83(8), 73(4), 23( $\text{Na}^+$ ; 12). Elemental analysis: 507.2406, error  $-4.7 \times 10^{-3}$  for  $\text{C}_{28}\text{H}_{44}\text{NaSi}_2\text{Ti}$ ; 386.1901, error  $-0.8 \times 10^{-3}$  for  $\text{C}_{23}\text{H}_{34}\text{SiTi}$ . IR (toluene)( $\text{cm}^{-1}$ ): 1945 (vs); 1935 (vs).

##### 2.4.3. $[(\eta^5\text{-C}_5\text{HMe}_4)_2\text{Ti}(\eta^1\text{-C}\equiv\text{CSiMe}_3)_2]^- [\text{K}]^+$ (**4**)

After 3 h reaction time the solution was separated from potassium metal and was evaporated in vacuo. The residue was extracted with 20 ml of hexane and the extract was separated and discarded. The residue was extracted by toluene to give a brown solution. The saturated toluene solution yielded brown crystals of **4** by cooling in a refrigerator overnight. Yield 0.44 g (85%). Occasionally, blue crystals were also obtained which dissolved in toluene to give the brown solution.

MS ( $190\text{ }^\circ\text{C}$ ;  $m/e$ , (%)): 523( $\text{M}^+$ ; 1.2), 386(19), 371(2), 290(100), 179(7), 168(11), 167(9), 166(13), 165(6), 164(7), 83(13), 73(5), 39( $\text{K}^+$ ; 17). IR (toluene)( $\text{cm}^{-1}$ ): 1944 (vs); 1937 (vs). EDX ( $\text{K}\alpha$ ): approximate ratio Ti:K = 1.

##### 2.4.4. $[(\eta^5\text{-C}_5\text{HMe}_4)_2\text{Ti}(\eta^1\text{-C}\equiv\text{CSiMe}_3)_2]^- [\text{Cs}]^+$ (**5**)

After 1 h reaction time a large amount of a black sediment was formed in the system. A light-brown solution was poured away from the sediment and discarded. The sediment was repeatedly extracted by 30 ml of toluene until the light-brown colour of the extracts faded. The soluble material obtained from the sediment was dissolved in hot toluene and was slowly cooled to room temperature. Grey needles of metallic appearance were obtained in the yield of 0.24 g (40%).

MS ( $220\text{ }^\circ\text{C}$ ;  $m/e$ , (%)): 617( $\text{M}^+$ ; 1), 386(19), 290(100), 179(6), 168(13), 167(13), 166(16), 165(8), 164(10), 133( $\text{Cs}^+$ ; 52), 83(56), 73(11). IR (toluene)( $\text{cm}^{-1}$ ): 1948 (s).

Infrared spectra of **2**–**5** were virtually identical, except in the region of  $\nu(\text{C}\equiv\text{C})$  vibrations.

#### 2.5. Preparation of $[(\eta^5\text{-C}_5\text{HMe}_4)_2\text{Ti}(\eta^1\text{-C}\equiv\text{CSiMe}_3)_2]^- [\text{M}(\text{THF})_n]^+$ ( $M = \text{Li, Na, K, and Cs}$ ; $n \leq 2$ ) (**2a**–**5a**) from **1** and alkali metals in THF

The reactions of **1** with alkali metals were carried out in the same way as described above except that toluene was replaced on a vacuum line by THF. The reaction was generally completed in shorter times, e.g. for Li in 1 day. The workup always began by evaporating THF in vacuo and extraction of the residue by hexane.

##### 2.5.1. $[(\eta^5\text{-C}_5\text{HMe}_4)_2\text{Ti}(\eta^1\text{-C}\equiv\text{CSiMe}_3)_2]^- [\text{Li}(\text{THF})_n]^+$ ( $n \leq 2$ ) (**2a**)

Compound **2a** was obtained as fine brownish-green crystals by cooling of the saturated hexane solution to  $-10\text{ }^\circ\text{C}$  for several days. Yield 0.48 g (76% for  $n = 2$ ).

EPR and UV–vis (THF): Table 1, the same as **2** in MTHF. MS (direct inlet;  $50\text{--}90\text{ }^\circ\text{C}$ : evolution of THF,

$m/e$  72, 71, 42; 90–120 °C: MS identical with that of **2**. IR (hexane)( $\text{cm}^{-1}$ ): identical with that of **2** except 1948 (sh) and 1941 (vs) ( $\nu(\text{C}\equiv\text{C})$ ) and 1040 (m) (coordinated THF). In toluene solution the band of free THF at  $1060\text{ cm}^{-1}$  probably interfered with the band of coordinated THF. Three-times repeated dissolution of **2a** in toluene and evaporation of the solvent in vacuo afforded **2**.

The products obtained with the other metals lost a coordinated THF more easily. Compound **3a** contained THF after evaporation of solvents in vacuo, but its extract in hexane showed IR absorption bands of both coordinated ( $1053\text{ cm}^{-1}$ ) and free THF ( $1075\text{ cm}^{-1}$ ) in comparable intensities. After evaporating the solvent and dissolving the residue in toluene only a weak absorption band of free THF was observed. Evaporation of the solvent afforded **3**. Most of the coordinated THF was evolved from **4a** and **5a** by evacuation. The subsequent washing of the remainders with hexane afforded **4** and **5**. The yields of compounds **2–5** prepared via **2a–5a** did not differ from the yields obtained in toluene. Conversely, compounds **2a–5a** were obtained by dissolving **2–5** in THF and their EPR and UV–vis spectra are given in Table 1 (the same as listed for the MTHF solvent).

## 2.6. Preparation of **2** from $(\text{C}_5\text{HMe}_4)_2\text{TiCl}$ and $\text{LiC}\equiv\text{CSiMe}_3$

The solution of BuLi in hexane (1.6 M, 1.3 ml) was added to  $(\text{C}_5\text{HMe}_4)_2\text{TiCl}_2$  (0.65 g, 2 mmol) in 30 ml of toluene and the mixture was warmed to 50 °C to give a blue solution. BuLi in hexane (1.6 M, 2.5 ml) was mixed with trimethylsilylethyne (0.6 ml, 4 mmol) in toluene (60 ml) and the mixture was stirred overnight. The blue reaction mixture containing  $(\text{C}_5\text{HMe}_4)_2\text{TiCl}$  was added to a yellow slurry containing  $\text{LiC}\equiv\text{CSiMe}_3$  and the mixture was stirred for 2 h at ambient temperature. The solvents were evaporated in vacuo and the residue was worked up as above. Yield of crystalline **2** was 0.41 g (85%).

## 2.7. X-ray crystal structure analysis of **4**

A dark-brown crystal fragment  $0.6 \times 0.5 \times 0.4\text{ mm}^3$  was mounted in a glass capillary under purified nitrogen in a glovebox (Braun) and was sealed by wax. The X-ray measurements were carried out on a Phillips PW 1100 four circle diffractometer equipped with a STOE electronic control system using graphite-monochromated Mo K $\alpha$  radiation ( $\lambda = 0.71069\text{ \AA}$ ) at room temperature.

### 2.7.1. Crystallographic data for **4**

$\text{C}_{28}\text{H}_{44}\text{KS}_2\text{Ti}$ ,  $M = 523.83$ , monoclinic,  $P2_1/c$ , No.14,  $a = 10.883(3)$ ,  $b = 18.047(8)$ ,  $c = 16.562(3)\text{ \AA}$ ,

Table 2  
Atomic coordinates for **4**

Atom	x	y	z	$U_{\text{eq}} (\text{\AA}^2)$
Ti	0.1950(1)	0.1555(1)	0.3385(1)	0.048(1)
K	0.1126(1)	0.2726(1)	0.1247(1)	0.094(1)
Si(1)	0.4295(1)	0.3843(1)	0.2656(1)	0.085(1)
Si(2)	-0.1955(1)	0.1497(1)	0.0875(1)	0.070(1)
C(1)	0.2770(3)	0.2501(2)	0.2926(2)	0.055(2)
C(2)	0.3315(4)	0.3038(2)	0.2721(3)	0.064(2)
C(3)	0.4792(7)	0.4270(3)	0.3729(4)	0.135(4)
C(4)	0.3371(8)	0.4532(3)	0.1925(4)	0.135(4)
C(5)	0.5733(6)	0.3576(5)	0.2328(5)	0.149(6)
C(6)	0.0383(3)	0.1587(2)	0.2314(2)	0.054(2)
C(7)	-0.0534(4)	0.1584(2)	0.1708(3)	0.064(2)
C(8)	-0.3334(6)	0.1301(5)	0.1311(4)	0.140(5)
C(9)	-0.2285(6)	0.2397(4)	0.0294(4)	0.124(4)
C(10)	-0.1698(7)	0.0756(4)	0.0148(4)	0.139(5)
C(11)	0.2299(5)	0.2099(3)	0.4744(3)	0.092(3)
C(111)	0.3633(6)	0.2254(5)	0.5228(4)	0.157(6)
C(12)	0.1466(5)	0.2624(3)	0.4246(3)	0.083(3)
C(121)	0.1716(8)	0.3439(3)	0.4175(5)	0.142(5)
C(13)	0.0322(4)	0.2273(3)	0.3918(3)	0.075(3)
C(131)	-0.0886(6)	0.2629(4)	0.3378(3)	0.122(4)
C(14)	0.0374(4)	0.1535(3)	0.4192(3)	0.073(3)
C(141)	-0.0714(6)	0.0988(3)	0.4006(4)	0.115(4)
C(15)	0.1595(5)	0.1428(3)	0.4712(3)	0.084(3)
C(16)	0.3973(4)	0.1042(2)	0.3308(4)	0.082(3)
C(161)	0.5178(5)	0.1472(3)	0.3453(7)	0.159(6)
C(17)	0.3099(4)	0.0870(2)	0.2553(3)	0.069(2)
C(171)	0.3178(8)	0.1113(3)	0.1694(4)	0.129(4)
C(18)	0.2194(4)	0.0371(2)	0.2717(3)	0.068(2)
C(181)	0.1196(6)	-0.0038(3)	0.2093(5)	0.138(5)
C(19)	0.2494(5)	0.0251(2)	0.3569(3)	0.082(3)
C(191)	0.184(1)	-0.0327(3)	0.3997(6)	0.185(7)
C(20)	0.3567(6)	0.0663(3)	0.3913(3)	0.092(3)

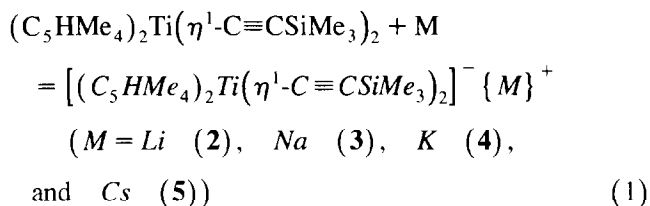
$\beta = 104.10(2)^\circ$ ,  $V = 3156(1)\text{ \AA}^3$ ,  $D_c = 1.102\text{ g cm}^{-3}$ ,  $Z = 4$ ,  $\mu = 4.46\text{ cm}^{-1}$ . Crystal data were collected by  $\theta/2\theta$  method;  $2\theta_{\text{max}} = 50^\circ$ . A total of 5460 unique reflections out of 5698 observed reflections were used in calculations. The positions of the heavy atoms (Ti, K, and Si) were determined by the Patterson method. Atomic coordinates and anisotropic thermal parameters of all non-hydrogen atoms were refined by the least squares method. Hydrogen atoms were included at their optimized positions. The final  $R$  indices were  $R = 0.064$ ,  $R_w = 0.073$  for the 3629 reflections with  $F_o > 1\sigma(F_o)$ . The PC ULM-package [12] was used for all the calculations. The atomic coordinates and thermal parameters are given in Table 2.

## 3. Results and discussion

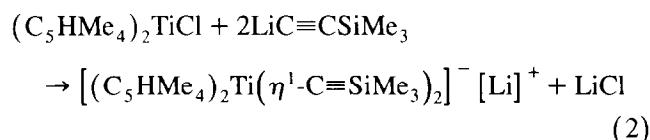
### 3.1. Synthesis of **2–5** in toluene

The titanocene ( $\text{Ti}^{\text{III}}$ ) diacetylide (tweezer) alkali metal complexes of the type  $[(\text{C}_5\text{HMe}_4)_2\text{Ti}(\eta^1\text{-C}\equiv\text{CSiMe}_3)_2]^-[\text{M}]^+$  were easily obtained by the redox reaction between bis(tetramethylcyclopentadienyl)-

titanium(IV) diacetylide (1) and the alkali metal in toluene according to Eq. (1).



Compounds 2–4 were obtained in high yields (70–90%); compound 5 was accompanied by an unknown byproduct which was insoluble in toluene. Compound 2 was also obtained in high yield by the dismutation reaction (2) in toluene.



All compounds form crystalline materials from the hexane or toluene solutions. Their solubility decreases from Li to Cs: whereas 2 is highly soluble in hexane, 5 dissolves only slightly in toluene. All compounds are thermally robust as they evaporate without decomposition in the vacuum of the mass spectrometer from 120 °C for 2 to 220 °C for 5. Their MS spectra showed the molecular ions corresponding to formulas 2–5 and the ions of alkali metals. The other fragment ions  $[(\text{C}_5\text{HMe}_4)_2\text{Ti}(\text{C}\equiv\text{CSiMe}_3)]^+$ ,  $[(\text{C}_5\text{HMe}_4)_2\text{Ti}]^+$  and ions probably from diyne  $(\text{C}\equiv\text{CSiMe}_3)_2$  were practically identical for all the compounds. The EPR, UV–vis and IR spectra of all compounds showed features similar to those of  $[(\text{C}_5\text{HMe}_4)_2\text{Ti}(\eta^1\text{-C}\equiv\text{CSiMe}_3)_2]^- [\text{Mg}(\text{THF})\text{Cl}]^+$  (6) [1] and  $[(\text{C}_5\text{HMe}_4)_2\text{Ti}(\eta^1\text{-C}\equiv\text{CC}\equiv\text{CSiMe}_3)_2]^- [\text{Li}(\text{THF})_2]^+$  (7) [3], the only structurally characterized Ti(III) tweezer complexes (vide infra). The X-ray single crystal analysis of 4 confirmed the tweezer structure with a potassium cation embedded between the trimethylsilylethynyl tweezer arms.

### 3.2. Crystal structure of 4

The PLUTO drawing of 4 with atom numbering scheme is shown in Fig. 1 and selected bond distances and bond angles are listed in Table 3. They demonstrate that the molecular structure of 4 is asymmetric in all parts. The titanocene moiety has the  $\eta^5\text{-C}_5\text{HMe}_4$  ligands in an irregularly staggered conformation with the proton-bearing ring atoms C(15) and C(20) close to positions where the ligands approach each other. The CE(1)–Ti–CE(2) (CE(1) is the centroid for the C(11)–C(15) ring; CE(2) is the centroid for the C(16)–C(20) ring) angle amounts to 136.9(2)°. This value is very close to that found for 7 (136.2(2)°) [3]. The CE(1), Ti, CE(2) plane is perpendicular to the tweezer plane defined by the

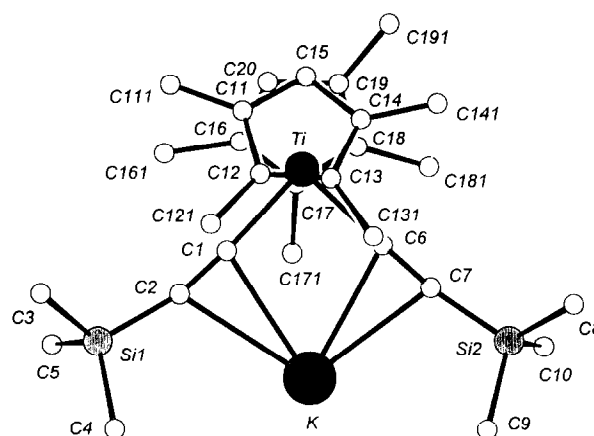


Fig. 1. Molecular structure and atom numbering scheme of  $[(\text{C}_5\text{HMe}_4)_2\text{Ti}(\eta^1\text{-C}\equiv\text{CSiMe}_3)_2]^- [\text{K}]^+$  (4). The view is perpendicular to the Ti, C(1), C(6) plane.

atoms of tweezer bite angle C(1)–Ti–C(6). The bite angle is 90.1(1)°, virtually the same as that in 7 (89.9(2)°). The Ti–C distances for the acetylide groups (average 2.146(4) Å) are slightly shorter than in the Mg complex 6 (average 2.165 Å). The C≡C bonds have approximately the same length in both compounds (average 1.229(4) Å against 1.22(1) Å). Both parameters are, however, slightly shorter in the diyne complex 7. The tweezer arms exert a mutually different outwards bending from an approximately linear structure (Table 3). The tweezer plane contains the acetylide atoms C(2) and C(7) within 0.005 Å; however, the K<sup>+</sup> ion is placed 0.363 Å away on the side containing CE(1), whereas the Si(1) atom is 0.149 Å and Si(2) 0.014 Å away on the other side of the plane. The potassium ion is located between the acetylide arms in a position which is negligibly closer to the inner acetylide carbon atoms (2.946(4) Å and 2.949(4) Å) than to the outer ones (3.021(4) Å and 2.961(4) Å). The K–C distances close to 3.00 Å are longer by ca. 0.2 Å than the sum of covalent radii of both atoms, 2.03 Å and 0.77 Å. The Ti–K distance of 4.033(1) Å does not imply any intermetallic interaction.

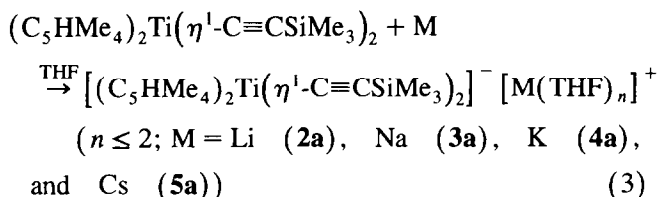
The distortion of the molecule seems to be brought about by a polymeric nature of the compound in the solid state, as is shown on a dimer fragment of the molecular chain (Fig. 2). The molecules are mutually bonded by a weak coordination of a cyclopentadienyl ring (CE(1)) to K' of the adjacent molecule. The mode of coordination formally resembles an  $\eta^5$ -mode; however, distances of ring carbon atoms to K' differ considerably from the shortest K'–C(11) 3.078(5) Å and K'–C(15) 3.112(5) Å to the longest K'–C(13) 3.741(5) Å. The average value K'–C<sub>av</sub> is 3.394(5) Å. The K'–CE(1) distance of 3.186(5) Å is only by 0.2 Å longer than the average distance from the potassium ion to acetylide carbon atoms. The zig-zag structure of the

polymer chain follows from the angles Ti–K'–Ti' 151.7° and K–Ti–K' 128.2°. The Ti–CE(1)–K' angle is 155.7°.

A very similar polymer arrangement of molecular units was previously found in  $[(C_5Me_5)_2Sm(\eta^1-C\equiv CPh)_2K]_n$  [5]. The distances between  $K^+$  and carbon atoms of the  $C_5Me_5$  ring of the adjacent molecule varied over the range 2.922(5)–3.229(6) Å to give the average value  $K'-C_{av}$  3.08(13) Å. The  $K'-CE(C_5Me_5)-Sm$  angle was close to linear (171.6°). The comparison of these intermolecular parameters with those of **4** shows that the phenyl substituents at tweezer arms do not hinder the contacts between the potassium ion and the adjacent cyclopentadienyl ring so severely as the trimethylsilyl groups in **4**.

### 3.3. The synthesis of $[(C_5HMe_4)_2Ti(\eta^1-C\equiv CSiMe_3)_2]^- [Li(THF)_n]^+$ (**2a**) and **2–5** in THF

The reaction (1) proceeded also in THF to give compounds **2–5** containing up to two equivalents of coordinated THF (Eq. (3)).



The limit of  $n = 2$  for the number of coordinated THF molecules corresponds to the maximum coordination of four ligands around  $Li^+$ . This upper limit was achieved in **7** [3]. Compounds **2a–5a** were of limited stability and lost THF with increasing ease on going from **2a** to **5a**. The workup of the reaction mixtures

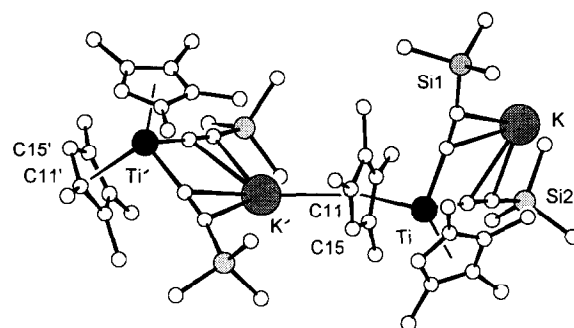


Fig. 2. PLUTO diagram showing the polymeric structure of  $[(C_5HMe_4)_2Ti(\eta^1-C\equiv CSiMe_3)_2]^- [K]^+$  (**4**).

consisting of the evaporation of THF in vacuo and extracting the residue with hexane led to a partial decomposition of **3a** and a complete decomposition of **4a** and **5a**. In this way compounds **4** and **5** were obtained in yields similar to those obtained in toluene (vide supra). Compound **3** was obtained after evaporation of the toluene solution of **3a** in vacuo. Only compound **2a** was isolated as a brownish-green crystalline solid from the hexane solution at  $-15^\circ C$ . The content of THF in **2a** has not yet been determined. It crystallizes from hexane probably with 1 or 2 molecules of THF coordinated to the  $Li^+$  ion; both cases of the THF coordination are known in  $(C_5Me_5)_2Y(C\equiv CCMe_3)_2Li(THF)$  [5] and **7** [3] respectively. The presence of compounds **2a–5a** in THF solutions was proven by electronic absorption spectra which differed from those of **2–5** in toluene in the region 1000–500 nm (vide infra). A remarkable efficiency of toluene in liberating THF from the complexes may result from the solvation of alkali metal cations by toluene, mimicking the coordination of  $C_5HMe_4$  ligand in the solid state.

### 3.4. Spectroscopic characterization of **2–5** and their THF adducts

The EPR spectra showed a narrow single line ( $\Delta H = 2.0\text{--}2.2$  G) at  $g = 1.9924\text{--}1.9935$  and much weaker satellite spectra reflecting the coupling to the  $^{49}Ti$  and  $^{47}Ti$  isotopes (natural abundances 5.5% and 7.7%) with nuclear spins  $I_N = 7/2$  and  $I_N = 5/2$  respectively. The value of  $g$ -factor is one of the highest values for titanocene derivatives, comparable with that for  $(C_5HMe_4)_2Ti(1\text{-methyl-}\eta^3\text{-allyl})$  with  $g = 1.9921$  [13]. The  $g$ -tensor of rhombic symmetry shows nearly equal components and a very low anisotropy (Table 1); this is a rare case amongst titanocene  $Ti(III)$  derivatives [14]. This indicates a considerable delocalization of the  $d^1$  unpaired electron density over the organic ligands, including the acetylide arms. The coupling constant  $a_{Ti}$  (equal for both isotopes) ranges between 7.8 and 8.4 G. A higher value of  $g$ -factor (1.9940) and a lower value

Table 3  
Selected interatomic distances (Å) and bond angles (deg) for **4**

Interatomic distances			
Ti–C(1)	2.149(4)	Ti–C(6)	2.142(4)
C(1)–C(2)	1.228(5)	C(6)–C(7)	1.231(5)
Si(1)–C(2)	1.821(4)	Si(2)–C(7)	1.812(4)
K–C(1)	2.946(4)	K–C(6)	2.949(4)
K–C(2)	3.021(4)	K–C(7)	2.961(4)
Ti–C(11)	2.399(5)	Ti–C(16)	2.422(5)
Ti–C(12)	2.528(5)	Ti–C(17)	2.415(4)
Ti–C(13)	2.523(5)	Ti–C(18)	2.450(4)
Ti–C(14)	2.418(5)	Ti–C(19)	2.428(5)
Ti–C(15)	2.333(5)	Ti–C(20)	2.389(5)
Ti–CE(1)	2.126(5)	Ti–CE(2)	2.111(5)
Si(1)–C(Me) <sub>av</sub>	1.862(7)	Si(2)–C(Me) <sub>av</sub>	1.865(7)
Ti–K	4.033(1)		
Bond angles			
C(1)–Ti–C(6)	90.1(1)	CE(1)–Ti–CE(2)	136.9(2)
Ti–C(1)–C(2)	174.9(3)	Ti–C(6)–C(7)	177.8(3)
Si(1)–C(2)–C(1)	167.6(4)	Si(2)–C(7)–C(6)	173.5(4)
K–C(1)–C(2)	81.6(3)	K–C(6)–C(7)	78.5(3)
K–C(2)–C(1)	74.7(2)	K–C(7)–C(6)	77.5(3)

of  $a_{Ti}$  (7.5 G) were observed in  $[(C_5HMe_4)_2Ti(\eta^1-C\equiv C\equiv CSiMe_3)_2]^- [Li(THF)_2]^+$ , probably as a result of higher delocalization capability of the diyne arms. The interaction of the unpaired electron with alkali metal was observed only for the  $Cs^+$  nucleus ( $I_N = 7/2$ ) in **5** both in toluene and MTHF. The  $\Delta H$  (peak-to-peak) of the central signal was the same in both solvents but the resolution into eight-line spectrum with  $a_{Cs} = 2.0$  G was obtained in MTHF. The nature of solvents affected the EPR spectra of all compounds only slightly. The values of  $g$ -factors were generally lower and  $a_{Ti}$  was negligibly higher in MTHF compared with toluene.

The electronic absorption spectra of **2–5** both in toluene and in THF or MTHF were characterized by a couple of very intense absorption bands in the range 350–390 nm (Table 1). Orange-brown toluene solutions of **2–4** further showed a broad absorption increasing in intensity from about 720 nm to shorter wavelengths. Poorly-discernible shoulders were observed for **3** and **4** near 500 nm, whereas the absorption band for **2** was observed at 460 nm. Compound **5** was only slightly soluble in toluene and thus the low-intensity part of the spectrum (750–500 nm) did not show any other feature except a weak absorption increasing towards short wavelengths. In THF or MTHF their colours turned to a much less intense green-yellow. The solutions showed a very weak absorption growing in intensity to shorter wavelengths from ca. 1000 nm. All compounds exerted a broad shoulder in the region 740–770 nm and an absorption band at 560–580 nm which should indicate the presence of compounds **2a–5a** in THF solutions. The intense bands below 400 nm were recently assigned to a  $d \rightarrow \pi^*$  transition [3], whereas the longest wavelengths' absorption band at 700 nm should belong to a  $d-d$  transition.

The IR spectra of **2–5** showed the  $\nu(C\equiv C)$  vibration in the region 1935–1948  $cm^{-1}$  as two poorly-resolved absorption bands in close vicinity. This splitting can result from coupling of triple bonds via the alkali metal ion. In **1**, no such splitting of  $\nu(C\equiv C)$  vibration at 2017  $cm^{-1}$  was observed. The presence of coordinated THF in the hexane solutions of **2a** and **3a** was proven by the absorption bands at 1040 and 1053  $cm^{-1}$  respectively. These wavenumbers are comparable with those of **6** (1020  $cm^{-1}$ ) [1] and **7** (two bands at 1057 and 1047  $cm^{-1}$ ) [3].

### 3.5. Concluding remarks

The method of preparation of **2–5** by the redox reaction of alkali metals with **1** as well as the EPR evidence for the presence of Ti(III) in the products leaves no doubt about the presence of alkali metal cations in **2–5**. The X-ray structure of **4** confirms the suggestion that the alkali metal cation is held between the anionic acetylide arms by an ionic bond [3]. The

coordinatively unsaturated  $K^+$  is weakly bonded to the CE(1) cyclopentadienyl ring of the adjacent molecule, thus creating a polymer chain structure. A striking and somewhat irreproducible difference in the colours of **3–5** in the hydrocarbon solution and in the solid state is apparently related to a different association in the solid state and the solvation or association in solutions. The coordination of THF to **2–5** is generally weak and decreases with increasing size of alkali metals. The magnitude of the tweezer bite angle and the mode of association and/or solvation (which depends on the size of the alkali metal cations) will be clarified by the structure investigation of **2**, **2a**, **3**, and **5** which is currently under way.

## 4. Supplementary material available

Listings of atomic coordinates and anisotropic thermal parameters, and all bond distances and angles are available upon request from the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-76012 Karlsruhe by quoting the deposition number CSD-58525, the name of the authors and the journal citation. Additional information, such as data for least squares planes, intermolecular distances and angles, observed and calculated structure factors and views of unit cell may be obtained from the authors.

## Acknowledgements

This investigation was supported by the Grant Agency of the Czech Republic, grant no. 203/93/0143 and by the Fonds der Chemischen Industrie. The authors thank Mrs. G. Dörfner for the EDX measurements.

## References

- [1] S.I. Troyanov, V. Varga and K. Mach, *Organometallics*, **12** (1993) 2820.
- [2] K. Mach, V. Varga and R. Gyepes, *XVIIth Int. Conf. Organometallic Chemistry, University of Sussex, July, 1994, Book of Abstracts*, OB17.
- [3] V. Varga, K. Mach, J. Hiller and U. Thewalt, *J. Organomet. Chem.*, **506** (1996) 109.
- [4] W.J. Evans, D.K. Drummond, T.P. Hanusa and J.M. Olofson, *J. Organomet. Chem.*, **376** (1989) 311.
- [5] W.J. Evans, R.A. Keyer and J.W. Ziller, *Organometallics*, **12** (1993) 2618.
- [6] H. Lang, S. Blau, B. Nuber and L. Zsolnai, *Organometallics*, **14** (1995) 3216.
- [7] H. Lang, M. Herres, L. Zsolnai and W. Imhof, *J. Organomet. Chem.*, **409** (1991) C7.
- [8] M.D. Janssen, M. Herres, L. Zsolnai, D.M. Grove, A.L. Spek, H. Lang and G. van Koten, *Organometallics*, **14** (1995) 1098.
- [9] H. Lang, M. Herres and L. Zsolnai, *Organometallics*, **12** (1993) 5008.

- [10] H. Antropiusová, A. Dosedlová, V. Hanuš and K. Mach, *Transition Met. Chem.*, **6** (1981) 90.
- [11] H. Lang and D. Scyferth, *Z. Naturforsch. Teil B*, **45** (1990) 212.
- [12] T. Brüggemann, B. Debaerdemaeker, G. Müller, Schmid and U. Thewalt, *ULM-Programmsystem, 1. Jahrestagung der Deutschen Gesellschaft für Kristallografie, Mainz, 9–12 June 1992, Abstr. p. 33* (includes G.M. Sheldrick, *SHELX-76 Program for Crystal Structure Determination*, University of Cambridge, Cambridge, UK, 1976).
- [13] K. Mach, H. Antropiusová, V. Varga and V. Hanuš, *J. Organomet. Chem.*, **358** (1988) 123.
- [14] K. Mach and J.B. Raynor, *J. Chem. Soc. Dalton Trans.*, (1992) 683.