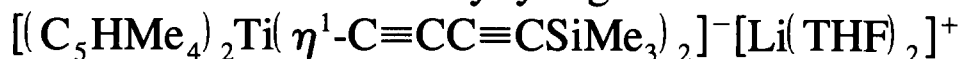


A titanium(III) tweezer complex with an embedded alkali metal ion between diyne ligands:



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Abstract

The complex $[(\eta^5-C_5HMe_4)_2Ti(\eta^1-C\equiv CC\equiv CSiMe_3)_2]^- [Li(THF)_2]^+$ (**1**) was obtained by the reaction of $(C_5HMe_4)_2TiCl$ with 2 equiv. of $LiC\equiv CC\equiv CSiMe_3$ in THF. X-Ray crystal structure determination of **1** revealed that the lithium ion is embedded between the inner triple bonds of the 4-trimethylsilyl-1,3-butadiyn-1-yl tweezer arms. The EPR spectrum of **1** shows a single line, $\Delta H = 2.5$ G at $g = 1.9940 (\pm 0.0003)$, and coupling to ^{49}Ti and ^{47}Ti isotopes ($a(Ti) = 7.5$ G).

Keywords: Titanium (III); Molecular tweezer; Lithium; Electron spin resonance; X-ray diffraction

1. Introduction

Titanocene(IV) tweezer complexes $[Cp'_2Ti(C\equiv CR)_2][ML_n]$ ($Cp' = C_5H_5$, $C_5H_4SiMe_3$; $R = SiMe_3$, Ph; $M =$ transition metal, $L =$ ligand) with a transition metal embedded between the two 2-substituted ethynyl ligands merit increasing attention in a prospect of finding materials with non-linear optical properties [1] and building blocks for molecular electronics (for examples with other metals, see Refs. [2,3]). The general method of preparation consists of the addition of a low-valent ML_{n+m} compound to $Cp'_2Ti(C\equiv CR)_2$ whereby a number of ligands mL are evolved. In this manner complexes containing the following metal species have been prepared: $FeCl_2$, $CuCl$ [4], $CuC\equiv CR$ [5], $Ni(CO)$ [6,7], $Co(CO)$ [8], $AgCl$, $AgCN$, $AgSCN$, $AgNO_2$, $AgClO_4$ [9] and $Pt(PR_3)$ [10]. The first titanocene(III) tweezer complex $[(\eta^5-C_5HMe_4)_2Ti(\eta^1-C\equiv CSiMe_3)_2]^- [Mg(THF)Cl]^+$ (**2**) was obtained as the sole product of the reduction of $(\eta^5-C_5HMe_4)_2TiCl_2$ by magnesium in the presence 1,4-bis(trimethylsilyl)buta-1,3-diyne in THF [11]. Permethyltitanocene–magnesium tweezer complexes of the same type were found to be catalytic

intermediates in the linear head-to-tail dimerization of terminal acetylenes [12].

Here we report the synthesis of the first titanocene tweezer complex containing trimethylsilylbutadiynyl arms and an embedded alkali metal ion.

2. Experimental details

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

2.1. Chemicals

Solvents THF, hexane and toluene were purified by conventional methods, dried by refluxing over $LiAlH_4$ and stored as solutions of dimeric titanocene $(C_{10}H_8)(C_5H_5)Ti(\mu-H)_2$ [13]. Methyl-lithium (MeLi) in hexane (1.6 M) was obtained from Aldrich. $(C_5HMe_4)_2TiCl$ was obtained from $(C_5HMe_4)_2TiCl_2$

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by reduction with LiAlH_4 [14]. 1,4-Bis(trimethylsilyl)buta-1,3-diyne was prepared by the described procedure [15] and was finally sublimed in vacuum.

2.2. Preparation of the title complex 1

1,4-Bis(trimethylsilyl)buta-1,3-diyne (0.78 g, 4 mmol) was dissolved in 20 ml of THF and MeLi (1.6 M, 2.5 ml) in diethyl ether was added. After stirring overnight, the solution of $\text{LiC}\equiv\text{CC}\equiv\text{CSiMe}_3$ [16] obtained was mixed with $(\text{C}_5\text{HMe}_4)_2\text{TiCl}$ (0.65 g, 2 mmol) and dissolved in 30 ml of THF. Reaction began immediately and the colour of the solution turned from blue to a final red. After 30 min, all volatiles were evaporated in vacuum at 30°C and the dark residue extracted with hexane. The extract was evaporated and the brown-red residue extracted again with a minimum amount of hexane in order to separate 1 from traces of LiCl. Dark brown-red crystals were obtained by cooling the extract. Yield 1.2 g (88%). The same crop of crystals was used for X-ray analysis, KBr pellets and for the preparation of solutions for spectroscopic measurements. MS (direct inlet, 150–220°C): decomposition, evolution of THF. UV-Vis (hexane, orange) (nm): 290 (sh >); 335 (sh); 363; 392; 420 (sh); 470; 514. EPR (toluene, 23°C): $g = 1.9940$, $\Delta H = 0.25$ mT, $a(\text{Ti}) = 0.75$ mT; (toluene, frozen glass at -140°C): $g_1 = 2.0013$, $g_2 = 1.9940$, $g_3 = 1.9893$, $g_{\text{av}} = 1.9948$. IR (KBr)(cm^{-1}): 2957 (s); 2901 (s); 2855 (s, sh); 2133 (s); 2101 (s); 1956 (m); 1450 (m); 1433 (m); 1379 (m);

1248 (s); 1057 (m) (THF); 1047 (m) (THF); 1024 (m, sh); 999 (w, sh); 843 (vs); 758 (m); 698 (w); 638 (m); 507 (m, br); 425 (w) IR(hexane): the same spectrum within ± 2 cm^{-1} was obtained, except that the band at 1956 cm^{-1} was split by about 5 cm^{-1} .

2.3. X-Ray crystal structure analysis of the title complex 1

A dark brown-red crystal fragment, $0.5 \times 0.5 \times 0.7$ mm, was mounted in a glass capillary under purified nitrogen. The X-ray measurements were carried out on a Philips PW 1100 four-circle diffractometer, graphite monochromator, using Mo K α radiation ($\lambda = 0.71069$ Å) at room temperature. Crystallographic data for 1: $\text{C}_{40}\text{H}_{60}\text{O}_2\text{LiSi}_2\text{Ti}$, $M = 683.93$; monoclinic, $C2/c$, No. 15; $a = 25.490(3)$, $b = 11.639(2)$, $c = 19.892(3)$ Å, $\beta = 132.921(5)^\circ$; $V = 4321(2)$ Å³; $D_c = 1.05$ g cm^{-3} ; $Z = 4$; $\mu = 2.44$ cm^{-1} . Crystal data were collected by $\theta/2\theta$ -method; $2\theta_{\text{max}} = 50^\circ$. A total of 2127 unique reflections with $F_o > 2\sigma(F_o)$ out of 4026 observed reflections were used in the calculations. The structure was solved by iterative symbolic addition. Hydrogen atoms were included in calculated positions as contributions to F_c . Refinement with anisotropic thermal parameters for the non-hydrogen atoms revealed high thermal motion for the carbon atoms of the trimethylsilyl group, in particular. The final R indices were $R = 0.064$, $R_w = 0.073$. The PC ULM package [17] was used for all the calculations. The atomic coordinates and thermal

Table 1
Atomic coordinates for 1

Atom ^a	x	y	z	U_{eq}
Ti(1)	0.0000	0.1127(1)	0.2500	0.053(1)
Li(1)	0.0000	0.389(1)	0.2500	0.095(4)
Si(1)	0.2356(1)	0.5846(1)	0.2917(1)	0.094(1)
C(1)	0.0637(2)	0.2421(4)	0.2592(3)	0.067(2)
C(2)	0.1023(3)	0.3137(4)	0.2673(3)	0.075(2)
C(3)	0.1467(3)	0.3948(5)	0.2755(4)	0.085(2)
C(4)	0.1830(3)	0.4681(5)	0.2819(4)	0.094(3)
C(5)	0.3298(4)	0.5640(8)	0.3877(6)	0.149(4)
C(6)	0.2185(8)	0.596(1)	0.1893(7)	0.404(4)
C(7)	0.2084(7)	0.7126(9)	0.307(1)	0.404(4)
C(8)	0.1150(3)	0.0437(5)	0.3873(3)	0.079(2)
C(81)	0.1817(3)	0.0351(6)	0.4019(5)	0.120(3)
C(9)	0.0991(3)	0.1326(4)	0.4177(3)	0.078(2)
C(91)	0.1461(3)	0.2351(6)	0.4715(4)	0.111(3)
C(10)	0.0380(3)	0.1015(5)	0.4011(3)	0.085(3)
C(101)	0.0082(4)	0.1669(7)	0.4353(4)	0.132(3)
C(11)	0.0148(3)	-0.0073(5)	0.3586(4)	0.086(3)
C(111)	-0.0447(4)	-0.0777(7)	0.3367(5)	0.133(3)
C(12)	0.0639(3)	-0.0426(4)	0.3515(3)	0.080(2)
O(1)	-0.0411(3)	0.4971(4)	0.1485(4)	0.139(3)
C(13)	-0.0202(5)	0.5266(9)	0.1009(8)	0.187(4)
C(14)	-0.0663(7)	0.620(1)	0.0385(9)	0.219(4)
C(15)	-0.1210(7)	0.6328(9)	0.0433(8)	0.211(4)
C(16)	-0.1015(6)	0.5663(9)	0.1143(9)	0.207(4)

^a Atoms Si(1'), C(1'), etc. are related to atoms Si(1), C(1), respectively, etc., by the symmetry operation $-x, y, \frac{1}{2} - z$.

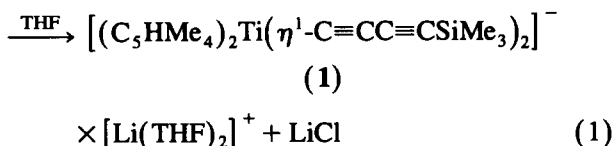
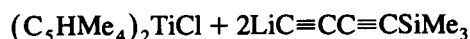
Table 2
Selected interatomic distances (Å) and bond angles (°) for **1** (e.s.d.s given in parentheses)

Interatomic distances			
Ti(1)—CE (C ₅ HMe ₄ ring)	2.096(6)	C(4)—Si(1)	1.822(7)
Ti(1)—C(C ₅ HMe ₄ ring) (av.)	2.411(6)	Si(1)—C(5–7) (av.)	1.776(16)
Ti(1)—C(1)	2.129(5)	Li(1)—C(1)	2.277(7)
C(1)—C(2)	1.213(8)	Li(1)—C(2)	2.541(7)
C(2)—C(3)	1.395(9)	Li(1)—O(1)	1.969(8)
C(3)—C(4)	1.200(10)	Li(1)—Ti(1)	3.215(4)
Bond angles			
CE(1)—Ti(1)—CE(1')	136.2(2)	C(3)—C(4)—Si(1)	177.2(6)
C(1)—Ti(1)—C(1')	89.9(2)	Ti(1)—C(1)—Li(1)	93.7(2)
C(1)—C(2)—C(3)	178.8(6)	C(1)—Li(1)—C(2)	28.5(2)
C(2)—C(3)—C(4)	177.2(7)	Ti(1)—C(1)—C(2)	177.5(5)

parameters are given in Table 1. Selected interatomic distances and angles are listed in Table 2.

3. Results and discussion

The complex $[(C_5HMe_4)_2Ti(\eta^1-C\equiv C\equiv CSiMe_3)_2]^- [Li(THF)_2]^+$ (**1**) was obtained in high yield from the reaction of $(C_5HMe_4)_2TiCl$ with 2 equiv. of $LiC\equiv C\equiv CSiMe_3$ in THF [Eq. (1)].



The X-ray single-crystal analysis of **1** revealed that the molecule has twofold crystallographic symmetry with the Ti and Li atoms located on the axis. A PLUTO drawing of **1** is shown in Fig. 1. Selected interatomic distances and bond angles of **1** are listed in Table 2. The titanocene part of **1** contains two C₅HMe₄ ligands in a staggered configuration. The hydrogen-bearing carbon

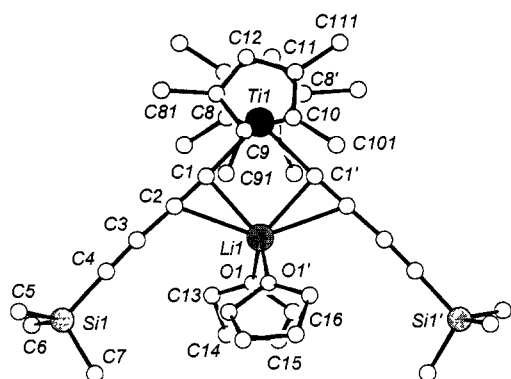


Fig. 1. Molecular structure and atom numbering scheme of $[(C_5HMe_4)_2Ti(\eta^1-C\equiv C\equiv CSiMe_3)_2]^- [Li(THF)_2]^+$ (**1**). The viewing direction is perpendicular to the Ti(1), C(1), C(1') plane.

atoms are in positions where the cyclopentadienyl rings have their closest contact. The titanium atom is pulled towards the apex of the angle α between the C₅HMe₄ rings ($\alpha = 51^\circ$) so that the distance from the titanium atom to C(12) is shorter by 0.1 Å than to C(9). The same effect has been observed in $(C_5HMe_4)_2TiCl_2$, $(C_5HMe_4)_2TiCl$ and $(C_5HMe_4)_2TiI$ [18]. The tweezer part is formed by the bis(4-trimethylsilyl-1,3-butadiyn-1-yl)titanium(III) segment which contains the Li⁺ ion embedded between the inner pair of triple bonds. The plane defined by CE(1) [centroid of the C(8)–C(12) ring], CE(1') and Ti is perpendicular to the tweezer plane defined by C(1), C(1') and Ti within 1.6°. The tweezer arms are approximately linear with a maximum outward deviation from the Ti–Si interconnection of ca. 0.1 Å for the C(3) and C(4) atoms. The Li⁺ ion acquires a pseudotetrahedral coordination by binding two molecules of THF. The angle O(1)–Li–O(1') is 100.5° and its plane deviates from the perpendicular orientation towards the tweezer plane by 7.4° (see the view of **1** in Fig. 1).

The molecular structure of **1** is similar to that of **2**. The common molecular parameters differ mainly in a larger angle between the tweezer arms C(1)–Ti–C(1') of 89.9(2)° and a slightly larger CE(1)–Ti–CE(1') angle of 136.2(2)° compared to 86.1(3)° and 134.8(3)°, respectively, in **2**. The Ti–C(1) σ -bond length of 2.129(5) Å is slightly shorter than the average of such bond lengths in **2** [2.165(7) Å]; however, the C≡C bond lengths in **2** [1.22(1) Å] and the two C≡C bonds in **1**, coordinated [1.213(8) Å] and uncoordinated [1.200(10) Å], differ to a smaller extent. The Li–C(1) and Li–C(2) distances are different, 2.277(7) Å and 2.541(7) Å, respectively. The Li–C(1) vector is nearly perpendicular to the tweezer arm. This circumstance and the virtually unchanged bond length of the inner triple bond imply the absence of covalent bonding between the arm and the Li⁺ ion. The Ti–Li distance of 3.215(4) Å excludes any direct interaction and the nature of the Li⁺ bonding to tweezer arms is thus essentially ionic. A similar arrangement of the $[Li(OEt_2)]^+$ ion towards the two

$\text{Cu}^{\text{I}}-\text{C}\equiv\text{CPh}$ moieties was found in a cluster of lithium phenylethynyl cuprate with the distance $\text{Li}-\text{C}_{\alpha} = 2.30-2.36 \text{ \AA}$ [19]. The molecular structures of **1** and **2** do not differ essentially from those of bis(trimethylsilylcyclopentadienyl)titanium(IV) tweezer complexes containing transition metals where, for example, the $\text{C}(1)-\text{Ti}-\text{C}(1')$ angles span the range $85.4^{\circ}-91.0^{\circ}$ (for $\text{ML}_n = \text{FeCl}_2$ and CuCl , respectively [4]). In the silver complexes, this angle attains a value as great as 93.8° for $\text{ML}_n = \text{Ag}(\text{NO}_2)$ [9].

The toluene solution of **1** affords the EPR spectrum consisting of a single line $\Delta H = 2.5 \text{ G}$ at $g = 1.9940$ accompanied by hyperfine splittings due to ^{49}Ti ($I_{\text{N}} = \frac{7}{2}$) and ^{47}Ti ($I_{\text{N}} = \frac{5}{2}$) isotopes [$a(\text{Ti}) = 7.5 \text{ G}$] in the wings of the spectrum with approx. 20-times lower intensity. A frozen toluene solution exhibited a nearly symmetrical rhombic g -tensor giving $g_{\text{av}} = 1.9948$. All the EPR parameters are very similar to those for **2** [11]. The presence of Ti^{III} justifies the ionic formulation of the structure. The electronic absorption spectrum of **1** contains two pairs of bands of high intensity (363/392, 470/514 nm) in contrast to one pair of such bands (380/400 nm) in **2**. This is apparently due to the conjugated system of triple bonds generating a LUMO orbital at lower energy than in **2**. These transitions are tentatively described as being of a $d \rightarrow \pi^*$ nature.

The infrared spectra of **1** in a KBr matrix allowed a distinction to be made between the outer and inner triple bonds, the former showing two strong bands at 2133 and 2101 cm^{-1} whereas the latter exhibited only one band at 1956 cm^{-1} of a lower intensity. The latter band is slightly but distinctly split in the spectrum of the hexane solution. The wavenumbers for the outer triple bond are higher than those for 1,4-bis(trimethylsilyl)buta-1,3-diyne (2064 and 2038 cm^{-1}) and fall in the range of wavenumbers typical of alkyl- or trimethylsilyl-disubstituted acetylenes [20] which readily coordinate to transition metal complexes [21]. Recently, hafnocene(IV) diacetylide has been shown to form complexes with iron and cobalt carbonyls where the metals were coordinated to acetylenic triple bonds outside the tweezer arms [22]. The potential of complex **1** to form a variety of multimetallic complexes via coordination inside the inner triple bonds by the replacement of the Li^+ ion, and inside or outside the outer triple bonds by coordinating, for example, metal carbonyls, is to be investigated.

4. Supplementary material available

Listings of atomic coordinates and anisotropic thermal parameters, and all bond distances and angles are available upon request from the Fachinformationszen-

trum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-76012 Karlsruhe by quoting the deposition number CSD-58522, the name of the authors and the journal citation.

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