Synthesis and characterization of thiolate derivatives of bis(trimethylsilylcyclopentadienyl)titanium(IV). The crystal and molecular structure of $[(\eta^5\text{-}C_5H_4SiMe_3)_2Ti(SC_6F_5)_2]$

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Abstract

A series of new compounds $[(\eta^5\text{-}C_5H_4SiMe_3)_2Ti(SR)_2]$ [R = C_6F_5 (**1**), C_6H_5 (**2**), $CH_2C_6H_5$ (**3**), or C_2H_5 (**4**)] and $[(\eta^5\text{-}C_5H_4SiMe_3)_2TiCl(SC_6H_{11})]$ (**5**) has been obtained. The ^1H NMR spectra in the cyclopentadienyl region show different patterns depending on the nature of the thiol group. The ^{13}C NMR spectra of the $[(\eta^5\text{-}C_5H_4SiMe_3)_2Ti(SR)_2]$ compounds show three resonances, whereas the spectrum of the complex $[(\eta^5\text{-}C_5H_4SiMe_3)_2TiCl(SC_6H_{11})]$ exhibits five. The crystal structure of compound **1** has been determined by X-ray diffraction. There is a pseudotetrahedral arrangement about the titanium atom. The molecule adopts an "*endo*" (*anti*) conformation of the cyclopentadienyl rings.

Key words: Titanium; Thiolate; Cyclopentadienyl; Crystal structure

1. Introduction

The chemistry of Ti^{IV} thiolates has attracted interest for several reasons, notably on account of their antitumour activity [1–2], the nature of bonding and conformational aspects [3–5], and recently thiolates of transition metals, including titanium, have been widely used in the synthesis of heterobimetallic compounds for their potential in catalysis [6,7]. In contrast to the wide knowledge of the thiolate derivatives of titanocene, the analogous compounds with trimethylsilylcyclopentadienyl ligand have been less studied. Here we describe the synthesis and characterization of new bis(thiolate) derivatives of bis(trimethylsilylcyclopentadienyl)-titanium(IV). An X-ray study of $[(\eta^5\text{-}C_5H_4SiMe_3)_2Ti(SC_6F_5)_2]$ compound is also included.

2. Experimental details

All reactions were carried out under dinitrogen using Schlenk techniques. Solvents were purified according to standard procedures [8]. The starting materials $[(\eta^5\text{-}C_5H_4SiMe_3)_2TiCl_2]$ [9], $[HSC_6H_2(Me)_3\text{-}2,4,6]$ and $[HSC_6H_2(^iPr)_3\text{-}2,4,6]$ [10] were prepared by literature methods and all other reagents were commercially available.

IR spectra (range 4000–200 cm^{-1}) were recorded on a Perkin-Elmer 1600 FT spectrophotometer, NMR spectra were recorded on Bruker WH-200-5Y (^1H and ^{13}C) and Varian Unity 300 (^{19}F) instruments. FAB positive ion mass spectra were measured on a VG Autospec spectrometer. Elemental analyses were performed with a Perkin-Elmer 2400 microanalyzer.

2.1. *Synthesis of* $[(\eta^5\text{-}C_5H_4SiMe_3)_2Ti(SC_6F_5)_2]$ *(1)*

To a solution of $[(\eta^5\text{-}C_5H_4SiMe_3)_2TiCl_2]$ (0.4 g, 1.02 mmol) in toluene (30 cm^3) was added HSC_6F_5

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(0.27 cm³, 2.04 mmol) and Et_3N (0.36 cm³, 2.5 mmol). After stirring for 24 h at room temperature, the solution was filtered through silica gel, and on removing the solvent *in vacuo* a deep dark red solid, compound **1**, was isolated and recrystallized from hexane at −20°C giving crystals suitable for a X-ray study (0.73 mmol, 72% yield). Found: C, 46.98; H, 3.72. Calc. for $C_{28}H_{26}F_{10}S_2Si_2Ti$: C, 46.68; H, 3.61%. ^{19}F [^1H] NMR (relative to CCl_3F)($CDCl_3$) δ (ppm) −131.0 (d, $o\text{-}C_6F_5$), −157.9 (t, $p\text{-}C_6F_5$), and −163.5 (t, $m\text{-}C_6F_5$).

2.2. Preparation of $[(\eta^5\text{-}C_5H_4SiMe_3)_2Ti(SR)_2]$ [$R = C_6H_5$ (2), $CH_2C_6H_5$ (3), C_2H_5 (4)] and $[(\eta^5\text{-}C_5H_4SiMe_3)_2TiCl(SC_6H_{11})]$ (5)

These complexes were obtained following the above procedure. **2**: 87% yield. Found: C, 61.5; H, 6.8. Calc. for $C_{28}H_{36}S_2Si_2Ti$: C, 58.3; H, 6.9%. **3**: 95% yield. Found: C, 64.0; H, 7.2. Calc. for $C_{30}H_{40}S_2Si_2Ti$: C, 63.4; H, 7.0%. **4**: 60% yield. Found: C, 53.1; H, 8.3. Calc. for $C_{20}H_{36}S_2Si_2Ti$: C, 54.0; H, 8.1%. **5**: 49% yield. Found: C, 56.7; H, 8.3. Calc. for $C_{22}H_{37}ClSSi_2Ti$: C, 55.9; H, 7.8%.

TABLE 1. Crystal data and structure refinement for compound **1**

Crystal data	
Formula	$C_{28}H_{26}F_{10}S_2Si_2Ti$
Crystal habit	Prism truncated
Colour	Ruby
Crystal size (mm)	0.36 × 0.10 × 0.20
Symmetry	Monoclinic, $P2_1/n$
Unit cell dimensions	12.579(3), 14.008(6), 17.803(4) Å 90.0, 96.44(2), 90.0(°)
Packing: V (Å³), Z	3117(2), 4
M, F(000)	720.69, 1464
D_{calc} (g cm^{-3})	1.536
μ (Cu Kα) (cm^{-1})	50.62
Experimental data	
Technique	Four circle diffractometer: Rigaku AFC6S. Graphite monochromated Cu Kα
2θ range max.	120
Scan type	ω–2θ
No. of reflections:	
Measured	4458
Observed (N_o)	2731 ($I < 3\sigma(I)$)
Variables (N_v)	388
Absorption	Absorption correction applied, DIFABS [11]
Solution and refinement	
Solution	Direct methods DIRDIF [12]
Refinement	Full-matrix least-squares, anisotropic for all atoms
H atoms	Included with Calc. or Diff. Map Pos.
w-scheme	Empirical as to give no trends in $[\Sigma w(F_o - F_c)2/(\text{No-Nv})]^{1/2}$
Max. peak final Diff. map. (e^-/Å³)	0.16
Average shift/error	0.002
Final R and R_w	0.036, 0.045
Scattering factors	*Int. Tables for X-Ray Crystallography*
Anomalous dispersion	Applied for Ti, Si, S, F and C [13]
Computer and programs	VAX-station 3520, TEXSAN crystallographic software package [14]

TABLE 2. Positional parameters for compound **1**

Atom	x	y	z
Ti(1)	0.60630(6)	0.32962(6)	0.26661(4)
S(1)	0.5343(1)	0.3430(1)	0.13405(7)
S(2)	0.6582(1)	0.1624(1)	0.27248(8)
Si(1)	0.8018(1)	0.3674(1)	0.45360(8)
Si(2)	0.4514(1)	0.5661(1)	0.29680(8)
F(2)	0.6788(2)	0.1940(2)	0.0772(2)
F(3)	0.8052(3)	0.2114(2)	−0.0333(2)
F(4)	0.8272(3)	0.3824(3)	−0.1004(2)
F(5)	0.7193(3)	0.5352(2)	−0.0577(2)
F(6)	0.5924(2)	0.5205(2)	0.0530(2)
F(8)	0.6168(3)	0.0650(2)	0.4155(2)
F(9)	0.4922(3)	−0.0854(3)	0.4325(2)
F(10)	0.3706(3)	−0.1610(2)	0.3120(2)
F(11)	0.3781(3)	−0.0847(3)	0.1740(2)
F(12)	0.5005(3)	0.0681(2)	0.1554(2)
C(1)	0.6284(4)	0.3561(4)	0.0690(3)
C(2)	0.6859(4)	0.2796(4)	0.0442(3)
C(3)	0.7514(4)	0.2876(4)	−0.0110(3)
C(4)	0.7622(4)	0.3736(5)	−0.0457(3)
C(5)	0.7068(4)	0.4506(4)	−0.0238(3)
C(6)	0.6429(4)	0.4412(4)	0.0324(3)
C(7)	0.5612(4)	0.0740(3)	0.2849(3)
C(8)	0.5562(4)	0.0312(4)	0.3537(3)
C(9)	0.4936(5)	−0.0458(4)	0.3642(3)
C(10)	0.4332(4)	−0.0845(4)	0.3034(4)
C(11)	0.4371(4)	−0.0453(4)	0.2338(3)
C(12)	0.4989(5)	0.0323(4)	0.2253(3)
C(13)	0.7974(3)	0.3172(4)	0.2949(3)
C(14)	0.7749(4)	0.3551(4)	0.2231(3)
C(15)	0.7267(4)	0.4435(4)	0.2299(3)
C(16)	0.7192(3)	0.4601(3)	0.3061(3)
C(17)	0.7622(3)	0.3795(4)	0.3485(2)
C(18)	0.5202(4)	0.3815(4)	0.3705(3)
C(19)	0.4981(4)	0.2840(4)	0.3602(3)
C(20)	0.4356(4)	0.2731(4)	0.2908(3)
C(21)	0.4183(4)	0.3646(4)	0.2599(3)
C(22)	0.4726(4)	0.4339(3)	0.3073(3)
C(23)	0.9483(5)	0.3484(6)	0.4637(4)
C(24)	0.7695(6)	0.4794(4)	0.5002(3)
C(25)	0.7383(6)	0.2651(4)	0.4959(3)
C(26)	0.4995(5)	0.6124(4)	0.2096(4)
C(27)	0.5175(5)	0.6276(4)	0.3811(4)
C(28)	0.3054(4)	0.5875(4)	0.2899(3)

2.3. Crystallographic section.

Suitable crystals of compound $[(\eta^5\text{-}C_5H_4SiMe_3)_2\text{-}Ti(SC_6F_5)_2]$ (**1**) were obtained from a hexane solution under dinitrogen at −20°C. X-ray diffraction data and experimental details on the structure solution and refinement [11–14] are given in Table 1. The final atomic coordinates are collected in Table 2. Tables of all bond distances and angles, anisotropic thermal parameters and list of structure factors can be obtained from the authors or from the Cambridge Crystallographic Data Centre.

3. Results and discussion

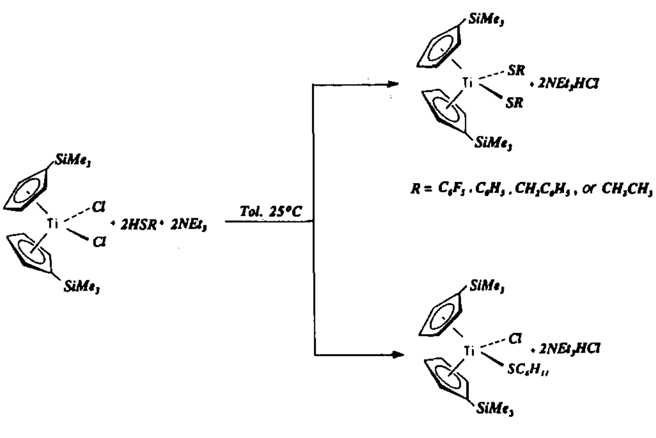
Compounds $[(\eta^5\text{-}C_5H_4SiMe_3)_2Ti(SR)_2]$ [R = C_6F_5 (1), C_6H_5 (2), $CH_2C_6H_5$ (3), or C_2H_5 (4)] and $[(\eta^5\text{-}C_5H_4SiMe_3)_2TiCl(SC_6H_{11})]$ (5) were synthesized by the reaction of $[(\eta^5\text{-}C_5H_4SiMe_3)_2TiCl_2]$ with the appropiate thiol, HSR, in 1:2 ratios in toluene in the presence of Et_3N (Scheme 1).

Different reaction times were required depending on the nature of the thiol, and the behaviour of HSC_6H_{11} may be due to its greater steric bulk. The use of exceedingly bulky thiols such as $[HSC_6H_2(Me)_3\text{-}2,4,6]$ and $[HSC_6H_2(^iPr)_3\text{-}2,4,6]$ in the above conditions did not give any positive results.

The new complexes were characterized by elemental analysis as well as by IR, ^1H and ^{13}C spectroscopies (Table 3), ^{19}F NMR spectroscopy and FAB mass spectrometry (Table 4).

The IR spectra show bands typical of substituted cyclopentadienyl rings and the various thiolates. The ^1H NMR spectra show the resonances expected for the different thiolate groups. The substituent in the cyclopentadienyl rings produces various patterns in the Cp region [9]. For the compounds $[(\eta^5\text{-}C_5H_4R)_2MCl_2]$ (M = Zr or Hf; R = Me, Et, ^iPr, or ^tBu) a complex AA′BB′ signal has been described whereas the starting material $[(\eta^5\text{-}C_5H_4SiMe_3)_2TiCl_2]$ exhibits an A_2B_2 pattern [9].

The new complexes $[(\eta^5\text{-}C_5H_4SiMe_3)_2Ti(SR)_2]$ behave differently in this range. Two pseudotriplets are exhibited by $[(\eta^5\text{-}C_5H_4SiMe_3)_2Ti(SC_6F_5)_2]$. Two superposed pseudotriplets giving rise to a multiplet were observed for $[(\eta^5\text{-}C_5H_4SiMe_3)_2Ti(SC_6H_5)_2]$ and $[(\eta^5\text{-}C_5H_4SiMe_3)_2Ti(SC_2H_5)_2]$, and a singlet was seen for $[(\eta^5\text{-}C_5H_4SiMe_3)_2\,Ti(SCH_2C_6H_5)_2]$. The nature of the thiolates can account for the degree of magnetic equivalence of the protons. In $[(\eta^5\text{-}C_5H_4SiMe_3)_2TiCl(SC_6H_{11})]$ the ^1H NMR spectrum shows three separate resonances with intensity ratios 1:2:1 for the cyclopentadienyl ring indicating that the four protons are magnetically inequivalent. The ^{13}C NMR spectra of the bis(thiolate) derivatives $[(\eta^5\text{-}C_5H_4SiMe_3)_2Ti(SR)_2]$ show three resonances in the cyclopentadienyl region. One of the signals is due to the carbon atom bearing the substituent (C^1), another to the two carbon atoms α to (C^1) and the third to the two carbon atoms β to (C^1). However, five resonances in the Cp region are observed for $[(\eta^5\text{-}C_5H_4SiMe_3)_2TiCl(SC_6H_{11})]$, showing that the five carbon atoms are inequivalent.



Scheme 1.

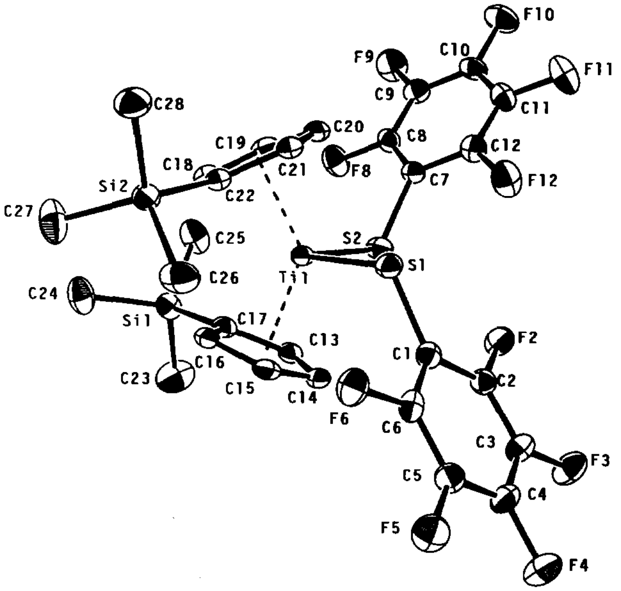


Fig. 1. Molecular structure of $[(\eta^5\text{-}C_5H_4SiMe_3)_2Ti(SC_6F_5)_2]$ (1) including the atom numbering scheme.

The chemical shifts in the ^{19}F NMR spectrum of $[(\eta^5\text{-}C_5H_4SiMe_3)_2Ti(SC_6F_5)_2]$ were similar to those reported for the SC_6F_5 group in the other perfluorophenyl thiolate derivatives [15,16]. The *ortho*- and *meta*-fluorine resonances appeared as a doublet and a triplet at 131.0 and 163.5 ppm, respectively, and the *para*-fluorine signal as a triplet at 157.9 ppm.

The positive ion FAB mass spectra of **1**–**5** were recorded using 3-nitrobenzyl alcohol as the matrix and tetrahydrofuran as solvent. The molecular ion signal (M^+) is always weak and $[(\eta^5\text{-}C_5H_4SiMe_3)_2Ti]^+$ was the most intense ion in most of the spectra. A similar fragmentation pattern was observed for all the compounds.

TABLE 3. ^1H and ^{13}C NMR data for complexes 1–5

Compound	^1H NMR (ppm) [a]	^{13}C NMR (ppm) [b]
1	0.22(s, 18H, $SiMe_3$) 6.04(t, 4H, C_5H_4, $J = 2.4$ Hz) 6.27(t, 4H, C_5H_4, $J = 2.4$ Hz)	
2	0.25(s, 18H, $SiMe_3$) 6.22–6.18(m, 8H, C_5H_4) 7.58–7.12(m, 10H, C_6H_5)	0.5(s, $SiMe_3$); 116.6(s, C_5H_4) [c] 120.0(s, C_5H_4) [d]; 121.7(s, C_5H_4) [e] 125.4–132.3(s, C_6H_5); 150.4(s, C_6H_5)
3	0.26(s, 18H, $SiMe_3$) 4.25(s, 4H, CH_2) 6.41(s, 8H, C_5H_4) 7.30–7.26(m, 10H, C_6H_5)	0.5(s, $SiMe_3$); 50.1(s, CH_2); 114.9 (s, C_5H_4) [e]; 119.1 (s, C_5H_4) [d]; 120.3 (s, C_5H_4) [c]; 126.2; 128.2; 143.5; (s, C_6H_5)
4	0.23(s, 18H, $SiMe_3$) 1.14(t, 6H, CH_3, $J = 7.4$ Hz) 3.05(q, 4H, CH_2, $J = 7.4$ Hz) 6.29(m, 8H, C_5H_4)	0.9(s, $SiMe_3$); 18.9(s, CH_3); 40.6(s, CH_2); 114.1 (s, C_5H_4) [e]; 118.7(s, C_5H_4) [d]; 120.8(s, C_5H_4) [c]
5	0.25(s, 18H, $SiMe_3$) 3.89; 2.08–1.19(m, 11H, C_6H_{11}) 6.14(m, 2H, C_5H_4) 6.47(m, 4H, C_5H_4) 6.57(m, 2H, C_5H_4)	0.6(s, $SiMe_3$); 26.2(s, CH_2) [f]; 27.1 (s, CH_2) [g]; 33.2(s, CH); 35.9(s, CH_2) [h]; 116.4(s, C_5H_4) [c]; 113.9; 118.2; 121.9; 124.0(s, C_5H_4) [d,e]

[a] Relative to trimethylsilane, $CDCl_3$ solvent. [b] Relative to trimethylsilane, C_6D_6 solvent. [c] C^1-C_5H_4. [d] $C^{2,5}$-C_5H_4. [e] $C^{3,4}$-C_5H_4. [f] C *para*. [g] C *meta*. [h] C *ortho*.

Theoretical and X-ray studies of the influence of electronic and steric factors in determining the conformational preferences of bent metallocene-thiolate complexes [3–5] confirm the relationship between the S–M–S angle and the orientation of the SR groups relative to the cyclopentadienyl rings. Structural data of the complexes $[(\eta^5\text{-}C_5H_5)_2Ti(SR)_2]$ [R = CH_3, C_2H_5, or C_6H_5)] [4,17,18] show an S–M–S angle in the range 93.6–99.3° and an *endo* (*anti*) conformation for all of them.

It was of interest to deduce how a trimethylsilylcyclopentadienyl affects the geometry of this type of compound, and the lack of crystallographic data concerning the SC_6F_5 group in this class of thiolate derivative prompted us to carry out a X-ray study of the $[(\eta^5\text{-}C_5H_4SiMe_3)_2Ti(SC_6F_5)_2]$. An ORTEP plot of the molecular structure is shown in Fig. 1.

Selected bond lengths and angles for 1 are given in Table 5. There is a pseudotetrahedral arrangement of ligands about the titanium atom made up of the cen-

TABLE 4. FAB Mass spectra of compounds 1–5 [a]

1	720 (M^+), 705 (M^+-Me), 583 (M^+-$C_5H_4SiMe_3$), 521 (M^+-SC_6F_5), 341 $[(C_5H_4SiMe_3)_2TiF]$, 322 $[(C_5H_4SiMe_3)_2Ti]$
2	540 (M^+), 525 (M^+-Me), 431 (M^+-SPh), 403 (M^+-$C_5H_4SiMe_3$), 322 $[(C_5H_4SiMe_3)_2Ti]$, 218 (PhSSPh)
3	568 (M^+), 553 (M^+-Me), 445 (M^+-SCH_2Ph), 431 (M^+-$C_5H_4SiMe_3$), 322 $[(C_5H_4SiMe_3)_2Ti]$, 246 ($PhCH_2SSCH_2Ph$)
4	444 (M^+), 429 (M^+-Me), 383 (M^+-SEt), 322 $[(C_5H_4SiMe_3)_2Ti]$, 307 (M^+-$C_5H_4SiMe_3$)
5	472 (M^+), 457 (M^+-Me), 437 (M^+-Cl), 357 (M^+-SC_6H_{11}), 335 (M^+-$C_5H_4SiMe_3$), 322 $[(C_5H_4SiMe_3)_2Ti]$

[a] Matrix: 3-nitrobenzyl alcohol.

TABLE 5. Selected bond lengths (Å) and angles (°) for compound 1 [a]

Bond lengths	
Ti(1)–S(1)	2.438(2)
Ti(1)–S(2)	2.431(2)
Ti(1)–cp(1)	2.061(1)
Ti(1)–cp(2)	2.056(1)
S(1)–C(1)	1.756(5)
S(2)–C(7)	1.769(5)
Si(1)–C(17)	1.889(5)
Si(2)–C(22)	1.877(5)
Mean Si–C (methyl groups)	1.846
Mean C–C (cp rings)	1.402
Mean C–C (benzene rings)	1.367
Mean C–F (benzene rings)	1.346
Bond angles	
S(1)–Ti(1)–S(2)	100.6(1)
cp(1)–Ti(1)–cp(2)	134.3(1)
Ti(1)–S(1)–C(1)	116.2(2)
Ti(1)–S(2)–C(7)	119.6(2)
Mean C–C–C (cp rings)	108.0
Mean C–C–C (benzene rings)	120.0
Mean F–C–C/C–C–F (benzene rings)	119.4

[a] cp(1) and cp(2), centroid of the cyclopentadienyl rings.

troids of the two trimethylsilylcyclopentadienyl rings and the two thiolate sulphur atoms. The Ti–S(1) and Ti–S(2) distances are 2.438(2) and 2.431(2) Å, respectively. These are slightly bigger than those seen for compounds [(η^5-C_5H_5)$_2$Ti(SR)$_2$] [R = CH_3, C_2H_5, or C_6H_5)] [4,17,18].

The S(1)–Ti–S(2) angle of 100.6(1)° and the *endo* (*anti*) conformation are consistent with earlier discussions [3–5]. The parent compound [(η^5-$C_5H_4SiMe_3$)$_2$TiCl$_2$] [21] has a Cl(1)–Ti–Cl(2) angle of 91.63(0)°, smaller than that for compound **1** where the thiolate ligands are more sterically demanding. On the other hand, the centroid(1)–Ti–centroid(2) angle of complex **1**, 134.3(1)°, is bigger than in [(η^5-$C_5H_4SiMe_3$)$_2$TiCl$_2$]. (131.0°) [19]. The two cyclopentadienyl rings exhibit a "staggered" conformation as shown by a projection onto the plane formed by the titanium and the two sulphur atoms.

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