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Preparation of the compounds $(\mu\text{-O})[\mathrm{Ti}(\mathrm{C_5Me_5})\mathrm{R_2}]_2$ ($\mathrm{R = Me, CH_2Ph}$, or $\mathrm{CH_2SiMe_3}$) and the crystal structure of the derivative with $\mathrm{R = CH_2SiMe_3}$

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Abstract

The complex $(\mu\text{-O})[\mathrm{Ti}(\mathrm{C_5Me_5})\mathrm{Cl_2}]_2$ can be readily alkylated with organo-lithium or -magnesium reagents to give $(\mu\text{-O})[\mathrm{Ti}(\mathrm{C_5Me_5})\mathrm{R_2}]_2$ ($\mathrm{R = Me, Ch_2Ph}$, or $\mathrm{CH_2SiMe_3}$) compounds which have been characterized by analytical and spectroscopic methods and, in the case of $\mathrm{R = CH_2SiMe_3}$, by an X-ray diffraction study. Crystals are trigonal, space group $P\bar{3}C1$ (no. 165); the values of R and R_w were 0.063 and 0.086 respectively. The compound has a crowded structure with a Ti–O–Ti angle of 155.9(1)°, and possibly with Ti...H–C interactions.

Introduction

We recently reported the preparation of the μ-oxopentamethylcyclopentadienyl di- and tri-nuclear species (**2** and **3**) through controlled hydrolysis of the trimethyl derivative **1** according to the sequence shown in eq. 1, where $\mathrm{Cp}^\star = \mathrm{C_5Me_5}$ [1].

$$\underset{(\mathbf{1})}{\mathrm{Cp^\star TiMe_3}} \rightarrow \underset{(\mathbf{2})}{[\mathrm{Cp^\star TiMe_2}]_2(\mu\text{-O})} \rightarrow \underset{(\mathbf{3})}{[\mathrm{Cp^\star TiMe}(\mu\text{-O})]_3} \qquad (1)$$

However, this simple procedure does not work in the case of other trialkyl analogues $\mathrm{Cp^\star TiR_3}$ ($\mathrm{R = CH_2Ph}$ or $\mathrm{CH_2SiMe_3}$) [2]. Compounds **2** and **3** have an interesting chemistry, giving rise for example to μ-η^2-acetone complexes upon reaction with CO [3] or undergoing insertion of $\mathrm{Ph_2CN_2}$ to forming polynuclear η^2-benzopherone-methylhydrazonate(-1) complexes [4]. The possibility of extending these and similar studies to other oxoalkyls titanium prompted us to devise an alternative route to them. We describe here an alternative way of making **2**, the synthesis of the new dimers $[Cp^{\star}TiR_2]_2(\mu\text{-}O)$ (**5**, R = CH_2SiMe_3 and **6**, R = CH_2Ph), and the crystal structure of **5**.

Results and discussion

The obvious alternative starting product for the preparation of the μ-oxo dimer species is the chloro-derivative **4** [5], which is readily alkylated by organo-lithium or -magnesium derivatives to give **2**, **5** and **6** in high yield (eqs. 2 and 3):

$$\underset{(\mathbf{4})}{[Cp^{\star}TiCl_2]_2(\mu\text{-}O)} + 4RLi \rightarrow \underset{\substack{(\mathbf{2}:\ R = Me,\\ \mathbf{5}:\ R = CH_2SiMe_3)}}{[Cp^{\star}TiR_2]_2(\mu\text{-}O)} + 4LiCl \tag{2}$$

$$\underset{(\mathbf{4})}{[Cp^{\star}TiCl_2]_2(\mu\text{-}O)} + 2Mg(CH_2Ph)_2 \rightarrow \underset{(\mathbf{6})}{[Cp^{\star}Ti(CH_2Ph)_2]_2(\mu\text{-}O)} + 2MgCl_2 \tag{3}$$

All the compounds were characterized by elemental analysis and NMR spectroscopy (see Experimental section). The methylene protons of **5** and **6** give rise to AB doublets, a situation similar to that for $Cp^{\star}TiClR_2$ (R = CH_2Ph and CH_2SiMe_3) in which the methylene hydrogens are also diastereotopic [6]. Noteworthy is the high field shift of the signals from the CH_2 protons of **5**, which are centered at δ 0.03 and −0.64, compared with a value for $Cp^{\star}Ti(CH_2SiMe_3)_3$ (**7**) of δ 1.37, and for $Cp^{\star}TiCl(CH_2SiMe_3)_2$ (**8**) of 2.03 and 1.41. A shift to high field is also found for the CH_2 carbon signal in the ^{13}C NMR spectrum; cf. δ 49.0 vs. 84.4 in **7** and 90.0 in **8**. These features are indicative of agostic Ti...H–C interactions [7], as found in the trialkyl $Cp^{\star}Ti(CH_2Ph)_3$ [2,6], and because of this we undertook an X-ray diffraction study of **5**.

Final atomic coordinates and anisotropic thermal parameters for nonhydrogen atoms of **5** are presented in Table 1. Selected bond lengths and angles involving non-hydrogen atoms are listed in Table 2. The atom labeling scheme is shown in Fig. 1. The molecular structure consists of two identical $Cp^{\star}Ti(CH_2SiMe_3)_2$ fragments connected by an oxygen bridging atom situated on a twofold axis, leading to a mutual *trans* arrangement of the Cp* rings. The bulk of the two Cp* rings and the four CH_2SiMe_3 groups control the structural disposition of the latter in such a way that within each fragment the Ti–CH_2–$SiMe_3$ bonds are oriented in a clockwise manner when viewed from the Cp* centroid (see Fig. 2). The mutual *trans* arrangement of the fragments means that two of the $SiMe_3$ groups (Si(2)Me_3 and Si(2A)Me_3) point away from each other and from the oxygen atom while the other two (Si(1)Me_3 and Si(1A)Me_3) point towards each other and toward the central part of the molecule. In order to minimize the mutual repulsion between the latter two, the Ti(1)–O–Ti(1A) angle bends to 155.9(1)° but even with this distortion their methyl groups remain rather close to one another: the C(13)–C(13A) contact of 3.77(1) Å is somewhat shorter than the sum of the van der Waals radii of the methyl groups (4.0 Å) [8]. The value of 155.9(1)° for the Ti(1)–O–Ti(1A) angle is the smallest so far reported for an M_2O early transition metal complex, in which the linear arrangement favours the oxygen to metal back bonding [9]. Nevertheless, the Ti–O distance in **5** of 1.842(1) Å is still rather small when compared with values for other μ-O derivatives [10].

Table 1

Atomic coordinates for **5**, with thermal parameters as $U_{eq} = \frac{1}{3}\Sigma[U_{ij}a_i \times a_j \times a_i a_j \cos(a_i a_j)] \times 10^3$

Atom	x	y	z	U_{eq}
Ti(1)	0.3765(1)	0.0492(1)	0.1827(1)	34(1)
Si(1)	0.4868(1)	−0.0525(1)	0.1144(1)	54(1)
Si(2)	0.1823(1)	−0.0634(1)	0.1015(1)	54(1)
O(1)	0.3731(2)	0.0000(0)	0.2500(0)	39(1)
C(1)	0.4066(2)	−0.0174(2)	0.1246(2)	47(2)
C(2)	0.2442(2)	−0.0044(2)	0.1639(2)	44(2)
C(11)	0.5732(3)	0.0155(4)	0.0643(2)	83(3)
C(12)	0.4304(4)	−0.1638(4)	0.0856(3)	88(3)
C(13)	0.5408(4)	−0.0522(4)	0.1797(2)	78(3)
C(21)	0.072394)	−0.0807(5)	0.1067(4)	128(5)
C(22)	0.2275(5)	−0.0074(4)	0.0345(3)	117(4)
C(23)	0.1724(4)	−0.1700(3)	0.0938(3)	95(3)
C(14)	0.3915(2)	0.1871(2)	0.2004(2)	49(2)
C(141)	0.3297(3)	0.2002(3)	0.2351(2)	67(2)
C(15)	0.4656(2)	0.1878(2)	0.2196(2)	46(2)
C(151)	0.4986(3)	0.2025(3)	0.2772(2)	67(2)
C(16)	0.5083(2)	0.1794(2)	0.1726(2)	51(2)
C(161)	0.5934(3)	0.1838(3)	0.1736(2)	77(2)
C(17)	0.4607(3)	0.1759(2)	0.1244(2)	54(2)
C(171)	0.4903(4)	0.1777(3)	0.0663(2)	83(3)
C(18)	0.3890(2)	0.1801(2)	0.1421(2)	49(2)
C(181)	0.3268(4)	0.1889(3)	0.1060(2)	77(3)

Table 2

Selected bond distances (Å) and angles (°)

Ti(1)–O(1)	1.842(1)	Si(1)–C(1)	1.869(5)
Ti(1)–C(1)	2.093(4)	Si(1)–C(11)	1.873(5)
Ti(1)–C(2)	2.135(3)	Si(1)–C(12)	1.879(6)
Ti(1)–C(14)	2.409(4)	Si(1)–C(13)	1.857(6)
Ti(1)–C(15)	2.377(3)	Si(2)–C(2)	1.864(4)
Ti(1)–C(16)	2.384(3)	Si(2)–C(21)	1.859(8)
Ti(1)–C(17)	2.466(3)	Si(2)–C(22)	1.869(6)
Ti(1)–C(18)	2.468(4)	Si(2)–C(23)	1.855(7)
C(14)–C(15)	1.414(6)	C(15)–C(16)	1.427(6)
C(14)–C(18)	1.414(6)	C(16)–C(17)	1.433(6)
Ti(1)–Cp*[a]	2.159	C(17)–C(18)	1.404(7)
C(1)–Ti(1)–C(2)	98.6(1)	Ti(1)–C(1)–Si(1)	138.9(2)
O(1)–Ti(1)–C(2)	102.1(1)	Ti(1)–C(2)–Si(2)	130.4(2)
O(1)–Ti(1)–C(1)	105.8(1)	C(12)–Si(1)–C(13)	108.7(2)
Ti(1)–O(1)–Ti(1A)	155.9(1)	C(11)–Si(1)–C(13)	106.5(2)
C(1)–Si(1)–C(13)	112.5(2)	C(11)–Si(1)–C(12)	106.9(3)
C(1)–Si(1)–C(12)	108.4(2)	C(22)–Si(2)–C(23)	105.4(3)
C(1)–Si(1)–C(11)	113.3(2)	C(21)–Si(2)–C(23)	107.0(3)
C(2)–Si(2)–C(23)	113.2(2)	C(21)–Si(2)–C(22)	106.9(3)
C(2)–Si(2)–C(21)	109.2(3)	C(2)–Si(2)–C(22)	114.7(2)

[a] Cp* is the centroid of C_5Me_5 ring, Sym. (1A) $x - y,\ -y,\ -z + \frac{1}{2}$.

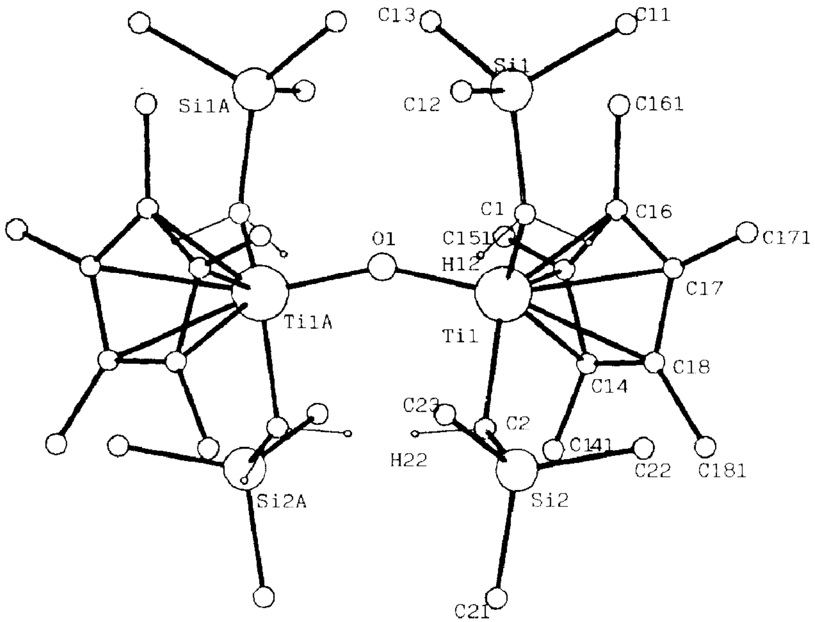

Fig. 1. View of the molecular structure of **5** with the atom numbering scheme.

The Cp*Ti(CH$_2$SiMe$_3$)$_2$(μ-O) fragments have the "three-legged piano stool" structure with Cp*-centroid–Ti–substituent angles between 111.4(1) and 114.4(1)° for the CH$_2$SiMe$_3$ groups and 121.41(5)° for O(1). The angles between the legs are 105.8(1)° for O(1)–Ti(1)–C(1), 102.1(1)° for O(1)–Ti(1)–C(2) and 98.6(1) for C(1)–Ti(1)–C(2).

The Ti–C(ring) distances show normal values for this type of compound [10] but the C$_5$Me$_5$ ring best plane is not perpendicular to the centroid–Ti axis, the mean

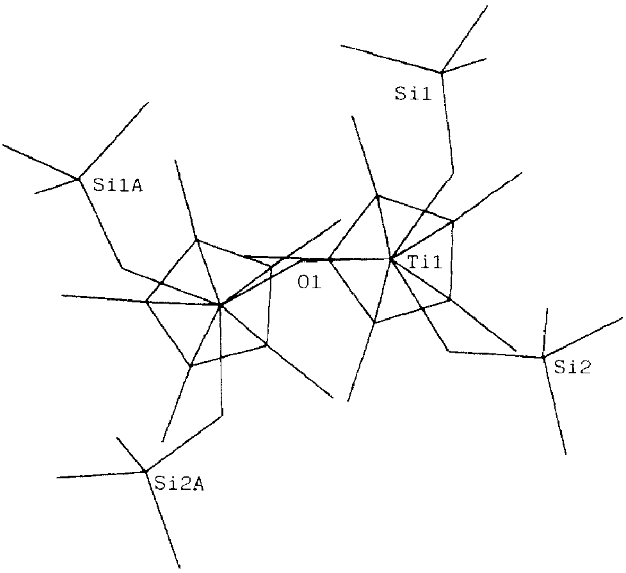

Fig. 2. Projection of the molecule of **5** on the Cp* plane.

value of the angles between this line and the normals to the plane being 3.03°. The reason for this is most probably again steric, and the Cp * rings are tilted in order to minimize repulsive interactions with some CH_2SiMe_3 methyls within the same fragment, especially with C(22); nevertheless, there is still a rather short contact between C(22) and C(181) [3.52(1) Å}.

The metal-trimethylsilylmethyl distances are also normal for Ti–alkyl bonds [10], Ti(1)–C(1) being somewhat shorter than Ti(1)–C(2). The former corresponds to the CH_2SiMe_3 groups that are pointing nearly towards one another, and the Ti–C–Si angles for them (138.8(2)°) are also higher than those for the other (130.4(2)°). An attempt was made to locate the methylenic hydrogen atoms in the difference Fourier map, and peaks at distances 2.422 and 2.489 Å from Ti(1) assigned to H(12) and H(22), respectively, were found. These Ti...H distances are of the same order as these in other Ti...H–C agostic systems studied by X-ray diffraction [2,11] and are also notably shorter than the distances to the other methylenic hydrogens in the molecule (from 2.525 to 2.686 Å). An agostic interaction thus seems to be present, probably favoured by steric effects.

Some signs of steric congestion are apparent between the two CH_2SiMe_3 groups bonded to the same atom: the contacts C(1)–Si(2) (3.754(4) Å) and C(1)–C(23) (3.79(1) Å) are somewhat short in terms of the van der Waals radii for CH_3 (2.0 Å) and Si (2.10 Å) [8,12].

Experimental

All manipulations were by conventional Schlenk techniques: Hexane was used freshly distilled from Na/K amalgam under N_2. ^1H NMR spectra were recorded on a Varian-FT 80A instrument and C, H analyses were performed with a Perkin–Elmer 240B microanalizer. $[Cp^*TiCl_2]_2(\mu\text{-}O)$ (**4**) was prepared as described elsewhere [5].

μ-Oxobis[pentamethylcyclopentadienyldimethyltitanium(IV)] (2)

3.1 ml of a 1.6 *M* ethereal solution of LiMe (4.96 mmol) diluted with 10 ml of diethyl ether was dropwise added to an ice-cooled suspension of 0.650 g (1.24 mmol) of **4** in 20 ml hexane. The yellow solution was allowed to warm to room temperature and then stirred for 5 h. It was slightly concentrated under reduced pressure, filtered, further concentrated, and cooled to −30°C to give **2** in 95% yield. Elemental analysis: Found: C, 65.30; H, 9.69. $C_{24}H_{42}OTi_2$ calcd.: C, 65.16; H, 9.57%. ^1H NMR (C_6D_6): δ (ppm) 1.91 (s, 30H, Cp *) and 0.66 (s, 12H,TiMe). ^{13}C NMR (gated decoupled; C_6D_6): δ (ppm) 122.1 (s, C_5Me_5), 52.4 (q, ^1J(CH) 121 Hz, TiMe) and 11.9 (q, ^1J(CH) 127 Hz, $C_5\mathit{Me}_5$).

μ-Oxobis[pentamethylcyclopentadienylbistrimethylsilylmethyltitanium(IV)] (5)

A mixture of 0.800 g (1.52 mmol) of **4** and 0.572 g (6.08 mmol) of $LiCH_2SiMe_3$ in 40 ml hexane was stirred at room temperature for 5 h and then filtered. The filtrate was concentrated under reduced pressure and cooled to −30°C to give yellow **5** in 90–95% yield. Elemental analysis: Found: C, 59.22; H, 10.80. $C_{36}H_{74}OSi_4Ti_2$ calcd.: C, 59.14; H, 10.20%. ^1H NMR ($CDCl_3$): δ (ppm) 1.94 (s, 30H, Cp *), 0.05 (s, 36H, $SiMe_3$), 0.03 (d, ^2J(HH) 12 Hz, 4H, CH_2) and −0.64 (d, ^2J(HH) 12 Hz, 4H, CH_2). ^{13}C NMR (gated decoupled, $CDCl_3$);δ (ppm) 118.0 (s,

$C_5\mathrm{Me}_5$), 49.0 (t, $^1J(\mathrm{CHa}) = {}^1J(\mathrm{CHb}) = 108$ Hz CH_2), 12.1 (q, $^1J(\mathrm{CH})$126 Hz, C_5Me_5) and 3.1 (q, $^1J(\mathrm{CH})$ 117 Hz, SiMe_3).

μ-Oxobis[pentamethylcyclopentadienyldibenzyltitanium(IV)] (6)

This complex was prepared as **5** from 0.650 g (1.24 mmol) of **4** and 0.870 g (2.48 mmol) $\mathrm{Mg(CH_2Ph)_2(THF)_2}$ in 30 ml hexane with stirring overnight. The yield of red **6** was ca. 85%. Elemental analysis: Found: C, 77.22; H, 7.80. $\mathrm{C_{48}H_{58}OTi_2}$ calcd.: C, 77.2; H, 7.83%. ^{1}H NMR ($\mathrm{C_6D_6}$): δ (ppm) 7.13–6.85 (m, Ph), 2.75 (d, ^2J(HH) 10 Hz, 4H, $\mathrm{CH_2}$), 2.41 (d, ^2J(HH) 10 Hz, 4 H, $\mathrm{CH_2}$) and 1.83, s, 30H, Cp*).

Crytal structure of complex 5

$\mathrm{C_{36}H_{74}OSi_4Ti_2}$, $M = 731.12$, trigonal, space $P\bar{3}C1$, no. 165, a 18.095(3), c 24.20(1) Å, V 68.63 Å^3, $D_{\mathrm{calcd}} = 1.06$ g cm^{-3} for $Z = 6$, $F(000) = 2388$, Mo-K_α radiation (λ 0.7107 Å), μ(Mo-K_α) 4.70 cm^{-1}.

A yellow crystal was mounted on a Enraf–Nonius four circle diffractometer with graphite monochromated Mo-K_α radiation; lattice parameters were determined by least squares refinement of values for 25 reflections. Reflections were recorded by the $\omega/2\theta$ scan technique in the range ($2 < \theta < 27°$) and h 0 to 23, k 0 to 23, and l -30 to 30.

Two standard reflections ($\bar{6}$ 3 1) and 3 $\bar{6}$ $\bar{1}$) were measured after every 100 reflections and showed no significant change. A total of 9395 unique reflections were collected, but only 5651 were considered observed (with $I > 3\sigma(I)$) and used in further calculations. Intensities were corrected for Lorentz and polarization effects in the usual way. The structure was solved by a combination of heavy atom direct methods and Fourier synthesis.

The structure was refined on F by full matrix least-squares calculations. Before refinement of all the non-hydrogen atoms anositropically an empirical absorption correction was made by the Walker and Stuart method [13]. In the later stages of refinement the difference synthesis map revealed most of the hydrogen atoms of the molecule, but finally we decided to place all the hydrogen atom of the methyl groups at calculated positions and take only the position of the H atoms of the $\mathrm{CH_2}$ groups from the Fourier difference synthesis map, and to include them all at fixed positions and with the temperature factors of the atoms to which they were attached.

Final R values of $R = 0.063$ and $R_w = 0.088$ (weighting scheme, empirical fit as to give no trends in $\langle W\Delta^2F\rangle$ vs. $\langle |F_o| \rangle$ and vs. $\langle \sin\theta/\lambda \rangle$, were obtained. Anomalous dispersion corrections and atomic scattering factors were taken from ref. 14. Calculations were performed with X-ray system 80 [15], DIRDIF [16], PARST [17] and PESOS [18] on a VAX 11750 computer.

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