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The Crystal and Molecular Structure of Bis(η^5-trimethylsilylcyclopentadienyl)titanium(IV) Dichloride, Ti(η^5-$C_5H_4SiMe_3$)$_2$Cl$_2$

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Summary. The crystal and molecular structure of the titanocene complex Ti(η^5-$C_5H_4SiMe_3$)$_2$Cl$_2$ has been determined by X-ray diffraction studies. The compound crystallizes in the triclinic crystal system [$a = 6.747(8)$, $b = 12.815(2)$, $c = 12.928(4)$ Å and $\alpha = 67.16(2)$, $\beta = 82.29(5)$, $\gamma = 74.83(4)°$] in the space group $P\bar{1}$ with 2 formula units in the unit cell. The coordination about the titanium atom formed by the two chlorine atoms and the centroids of the cyclopentadienyl rings is that of a distorted tetrahedron. The Cl – Ti – Cl angle is 91.63° while the (centroid) – Ti – (centroid) angle is 131.02°.

Keywords. Ring substituted titanocenes; Molecular structure; X-ray analysis.

Die Kristall- und Molekülstruktur von Bis(η^5-trimethylsilylcyclopentadienyl)titan(IV)dichlorid, Ti(η^5-$C_5H_4SiMe_3$)$_2$Cl$_2$

Zusammenfassung. Die Kristall- und Molekülstruktur des Titanocen-Komplexes Ti(η^5-$C_5H_4SiMe_3$)$_2$Cl$_2$ wurde durch eine Röntgenstrukturanalyse bestimmt. Die Verbindung kristallisiert im triklinen Kristallsystem [$a = 6.747(8)$, $b = 12.815(2)$, $c = 12.928(4)$ Å und $\alpha = 67.16(2)$, $\beta = 82.29(5)$, $\gamma = 74.83(4)°$] in der Raumgruppe $P\bar{1}$ mit 2 Formeleinheiten pro Elementarzelle. Das Titanatom ist von zwei Chloratomen und den Centroiden der Cyclopentadienylringe umgeben, wobei die Koordination des Titanatoms verzerrt tetraedrisch ist. Die Winkel Cl – Ti – Cl und (Centroid) – Ti – (Centroid) betragen 91.63° bzw. 131.02°.

Introduction

The comparison of the structure of the parent compound Ti(η^5-C_5H_5)$_2$Cl$_2$ with that of Ti(η^5-$C_5H_4CH_3$)$_2$Cl$_2$ demonstrates that the substitution of the H atom by a CH_3 group on each cyclopentadienyl (*Cp*) ring has a negligible effect on the basic molecular configuration. Specifically, the corresponding bond distances and angles differ by less than 0.01 Å and 1.3°, respectively [1, 2]. On the contrary, when the cyclopentadienyl rings are linked together by a methylene or dimethylsilyl bridge, as in the complexes Ti[(η^5-C_5H_4)$_2$CH$_2$]Cl$_2$ [3] and Ti[(η^5-C_5H_4)$_2$SiMe_2]Cl$_2$ [4, 5], an essential alteration in the degree of canting of the rings is produced. Moreover, the two cyclopentadienyl rings in these compounds are not planar any more.

In order to study further the effect on the titanium environment of incorporating substituents bulkier than methyl groups in each of the cyclopentadienyl ligands, we have undertaken an X-ray structure determination on the silylated titanocene dihalide $Ti(\eta^5\text{-}C_5H_4SiMe_3)_2Cl_2$. Another reason for this structural investigation was the confirmation of our earlier conclusions about the structure of the title and similar complexes, derived from ^1H NMR studies [6].

Experimental

The title compound has been prepared by metallation of $Me_3SiC_5H_5$ with *n-Bu*Li followed by reaction with $TiCl_4$ in *THF* [6]. After recrystallisation from $CHCl_3$ copper-brown crystals were obtained. The air-stable compound melts at 189 to 191°C and its molecular weight (392), determined by mass spectroscopy, corresponds to the formula $C_{16}H_{26}Cl_2Si_2Ti$. The ^1H NMR spectrum ($CDCl_3$) shows two pseudo-triplets at $\delta = 6.81$ and 6.56 ppm (C_5H_4) and a singlet at $\delta = 0.30$ ppm [$Si(CH_3)_3$].

X-Ray Structure Analysis (**1**)

Crystal dimensions $0.15 \times 0.30 \times 0.45$ mm, triclinic, space group $P\bar{1}$, $a = 6.747(8)$, $b = 12.815$ (2), $c = 12.928(4)$ Å; $\alpha = 67.16(2)$, $\beta = 82.29(5)$, $\gamma = 74.83(4)°$, $V = 993.6(12)$ Å^3, $Z = 2$, $D = 1.31$ g/cm^3, $\lambda(MoK\alpha) = 0.71069$ A, $\mu = 8.21$ cm^{-1}, $F(000) = 412$, room temperature. Enraf-Nonius CAD-4 diffractometer, 25 reflections with $7 < \theta < 12°$ used for determining lattice parameters, data collected using ω-2θ scans up to $2\theta = 50°$, one standard reflection monitored after every 50 measurements showed no significant deviation from its mean intensity, absorption correction applied, 2821 unique reflections measured of which 2810 with $I > 2.5\sigma(I)$ were considered "observed" and used in refinement, range of *hkl*: $-7 \leqslant h \leqslant 8$, $-13 \leqslant k \leqslant 15$, $0 \leqslant l \leqslant 15$.

The structure was solved by means of direct methods (SHELXS 86) [7] and refined by the full-matrix least squares technique (SHELX 76) [8]. Final $R = 0.031$, $R_w = 0.036$, $\Sigma w(\Delta F)^2$ minimized, reflection weights were $[\sigma^2(F) + 0.00124F^2]^{-1}$, goodness-of-fit parameter 1.15, $(\Delta/\sigma)_{max} = 0.69$, max. and min. electron densities in final difference synthesis 0.38 and -0.29 eÅ^{-3}, respectively. Atomic scattering factors from SHELX 76, non-H atoms refined with anisotropic temperature factors, H atoms constrained to idealized positions using $C-H = 1.08$ Å with fixed overall isotropic temperature factors. Computer programs used: SHELXS 86, SHELX 76, XANADU [9], PARST [10], PLUTO [11].

Results and Discussion

The molecular structure of $Ti(\eta^5\text{-}C_5H_4SiMe_3)_2Cl_2$ (**1**) with the atomic numbering is shown in Fig. 1. The positional parameters and the equivalent isotropic temperature factors for the heavy atoms are given in Table 1. Important bond lengths and angles are illustrated in Tables 2 and 3. The molecular parameters about the Ti-atom for $Ti(\eta^5\text{-}C_5H_4SiMe_3)_2Cl_2$ are comparable to those reported for $Ti(\eta^5\text{-}C_5H_4CH_3)_2Cl_2$ (**2**) and other similar titanocene dichlorides characterized by a pseudo-tetrahedral ligand arrangement about the Ti-atom (Table 4).

The Ti – Cl distance in complex **1** is practically identical with that found in the parent compound $Ti(\eta^5\text{-}C_5H_5)_2Cl_2$ (**3**) and the Si-bridged derivative $Ti[(\eta^5\text{-}C_5H_4)_2SiMe_2]Cl_2$ (**4**). The Cl – Ti – Cl bond angle of 91.63° is slightly smaller than the corresponding angle in the methyl substituted compound **2**. The differences to the complexes **3** and **4**, observed also in analogous zirconocene complexes [12], are not significant.

Similarly, the Ti – Cp(centroid) distances and *Cp* – Ti – *Cp* angles are essentially the same for the complexes **1**–**4**. The smallest value of the *Cp* – Ti – *Cp* angle for the complex **4** is expected because of the canting of the rings linked by the dimethylsilyl bridge.

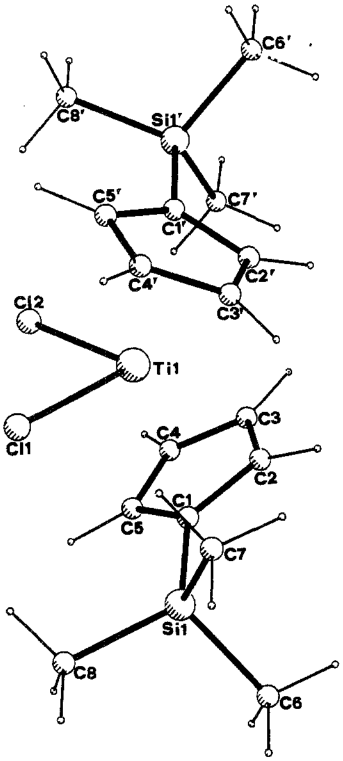

Fig. 1. The molecular structure of Ti(η^5-$C_5H_4SiMe_3$)$_2$$Cl_2$ with the atom numbering scheme

Table 1. Atomic positional parameters ($\cdot 10^4$) and equivalent isotropic temperature factors (Å^2) with e.s.d.'s in parentheses. $B_{eq} = (4/3)\Sigma_i \Sigma_j \beta_{ij} a_i \cdot a_j$

	X	Y	Z	B_{eq}
Ti	1 397 (1)	2 319 (0)	2 496 (0)	2.35 (1)
Cl (1)	−924 (1)	1 081 (1)	3 228 (1)	3.63 (2)
Cl (2)	−1 306 (1)	3 959 (1)	1 739 (1)	3.84 (2)
Si (1)	2 925 (1)	−663 (1)	2 164 (1)	3.55 (2)
Si (1′)	1 923 (1)	5 122 (1)	2 802 (1)	3.37 (3)
C (1)	2 866 (4)	934 (2)	1 604 (2)	2.95 (8)
C (2)	4 439 (4)	1 420 (2)	1 724 (2)	3.41 (9)
C (3)	4 011 (5)	2 626 (3)	1 069 (3)	4.04 (10)
C (4)	2 180 (5)	2 893 (2)	519 (2)	4.20 (11)
C (5)	1 459 (5)	1 874 (2)	861 (2)	3.56 (9)
C (6)	4 970 (6)	−1 316 (3)	1 320 (3)	5.52 (12)
C (7)	3 648 (6)	−1 346 (3)	3 659 (3)	5.25 (12)
C (8)	437 (6)	−907 (3)	1 940 (4)	6.50 (17)
C (1′)	2 126 (4)	3 513 (2)	3 379 (2)	2.78 (8)
C (2′)	3 946 (4)	2 674 (2)	3 338 (2)	3.10 (8)
C (3′)	3 636 (5)	1 563 (2)	3 995 (2)	3.70 (9)
C (4′)	1 658 (5)	1 692 (2)	4 486 (2)	3.88 (9)
C (5′)	690 (4)	2 883 (2)	4 089 (2)	3.36 (8)
C (6′)	3 670 (6)	5 323 (3)	3 673 (3)	5.90 (15)
C (7′)	2 875 (5)	5 638 (3)	1 316 (3)	4.66 (11)
C (8′)	−758 (5)	5 897 (3)	2 982 (4)	6.09 (14)

Table 2. Bond distances (Å) in $Ti(\eta^5\text{-}C_5H_4SiMe_3)_2Cl_2$

Ti Environment		C−C Distances in the cyclopentadienyl rings		Si Environment	
Bond	Distance	Bond	Distance	Bond	Distance
Ti−Cl(1)	2.367(1)	Ring 1 C(1)−C(2)	1.415(4)	Si(1)−C(1)	1.879(2)
−Cl(2)	2.362(1)	C(2)−C(3)	1.416(4)	Si(1)−C(6)	1.870(3)
−C(1)	2.413(2)	C(3)−C(4)	1.405(4)	Si(1)−C(7)	1.859(3)
−C(2)	2.375(3)	C(4)−C(5)	1.401(4)	Si(1)−C(8)	1.864(3)
−C(3)	2.365(3)	C(5)−C(1)	1.423(4)		
−C(4)	2.395(3)				
−C(5)	2.387(3)				
−C(1′)	2.406(2)	Ring 1′ C(1′)−C(2′)	1.416(3)	Si(1′)−C(1′)	1.874(2)
−C(2′)	2.376(2)	C(2′)−C(3′)	1.401(4)	Si(1′)−C(6′)	1.861(3)
−C(3′)	2.353(3)	C(3′)−C(4′)	1.397(4)	Si(1′)−C(7′)	1.857(3)
−C(4′)	2.395(3)	C(4′)−C(5′)	1.407(4)	Si(1′)−C(8′)	1.854(3)
−C(5′)	2.388(3)	C(5′)−C(1′)	1.424(4)		
Aver. Ti−Cl	2.365	Ring 1, mean C−C	1.412		
Aver. Ti−C	2.385	Ring 1′, mean C−C	1.409		
Ti−Cp	2.063				
Ti−Cp′	2.061				
Aver. Ti−Cp	2.062				

Table 3. Bond angles (°) in Ti $(\eta^5\text{-}C_5H_4SiMe_3)_2Cl_2$

Around the Ti tetrahedron		On the cyclopentadienyl rings		Around the Si tetrahedron	
Bonds	Angle	Bonds	Angle	Bonds	Angle
Cl(1)−Ti−Cl(2)	91.63(0)	Ring 1′ C(5)−C(1)−C(2)	105.7(2)	C(1)−Si(1)−C(6)	106.4(1)
Cl(2)−Ti−Cp	106.61	C(1)−C(2)−C(3)	109.4(2)	C(1)−Si(1)−C(7)	110.4(1)
Cp−Ti−Cp′	131.02	C(2)−C(3)−C(4)	107.3(2)	C(1)−Si(1)−C(8)	110.7(1)
Cl(1)−Ti−Cp	107.04	C(3)−C(4)−C(5)	108.1(2)	C(6)−Si(1)−C(7)	108.4(2)
Cl(1)−Ti−Cp′	106.23	C(4)−C(5)−C(1)	109.5(3)	C(6)−Si(1)−C(8)	107.8(2)
Cl(2)−Ti−Cp′	107.29	Average C−C−C	108.0	C(7)−Si(1)−C(8)	113.0(2)
		Ring 1′ C(5′)−C(1′)−C(2′)	106.3(2)	C(1′)−Si(1′)−C(6′)	104.0(1)
		C(1′)−C(2′)−C(3′)	109.1(2)	C(1′)−Si(1′)−C(7′)	111.4(1)
		C(2′)−C(3′)−C(4′)	108.0(2)	C(1′)−Si(1′)−C(8′)	110.0(1)
		C(3′)−C(4′)−C(5′)	108.3(2)	C(6′)−Si(1′)−C(7′)	108.6(2)
		C(4′)−C(5′)−C(1′)	108.3(2)	C(6′)−Si(1′)−C(8′)	110.6(2)
		Average C−C−C	108.0	C(7′)−Si(1′)−C(8′)	112.0(2)

Table 4. Comparison of structural parameters (averaged values) for the complexes **1–4**

Formula		Ti−Cl	Cl−Ti−Cl	Ti−*Cp*	*Cp*−Ti−*Cp*	*Cp*−Ti−Cl
$Ti(\eta^5\text{-}C_5H_4SiMe_3)_2Cl_2$	**(1)**	2.365	91.63	2.062	131.02	106.79
$Ti(\eta^5\text{-}C_5H_4CH_3)_2Cl_2$	**(2)**	2.361	93.15	2.067	130.2	106.8
$Ti(\eta^5\text{-}C_5H_5)_2Cl_2$	**(3)**	2.364	94.53	2.059	130.97	106.40
$Ti(\eta^5\text{-}C_5H_4)_2SiMe_2]Cl_2$	**(4)**	2.361	95.8	2.078	128.9	

An examination of the structural parameters associated with the cyclopentadienyl rings indicates that the Me_3Si-substitution has not introduced any distinct structural alterations. The differences in C − C bond lengths and C − C − C angles (Tables 2 and 3) are not significant and the least-squares plane calculations show that the two cyclopentadienyl rings are planar to within 0.011 and 0.017 Å. The angle between the normals to planes is 50.55°.

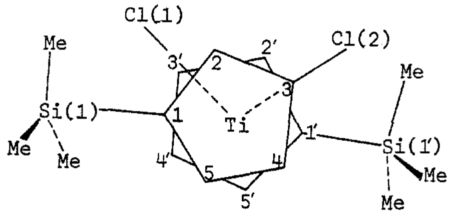

Fig. 2. Representation of the structure of $Ti(\eta^5\text{-}C_5H_4SiMe_3)_2Cl_2$ in projection down the line through the *Cp*-ring centroids

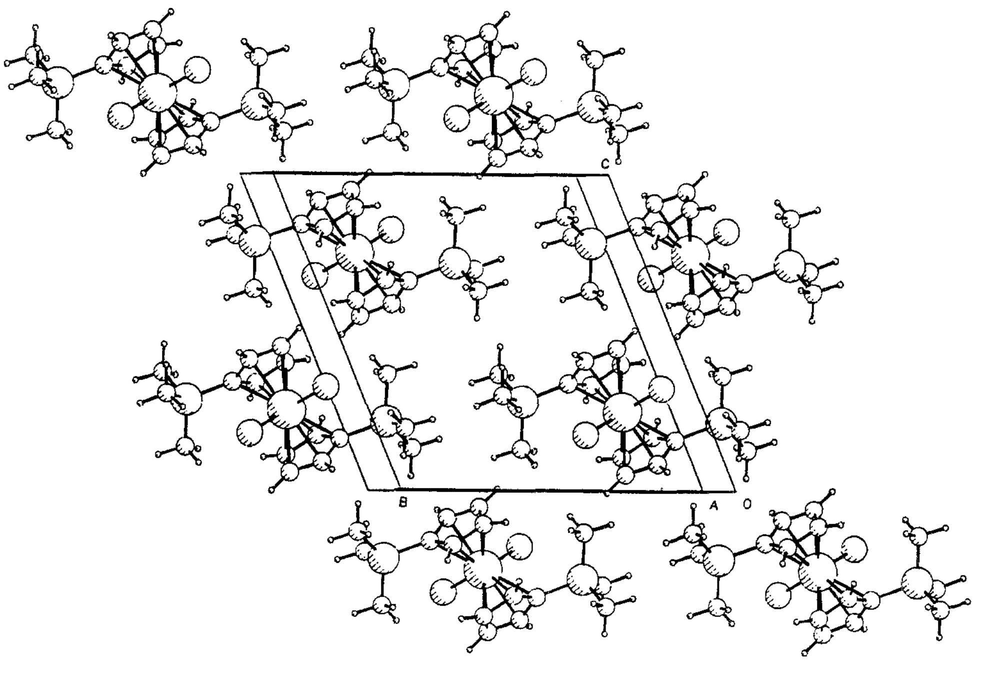

Fig. 3. Drawing of the packing of $Ti(\eta^5\text{-}C_5H_4SiMe_3)_2Cl_2$

The Me_3Si-substituents in the title compound are opposite to each other and the two *Cp*-rings have a "staggered" conformation, as indicated by a projection down the line through their centroids (Fig. 2). The rings are "staggered" also in the zirconocene analogue $Zr(\eta^5\text{-}C_5H_4SiMe_3)_2Cl_2$ [12]. The Si–C bond lengths range from 1.854 to 1.879 Å and the average value of 1.860 Å is very close to that given for related compounds [4, 5, 13]. The coordination about the silicon atom is that of a slightly distorted tetrahedron.

The crystalline arrangement of the two $Ti(\eta^5\text{-}C_5H_4SiMe_3)_2Cl_2$ molecules in the triclinic unit cell of $P\bar{1}$ symmetry is shown in Fig. 3.

The results of our X-ray study for the complex **1** are in complete agreement with our earlier assumption (arising from ^1H NMR studies [6]), that no significant change occurs in the basic molecular configuration, even if a voluminous group, like Me_3Si, is introduced in each cyclopentadienyl ring.

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