

# Preparation and characterization of $(C_5Me_4Ph)TiCl_3$ , the oxochloride complexes $[(C_5Me_4Ph)TiCl_2]_2(\mu-O)$ and $[(C_5Me_4Ph)TiCl(\mu-O)]_3$ and the oxo-complex $[(C_5Me_4Ph)Ti]_4(\mu-O)_6$ . The X-ray crystal structures of $[(C_5Me_4Ph)TiCl_2]_2(\mu-O)$ and $[(C_5Me_4Ph)Ti]_4(\mu-O)_6$

Mar Björgvinsson<sup>a,\*</sup>, Snorri Halldorsson<sup>a</sup>, Ingvar Arnason<sup>a</sup>, Jörg Magull<sup>b,1</sup>, Dieter Fenske<sup>b</sup>

<sup>a</sup> Science Institute, University of Iceland, Dunhaga 3, 107 Reykjavík, Iceland

<sup>b</sup> Institut für Anorganische Chemie der Universität Karlsruhe, Engesserstraße, D-76128 Karlsruhe, Germany

Received 7 February 1997; revised 12 May 1997

## Abstract

The titanium compound  $(C_5Me_4Ph)TiCl_3$  (**1**) can be prepared by the reaction of  $(C_5Me_4Ph)SiMe_3$  with  $TiCl_4$ . Hydrolysis of **1** in the presence of  $HNEt_2$  or  $Ag_2O$  has allowed for the isolation of the oxochloride complexes  $[(C_5Me_4Ph)TiCl_2]_2(\mu-O)$  (**2**) and  $[(C_5Me_4Ph)TiCl(\mu-O)]_3$  (**3**), respectively. The NMR spectra of **3** are consistent with a nearly flat  $Ti_3O_3$  ring having down-up-up or E-Z-Z arrangement of  $(C_5Me_4Ph)$ -ligands around the ring. The X-ray crystal structure of **2** (monoclinic, space group  $C2/c$ ,  $a = 19.847(12)$ ,  $b = 9.089(5)$ ,  $c = 20.405(13)$  Å,  $\beta = 124.06(5)^\circ$ ) consists of *trans*  $[(C_5Me_4Ph)TiCl_2]_2(\mu-O)$  molecules of  $C_2$  symmetry with nearly linear Ti–O–Ti units ( $169.3(2)^\circ$ ). Reaction of **1** with an excess of  $H_2O/HNEt_2$  results in the formation of the oxo-complex  $[(C_5Me_4Ph)Ti]_4(\mu-O)_6$  (**4**). The X-ray crystal structure of **4** (triclinic, space group  $P\bar{1}$ ,  $a = 11.861(5)$ ,  $b = 12.706(5)$ ,  $c = 18.218(8)$  Å,  $\alpha = 87.58(3)^\circ$ ,  $\beta = 89.00(3)^\circ$ ,  $\gamma = 86.60(3)^\circ$ ) reveals that the molecules of **4** have an adamantane-like  $Ti_4O_6$  cage of nearly  $T_d$  symmetry. The NMR spectra and molecular structures of **1**, **2**, **3** and **4** are discussed. © 1997 Elsevier Science S.A.

**Keywords:** Phenyltetramethylcyclopentadiene;  $C_5Me_4Ph$  ligand;  $(\eta^5$ -cyclopentadienyl)titanium; Oxochloride complexes;  $Ti_4O_6$  cage; X-ray structure

## 1. Introduction

The moisture sensitive mono-(cyclopentadienyl)titanium trichloride,  $CpTiCl_3$  ( $Cp = \eta^5-C_5H_5$ ), was first described in a patent more than 40 years ago [1]. The hydrolysis of  $CpTiCl_3$  is complex [2] but by controlled hydrolysis the oxochloride  $[CpTiCl_2]_2(\mu-O)$  [3,4] and the cyclic tetramer  $[CpTiCl(\mu-O)]_4$  [5,6] have been isolated and structurally characterized. Full hydrolysis of  $CpTiCl_3$  results in formation of a  $(CpTi)_2O_3$  polymer [2,7,8].

When the more bulky  $Cp^*$  ligand ( $Cp^* = \eta^5-C_5Me_5$ ) is bonded to titanium, full hydrolysis of  $Cp^*TiCl_3$  results in formation of an adamantane-like cage  $(Cp^*Ti)_4O_6$  [9]. The intermediate oxochloride

$[Cp^*TiCl_2]_2(\mu-O)$  is formed by controlled hydrolysis of  $Cp^*TiCl_3$  and further hydrolysis results in the cyclic trimer  $[Cp^*TiCl(\mu-O)]_3$  but not a cyclic tetramer [10]. However, the formation of  $(Cp^*Ti)_4O_6$  can be rationalized by the intermediate oxochloride complexes  $(Cp^*TiCl_2)_2O$ ,  $(Cp^*TiClO)_4$  and  $(Cp^*Ti)_4O_5Cl_2$  in the hydrolysis of  $Cp^*TiCl_3$  [10]. The ‘missing’ oxochloride intermediates in the hydrolysis, the bicyclo  $(Cp^*Ti)_4O_5Cl_2$  and the cyclic tetramer  $[Cp^*TiCl(\mu-O)]_4$ , are formed by retrohydrolysis when  $(Cp^*Ti)_4O_6$  is allowed to react with  $TiCl_4$  [10]. Recently the bicyclo  $(Cp^*Ti)_4O_5Cl_2$ , could be prepared in good yields, by heating  $[(Cp^*Ti)_3Cl_2(NMe_2)](\mu-O)_3$  in an autoclave, and subsequently its methyl analogue,  $(Cp^*Ti)_4O_5Me_2$ , synthesized and structurally characterized by X-ray crystallography [11]. Hydrolysis of  $Cp^*TiMe_3$  follows the same course as  $Cp^*TiCl_3$  with subsequent formation of  $[Cp^*TiMe_2]_2(\mu-O)$ ,  $[Cp^*TiMe(\mu-O)]_3$  and finally  $(Cp^*Ti)_4O_6$  [12,13]. However, the cyclic tetramer,

\* Corresponding author.

<sup>1</sup> Author for crystal structure enquiry.

$[\text{Cp}^* \text{TiBr}(\mu\text{-O})]_4$  [14], and trimer,  $[\text{Cp}^* \text{TiBr}(\mu\text{-O})]_3$  [15], are formed in the hydrolysis of  $\text{Cp}^* \text{TiBr}_3$ , depending on the conditions used. It is therefore evident that subtle factors effect the stability and chemistry of species formed by hydrolysis of mono(cyclopentadienyl)titanium complexes.

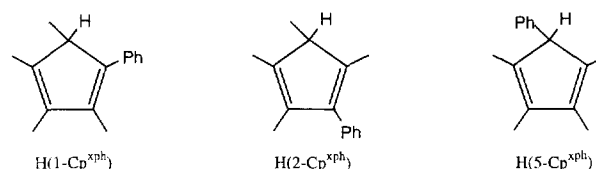
In order to extend the series of mono(cyclopentadienyl)titanium oxochloro complexes we report here the synthesis and characterization of the new compound mono(phenyltetramethylcyclopentadienyl)titanium trichloride  $\text{Cp}^{\text{xph}} \text{TiCl}_3$  (**1**,  $\text{Cp}^{\text{xph}} = \eta^5\text{-C}_5\text{Me}_4\text{Ph}$ ) and its oxochloro and oxo derivatives  $[\text{Cp}^{\text{xph}} \text{TiCl}_2]_2(\mu\text{-O})$  (**2**),  $[\text{Cp}^{\text{xph}} \text{TiCl}(\mu\text{-O})]_3$  (**3**) and  $(\text{Cp}^{\text{xph}} \text{Ti})_4(\mu\text{-O})_6$  (**4**). Threlkel and Bercaw [16] have previously prepared the dichloro titanocene complex  $(\text{Cp}^{\text{xph}})_2 \text{TiCl}_2$  containing a  $\eta^5\text{-C}_5\text{Me}_4\text{Ph}$  ligand bonded to titanium and during the course of this work we learned of the synthesis of series of titanocene(III) complexes  $(\text{Cp}^{\text{xph}})_2 \text{TiX}$  ( $\text{X} = \text{Cl}, \text{Me}, \text{H}$ ) by de Wolf et al. [17].

## 2. Results and discussion

### 2.1. Synthetic results

#### 2.1.1. $\text{Cp}^{\text{xph}} \text{TiCl}_3$ (**1**)

The phenyltetramethylcyclopentadiene  $\text{HCp}^{\text{xph}}$  was prepared by a similar method as used by Fischer et al. [18] except that  $\text{PhLi}$ , instead of  $\text{PhMgBr}$ , was allowed to react with 2,3,4,5-tetramethylcyclopenta-2-enone. A mixture of three isomers of  $\text{HCp}^{\text{xph}}$

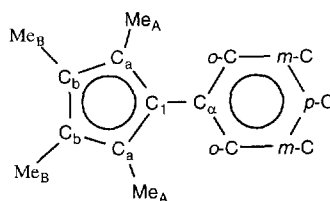


was formed in the synthesis but each isomer in the mixture could easily be identified by  $^1\text{H}$  NMR spec-

Table 1  
Proton and carbon-13 chemical shifts of **1**, **2**, **3** and **4**

$^{13}\text{C}$ -NMR <sup>a,b</sup>	$\text{Cp}^{\text{xph}} \text{TiCl}_3$ <b>1</b>	$[\text{Cp}^{\text{xph}} \text{TiCl}_2]_2 \text{O}$ <b>2</b>	$\text{E-Z-Z} - [\text{Cp}^{\text{xph}} \text{TiOCl}]_3$ <sup>c</sup> <b>3</b>			$(\text{Cp}^{\text{xph}} \text{Ti})_4 \text{O}_6$ <b>4</b>
			E(1)	Z-Z(2)	Ratio	
$\text{C}_5\text{Me}_4$	142.91	138.37	134.11	134.34	1:2	135.90
$\text{C}_1$						122.90
$\text{C}_a/\text{C}_{a'}$	138.77	134.81	130.38/129.36/129.08 129.08/128.81/127.89		1:1:(1:1):1:1	
$\text{C}_b/\text{C}_{b'}$	136.16	133.36				122.33
$\text{Me}_A/\text{Me}_{A'}$	15.50	14.61	13.27	13.48/13.48	1:(1:1)	12.22
$\text{Me}_B/\text{Me}_{B'}$	14.61	13.42	12.05	12.21/12.18	1:1:1	11.27
$\text{C}_6\text{H}_5$						
$\text{C}_\alpha$	132.94	133.32	132.56	132.16	1:2	126.08
o-C	130.34	130.46	130.46	130.57	1:2	130.80
m-C	128.31	128.12	127.84	127.95	1:2	127.59
p-C	128.61	127.92	127.08	127.08	(1:2)	127.50
$^1\text{H}$ -NMR <sup>a,b,d</sup>						
$\text{C}_5\text{Me}_4$						
$\text{Me}_A$	2.48	2.37	2.23/2.17/2.16/2.06/2.04/1.98		1:1:1:1:1	1.93
$\text{Me}_B$	2.44	2.34				1.88

<sup>a</sup> All spectra were measured at 25°C in  $\text{CDCl}_3$ . Atom labelling for the  $\text{Cp}^{\text{xph}}$ -ligand



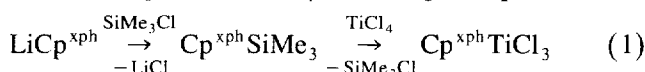
<sup>b</sup> The  $\text{Me}_A$  groups are tentatively assigned to be more deshielded than the  $\text{Me}_B$  groups ( $^1\text{H}$  and  $^{13}\text{C}$  NMR) and  $\text{C}_a$  more deshielded than  $\text{C}_b$ .

<sup>c</sup> Ratio of unresolved NMR resonances are in parenthesis.

<sup>d</sup> The  $^1\text{H}$ -NMR resonances for the phenyl groups come as complex multiplets in the range 7.2–7.4 ppm for **2**, **3** and **4**. The phenyl resonances of **1** could be fitted to a  $\text{AA}'\text{BB}'\text{C}$  spin system with  $\delta\text{H}_o = 7.37$ ,  $\delta\text{H}_m = 7.46$ ,  $\delta\text{H}_p = 7.40$  ppm and  $J(\text{H}_o - \text{H}_{o'}) = 1.91$ ,  $J(\text{H}_o - \text{H}_m) = 7.74$ ,  $213J(\text{H}_o - \text{H}_{m'}) = 0.59$ ,  $J(\text{H}_o - \text{H}_p) = 1.23$ ,  $J(\text{H}_m - \text{H}_{m'}) = 1.47$ ,  $J(\text{H}_m - \text{H}_p) = 7.56$  Hz.

troscopy from the multiplet of the acidic cyclopentadienyl proton.

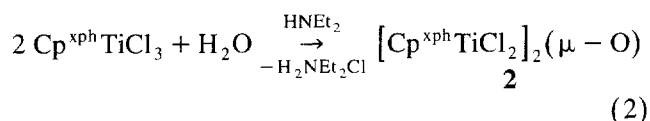
Compound **1** was synthesized by first preparing the trimethylsilyl derivative of the ligand,  $\text{Cp}^{\text{xph}}\text{SiMe}_3$ , and then reacting it with  $\text{TiCl}_4$  according to Eq. (1).



The red **1** was characterized by  $^1\text{H}$  and  $^{13}\text{C}$  NMR (Table 1), mass spectroscopy and elemental analysis. The  $^1\text{H}$  NMR spectrum of **1** showed a pair of singlets for the methyl groups as expected for a pentahapto bonded  $\text{C}_5\text{Me}_4\text{Ph}$ -ligand. The methyl groups next to the phenyl ring are labelled  $\text{Me}_\text{A}$  but the ones further away are labelled  $\text{Me}_\text{B}$ . There is no indication of restricted rotation of the phenyl group relative to the cyclopentadienyl ring at room temperature as the aromatic resonances could be fitted to a  $\text{AA}'\text{BB}'\text{C}$ -spin system. Compound **1** can be handled in air as a solid but it is less stable in solution.

### 2.1.2. $[\text{Cp}^{\text{xph}}\text{TiCl}_2]_2(\mu\text{-O})$ (**2**), $[\text{Cp}^{\text{xph}}\text{TiCl}(\mu\text{-O})]_3$ (**3**) and $(\text{Cp}^{\text{xph}}\text{Ti})_4(\mu\text{-O})_6$ (**4**)

When a toluene or ether solution of **1** was moistened, a new pair of singlets in the  $^1\text{H}$ -NMR methyl region gradually increased in intensity. The singlets were assigned to the new oxochloride complex **2** as could be further verified by  $^{13}\text{C}$ -NMR (Table 1), mass spectroscopy, elemental analysis and X-ray crystallography (vide infra) from a isolated sample of **2**. A pure sample of **2** can be prepared by controlled base hydrolysis of **1** in toluene according to Eq. (2)



When a solution of **1** and **2** was hydrolyzed further a

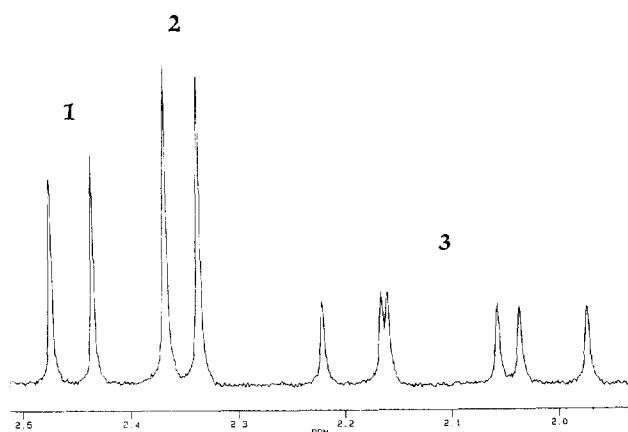


Fig. 1.  $^1\text{H}$ -NMR methyl resonances ( $\text{Me}_\text{A}$  and  $\text{Me}_\text{B}$ ) of the  $\text{C}_5\text{Me}_4\text{Ph}$  ligands in  $(\text{Cp}^{\text{xph}}\text{Ti})\text{Cl}_3$  (**1**),  $[\text{Cp}^{\text{xph}}\text{TiCl}_2]_2(\mu\text{-O})$  (**2**) and  $[\text{Cp}^{\text{xph}}\text{TiCl}(\mu\text{-O})]_3$  (**3**). The six 1:1:1:1:1:1 resonances of **3** result from geometric and dia stereotopic ( $\text{Z-C}_5\text{Me}_4\text{Ph}$ ) non-equivalent methyl groups.

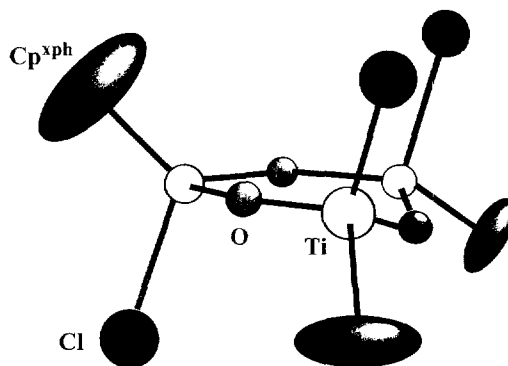
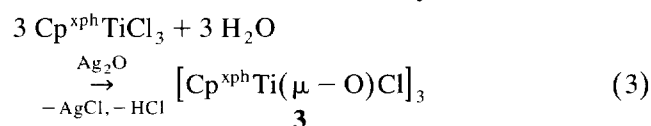


Fig. 2. A proposed molecular structure for  $[\text{Cp}^{\text{xph}}\text{TiCl}(\mu\text{-O})]_3$  (**3**).

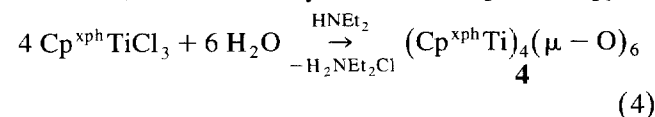
six line 1:1:1:1:1:1 pattern appeared further upfield in the methyl region of the  $^1\text{H}$ -NMR spectrum (Fig. 1). The compound giving rise to the six line pattern could be formed as the dominating species in toluene solution by adding  $\text{H}_2\text{O}$  dropwise to a 1:1 mixture of **1** and  $\text{Ag}_2\text{O}$  (Eq. (3)) and was subsequently isolated as a bright yellow solid and identified as **3** by  $^1\text{H}$  and  $^{13}\text{C}$  NMR (Table 1) and elemental analysis.

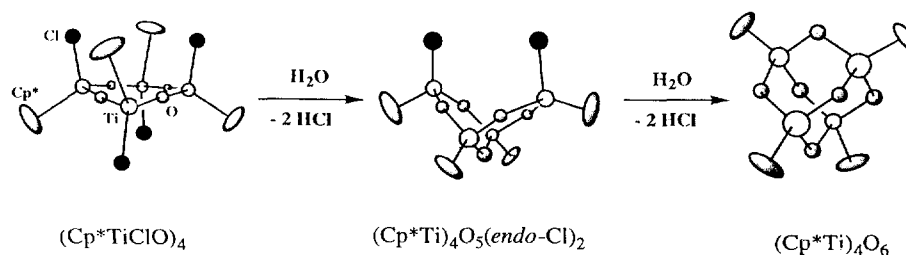


The composition of the trimer **3** could be verified from the isotopomer pattern of the molecular peak in the mass spectra of the compound.

The trimer **3** is analogous to the isostructural molecules  $[\text{Cp}^*\text{TiMe}(\mu\text{-O})]_3$  [12],  $[\text{Cp}^*\text{TiBr}(\mu\text{-O})]_3$  [15] and  $[\text{Cp}^*\text{TiCl}(\mu\text{-O})]_3$  [18] and is assigned to have the same molecular structure i.e. nearly a flat  $\text{Ti}_3\text{O}_3$ -ring with up-down-down or E-Z-Z arrangement of the  $\text{Cp}^{\text{xph}}$  ligands around the ring (Fig. 2). The E-Z-Z arrangement and the diastereotopic protons of the  $\text{Me}_\text{A}/\text{Me}_\text{A}'$  and  $\text{Me}_\text{B}/\text{Me}_\text{B}'$ -groups in the Z- $\text{Cp}^{\text{xph}}$  ligands, give rise to the six line pattern of 1:1:1:1:1:1 intensity. However, the six resonances cannot be unambiguously assigned to each Me environment.

Further base hydrolysis of **3** resulted in a number of resonances in the  $^1\text{H}$ -NMR methyl region of the  $\text{Cp}^{\text{xph}}$  ligand, indicating a more complex mixture of  $\text{Cp}^{\text{xph}}\text{Ti}$ -oxochloro complexes. However, after an extensive hydrolysis, a pair of singlets further upfield (1.93 and 1.88 ppm) gradually increased in intensity and finally became the most intensive resonances in the  $^1\text{H}$ -NMR spectrum. When **1** was allowed to react with an excess of  $\text{H}_2\text{O}/\text{HNEt}_2$  solution the species giving rise to the high field pair of singlets could be isolated and identified as **4** (Eq. (4)) by  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectroscopy (Table 1), elemental analysis and mass spectroscopy.





Scheme 1.

The molecules of **4** have an adamantane-like structure as was confirmed by X-ray crystallography (vide infra).

The intermediate species formed from the hydrolysis of **3**, and before the formation of **4**, could not be isolated and identified. The bicyclo  $(\text{Cp}^*\text{Ti})_4(\mu\text{-}$

$\text{O})_5(\text{endo-Cl})_2$  has been rationalized as an intermediate in the formation of  $(\text{Cp}^*\text{Ti})_4(\mu\text{-O})_6$  as shown in Scheme 1 [10,18].

However, Gómez-Sal et al. [11] have recently shown that the chlorine atoms in the butterfly shaped

Table 2  
Crystal data and structure refinement of **2** and **4**

	<b>2</b>	<b>4</b>
Formula	$\text{C}_{15} \text{H}_{17} \text{Cl}_2 \text{O}_{1/2} \text{Ti}$	$\text{C}_{60} \text{H}_{68} \text{O}_6 \text{Ti}_2$
Formula weight	324.09	1076.79
Crystal system	monoclinic	triclinic
Space group	$\text{C}2/c$	$\text{P}\bar{1}$
Z	8	2
Unit cell dimension		
$a$ (Å)	19.847(12)	11.861(5)
$b$ (Å)	9.089(5)	12.706(5)
$c$ (Å)	20.405(13)	18.218(8)
$\gamma$ (°)	90	86.60(3)
$\beta$ (°)	124.06(5)	89.00(3)
$\alpha$ (°)	90	87.58(3)
Temperature (K)	293(2)	290(2)
Volume (Å <sup>3</sup> )	3049(3)	2738(2)
$d_{\text{calc}}$ (g cm <sup>-3</sup> )	1.412	1.306
Wavelength (Mo K $\alpha$ )	0.71069 Å	0.71069 Å
Absorption coefficient	0.896 mm <sup>-1</sup>	0.611 mm <sup>-1</sup>
$F(000)$	1336	1128
Theta range for data collection	2.29° to 24.97°	1.61° to 22.50°
Index ranges	$-23 \leq h \leq 23$ $0 \leq k \leq 10$ $-24 \leq l \leq 24$	$-12 \leq h \leq 7$ $-13 \leq k \leq 13$ $0 \leq l \leq 19$
Reflections collected	4630	6070
Independent reflections	2676 ( $R(\text{int}) = 0.0557$ )	6070 ( $R(\text{int}) = 0.0000$ )
Observed Reflections ( $I > 2\sigma(I)$ )		4329
Refinement method	Full-matrix least-squares on $F^2$	Full-matrix least-squares on $F^2$
Data/restraints/parameters	2676/0/172	6027/0/399
Goodness-of-fit on $F^2$	1.017	1.118
Final $R$ indices ( $I > 2\sigma(I)$ )		
$R_1 = \sum   F_o  -  F_c   / \sum  F_o $	0.0400	0.0789
$wR^2 = (\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2)^{1/2}$	0.0936	0.1753
$R$ indices (all data)		
$R_1$	0.0692	0.1172
$wR^2$	0.1070	0.2262
Largest diff. peak and hole (e Å <sup>-3</sup> )	0.305 and $-0.377$	0.979 and $-0.574$

Further details of the crystal structure determination are available from the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen (Germany) on quoting the depository numbers CSD-406962 (**2**) and CSD-406963 (**4**).

Table 3

Atomic coordinates and equivalent isotropic displacement parameters ( $\text{\AA}^2 \times 10^3$ ) for **2**.  $U(\text{eq})$  is defined as one third of the trace of the orthogonalized  $U_{ij}$  tensor

	x	y	z	$U(\text{eq})$
C(1)	0.5003(2)	0.2418(3)	0.3921(2)	34 (1)
C(2)	0.4178(2)	0.2568(3)	0.3670(2)	38 (1)
C(3)	0.3873(2)	0.1154(4)	0.3648(2)	44 (1)
C(4)	0.4502(2)	0.0124(3)	0.3889(2)	45 (1)
C(5)	0.5204(2)	0.0894(3)	0.4053(2)	39 (1)
C(6)	0.5555(2)	0.3650(3)	0.4064(2)	38 (1)
C(7)	0.6304(2)	0.3757(4)	0.4780(2)	50 (1)
C(8)	0.6808(2)	0.4948(5)	0.4922(2)	65 (1)
C(9)	0.6580(3)	0.5995(4)	0.4354(3)	70 (1)
C(10)	0.5839(3)	0.5901(4)	0.3646(3)	65 (1)
C(11)	0.5331(2)	0.4735(3)	0.3508(2)	48 (1)
C(12)	0.3740(2)	0.3988(4)	0.3562(2)	56 (1)
C(13)	0.3023(2)	0.0833(5)	0.3407(3)	67 (1)
C(14)	0.4472(3)	-0.1492(4)	0.4027(2)	69 (1)
C(15)	0.6012(2)	0.0228(4)	0.4339(2)	57 (1)
Ti(1)	0.42259(3)	0.11773(6)	0.27001(3)	33 (1)
Cl(1)	0.32349(6)	0.26926(11)	0.18188(5)	61 (1)
Cl(2)	0.36667(6)	-0.10354(9)	0.21725(5)	60 (1)
O(1)	0.5000	0.1363(3)	0.2500	42 (1)

Symmetry transformations used to generate equivalent atoms:  $1 - x$ ,  $y$ ,  $1/2 - z$ .

$(\text{Cp}^* \text{Ti})_4(\mu\text{-O})_5\text{Cl}_2$  are most likely *exo* but not *endo*. The hydrolysis of  $\text{Cp}^* \text{Ti}$ -oxochloro complexes is, therefore, probably more complex as is also evident from the hydrolysis of the  $\text{Cp}^{\text{xph}} \text{Ti}$ -oxochloro complexes. Formation of a mixture of *exo-exo*, *exo-endo* and *endo-endo* bicyclo  $(\text{Cp}^{\text{xph}} \text{Ti})_4(\mu\text{-O})_5\text{Cl}_2$  complexes could, however, account for some of the intermediate species resulting from the hydrolysis of **3**. Furthermore, formation of other species such as oxochlorohydroxide and oxohydroxide  $\text{Cp}^{\text{xph}} \text{Ti}$  complexes cannot be ruled out at present.

## 2.2. Crystal structure of **2**

Compound **2** crystallizes in a monoclinic system of space group  $\text{C2/c}$ . Crystal data and the unit cell atomic coordinates are given in Tables 2 and 3, respectively. There are four molecules per unit cell where twofold axis go through the oxygen atoms. The molecular structure is shown in Fig. 3. Selected bond lengths and bond angles are given in Table 4.

The molecules of **2** consist of a nearly linear  $(\text{Cp}^{\text{xph}} \text{Cl}_2)_2 \text{Ti}-\text{O}-\text{Ti}(\text{Cl}_2 \text{Cp}^{\text{xph}})$  unit with the  $\text{Cp}^{\text{xph}}$  ligands in *trans* position (Fig. 3). The Ti–O (1.805(11) Å) and Ti–Cl (2.244(2), 2.2577(14) Å) bond lengths fall within the range observed for related  $\text{Cp}^{\text{y}} \text{Ti}$ -oxohalide ( $\text{Cp}^{\text{y}} = \text{C}_5\text{H}_n\text{X}_{5-n}$ , X = substituent,  $n = 0-5$ ) and  $\text{Cp}^{\text{y}} \text{Ti}$ -oxoalkyl complexes; Ti–O = 1.78–1.84 Å and Ti–Cl = 2.24–2.29 Å [3,4,6,9,12,14,15,18,19]. The centroid  $\text{Cp}^{\text{xph}}\text{--Ti}$  distance of 2.04 Å is also within the range observed for other centroid  $\text{Cp}^{\text{y}}\text{--Ti}$  distances

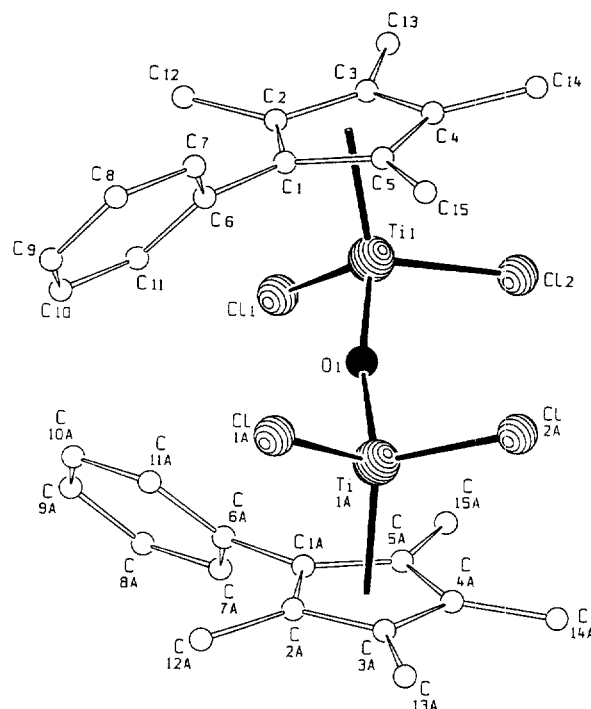


Fig. 3. Molecular structure of  $[\text{Cp}^{\text{xph}} \text{TiCl}_2]_2(\mu\text{-O})$  (**2**) and atom labels. The hydrogen atoms have been omitted for clarity.

(2.01–2.06 Å) and the centroid  $\text{Cp}^{\text{xph}}\text{--Ti}$  distance of 2.03 Å for the recently reported  $(\text{Cp}^{\text{xph}})_2 \text{TiH}$  compound [17].

The structure of **2** is similar to its cyclopentadienyl analogue  $(\text{CpTiCl}_2)_2(\mu\text{-O})$  [3,4]. However, the Ti–O–Ti unit in **2** is slightly bent ( $169.3(2)^\circ$ ) but is linear in  $(\text{CpTiCl}_2)_2(\mu\text{-O})$ . This might indicate less  $\pi$  Ti–O backbonding in **2** owing to the less need for electrons by titanium when bonded to a more electron donating alkylated cyclopentadienyl ligand. The difference in Ti–O–Ti bond angle for the two molecules could, however, be caused by different crystal environments and/or minimization of intramolecular steric effects in **2**.

Table 4

Selected bond lengths (Å) and bond angles ( $^\circ$ ) for **2**

Selected bond lengths (Å) <sup>a</sup>			
C(1)–Ti(1)	2.357(3)	cCp <sup>xph</sup> –Ti(1)	2.04
C(2)–Ti(1)	2.395(3)		
C(3)–Ti(1)	2.398(4)	Ti(1)–O(1)	1.8050(11)
C(4)–Ti(1)	2.370(3)	Ti(1)–Cl(1)	2.244(2)
C(5)–Ti(1)	2.336(4)	Ti(1)–Cl(2)	2.2577(14)
Selected bond angles ( $^\circ$ )			
Ti(1)–O(1)–Ti(1)	169.3(2)	cCp <sup>xph</sup> –Ti–O(1)	118.7
O(1)–Ti(1)–Cl(1)	103.68(8)	cCp <sup>xph</sup> –Ti–Cl(1)	114.8
O(1)–Ti(1)–Cl(2)	103.23(9)	cCp <sup>xph</sup> –Ti–Cl(2)	113.4
Cl(1)–Ti(1)–Cl(2)	100.86(7)		

<sup>a</sup> cCp<sup>xph</sup> is the centroid of the  $\text{Cp}^{\text{xph}}$ -ligand  $\text{C}_5$ -ring.

Table 5

Atomic coordinates and equivalent isotropic displacement parameters ( $\text{\AA}^2$ ) for **4**.  $U(\text{eq})$  is defined as one third of the trace of the orthogonalized  $U_{ij}$  tensor

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> (eq)
C(1)	0.3199(9)	0.4621(7)	0.3484(5)	0.045(3)
C(2)	0.4135(9)	0.4852(7)	0.3014(5)	0.043(3)
C(3)	0.4725(9)	0.5652(7)	0.3329(5)	0.042(2)
C(4)	0.4149(9)	0.5921(7)	0.3991(5)	0.040(2)
C(5)	0.3223(9)	0.5278(8)	0.4084(5)	0.049(3)
C(6)	0.2343(11)	0.3803(10)	0.3358(7)	0.082(4)
C(7)	0.4450(10)	0.4330(8)	0.2304(6)	0.059(3)
C(8)	0.5819(10)	0.6045(9)	0.3032(6)	0.063(3)
C(9)	0.4473(7)	0.6757(5)	0.4491(4)	0.053(3)
C(10)	0.4554(7)	0.6524(5)	0.5241(4)	0.079(4)
C(11)	0.4872(8)	0.7288(7)	0.5708(3)	0.108(5)
C(12)	0.5108(8)	0.8285(6)	0.5424(4)	0.107(5)
C(13)	0.5027(7)	0.8518(5)	0.4674(5)	0.091(4)
C(14)	0.4710(7)	0.7754(6)	0.4207(3)	0.064(3)
C(15)	0.2383(10)	0.5265(9)	0.4715(6)	0.072(3)
C(16)	0.3061(9)	1.0344(7)	0.1536(5)	0.041(3)
C(17)	0.3937(8)	1.0070(6)	0.2032(5)	0.037(2)
C(18)	0.4657(8)	0.9265(7)	0.1733(5)	0.036(2)
C(19)	0.4190(8)	0.9017(7)	0.1046(5)	0.036(2)
C(20)	0.3207(8)	0.9703(7)	0.0924(4)	0.036(2)
C(21)	0.2139(9)	1.1190(8)	0.1634(6)	0.058(3)
C(22)	0.4106(9)	1.0548(8)	0.2760(5)	0.057(3)
C(23)	0.5733(9)	0.8790(8)	0.2047(5)	0.052(3)
C(24)	0.4645(6)	0.8186(4)	0.0545(3)	0.040(2)
C(25)	0.4872(6)	0.7155(5)	0.0812(3)	0.050(3)
C(26)	0.5285(7)	0.6386(4)	0.0340(4)	0.067(3)
C(27)	0.5471(7)	0.6648(5)	−0.0399(3)	0.072(3)
C(28)	0.5245(7)	0.7678(5)	−0.0666(2)	0.067(3)
C(29)	0.4832(6)	0.8447(4)	−0.0194(3)	0.055(3)
C(30)	0.2463(9)	0.9721(8)	0.0276(5)	0.057(3)
C(31)	0.0584(9)	0.8926(8)	0.4356(5)	0.046(3)
C(32)	−0.0216(8)	0.8152(8)	0.4313(5)	0.041(2)
C(33)	−0.0969(8)	0.8478(7)	0.3756(5)	0.037(2)
C(34)	−0.0665(8)	0.9457(7)	0.3447(5)	0.038(2)
C(35)	0.0287(9)	0.9758(7)	0.3834(5)	0.040(2)
C(36)	0.1553(10)	0.8905(9)	0.4869(6)	0.064(3)
C(37)	−0.0248(10)	0.7143(8)	0.4771(6)	0.063(3)
C(38)	−0.1965(9)	0.7899(8)	0.3549(6)	0.060(3)
C(39)	−0.1285(6)	1.0078(5)	0.2851(3)	0.041(2)
C(40)	−0.0883(5)	1.0076(5)	0.2130(4)	0.067(3)
C(41)	−0.1467(7)	1.0662(6)	0.1582(3)	0.079(4)
C(42)	−0.2454(6)	1.1251(6)	0.1756(3)	0.076(4)
C(43)	−0.2856(5)	1.1254(5)	0.2477(4)	0.074(3)
C(44)	−0.2272(6)	1.0667(5)	0.3025(3)	0.058(3)
C(45)	0.0885(9)	1.0765(8)	0.3706(6)	0.057(3)
C(46)	0.0872(10)	0.6187(10)	0.0517(5)	0.060(3)
C(47)	−0.0066(10)	0.6898(8)	0.0636(5)	0.050(3)
C(48)	−0.0729(8)	0.6470(7)	0.1199(5)	0.042(2)
C(49)	−0.0195(9)	0.5487(7)	0.1447(5)	0.045(3)
C(50)	0.0784(10)	0.5330(8)	0.1003(6)	0.055(3)
C(51)	0.1831(12)	0.6361(11)	−0.0040(8)	0.095(4)
C(52)	−0.0305(11)	0.7939(10)	0.0227(7)	0.083(4)
C(53)	−0.1848(10)	0.6961(9)	0.1470(6)	0.068(3)
C(54)	−0.0502(8)	0.4774(6)	0.2059(4)	0.065(3)
C(55)	−0.0480(9)	0.3697(7)	0.1948(4)	0.111(5)
C(56)	−0.0758(10)	0.3000(5)	0.2522(6)	0.132(6)
C(57)	−0.1057(9)	0.3379(7)	0.3207(5)	0.128(6)
C(58)	−0.1079(8)	0.4455(8)	0.3319(4)	0.093(4)
C(59)	−0.0801(8)	0.5153(5)	0.2745(5)	0.083(4)
C(60)	0.1658(12)	0.4402(11)	0.1037(8)	0.098(5)

Table 5 (continued)

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> (eq)
Ti(1)	0.2890(1)	0.6408(1)	0.3009(1)	0.0318(4)
Ti(2)	0.2851(1)	0.8554(1)	0.1977(1)	0.0304(4)
Ti(3)	0.0858(1)	0.8199(1)	0.3187(1)	0.0333(5)
Ti(4)	0.1034(1)	0.6811(1)	0.1731(1)	0.0337(5)
O(1)	0.3605(5)	0.7473(4)	0.2507(3)	0.0333(15)
O(2)	0.1819(5)	0.9043(4)	0.2663(3)	0.036(2)
O(3)	0.0207(5)	0.7523(4)	0.2443(3)	0.038(2)
O(4)	0.2025(5)	0.5949(4)	0.2283(3)	0.0355(15)
O(5)	0.1840(5)	0.7147(4)	0.3568(3)	0.036(2)
O(6)	0.1956(5)	0.7843(4)	0.1380(3)	0.0344(15)

The angle between the  $\text{C}_5$ -ring and the phenyl group in the  $\text{Cp}^{\text{xph}}$ -ligand is  $50.4^\circ$ , similar to those observed in  $(\text{Cp}^{\text{xph}})_2\text{TiH}$  ( $49.61(9)^\circ$  and  $53.66(9)^\circ$ ) [17] and  $(\text{Cp}^{\text{xph}})_2\text{Zn}$  ( $46.72(18)^\circ$ ) [20]. An interesting feature in the structure of **2** is that both phenyl rings are on the same side of the molecule. A possible cause for this orientation of the phenyl rings is that the  $\text{Cl}(1)\text{--Ti}(1)\text{--Ti}(1\text{A})\text{--Cl}(1\text{A})$  and  $\text{Cl}(2)\text{--Ti}(1)\text{--Ti}(1\text{A})\text{--Cl}(2\text{A})$  dihedral angles can be varied in order to prevent too much steric crowding of the  $\text{Cp}^{\text{xph}}\text{TiCl}_2$ -units. Thus the  $\text{Cl}(1)\text{--Ti}(1)\text{--Ti}(1\text{A})\text{--Cl}(1\text{A})$  dihedral angle is relatively wide or  $-100.33^\circ$  and the  $\text{Cl}(2)\text{--Ti}(1)\text{--Ti}(1\text{A})\text{--Cl}(2\text{A})$  dihedral angle is relatively small or  $51.47^\circ$ . The shortest  $\text{Cl}\cdots\text{C}_{\text{ph}}$  and  $\text{Cl}\cdots\text{C}_{\text{Me}}$  distances between opposite  $\text{Cp}^{\text{xph}}\text{TiCl}_2$ -units of  $3.575\text{ \AA}$  ( $\text{Cl}(1\text{A})\cdots\text{C}(11)$ ) and  $3.665\text{ \AA}$  ( $\text{Cl}(2\text{A})\cdots\text{C}(15)$ ), respectively, are both longer than the corresponding van der Waals distances of  $\text{Cl}\cdots\text{C}_{\text{arom}} = 3.50\text{ \AA}$  [21] or  $3.52\text{ \AA}$  [22] and

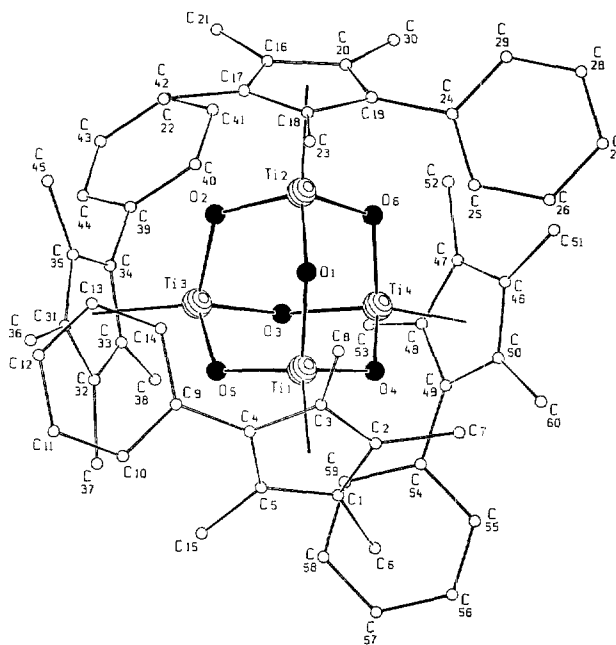


Fig. 4. Molecular structure of  $(\text{Cp}^{\text{xph}}\text{Ti})_4(\mu\text{--O})_6$  (**4**) and atom labels. The hydrogen atoms have been omitted for clarity.

$\text{Cl} \cdots \text{C}_{\text{aliph}} = 3.45 \text{ \AA}$  [22]. The shortest  $\text{Cl} \cdots \text{C}_{\text{Me}}$  distance is, however, slightly shorter than the van der Waals  $\text{Cl} \cdots \text{Me}$  distance of  $3.75 \text{ \AA}$  [21]. If the phenyl rings are arranged on the opposite side of the molecule, for example with one of the phenyl rings in position of atom C(15), there will be too much crowding of the  $\text{Cp}^{\text{xph}}\text{TiCl}_2$ -groups unless the two  $\text{Cl}(1)\text{--Ti}(1)\text{--Ti}(1\text{A})\text{--Cl}(1\text{A})$  and  $\text{Cl}(2)\text{--Ti}(1)\text{--Ti}(1\text{A})\text{--Cl}(2\text{A})$  dihedral angles are nearly equal. Furthermore, a simple computer model of such an arrangement of phenyl rings also indicates too much steric crowding as the  $\text{Cl} \cdots \text{C}_{\text{Ph}}$  and  $\text{Cl} \cdots \text{C}_{\text{Me}}$  distances between opposite  $\text{Cp}^{\text{xph}}\text{TiCl}_2$ -groups will be close to or shorter than the corresponding van der Waals distances. Finally, the slight bending of the  $\text{Ti--O--Ti}$  unit in **2** should also favor the observed arrangement of the phenyl rings.

### 2.3. Crystal structure of **4**

Compound **4** crystallizes in a triclinic system of space group  $\text{P}\bar{1}$ . Crystal data and the unit cell atomic

Table 6  
Selected bond lengths ( $\text{\AA}$ ) and angles ( $^\circ$ ) for **4**

Selected bond lengths ( $\text{\AA}$ ) <sup>a</sup>			
$\text{C}(1)\text{--Ti}(1)$	2.405(9)	$\text{cCp}^{\text{xph}}\text{--Ti}(1)$	2.07
$\text{C}(2)\text{--Ti}(1)$	2.396(9)		
$\text{C}(3)\text{--Ti}(1)$	2.397(10)	$\text{Ti}(1)\text{--O}(4)$	1.824(6)
$\text{C}(4)\text{--Ti}(1)$	2.387(9)	$\text{Ti}(1)\text{--O}(5)$	1.835(6)
$\text{C}(5)\text{--Ti}(1)$	2.403(9)	$\text{Ti}(1)\text{--O}(1)$	1.842(5)
$\text{C}(16)\text{--Ti}(2)$	2.405(8)	$\text{cCp}^{\text{xph}}\text{--Ti}(2)$	2.07
$\text{C}(17)\text{--Ti}(2)$	2.387(9)		
$\text{C}(18)\text{--Ti}(2)$	2.401(9)	$\text{Ti}(2)\text{--O}(6)$	1.833(6)
$\text{C}(19)\text{--Ti}(2)$	2.383(8)	$\text{Ti}(2)\text{--O}(2)$	1.835(6)
$\text{C}(20)\text{--Ti}(2)$	2.408(8)	$\text{Ti}(2)\text{--O}(1)$	1.841(6)
$\text{C}(31)\text{--Ti}(3)$	2.366(8)	$\text{cCp}^{\text{xph}}\text{--Ti}(3)$	2.07
$\text{C}(32)\text{--Ti}(3)$	2.396(8)		
$\text{C}(33)\text{--Ti}(3)$	2.400(9)	$\text{Ti}(3)\text{--O}(2)$	1.839(6)
$\text{C}(34)\text{--Ti}(3)$	2.395(9)	$\text{Ti}(3)\text{--O}(3)$	1.840(6)
$\text{C}(35)\text{--Ti}(3)$	2.404(8)	$\text{Ti}(3)\text{--O}(5)$	1.841(6)
$\text{C}(46)\text{--Ti}(4)$	2.395(9)	$\text{cCp}^{\text{xph}}\text{--Ti}(4)$	2.07
$\text{C}(47)\text{--Ti}(4)$	2.398(10)		
$\text{C}(48)\text{--Ti}(4)$	2.390(10)	$\text{Ti}(4)\text{--O}(4)$	1.841(6)
$\text{C}(49)\text{--Ti}(4)$	2.370(10)	$\text{Ti}(4)\text{--O}(6)$	1.844(6)
$\text{C}(50)\text{--Ti}(4)$	2.383(9)	$\text{Ti}(4)\text{--O}(3)$	1.847(5)
Selected angles ( $^\circ$ )			
$\text{O}(4)\text{--Ti}(1)\text{--O}(5)$	102.0(3)	$\text{Ti}(2)\text{--O}(1)\text{--Ti}(1)$	123.5(3)
$\text{O}(4)\text{--Ti}(1)\text{--O}(1)$	100.6(3)	$\text{Ti}(2)\text{--O}(2)\text{--Ti}(3)$	123.9(3)
$\text{O}(5)\text{--Ti}(1)\text{--O}(1)$	102.2(2)	$\text{Ti}(3)\text{--O}(3)\text{--Ti}(4)$	123.2(3)
$\text{O}(6)\text{--Ti}(2)\text{--O}(2)$	101.5(3)	$\text{Ti}(1)\text{--O}(4)\text{--Ti}(4)$	124.1(3)
$\text{O}(6)\text{--Ti}(2)\text{--O}(1)$	102.5(3)	$\text{Ti}(1)\text{--O}(5)\text{--Ti}(3)$	123.4(3)
$\text{O}(2)\text{--Ti}(2)\text{--O}(1)$	101.2(2)	$\text{Ti}(2)\text{--O}(6)\text{--Ti}(4)$	122.9(3)
$\text{O}(2)\text{--Ti}(3)\text{--O}(3)$	101.2(3)		
$\text{O}(2)\text{--Ti}(3)\text{--O}(5)$	102.0(3)	$\text{Ph--C}_5(\text{Me}_4\text{Ti}(1))$ <sup>b</sup>	48.9
$\text{O}(3)\text{--Ti}(3)\text{--O}(5)$	101.5(3)	$\text{Ph--C}_5(\text{Me}_4\text{Ti}(2))$	51.9
$\text{O}(4)\text{--Ti}(4)\text{--O}(6)$	101.6(3)	$\text{Ph--C}_5(\text{Me}_4\text{Ti}(3))$	79.4
$\text{O}(4)\text{--Ti}(4)\text{--O}(3)$	102.3(3)	$\text{Ph--C}_5(\text{Me}_4\text{Ti}(4))$	48.2
$\text{O}(6)\text{--Ti}(4)\text{--O}(3)$	101.0(3)		

<sup>a</sup>  $\text{cCp}^{\text{xph}}$  is the centroid of the  $\text{Cp}^{\text{xph}}$ -ligand  $\text{C}_5$ -ring.

<sup>b</sup> The angle between the phenyl and  $\text{C}_5$ -rings for the  $\text{Cp}^{\text{xph}}$ -ligands.

coordinates are given in Tables 2 and 5, respectively. There are two molecules per unit cell, related by inversion center. The molecular structure is shown in Fig. 4 and selected bond lengths and bond angles are given in Table 6.

The most interesting feature of the molecular structure of **4** is the adamantane-like  $\text{Ti}_4\text{O}_6$  cage. The  $\text{Ti}_4\text{O}_6$  cage is of nearly tetrahedral symmetry with  $\text{Ti} \cdots \text{Ti}$  distances ranging only between  $3.230(3)\text{--}3.244(2) \text{ \AA}$ . The  $\text{Ti--O}$  bond lengths and the  $\text{Ti--O--Ti}$  and  $\text{O--Ti--O}$  bond angles vary little or  $1.824(6)\text{--}1.847(5) \text{ \AA}$ ,  $122.9(3)\text{--}124.1(3)^\circ$  and  $100.6(3)\text{--}102.5(3)^\circ$ , respectively, and are similar to the corresponding  $(\text{Cp}^* \text{Ti})_4\text{O}_6$  cage average values of  $1.837 \text{ \AA}$  ( $\text{Ti--O}$ ),  $123.0^\circ$  ( $\text{Ti--O--Ti}$ ) and  $101.9^\circ$  ( $\text{O--Ti--O}$ ) [9]. The centroid  $\text{Cp}^{\text{xph}}\text{--Ti}$  distances are  $2.07 \text{ \AA}$ .

The dihedral angle between the planes of the  $\text{Cp}$  and phenyl rings for the  $\text{Cp}^{\text{xph}}\text{Ti}$ -groups are  $48.9^\circ$  ( $\text{Cp}^{\text{xph}}\text{Ti}(1)$ ),  $51.9^\circ$  ( $\text{Cp}^{\text{xph}}\text{Ti}(2)$ ) and  $48.2^\circ$  ( $\text{Cp}^{\text{xph}}\text{Ti}(4)$ ) but the dihedral angle is considerably larger for the  $\text{Cp}^{\text{xph}}\text{Ti}(3)$  group or  $79.7^\circ$ . The phenyl rings of each  $\text{Cp}^{\text{xph}}$ -ligand are staggered with the  $\text{TiO}_3$  unit which the ligand is bonded to and the phenyl-rings are arranged around the  $\text{Ti}_4\text{O}_6$ -core in such a way that there is an approximate  $S_4$ -axis going through the  $\text{O}(1)$  and  $\text{O}(3)$  atoms. The approximate  $S_4$  symmetry of **4** is mainly broken by the large dihedral angle of the  $\text{Cp}^{\text{xph}}\text{Ti}(3)$  group. There are no significant close intermolecular contacts in the crystal structure of **4** but the large dihedral angle of the  $\text{Cp}^{\text{xph}}\text{Ti}(3)$  group could be due to a more efficient packing of the molecules.

### 3. Experimental

All manipulations of organometallic compounds were performed under an inert atmosphere of dry nitrogen gas in Schlenk apparatus or in a dry box (Vacuum Atmospheres, TS-4000). Analytical grade THF,  $\text{Et}_2\text{O}$ , *n*-pentane, *n*-hexane and toluene solvents (Merck) were dried over sodium metal wire and benzophenone and distilled prior to use. Triglyme was added to the *n*-pentane, *n*-hexane and toluene solvents in order to induce a blue colour before distillation. The reagents  $\text{SiMe}_3\text{Cl}$  (Aldrich), Li-wire (Merck) and  $\text{MeLi/Et}_2\text{O}$  (Janssen) were used as received but  $\text{C}_6\text{H}_5\text{Br}$  (Merck) was distilled prior to use. The 2,3,4,5-tetramethylcyclopenta-2-enone was prepared according to literature methods [23] and  $\text{TiCl}_4$  was distilled from copper-chips prior to use.

Proton and carbon-13 NMR spectra were recorded on a AC-250 MHz Bruker NMR spectrometer. Mass spectra were obtained with Finnigan MAT 711 and MAT 8230 instruments and elemental analyses (H and C) were performed with a Carlo Erba CHN Mod.1106 instrument.

### 3.1. Syntheses

#### 3.1.1. $\text{HCp}^{\text{xph}}$

A  $\text{PhLi}/\text{Et}_2\text{O}$  solution was prepared by adding dropwise 55 ml of  $\text{C}_6\text{H}_5\text{Br}$  (520 mmol) to 6.2 g of lithium wire (890 mmol) in 100 ml of freshly distilled  $\text{Et}_2\text{O}$  and boiling the solution for 1 h. The solution was then cooled ( $0^\circ\text{C}$ ) and 59 g of 2,3,4,5-tetramethylcyclopent-2-enone (430 mmol) added dropwise (2 h) and the solution stirred overnight. The solution was poured onto ice, acidified with 60 ml conc.  $\text{HCl}$  and finally extracted with  $\text{Et}_2\text{O}$  ( $2 \times 50$  ml) and dried over  $\text{Na}_2\text{CO}_3$ . After removing the solvent in vacuo the remaining solution was distilled (Vigreux column) at low pressure. A total of 53 g of yellow liquid was collected ( $99\text{--}120^\circ\text{C}/0.3\text{--}0.8$  mm Hg) which contained a mixture of three isomers of  $\text{HCp}^{\text{xph}}$  (270 mmol, 63% yield). MS (EI):  $m/z$  (inten. (%)): 198 ( $\text{M}^+$ , 100). Each isomer in the mixture can be identified by the characteristic multiplets of the Cp-ring proton,  $\text{HCp}^{\text{xph}}$ ,  $^1\text{H}$ -NMR resonance. Thus 1-phenyl-2,3,4,5-tetramethylcyclopenta-1,3-diene ( $\text{H}(1\text{-Cp}^{\text{xph}})$ ) gives a quartet-of-quartets (2.78 ppm), 2-phenyl-1,3,4,5-tetramethylcyclopenta-1,3-diene ( $\text{H}(2\text{-Cp}^{\text{xph}})$ ) a quartet-of-septets (3.28 ppm) and 5-phenyl-1,2,3,4-tetramethylcyclopenta-1,3-diene ( $\text{H}(5\text{-Cp}^{\text{xph}})$ ) an ill-resolved septet (3.65 ppm). The relative amount of each isomer varied but typical values were 85%, 10% and 5% for  $\text{H}(2\text{-Cp}^{\text{xph}})$ ,  $\text{H}(1\text{-Cp}^{\text{xph}})$  and  $\text{H}(5\text{-Cp}^{\text{xph}})$ , respectively. The  $\text{HCp}^{\text{xph}}$  was used without further purification.

#### 3.1.2. $\text{LiCp}^{\text{xph}}$

To a cooled ( $0^\circ\text{C}$ ) 100 ml  $\text{Et}_2\text{O}$  solution containing 6.83 g of  $\text{HCp}^{\text{xph}}$  (34.4 mmol) was added dropwise 23 ml of a 1.6 M  $\text{MeLi}/\text{Et}_2\text{O}$  solution (37 mmol). A white precipitate of  $\text{LiCp}^{\text{xph}}$  formed which was filtered from the solution, dried on a vacuum line and isolated in a dry box and used without further purification. Yield 6.16 g (30.2 mmol), 88%.

#### 3.1.3. $\text{Cp}^{\text{xph}}\text{SiMe}_3$ and $\text{Cp}^{\text{xph}}\text{TiCl}_3$ (**1**)

To 1.44 g (7.05 mmol) of  $\text{LiCp}^{\text{xph}}$  dissolved in 100 ml THF was added 1.25 g of  $\text{SiMe}_3\text{Cl}$  (11.5 mmol) via syringe and the solution refluxed for 24 h. After distilling the THF off in vacuo and adding 60 ml of *n*-pentane the white precipitate ( $\text{LiCl}$ ) was filtered from the solution. The  $\text{Cp}^{\text{xph}}\text{SiMe}_3/\text{n-pentane}$  solution was freeze-dried, 1.30 g  $\text{TiCl}_4$  (6.85 mmol) added and after thawing, the solution was allowed to warm up slowly to room temperature and stirred further for 10 h. Red crystals of **1**, which precipitated from the solution, were isolated in a drybox. Yield 1.15 g (3.27 mmol), 46%. Anal. Found: C, 51.66; H, 4.96.  $\text{C}_{15}\text{H}_{17}\text{Cl}_3\text{Ti}$ , (351.56) Calc.: C, 51.25; H, 4.87. MS (FI):  $m/z$  ( $^{48}\text{Ti}/^{35}\text{Cl}$ , inten. (%)): 350 ( $\text{M}^+$ , 100).  $^1\text{H}$  and  $^{13}\text{C}$  NMR: ( $\text{CDCl}_3$ ,  $25^\circ\text{C}$ ) Table 1.

#### 3.1.4. $[\text{Cp}^{\text{xph}}\text{TiCl}_2]_2(\mu\text{-O})$ (**2**)

To a cooled ( $0^\circ\text{C}$ ) 60 ml toluene solution containing 0.29 g of **1** (0.82 mmol) were added 0.11 g of a 1:2  $\text{H}_2\text{O}/\text{HNEt}_2$  solution (0.67 mmol  $\text{H}_2\text{O}$ , 1.3 mmol  $\text{HNEt}_2$ ). A white precipitate formed ( $\text{H}_2\text{NEt}_2\text{Cl}(s)$ ) and  $^1\text{H}$  NMR spectrum of the solution showed it to be mainly a mixture of **2** and **3**. The solution was filtered, the toluene distilled off in vacuo and the red residue heated in 60 ml of *n*-pentane in order to dissolve **3**. After filtration a red solid of **2** was isolated in a dry box. Yield: 0.16 g (0.24 mmol), 58%. Anal. Found: C, 55.38; H, 5.24.  $\text{C}_{30}\text{H}_{34}\text{OCl}_4\text{Ti}_2$  (648.22) Calc.: C, 55.59; H, 5.29. MS (EI):  $m/z$  ( $^{48}\text{Ti}/^{35}\text{Cl}$ , inten. (%)), 648 ( $\text{M}^+$ , 10), 451 ( $\text{M}^+ - \text{C}_5\text{Me}_4\text{Ph}$ , 20).  $^1\text{H}$  and  $^{13}\text{C}$  NMR: ( $\text{CDCl}_3$ ,  $25^\circ\text{C}$ ) Table 1.

#### 3.1.5. $[\text{Cp}^{\text{xph}}\text{Ti}(\mu\text{-O})\text{Cl}]_3$ (**3**)

An  $\text{Ag}_2\text{O}$  solid was prepared by adding excess  $\text{NaOH}$  solution to 8.54 ml of a 0.09991 M  $\text{AgNO}_3$  (0.853 mmol), centrifuging the dark grey  $\text{Ag}_2\text{O}$  precipitate and decanting off the liquid. The precipitate was washed with  $6 \times 10$  ml  $\text{H}_2\text{O}$  and  $4 \times 10$  ml  $\text{EtOH}$  (96%) by stirring, centrifuging and decanting. The solid was dried briefly in vacuo and added to a toluene solution (60 ml) containing 0.30 g of **1** (0.85 mmol). After stirring for few days and refluxing, the solution contained mainly **1** and **2** ( $^1\text{H}$ -NMR). Adding approximately 0.15 g of  $\text{H}_2\text{O}$  (9 mmol) and refluxing the solution over night resulted in the formation of **3** as the dominating species in solution. The solution was then filtered, the solvent removed in vacuo and 60 ml of *n*-pentane added to the viscous yellow residue. After stirring the solution for 30 min a bright yellow solid of **3** precipitated from solution. The precipitate was filtered, dried and finally isolated in a dry box. Yield: 0.153 g (0.516 mmol), 60%. Anal. Found: C, 61.50; H, 5.86.  $\text{C}_{45}\text{H}_{51}\text{O}_3\text{Cl}_3\text{Ti}_3$  (889.97) Calc.: C, 60.73; H, 5.78. MS (EI):  $m/z$  ( $^{48}\text{Ti}/^{35}\text{Cl}$ , inten. (%)), 888.2 ( $\text{M}^+$ , 10), 691 ( $\text{M}^+ - \text{C}_5\text{Me}_4\text{Ph}$ , 95).  $^1\text{H}$  and  $^{13}\text{C}$  NMR: ( $\text{CDCl}_3$ ,  $25^\circ\text{C}$ ) Table 1.

#### 3.1.6. $(\text{Cp}^{\text{xph}}\text{Ti})_4(\mu\text{-O})_6$ (**4**)

To a cooled ( $0^\circ\text{C}$ ) 70 ml *n*-pentane solution, containing 0.37 g of **1** (1.1 mmol), were added 24 ml of a 17% (*v/v*)  $\text{HNEt}_2/\text{H}_2\text{O}$  solution. The solution was allowed to warm up to room temperature and stirred further for 2 days. A yellow material precipitated after the aqueous phase had been separated and the *n*-pentane solvent pumped off in vacuo. The yellow material of **4** was washed with little *n*-pentane, dried and isolated in a dry box. A pure sample can be prepared by recrystallizing **4** in warm *n*-hexane. Yield: 0.063 g (0.06 mmol), 22%. Anal. Found: C, 67.20; H, 6.26.  $\text{C}_{60}\text{H}_{68}\text{O}_6\text{Ti}_4$  (1076.79) Calc.: C, 66.93; H, 6.36. MS (EI):  $m/z$  ( $^{48}\text{Ti}/^{35}\text{Cl}$ , inten. (%)), 1076 ( $\text{M}^+$ , 100).  $^1\text{H}$  and  $^{13}\text{C}$  NMR: ( $\text{CDCl}_3$ ,  $25^\circ\text{C}$ ) Table 1.



### 3.2. Crystal growth and X-ray measurements of **2** and **4**

An impure sample of **1** was Soxhlet extracted with *n*-pentane. The resulting orange solution was allowed to stand in the dark for two weeks where red crystals of **2** formed as shown by <sup>1</sup>H-NMR spectroscopy. Single crystals of **2** were selected for X-ray diffraction measurements.

Single crystals of **4** were grown by dissolving a sample of **4** in warm *n*-hexane and storing the solution for few days in a refrigerator (5°C).

Information about the single crystal X-ray diffraction data collection, crystal data and structure refinement can be found in Table 2. The programs SHELX86 [24], SHELX93 [25] and SCHAKAL [26] were used for solving and displaying the crystal structures.

### 4. Supplementary material available

Further details of the crystal structure investigation are available on request from the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen, on quoting the depository number CSD-406962 for **2** and CSD-406963 for **4**.

### Acknowledgements

We wish to thank S. Jonsdottir, S. Stefansdottir and D. Müller for the NMR, elemental analyses and MS measurements, respectively. MB and IA wish to thank the Science Research Council of Iceland for financial support.

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