

Synthesis of Group 4 metal compounds containing cyclopentadienyl ligands with a pendant alkoxide function: molecular structure of $\{[\eta^5 : \eta^1\text{-C}_5\text{H}_4(\text{CH}_2)_2\text{O}]\text{TiCl}_2\}_2$ and $[\eta^5 : \eta^1\text{-C}_5\text{H}_4(\text{CH}_2)_3\text{O}]\text{TiCl}_2$ ¹

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Received 11 August 1995

Abstract

Trimethylsilylcyclopentadiene–siloxo ethers $\text{Me}_3\text{SiC}_5\text{H}_4(\text{CH}_2)_n\text{OSiMe}_3$ ($n = 2, 3$) react with TiCl_4 to give (2-(cyclopentadienyl)-ethyl-oxy)titanium dichloride, $[[\eta^5 : \eta^1\text{-C}_5\text{H}_4(\text{CH}_2)_2\text{O}]\text{TiCl}_2]_2$ and (3-(cyclopentadienyl)-prop-1-oxy)titanium dichloride $[\eta^5 : \eta^1\text{-C}_5\text{H}_4(\text{CH}_2)_3\text{O}]\text{TiCl}_2$, by release of two equivalents of Me_3SiCl . Molecular structure determination shows that $[[\eta^5 : \eta^1\text{-C}_5\text{H}_4(\text{CH}_2)_2\text{O}]\text{TiCl}_2]_2$ is dimeric in the solid state with the alkoxide function bridging two titanium centers, whereas $[\eta^5 : \eta^1\text{-C}_5\text{H}_4(\text{CH}_2)_3\text{O}]\text{TiCl}_2$ is a monomer with a bidentate cyclopentadienyl–alkoxide ligand. $[[\eta^5 : \eta^1\text{-C}_5\text{H}_4(\text{CH}_2)_2\text{O}]\text{TiCl}_2]_2$ crystallizes in the triclinic space group $P\bar{1}$ with $a = 7.702(1)$ Å, $b = 7.942(2)$ Å, $c = 8.251(1)$ Å, $\alpha = 71.39(1)^\circ$, $\beta = 89.92(1)^\circ$, $\gamma = 61.25(2)^\circ$, $V = 412.27(16)$ Å³ and $Z = 1$. The basic structure consists of a dimer molecule with a crystallographic center of inversion, coupled by two Ti–O–Ti bridges. Crystals of $[\eta^5 : \eta^1\text{-C}_5\text{H}_4(\text{CH}_2)_3\text{O}]\text{TiCl}_2$ are triclinic, space group $P\bar{1}$ with $a = 8.194(1)$, $b = 11.002(1)$, $c = 11.192(1)$ Å, $\alpha = 84.339(5)$, $\beta = 88.035(5)$, $\gamma = 76.256(6)^\circ$, $V = 975.2$ Å³ and $Z = 4$. Two crystallographically independent molecules are present in the asymmetric unit.

Keywords: Group 4; Titanium; Cyclopentadienyl; Alkoxide; Crystal structure; X-ray diffraction; Synthesis

1. Introduction

There is a strong interest in cyclopentadienyl complexes of early transition and lanthanide metals with neutral or anionic Lewis base substituents on the cyclopentadienyl ligands. The main reason is the rapid development of catalytic olefin polymerisation and the striking dominance of lanthanide and early transition metal metallocene and functionalised cyclopentadienyl compounds [1]. Replacing the dicyclopentadienyl ligand system on scandium by a combination of an amide and a cyclopentadienyl ligand turns on catalytic polymerization of propene [2]. For lanthanides, Group 3 and Group 4 metals with a bidentate, amido or phosphido substituted cyclopentadienyl ligand system high catalytic activity for (co)polymerisation of α -olefins is claimed [3]. The synthetic activity in this and closely related areas is

growing rapidly, as recent examples of amido–cyclopentadienyl and amido–fluorenyl zirconium complexes and of amido–/imido–cyclopentadienyl Group 5 compounds illustrate [4]. Not only nitrogen, but also alkoxy- and siloxy-functionalized cyclopentadienyl compounds have been reported recently for titanium [5,6].

Part of our current research is on the synthesis of cyclopentadienyl-functionalized monocyclopentadienyl titanium compounds, e.g. the preparation of (3-(tetramethylcyclopentadienyl)-prop-1-oxy)titaniumdichloride via intramolecular C–O activation in a titanium ylide $[\text{C}_5\text{Me}_4(\text{CH}_2)_3\text{OMe}]\text{TiCl}_2(\text{CHPh}_3)$ [6] or insertion of basic functions into titanium–fulvene bonds [7]. However, these methods do not seem to have a broad scope and a more generally applicable methodology has to be worked out.

Trimethylsilyl-functionalized cyclopentadienes have been used to introduce cyclopentadienyl ligands on Group 4 and 5 metal centers [5b,8]. It has been established that the reaction between silylated cyclopentadienes and titanium tetrachloride is an efficient route to monocyclopentadienyltitanium complexes. In addition,

¹ Dedicated to Professor Dr. Herbert Schumann on the occasion of his 60th birthday.

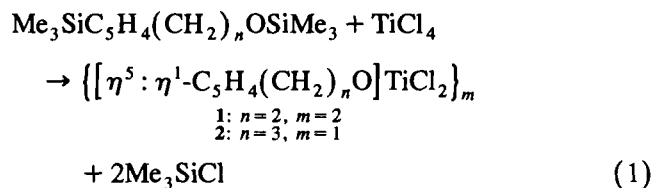
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the method is also useful for formation of M–OAr bonds for Group 4, 5 and 6 metals by reaction with phenyltrimethylsilyl ether to afford phenoxy metal complexes with release of chlorotrimethylsilane [9]. Green and coworkers [4c] used trimethylsilyl extrusion for the preparation of cyclopentadienylalkyl–amido and –imido derivatives of Group 5 metals.

We decided to investigate whether it is possible to introduce a cyclopentadienyl and an alkoxy function in one step onto a metal center starting from the corresponding trimethylsilyl- ω -(trimethylsilylcyclopentadienyl)alkyl ethers, $\text{Me}_3\text{SiC}_5\text{H}_4(\text{CH}_2)_n\text{OSiMe}_3$ ($n = 2, 3$). Here we report a new, efficient route for the preparation of cyclopentadienyl–alkoxy titanium complexes.

2. Results and discussion

Reaction of 1-(trimethylsilylcyclopentadienyl)-2-(trimethylsilyloxy)ethane and 1-(trimethylsilylcyclopentadienyl)-3-(trimethylsilyloxy)propane with titanium tetrachloride in pentane at 0°C instantaneously gives the cyclopentadienyl–alkoxy titanium dichlorides $\{[\eta^5 : \eta^1\text{-C}_5\text{H}_4(\text{CH}_2)_2\text{O}]\text{TiCl}_2\}_2$ (**1**, orange–red) and $[\eta^5 : \eta^1\text{-C}_5\text{H}_4(\text{CH}_2)_3\text{O}]\text{TiCl}_2$ (**2**, yellow) with formation of two equivalents of Me_3SiCl (Eq. (1)):



The new compounds have been characterized by ^1H and ^{13}C NMR and IR spectroscopy, mass spectrometry, elemental analysis and single crystal X-ray structure determination. Compound **1** is a dimer, while **2** is a monomer in the solid state. In crystalline form the compounds are air-stable, although in solution they have to be kept under an inert atmosphere. $\{[\eta^5 : \eta^1\text{-C}_5\text{H}_4(\text{CH}_2)_2\text{O}]\text{TiCl}_2\}_2$ (**1**) is poorly soluble in pentane, ether, toluene, benzene and chlorinated solvents, but dissolves quite well in tetrahydrofuran. The solubility of $[\eta^5 : \eta^1\text{-C}_5\text{H}_4(\text{CH}_2)_3\text{O}]\text{TiCl}_2$ (**2**) in common organic solvents ranges from quite good (alkanes) to excellent (aromatic solvents, ethers) and reflects the monomeric structure of the compound. In the ^1H NMR spectra (C_6D_6) of both compounds the four cyclopentadienyl protons show up as a pair of pseudo-triplets. The α -protons are found at 5.78 ppm (**1**) and 5.42 ppm (**2**), while the two β -protons are at 6.07 ppm and 6.42 ppm respectively. For **1** the methylene protons of the carbon chain give triplets at 2.19 ppm (CpCH_2) and at 4.68 ppm (OCH_2). The chain methylene resonances for **2** are observed at 1.79 ppm (m, CpCH_2CH_2 –), at 1.30

ppm (m, $-\text{CH}_2\text{CH}_2\text{CH}_2$ –) and at 3.51 ppm (t, OCH_2). The assignment of the ^{13}C NMR spectra is also straightforward. For **1** ($\text{THF-}d_8$) the *ipso*-C of the cyclopentadienyl ring is found at 149.36 ppm, and the other ring carbon atoms form doublets at 118.89 and 122.35 ppm; the chain carbon atom α with respect to the cyclopentadienyl ring is observed as a doublet at 33.21 ppm and the alkoxy C gives a doublet at 97.95 ppm. For compound **2** (C_6D_6), the ring resonances are at 131.39, 120.89 and 116.53 ppm, while the chain carbon resonances are at 32.75 ppm (α -C), 24.78 ppm (central chain carbon) and 76.07 ppm (alkoxy C). Chemical shifts and coupling constants (see Section 5) of the ^1H and ^{13}C NMR spectra are comparable with those found in the literature for other *ansa*-titanocene complexes [6,10]. The IR spectra show a number of diagnostic bands. The most prominent is the intense $\nu(\text{C–O})$ absorption, observed at 1066 cm^{-1} for **2**, while for **1** it has shifted to 985 cm^{-1} . Mass spectra show for both **1** and **2** monomeric molecular ion (M^+) peaks, respectively at m/e values of 226 and 240 mass units, and related fragments such as $[\text{M–OCH}_2]^+$ and $[\text{M–CH}_2\text{OTiCl}_2]^+$ ($[\text{M–OCH}_2]^+$ is in both cases the most abundant ion); all fragments have the fine structure corresponding to the natural isotope (Cl, Ti) distribution. It appears that compound **1** easily dissociates in the gas phase.

3. Molecular structures

The molecular structures of **1** and **2** were determined by single-crystal X-ray diffraction. Figs. 1 and 2 show PLUTO drawings of the respective compounds. X-ray diffraction data were collected under the conditions summarized in Table 1. Selected bond lengths, bond angles and positional parameters are summarized in Tables 2–5.

Compound **1** crystallizes in the triclinic space group $\bar{P}1$. The basic structure is a dimeric molecule with a

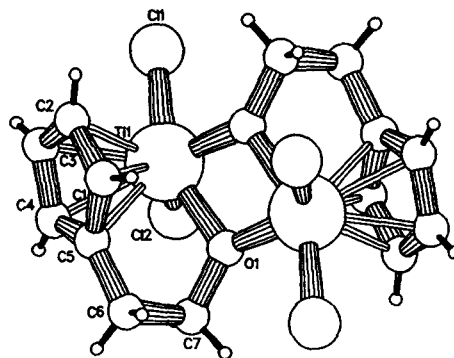


Fig. 1. PLUTO drawing of the molecular structure of $[[\eta^5 : \eta^1\text{-C}_5\text{H}_4(\text{CH}_2)_2\text{O}]\text{TiCl}_2]_2$ (**1**).

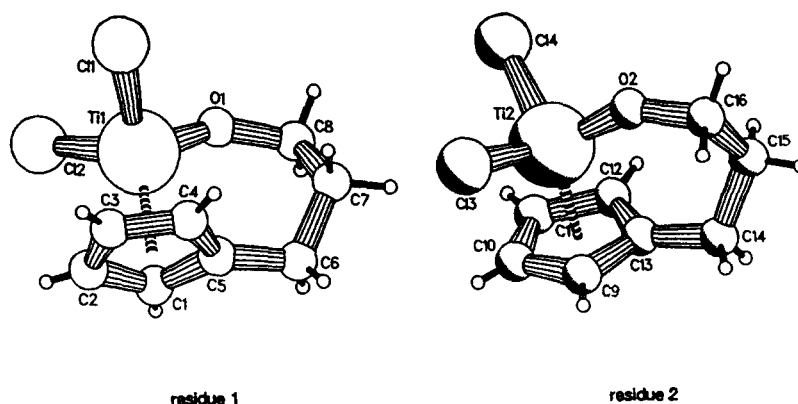


Fig. 2. PLUTO drawing of the molecular structure of $[\eta^5:\eta^1\text{-C}_5\text{H}_4(\text{CH}_2)_3\text{O}]\text{TiCl}_2$, (2); the two crystallographically independent molecules (residue 1 and 2) are shown.

crystallographically imposed center of inversion, in which two Ti–O–Ti bridges form a non-symmetric quadrangle in the center of the molecule. The bridging alkoxy group is bonded in a very interesting way. The Ti–O distances clearly show that the interaction between the alkoxy oxygen and the metal atoms is different, and that the alkoxide function binds intermolecu-

larly and coordinates in an intramolecular fashion. The bond Ti(1)–O(1) is long (2.0726(17) Å) whereas Ti(1)–O(1)a is short (1.9472(17) Å), indicating that the first is a coordinative and the latter a normal alkoxy–Ti bond. Closer inspection reveals, however, that there is more to it. The Ti(1)–O(1) bond is shorter than typical Ti–O dative bonds, like those observed in $(\eta^5\text{-Cp})_3(\text{C}_5\text{H}_4\text{-})$

Table 1
Experimental crystallographic data for 1 and 2

	Compound	
	1	2
Empirical formula	$\text{C}_{14}\text{H}_{16}\text{Cl}_4\text{O}_2\text{Ti}_2$	$\text{C}_8\text{H}_{10}\text{Cl}_2\text{OTi}$
Molecular weight	453.85	240.95
Crystal system	triclinic	triclinic
Space group	$\text{P}\bar{1}$ (No. 2)	$\text{P}\bar{1}$ (No. 2)
a (Å)	7.702(1)	8.194(1)
b (Å)	7.942(2)	11.002(1)
c (Å)	8.251(1)	11.192(1)
α (°)	71.39(1)	84.339(5)
β (°)	89.92(1)	88.035(5)
γ (°)	61.25(2)	76.256(6)
V (Å ³)	412.27(16)	975.2(2)
Z	1	4
d_{calc} (g cm ⁻³)	1.828	1.641
μ (Mo K α) (cm ⁻¹)	16.1	13.7
Approx. crystal dimension (mm ³)	$0.25 \times 0.37 \times 0.38$	$0.20 \times 0.25 \times 0.31$
Radiation	Mo K α	Mo K α
Monochromator	graphite	graphite
θ range (min, max) (°)	1.75, 30.00	1.83, 27.0
$\omega/2\theta$ scan deg (°)	$\Delta\omega = 0.80 + 0.34\text{tg } \theta$	$\Delta\omega = 0.95 + 0.34\text{tg } \theta$
X-ray exposure time (h)	51.4	108.4
Total data	2897	5567
Unique data	2402	5143
Observed data ($I \geq 2.5\sigma(I)$)	2387	4321
Number of refined parameters	133	297
Final agreement factors		
$R_F = \Sigma(F_o - F_c) / \Sigma F_o $	0.035	0.033
$R_w = [\Sigma(\omega(F_o - F_c)^2) / \Sigma\omega F_o ^2]^{1/2}$	0.042	0.040
Weighting scheme	1	1
Max (shift/ σ) final cycle	0.0261	0.392
Average (shift/ σ) final cycle	0.0026	0.020

Table 2
Selected bond distances and angles for 1

Distance (Å)			
Ti(1)–Cl(1)	2.3419(10)	Ti(1)–C(3)	2.366(3)
Ti(1)–Cl(2)	2.3149(10)	Ti(1)–C(4)	2.383(3)
Ti(1)–O(1)	2.0726(17)	Ti(1)–C(5)	2.371(3)
Ti(1)–O(1)a	1.9472(17)	O(1)–C(7)	1.446(3)
Ti(1)–C(1)	2.346(3)	C(5)–C(6)	1.499(4)
Ti(1)–C(2)	2.343(3)	C(6)–C(7)	1.529(4)
Angle (°)			
Cl(1)–Ti(1)–Cl(2)	87.93(4)	O(1)–Ti(1)–O(1)a	72.07(7)
Cl(1)–Ti(1)–O(1)	149.62(6)	Ti(1)–O(1)–C(7)	115.71(14)
Cl(1)–Ti(1)–C(1)	118.80(8)	Ti(1)–O(1)–Ti(1)a	107.93(8)
Cl(1)–Ti(1)–O(1)a	87.85(6)	Ti(1)–C(5)–C(6)	113.16(19)
Cl(2)–Ti(1)–O(1)	83.97(5)	C(5)–C(6)–C(7)	107.0(3)
Cl(2)–Ti(1)–O(1)a	121.93(6)	O(1)–C(7)–C(6)	106.2(2)
Ti(1)a–O(1)–C(7)	134.0(2)		

Ti₂(C₄H₈O).C₄H₈O (2.26 Å) [11] and in the tetrahydrofuran functionalized cyclopentadienyl Cp'TiCl₃ (Cp'-tetrahydrofurfurylcyclopentadienyl, Ti–O = 2.16 Å) [12], suggesting that the bond has more regular σ -bond Ti–alkoxy character. The bond between Ti(1) and the oxygen atom of the other bridge (Ti(1)–O(1)a, 1.947(2) Å) is longer than reported for regular titanium alkoxides of bent metallocene Ti(IV) and Ti(III) complexes such as Cp₂Ti(OCH=CH₂)₂ (1.903(2) Å) [13], Cp₂Ti(OEt)Cl (1.855 Å) [14] and Cp₂TiO(2,6-(CH₃)₂C₆H₃) (1.892(2) Å) [15] where a (partial) dou-

ble bond can be assumed as a consequence of the combination of both σ and π bonds between metal and oxygen. The bonding of the cyclopentadienyl ring to titanium in 1 is close to, but not fully, η^5 , indicating strain in this part of the molecule due to the limited geometric tolerance of the bidentate cyclopentadienyl–alkoxide with only two methylene groups linking the cyclopentadienyl and the alkoxide function. The Ti–C bonds to the cyclopentadienyl fragment separate into two relatively short (Ti–C(1), Ti–C(2), 2.346(3) and 2.343(3) Å respectively) and three long (Ti–C(3), Ti–

Table 3
Selected bond distances and angles for 2

Residue 1		Residue 2	
Distance (Å)			
Ti(1)–Cl(1)	2.276(1)	Ti(2)–Cl(3)	2.275(1)
Ti(1)–Cl(2)	2.269(1)	Ti(2)–Cl(4)	2.273(1)
Ti(1)–O(1)	1.762(2)	Ti(2)–O(2)	1.755(2)
Ti(1)–C(1)	2.329(3)	Ti(2)–C(9)	2.320(3)
Ti(1)–C(2)	2.354(3)	Ti(2)–C(10)	2.342(3)
Ti(1)–C(3)	2.356(3)	Ti(2)–C(11)	2.365(3)
Ti(1)–C(4)	2.336(3)	Ti(2)–C(12)	2.343(3)
Ti(1)–C(5)	2.354(3)	Ti(2)–C(13)	2.351(3)
O(1)–C(8)	1.434(4)	O(2)–C(16)	1.429(5)
C(5)–C(6)	1.512(5)	C(13)–C(14)	1.506(5)
C(6)–C(7)	1.531(5)	C(14)–C(15)	1.527(5)
C(7)–C(8)	1.505(5)	C(15)–C(16)	1.509(6)
Angle (°)			
Cl(1)–Ti(1)–Cl(2)	102.63(4)	Cl(3)–Ti(2)–Cl(4)	103.25(4)
Cl(1)–Ti(1)–O(1)	102.83(8)	Cl(3)–Ti(2)–O(2)	104.66(8)
Cl(1)–Ti(1)–C(1)	146.26(9)	Cl(3)–Ti(2)–C(9)	91.42(9)
Cl(2)–Ti(1)–O(1)	104.41(8)	Cl(4)–Ti(2)–O(2)	103.77(8)
Cl(2)–Ti(1)–C(1)	96.81(9)	O(2)–Ti(2)–C(9)	102.8(1)
O(1)–Ti(1)–C(1)	98.6(1)	Ti(2)–O(2)–C(16)	146.7(2)
Ti(1)–O(1)–C(8)	145.8(2)	C(12)–C(13)–C(14)	127.2(3)
C(4)–C(5)–C(6)	126.8(3)	C(13)–C(14)–C(15)	113.6(3)
C(5)–C(6)–C(7)	113.1(3)	C(14)–C(15)–C(16)	113.3(3)
C(6)–C(7)–C(8)	112.7(3)	O(2)–C(16)–C(15)	111.9(3)
O(1)–C(8)–C(7)	110.8(3)		

Table 4

Final fractional atomic coordinates and equivalent isotropic thermal displacement parameters for non-H atoms with ESDs in parentheses for 1

Atom in the asymmetric unit	x	y	z	U_{eq} (Å ²) [*]
Ti(1)	0.67188(6)	0.31432(6)	0.16612(5)	0.0093(1)
Cl(1)	1.01409(8)	0.15153(9)	0.14806(8)	0.0152(2)
Cl(2)	0.73694(9)	0.48027(9)	0.32190(8)	0.0155(2)
O(1)	0.3882(2)	0.5765(2)	0.0871(2)	0.0109(4)
C(1)	0.4972(4)	0.1387(4)	0.1746(3)	0.0151(6)
C(2)	0.7047(4)	−0.0096(4)	0.2264(4)	0.0169(6)
C(3)	0.7739(4)	−0.0095(4)	0.3857(3)	0.0186(6)
C(4)	0.6096(4)	0.1390(4)	0.4322(3)	0.0180(6)
C(5)	0.4372(4)	0.2315(4)	0.3018(3)	0.0144(6)
C(6)	0.2372(4)	0.4178(4)	0.2831(3)	0.0162(6)
C(7)	0.2665(4)	0.6040(4)	0.2205(3)	0.0137(6)

$$^* U_{eq} = 1/3 \sum_i \sum_j U_{ij} a_i^* a_j^* a_i a_j$$

C(4), Ti–C(5), 2.366(3), 2.383(3) and 2.371(3) Å distances. The bite angle, Cp(center)–Ti–O, of the bidentate cyclopentadienyl–alkoxide ligand is 100.8°, and the ligand seems quite rigid and exerts considerable steric constraints on the molecule as indicated by the long Ti(1)–O(1) bond (2.072(6) Å) and the obtuse angle Ti(1)–O(1)–C(7) (115.71(1)°). The strain also forces the carbon atom of the alkoxy functionalized carbon chain next to the Cp group, C(6), 0.2 Å out of the plane of the cyclopentadienyl group. The carbon atoms C(1)–C(5) of the cyclopentadienyl fragment itself are in a

plane within experimental error. Within the bidentate ligand the distances and other features seem completely normal and correspond well to those in the analogous part of complex 2. It is clear that, apart from the strain-induced distortions, the bonding between titanium and the cyclopentadienyl–alkoxy fragment is quite normal and can be compared well with other cyclopentadienyl titanium complexes [11–15]. Compared with the structure of 2, all distances between metal and ligands appear to be larger for 1, reflecting the steric strain in the cyclopentadienyl–alkoxide, the higher coordination

Table 5

Final fractional atomic coordinates and equivalent isotropic thermal displacement parameters for non-H atoms with ESDs in parentheses for 2

Atom in the asymmetric unit	x	y	z	U_{eq} (Å ²) [*]
<i>Residue 1</i>				
Ti(1)	0.11333(7)	0.22407(5)	0.37756(4)	0.0124(1)
Cl(1)	−0.0834(1)	0.29560(8)	0.51872(7)	0.0262(2)
Cl(2)	−0.0425(1)	0.17496(7)	0.23384(7)	0.0217(2)
O(1)	0.1687(3)	0.3623(2)	0.3151(2)	0.0173(6)
C(1)	0.3626(4)	0.0801(3)	0.3373(3)	0.0189(8)
C(2)	0.2535(4)	0.0100(3)	0.3952(3)	0.021(1)
C(3)	0.2204(4)	0.0461(3)	0.5116(3)	0.020(1)
C(4)	0.3116(4)	0.1383(3)	0.5266(3)	0.0177(8)
C(5)	0.4020(4)	0.1586(3)	0.4202(3)	0.0160(6)
C(6)	0.5154(4)	0.2488(3)	0.3972(3)	0.021(1)
C(7)	0.4228(4)	0.3863(3)	0.4040(3)	0.0197(8)
C(8)	0.2952(4)	0.4333(3)	0.3064(3)	0.0188(8)
<i>Residue 2</i>				
Ti(2)	0.37742(7)	0.27769(5)	0.88660(5)	0.0130(1)
Cl(3)	0.5491(1)	0.25203(7)	1.04729(7)	0.0236(2)
Cl(4)	0.5545(1)	0.28833(7)	0.72717(6)	0.0214(2)
O(2)	0.3287(3)	0.1312(2)	0.8826(2)	0.0225(6)
C(9)	0.1525(4)	0.3887(3)	0.9933(3)	0.0185(6)
C(10)	0.2491(4)	0.4751(3)	0.9495(3)	0.023(1)
C(11)	0.2422(4)	0.4882(3)	0.8241(3)	0.023(1)
C(12)	0.1432(4)	0.4091(3)	0.7886(3)	0.0204(8)
C(13)	0.0835(4)	0.3496(3)	0.8933(3)	0.0168(6)
C(14)	−0.0317(4)	0.2609(3)	0.8996(3)	0.021(1)
C(15)	0.0374(5)	0.1434(3)	0.8346(3)	0.025(1)
C(16)	0.1997(5)	0.0633(3)	0.8864(4)	0.036(1)

$$^* U_{eq} = 1/3 \sum_i \sum_j U_{ij} a_i^* a_j^* a_i a_j$$

number and consequently the higher steric burden on the metal in the latter.

Complex **2** crystallizes in space group $P\bar{1}$. Two crystallographically independent molecules (residues 1 and 2, Fig. 2) are present in the asymmetric unit, separated by normal van der Waals distances. Both molecules **2** have a perfect three-legged piano stool structure as expected for organotitanium compounds of the type $\text{CpTi}(\text{X})\text{Cl}_2$, and show practically identical bonding features. The bidentate cyclopentadienyl-alkoxide ligand is very flexible and fits well around titanium, exerting no apparent strain on the molecule. The carbon atom of the side chain next to the Cp ligand is located perfectly well in the plane of the cyclopentadienyl ring, all Ti–C(Cp) distances are identical within error limits, and so are the distances within the Cp-ring. The short titanium–oxygen bond (Ti(1)–O(1) = 1.762(2) Å, a typical Ti–O double bond) and the rather large angle Ti(1)–O(1)–C(8) (145.8(2)°), indicate strong π -type donation from oxygen to the metal in addition to the regular σ -interaction. Bond lengths (Ti–O; Ti–Cl; Ti–C(Cp) and C–C(Cp)) and angles (Ti–O–C; O–Ti–Cl and Cl–Ti–Cl) within the molecules **2** are very similar to those found in the per-methyl analogue of **2**, (3-(2,3,4,5-tetramethylcyclopentadienyl)propoxy)-titanium dichloride, described before by Fandos et al. [4]. The C–C distances within the Cp-rings, the C–C and C–O bonds in the chain connecting the Cp with the alkoxide, the Ti–C_{Cp} and the Ti–O distances are identical for both complexes. The only difference is found in the Ti–Cl bonds which are slightly shorter (0.01 Å) in the compound reported here.

4. Conclusions

One-step introduction of a bifunctional bidentate ligand system on titanium, like a cyclopentadienyl-alkoxide, starting from titanium tetrachloride and the bis-trimethylsilyl derivative of the ligand system, is a convenient synthetic methodology. The conversion is fast and essentially quantitative and purification is relatively easy because of the high volatility of the side product Me_3SiCl .

Small differences in the chain linking the two functions appear to have a dramatic influence on the molecular structure of the product formed. With a (short) C_2H_4 chain between the cyclopentadienyl and the alkoxide function, a dimeric complex is obtained in which the alkoxide function forms a non-symmetric bridge such that the cyclopentadienyl binds to one and the alkoxide binds strongly to the other titanium atom, while at the same time it also forms a dative interaction with the other titanium atom. A C_3H_6 chain between the cyclopentadienyl and alkoxide functions gives the bidentate ligand system more flexibility to adjust the

relative geometry of both functions, and a strictly normal CpTiCl_2OR derivative is formed.

5. Experimental section

All manipulations were performed under nitrogen using standard glovebox and Schlenk techniques. The solvents used (toluene, ether, THF and pentane) were dried over sodium/potassium alloy. Characterization was made with Bruker WH-90 (^1H NMR) and Varian VXR-300 (^1H and ^{13}C NMR) spectrometers and a Mattson-4020 Galaxy FT-IR spectrophotometer. Mass spectrometry was performed on a Ribermag R10-10C mass spectrometer, operating at 70 eV. Elemental analysis was carried out at the Microanalytical Department of the University of Groningen. Values given are the average of at least two independent determinations. Titanium tetrachloride was used as received from Fluka. The lithium salts $[\text{C}_5\text{H}_4(\text{CH}_2)_n\text{OSiMe}_3]^- \text{Li}^+$ ($n = 2, 3$) were prepared in a straightforward way from the corresponding cyclopentadienes [16,17].

$\text{Me}_3\text{SiC}_5\text{H}_4(\text{CH}_2)_2\text{OSiMe}_3$. Prepared by adding at room temperature 6.6 ml (52 mmol) of Me_3SiCl to a suspension of 9.78 g (52 mmol) of $\text{C}_5\text{H}_4(\text{CH}_2)_2\text{OSiMe}_3\text{Li}$ in 110 ml of ether. After stirring for 1 h, the solvent was evaporated and 60 ml of pentane was added. The mixture was filtrated to remove LiCl. Evaporation of the solvent afforded 8.00 g (31.50 mmol, 60%) of a pale yellow liquid (mixture of isomers). ^1H NMR (CDCl_3 , ppm): δ –0.04 (s, 9H); 0.12 (s, 9H), 2.26 (t, 2H); 3.26 (m, 1H); 3.72 (t, 2H); 6.11 (m, 1H); 6.40 (m, 1H); 6.43 (m, 1H). ^{13}C NMR (CDCl_3 , ppm): δ –2.07 (q, $^1J(\text{C-H}) = 119.77$ Hz); –0.47 (q, $^1J(\text{C-H}) = 118.62$ Hz); 33.43 (t, $^1J(\text{C-H}) = 126.68$ Hz); 51.27 (d, $^1J(\text{C-H}) = 131.29$ Hz); 62.87 (t, $^1J(\text{C-H}) = 141.65$ Hz); 128.54 (d, $^1J(\text{C-H}) = 141.65$ Hz); 132.13 (d, $^1J(\text{C-H}) = 158.93$ Hz); 133.78 (d, $^1J(\text{C-H}) = 164.73$ Hz); 141.72 (s).

$\text{Me}_3\text{SiC}_5\text{H}_4(\text{CH}_2)_3\text{OSiMe}_3$. Prepared by adding at room temperature 1.90 ml (15.0 mmol) of ClSiMe_3 to a suspension of 3.00 g (14.9 mmol) of $\text{C}_5\text{H}_4(\text{CH}_2)_3\text{OSiMe}_3\text{Li}$ in 50 ml of ether. After stirring for 3 h at room temperature, the solvent was evaporated and 50 ml of pentane added. Filtration and evaporation of the pentane afforded 2.75 g (10.26 mmol, 69%) of an orange viscous oil. ^1H NMR (CDCl_3 , ppm): δ –0.06 (s, 9H); 0.09 (s, 9H); 1.77 (m, 2H); 2.43 (m, 2H); 3.23 (m, 1H); 3.59 (t, 2H); 6.06 (m, 1H); 6.41 (m, 1H); 6.43 (m, 1H). ^{13}C NMR (CDCl_3 , ppm): δ –2.07 (q, $^1J(\text{C-H}) = 122.07$ Hz); –0.47 (q, $^1J(\text{C-H}) = 118.62$ Hz); 26.02 (t, $^1J(\text{C-H}) = 127.83$ Hz); 32.82 (t, $^1J(\text{C-H}) = 126.68$ Hz); 50.91 (d, $^1J(\text{C-H}) = 125.53$ Hz); 62.46 (t, $^1J(\text{C-H}) = 140.50$ Hz); 127.08 (d, $^1J(\text{C-H}) = 162.40$ Hz); 132.11 (d, $^1J(\text{C-H}) = 160.06$ Hz); 133.86 (d, $^1J(\text{C-H}) = 168.13$ Hz); 145.09 (s).

$[\eta^5 : \eta^1\text{-C}_5\text{H}_4(\text{CH}_2)_2\text{O}]\text{TiCl}_2$ (**1**). To a solution of 2.22 g (8.74 mmol) of $\text{Me}_3\text{SiC}_5\text{H}_4(\text{CH}_2)_2\text{OSiMe}_3$ in 40 ml of pentane at 0°C, 0.8 ml (7.28 mmol) of TiCl_4 was added. Immediately a yellow–orange powder precipitated. The reaction mixture was warmed to room temperature and stirred overnight. The solvent was removed and the solid washed with pentane and dried in vacuum. The solid was dissolved in 80 ml of hot toluene. The hot solution was filtered, cooled to –20°C and yielded 0.34 g (1.50 mmol, 21%, m.p. 179°C) of $[\eta^5 : \eta^1\text{-C}_5\text{H}_4(\text{CH}_2)_2\text{O}]\text{TiCl}_2$ (**1**) as orange–red crystals. ^1H NMR (C_6D_6 , ppm): δ 2.19 (t, 2H, $^3J(\text{H-H}) = 6.74$ Hz); 4.68 (t, 2H, $^3J(\text{H-H}) = 6.74$ Hz); 5.78 (pt, 2H, $^3J(\text{H-H}) = 2.6$ Hz); 6.07 (pt, 2H, $^3J(\text{H-H}) = 2.6$ Hz). ^{13}C NMR ($\text{THF-}d_8$, ppm): δ 33.21 (t, $^1J(\text{C-H}) = 131.34$ Hz); 97.95 (t, $^1J(\text{C-H}) = 148.04$ Hz); 118.89 (d, $^1J(\text{C-H}) = 179.17$ Hz); 122.35 (d, $^1J(\text{C-H}) = 176.13$ Hz); 149.36 (s). IR (Nujol, cm^{-1}): 3109 (vw); 3096 (vw); 1484 (m); 1440 (m); 1309 (w); 1224 (vw); 1172 (m); 1047 (w); 1042 (w); 985 (s); 952 (m); 914 (w); 897 (w); 873 (m); 835 (s); 688 (m); 575 (s); 472 (m); 416 (s). Mass spectrometry: 226 (M^+); 196 (M-OCH_2) $^+$; 118 ($\text{M-C}_5\text{H}_4(\text{CH}_2)_2\text{O}$) $^+$; 91 (C_7H_7) $^+$; 78 ($\text{M-CH}_2\text{OTiCl}_2$) $^+$. Anal. Found: C, 37.21; H, 3.55; Cl, 30.63; Ti, 21.22. $\text{C}_{14}\text{H}_{16}\text{Cl}_4\text{O}_2\text{Ti}_2$. Calc.: C, 37.05; H, 3.55; Cl, 31.25; Ti, 21.10.

$[\eta^5 : \eta^1\text{-C}_5\text{H}_4(\text{CH}_2)_3\text{O}]\text{TiCl}_2$ (**2**). To a solution of 1.60 g (5.97 mmol) of $\text{Me}_3\text{SiC}_5\text{H}_4(\text{CH}_2)_3\text{OSiMe}_3$ in 30 ml of pentane at 0°C, 0.55 ml (4.98 mmol) of TiCl_4 was added. Immediately a yellow powder precipitated. The reaction mixture was warmed to room temperature and stirred overnight. The solvent was removed and the solid was washed twice with pentane. Extraction with 40 ml of toluene and filtration gave after cooling to room temperature 0.25 g (1.03 mmol, 21%) of dark yellow–green crystals of **2**. ^1H NMR (C_6D_6 , ppm): δ 1.30 (m, 2H); 1.79 (m, 2H); 3.51 (t, 2H); 5.42 (pt, 2H); 6.42 (pt, 2H). ^{13}C NMR (C_6D_6 , ppm): δ 24.78 (t, $^1J(\text{C-H}) = 128.84$ Hz); 32.75 (t, $^1J(\text{C-H}) = 128.84$ Hz); 76.07 (d, $^1J(\text{C-H}) = 147.36$ Hz); 116.53 (d, $^1J(\text{C-H}) = 177.16$ Hz); 120.89 (d, $^1J(\text{C-H}) = 172.33$ Hz); 131.39 (s). IR (Nujol, cm^{-1}): 3097 (vw); 3084 (vw); 1491 (w); 1415 (vw); 1332 (vw); 1271 (vw); 1240 (vw); 1211 (w); 1066 (s); 1031 (w); 1014 (m); 939 (m); 873 (w); 827 (s); 611 (m); 524 (m); 464 (m); 405 (s). Mass spectrometry: 240 (M^+); 210 (M-OCH_2) $^+$; 176 ($\text{M-OCH}_2\text{Cl}$) $^+$; 78 ($\text{C}_5\text{H}_4\text{CH}_2$) $^+$; 36 (Cl) $^+$. Anal. Found: C, 39.67; H, 4.12; Cl, 29.09; Ti, 19.95. $\text{C}_8\text{H}_{10}\text{Cl}_2\text{OTi}$. Calc.: C, 39.89; H, 4.15; Cl, 23.43; Ti, 19.88.

5.1. Structure determination of **1** and **2**

The crystals used for characterization were selected and glued on a glass fiber using inert-atmosphere handling techniques and cooled to 130 K using an on-line

liquid nitrogen cooling system mounted on an Enraf-Nonius CAD-4F diffractometer interfaced to a VAX-11/730 computer. Unit cell parameters and orientation matrices were determined from least-squares treatment of the SET4 [18] setting angles of 22 reflections in the range $13.43^\circ < \theta < 20.63^\circ$ for **1** and 21 reflections in the range $15.24^\circ < \theta < 20.50^\circ$ for **2**. The structures were solved by Patterson methods and subsequent partial structure expansion (SHELXS86) [19]. For **1** and **2**, positional and anisotropic thermal displacement parameters for the non-hydrogen atoms were refined with block-diagonal least-squares procedures (CRYLSQ) [20] minimizing the function $Q = \sum_h [w(\|F_o\| - \|F_c\|)^2]$. A subsequent difference Fourier synthesis gave all the hydrogen atoms of which coordinates and isotropic thermal displacement parameters were refined. Refinements on F_o by full-matrix least-squares techniques with anisotropic thermal displacement parameters for the non-hydrogen atoms and isotropic thermal displacement parameters for the hydrogen atoms converged at $R_F = 0.035$ ($wR = 0.042$, $w = 1$, **1**) and $R_F = 0.033$ ($wR = 0.040$, $w = 1$, **2**). For **1**, a final difference Fourier synthesis showed no unusual features. The crystal exhibited some secondary extinction for which the F_c values were corrected by refinement of an empirical isotropic extinction parameter [21]. For **2**, a final difference Fourier synthesis reveals residual densities between -0.90 and $0.56 \text{ e}\text{\AA}^{-3}$. Crystal data and experimental details of the structure determination are compiled in Table 2. The final fractional atomic coordinates and equivalent isotropic displacement parameters for the non-hydrogen atoms are given in Tables 4 and 5. Scattering factors were taken from Cromer and Mann [22]. Anomalous dispersion factors given by Cromer and Liberman [23] were included in F_c . All calculations were carried out on the CDC-Cyber 962-31 computer of the University of Groningen with the program packages XTAL [22], PLATON [24] (calculation of geometric data) and a locally modified version of the program PLUTO [25] (preparation of illustrations).

Tables of H-atom coordinates and thermal parameter and a complete list of bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre.

Acknowledgement

The European Community is acknowledged for granting a postdoctoral fellowship (G.T.).

Supplementary material available

Further details of the structure determinations, the refinement parameters used, atomic coordinates and

isotropic displacement parameters, bond distances, angles and torsion angles, listings of observed and calculated structure factors for **1** and **2** are available from the authors.

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