

New $[\text{Ti}(\eta^5\text{-C}_5\text{H}_5)\text{Cl}_2(\text{OR})]$ Complexes. Crystal and Molecular Structure of η^5 -Cyclopentadienyl(cyclohexoxy)titanium(IV) Dichloride

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Summary. A series of new compounds with molecular formula $[\text{Ti}(\eta^5\text{-C}_5\text{H}_5)\text{Cl}_2(\text{OR})]$ ($R = \text{C}_6\text{H}_{11}$ (cyclohexyl, **1**), $\text{CH}_2\text{CH}(\text{CH}_3)_2$ (**2**), $\text{CH}(\text{C}_2\text{H}_5)_2$ (**3**), and $\text{CH}_2\text{C}_6\text{H}_5$ (**4**)) has been obtained by the reaction of $[\text{Ti}(\eta^5\text{-C}_5\text{H}_5)\text{Cl}_3]$ with the appropriate alcohol. All complexes were characterized by elemental analysis and by IR and ^1H NMR spectroscopy. The structure of **1** was determined by X-ray diffraction studies; crystal data: triclinic, $a = 11.334(2)$, $b = 13.590(2)$, $c = 12.237(2)$ Å, $\alpha = 113.501(5)$, $\beta = 118.182(5)$, $\gamma = 101.993(6)$, $V = 1328.2(4)$ Å³, $T = 298\text{K}$, space $\text{P}\bar{1}$, $Z = 4$, two crystallographically independent molecules in the unit cell. Final R and R_w values are 0.0583 and 0.0632, respectively. Compound **1** exhibits surprisingly short Ti–Cl and Ti–O distances, suggesting strong π donation by the chloride and in particular by the alkoxide ligand. The Ti–O–C angle is unusually large.

Keywords. Titanium; Cyclopentadienyl; Akloxytitanium complexes; X-ray analysis.

Neue $[\text{Ti}(\eta^5\text{-C}_5\text{H}_5)\text{Cl}_2(\text{OR})]$ -Komplexe. Kristall- und Molekülstruktur von η^5 -Cyclopentadienyl(cyclohexoxy)titan(IV) Dichlorid

Zusammenfassung. Durch Umsetzung von $[\text{Ti}(\eta^5\text{-C}_5\text{H}_5)\text{Cl}_3]$ mit dem geeigneten Alkohol wurde eine Reihe von neuen Verbindungen der Formel $[\text{Ti}(\eta^5\text{-C}_5\text{H}_5)\text{Cl}_2(\text{OR})]$ ($R = \text{C}_6\text{H}_{11}$ (cyclohexyl, **1**), $\text{CH}_2\text{CH}(\text{CH}_3)_2$ (**2**), $\text{CH}(\text{C}_2\text{H}_5)_2$ (**3**) und $\text{CH}_2\text{C}_6\text{H}_5$ (**4**)) erhalten. Alle Komplexe wurden elementaranalytisch sowie IR- und ^1H -NMR-spektroskopisch charakterisiert. Die Struktur von **1** wurde röntgenographisch bestimmt; Kristalldaten: triklin, $a = 11.334(2)$, $b = 13.590(2)$, $c = 12.237(2)$ Å, $\alpha = 113.501(5)$, $\beta = 118.182(5)$, $\gamma = 101.993(6)$, $V = 1328.2(4)$ Å³, $T = 298\text{K}$, Raumgruppe $\text{P}\bar{1}$, $Z = 4$, zwei kristallographisch unabhängige Moleküle in der Elementarzelle; abschließende R -Werte: $R = 0.0583$ und $R_w = 0.0632$. Verbindung **1** zeigt überraschend kurze Ti–Cl- und Ti–O-Abstände; dies deutet auf eine starke π -Elektronendonorkwirkung des Chlorid- und vor allem des Alkoxidliganden hin. Der Ti–O–C-Bindungswinkel ist ungewöhnlich groß.

Introduction

Cyclopentadienylalkoxytitanium(IV) dichlorides with the formula $[\text{Ti}(\eta^5\text{-C}_5\text{H}_5)\text{Cl}_2(\text{OR})]$ have been prepared either from $[\text{Ti}(\eta^5\text{-C}_5\text{H}_5)_2\text{Cl}_2]$ and the corresponding

alcohol by substitution of one *Cp* ligand in the presence of triethylamine [1] or from $[\text{Ti}(\eta^5\text{-C}_5\text{H}_5)\text{Cl}_3]$ by replacement of a chlorine atom by the alkoxy group [2, 3]. Some of them can be used as potential chiral inductor complexes for enantioselective alkylation of carbonyl compounds [1].

Up to now, reports about this family of complexes are limited, particularly with respect to their preparation methods. A recent paper describes, apart from the synthesis, the electrochemical behaviour of $[\text{Ti}(\eta^5\text{-C}_5\text{H}_5)\text{Cl}_2(\text{OR})]$ complexes [3]. In the present work we describe the synthesis and characterization of some new stable monocyclopentadienylalkoxytitanium complexes and the crystal structure of $[\text{Ti}(\eta^5\text{-C}_5\text{H}_5)\text{Cl}_2(\text{OC}_6\text{H}_{11})]$. This appears to be the first crystallographic study on a complex of this class.

Results and Discussion

Complexes **1–4** were obtained as yellow, air-stable needles *via* treatment of $[\text{Ti}(\eta^5\text{-C}_5\text{H}_5)\text{Cl}_3]$ with an excess of ROH in petroleum ether. They are readily soluble in all usual organic solvents. Their melting points are low, ranging from 50 to 80 °C. The IR spectra show the characteristic absorptions of the η^5 -bonded cyclopentadienyl ring [6] and bands due to alkyl groups. Strong bands appearing in the 1050–1110 cm^{-1} region are assigned to the Ti–O–C vibrations [13]. The ^1H NMR spectra exhibit the expected signals and relative intensities (see Experimental).

Crystal structure of **1**

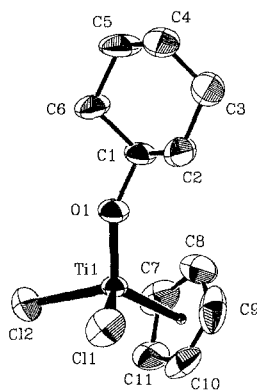
The unit cell of **1** contains two crystallographically independent but – in their main features – almost identical molecules. The structure of one of them is shown in Fig. 1, together with the atomic numbering scheme. The two chlorine atoms, together with the centroid of the cyclopentadienyl ring and the oxygen atom form a distorted tetrahedral coordination geometry around titanium. The angles subtending the Ti atom range from 103.53 to 117.3° (101.86 to 117.7°)¹. Examination of the structural parameters involving the *Cp* ring indicates that the Ti–C bond lengths do not differ significantly, suggesting that the ring carbon atoms interact with the metal in a nearly symmetrical η^5 -fashion. The distance between titanium and the centroid of cyclopentadienyl ring is by *ca.* 0.050 Å shorter than the corresponding distances in «open clamshell» titanium-complexes (Table 1), indicating a somewhat stronger interaction in *mono-Cp* compounds. The cyclopentadienyl ring is planar to within 0.009 Å (0.004 Å). The C–C distances within the ring range from 1.336 to 1.403 Å (1.359 to 1.385 Å).

The Ti–Cl distances and especially the Ti–O distance are remarkably shorter in **1** than in the titanocene complexes. This can be attributed to their partial double bond character [7, 8, 11]. Since the OC_6H_{11} group is a more effective π donor than Cl, the Ti–O bond undergoes a larger contraction than the Ti–Cl bonds. The strong $p_\pi\text{-}d_\pi$ donation from oxygen to titanium, suggesting an *sp* hybridization of

¹ Here and in the following, values in parentheses refer to the second independent molecule.

Table 1. Titanium coordination distances (Å, averaged values) in **1** and related complexes

	Ti–C _p	Ti–Cl	Ti–O	Ref.
[Ti(η^5 -C ₅ H ₅)Cl ₂ (OC ₆ H ₁₁)]	2.020	2.267	1.723	this work
[Ti(η^5 -C ₅ H ₅)Cl ₃]	2.04	2.28	–	[12]
[Ti(η^5 -C ₅ H ₅) ₂ Cl] ₂ O	2.090	2.409	1.837	[7]
[Ti(η^5 -C ₅ H ₅) ₂ Cl(OC ₂ H ₅)]	2.087	2.405	1.855	[8]
[Ti(η^5 -C ₅ H ₅) ₂ (OC ₆ H ₅) ₂]	2.089	–	1.907	[9]
[Ti(η^5 -C ₅ H ₅) ₂ Cl ₂]	2.059	2.364	–	[10]

**Fig. 1.** ORTEP view of the structure of [Ti(η^5 -C₅H₅)Cl₂(OC₆H₁₁)]; hydrogen atoms have been omitted for clarity

the oxygen atom [11], is also evident in the unusually large Ti–O–C angle of 153° (159.8°). The corresponding angle in the *bis*(cyclopentadienyl) derivative [Ti(η^5 -C₅H₅)₂Cl(OC₂H₅)] [8] is only 133°.

The cyclohexyl ring in each molecule has the stable chair conformation with atoms C(1) and C(4) deviating by -0.664 Å and 0.640 Å (0.541 Å and -0.478 Å), respectively, from the best mean plane of the remaining atoms. The C–C distances within this ring range from 1.496 to 1.536 Å (1.412 to 1.516 Å) with the C(2)–C(3) bond longer than the other ones. Differences can also be observed in the corresponding C–C–C bond angles of rings **A** and **B**. However, the main difference between the six-membered rings concerns the inequalities in torsion angles (Table 3). As a consequence, the closest contact of atom C(1) to C(8) (Fig. 1) is 3.345 Å in molecule **A** and 3.538 Å in molecule **B**. This intramolecular effect is probably responsible for the presence of two crystallographically independent molecules in the triclinic unit cell.

Experimental

Air-sensitive substances were handled under argon by *Schlenk* techniques. Solvents were purified by standard methods. Cyclohexanol, isobutanol, 3-pentanol, and benzyl alcohol were dried with K₂CO₃ and fractionally distilled before use. [Ti(η^5 -C₅H₅)Cl₃] was prepared by the procedure of *Gorsich*

Table 2. Summary of x-ray data

Empirical formula	C ₁₁ H ₁₆ Cl ₂ OTi
Formula weight	283.04
Temperature (K)	298
Wavelength	CuK _α , 1.54180 nm
Space group	P $\bar{1}$
<i>a</i> (Å)	11.334(2)
<i>b</i> (Å)	13.590(2)
<i>c</i> (Å)	12.237(2)
α (°)	113.501(5)
β (°)	118.182(5)
γ (°)	101.993(6)
<i>V</i> (Å ³)	1328.2(4)
<i>Z</i>	4
<i>D</i> _{calcd} / <i>D</i> _{measd} (Mg·m ⁻³)	1.415/1.40
Abs. coeff (μ , mm ⁻¹)	8.940
Max. abs. correction mode	1.59
Scan mode/speed (°/min)	θ -2 θ /3.0
Scan range (°)	2.5 + $\alpha_1\alpha_2$ separation
θ range (°)	4.07 to 61.98
Reflections collected	4355
Independent reflections	4136 (<i>R</i> (int) = 0.0348)
Range of <i>h, k, l</i>	-12 → 11, -15 → 14, 0 → 14
<i>F</i> (000)	584
(Δ/σ) _{max}	0.050
<i>W</i> ^a	<i>a</i> = 0.1042, <i>b</i> = 1.5547
($\Delta\rho$) _{max} /($\Delta\rho$) _{min} /(e/Å ³)	0.977/-0.705
Refinement method	Full-matrix least-squares on <i>F</i> ²
Data/restraints/parameters	4136/0/336
Goodness-of-fit on <i>F</i> ²	1.026
<i>R</i> indices (3693 refs <i>I</i> > 2 σ (<i>I</i>)) ^b	<i>R</i> ₁ = 0.0583, <i>wR</i> ₂ = 0.1561
<i>R</i> indices (all data)	<i>R</i> ₁ = 0.0632, <i>wR</i> ₂ = 0.1638

^a $W = 1/(\sigma^2(F_o^2) + (a * P)^2 + b * P)$ and $P = (\text{Max}(F_o^2, 0) + 2 * F_c^2)/3$; ^b *R*₁ based on *F*, *wR*₂ based on *F*²; extinction coefficient: 0.022(2)

[2]. The product was purified by sublimation. ¹H NMR (CDCl₃): δ = 7.06 (s) ppm; melting point: 211 °C.

IR spectra (range: 4000–400 cm⁻¹) were obtained as KBr discs on a Perkin-Elmer 16PC FT-IR Spectrophotometer; ¹H and ¹³C NMR spectra (CDCl₃) were recorded on a Bruker AM-300 spectrometer. All compounds afforded satisfactory C,H-analyses.

Preparation of [Ti(η^5 -C₅H₅)Cl₂(OC₆H₁₁)] (1)

[Ti(η^5 -C₅H₅)Cl₃] (1.0 g, 4.6 mmol) was suspended in 10 ml petroleum ether (40–60 °C) and an excess of cyclohexanol (10 ml, 95 mmol) was added. The reaction mixture was stirred for 15 min at room temperature and then for 20 min at 45 °C. After cooling with ice and decantation of the mother liquor, the yellow solid obtained was dried under high vacuum. Extraction of the residue with 5 ml petroleum ether afforded pure **1** as yellow needles (0.72 g, 56%). Melting point: 66 °C; ¹H NMR: δ = 6.71 (s, 5H,

Table 3. Positional and equivalent thermal parameters ($\times 10^4$) of non-H atoms
E.s.d.'s in parentheses; $U_{eq} = 1/3(U_{11} + U_{22} + U_{33})$

Atom	x	y	z	U_{eq}
Molecule A				
Ti	1468(1)	3559(1)	-562(1)	38(1)
Cl(1)	2946(1)	4853(1)	2007(1)	76(1)
Cl(2)	1068(2)	4804(1)	-1329(2)	71(1)
O	2740(3)	3248(3)	-848(4)	55(1)
C(1)	3334(5)	2454(4)	-1278(5)	51(1)
C(2)	4136(7)	2245(6)	-78(8)	73(2)
C(3)	4832(8)	1438(7)	-481(10)	85(2)
C(4)	5884(6)	1995(6)	-736(8)	74(1)
C(5)	5093(7)	2238(7)	-1900(7)	76(2)
C(6)	4403(6)	3031(6)	-1509(7)	64(1)
C(7)	-947(5)	1947(5)	-2717(6)	73(1)
C(8)	-126(6)	1451(4)	-2103(9)	90(2)
C(9)	195(6)	1882(6)	-692(9)	88(2)
C(10)	-475(5)	2610(5)	-503(6)	67(1)
C(11)	-1167(5)	2639(5)	-1717(7)	66(1)
Molecule B				
Ti	674(1)	2165(1)	3632(1)	43(1)
Cl(1)	-1335(2)	933(1)	1131(1)	81(1)
Cl(2)	-50(2)	1186(1)	4516(2)	75(1)
O	2073(4)	1849(3)	3659(4)	70(1)
C(1)	3580(7)	2037(6)	4115(9)	83(2)
C(2)	4005(6)	2551(5)	3390(7)	73(1)
C(3)	5501(8)	2630(8)	3716(10)	106(2)
C(4)	5672(8)	1588(7)	3559(11)	107(2)
C(5)	5166(6)	1033(5)	4206(7)	74(1)
C(6)	3683(6)	962(6)	3874(8)	82(2)
C(7)	173(9)	3703(5)	4772(9)	87(2)
C(8)	119(11)	3728(6)	3630(9)	99(3)
C(9)	1558(10)	4052(5)	4002(8)	90(2)
C(10)	2489(8)	4238(4)	5377(7)	85(2)
C(11)	1661(8)	4030(4)	5856(6)	75(2)

C₅H₅, 3.49 (m, 1H), 1.33–2.43 (m, 10H) ppm; ¹³C NMR: δ = 118.8(s), 93.3(s), 34.8(s), 25.2(s), 23.2(s) ppm.

*Preparation of [Ti(η^5 -C₅H₅)Cl₂(OR)] (R = CH₂CH(CH₃)₂ (2),
CH(C₂H₅)₂ (3), and CH₂C₆H₅ (4))*

These complexes were obtained following the above procedure.

2: Yield: 28%; m.p.: 69 °C; ¹H NMR: δ = 6.75 (s, 5H, C₅H₅), 3.43 (d, 2H), 1.72 (m, 1H), 0.99 (d, 6H) ppm.

3: Yield: 71%; m.p.: 79 °C; ¹H NMR: δ = 6.70 (s, 5H, C₅H₅), 4.58 (m, 1H), 1.64 (m, 4H), 1.00 (t, 6H) ppm.

4: Yield: 5%; m.p.: 50 °C; ¹H NMR: δ = 7.37 (m, 5H, C₆H₅), 6.83 (s, 5H, C₅H₅), 4.71 (s, 2H) ppm.

Table 4. Selected bond lengths (Å) and angles (°) in [Ti(η^5 -C₅H₅)Cl₂(OC₆H₁₁)]

	Molecule A	Molecule B
Bond lengths		
Ti–Cl(1)	2.274(1)	2.258(2)
Ti–Cl(2)	2.266(1)	2.269(1)
Ti–O	1.731(3)	1.715(3)
Ti–C(7)	2.308(5)	2.351(5)
Ti–C(8)	2.312(5)	2.318(5)
Ti–C(9)	2.328(5)	2.316(5)
Ti–C(10)	2.358(4)	2.338(5)
Ti–C(11)	2.351(4)	2.358(5)
Aver. Ti–C	2.331	2.336
Ti–Cp	2.017(1)	2.022(1)
C(7)–C(8)	1.375(9)	1.359(9)
C(8)–C(9)	1.403(9)	1.372(9)
C(9)–C(10)	1.380(9)	1.379(11)
C(10)–C(11)	1.336(8)	1.385(10)
C(11)–C(7)	1.382(8)	1.381(9)
mean C–C	1.375	1.375
O–C(1)	1.441(5)	1.449(6)
C(1)–C(2)	1.497(7)	1.505(7)
C(2)–C(3)	1.536(8)	1.516(8)
C(3)–C(4)	1.503(8)	1.418(10)
C(4)–C(5)	1.496(8)	1.501(9)
C(5)–C(6)	1.515(7)	1.502(7)
C(6)–C(1)	1.507(6)	1.412(8)
Bond angles		
Cl(1)–Ti–Cl(2)	103.5(6)	101.9(6)
Cl(1)–Ti–Cp	114.6(1)	116.1(1)
Cl(1)–Ti–O	103.2(1)	102.3(1)
Cl(2)–Ti–Cp	112.8(1)	113.2(1)
Cl(2)–Ti–O	103.9(1)	103.7(1)
Cp–Ti–O	117.3(1)	117.7(1)
Ti–O–C(1)	153.0(3)	159.8(4)
C(7)–C(8)–C(9)	107.5(5)	109.5(7)
C(8)–C(9)–C(10)	107.0(5)	106.9(6)
C(9)–C(10)–C(11)	108.8(5)	108.4(6)
C(10)–C(11)–C(7)	109.4(5)	107.3(7)
C(11)–C(7)–C(8)	107.3(5)	107.9(6)
C(1)–C(2)–C(3)	110.6(5)	111.3(5)
C(2)–C(3)–C(4)	110.8(5)	116.1(5)
C(3)–C(4)–C(5)	111.6(5)	115.9(6)
C(4)–C(5)–C(6)	112.2(5)	112.6(5)
C(5)–C(6)–C(1)	110.2(5)	115.2(5)
C(6)–C(1)–C(2)	111.4(4)	114.8(5)
Torsional angles		
C1C2C6/C2C3C5C6	51.7	43.6
C2C3C5C6/C3C4C5	49.4	38.1

Cp denotes the centroid of the cyclopentadienyl ring

Crystallographic Section

Suitable crystals of **1** were obtained by recrystallization from petroleum ether at -20°C . A crystal with approximate dimensions of $0.25 \times 0.45 \times 0.50$ mm was mounted in air and covered with epoxy glue. Diffraction measurements were performed on a P2₁ Nicolet diffractometer upgraded by Crystal Logic using Ni-filtered Cu radiation. Unit cell dimensions were determined and refined by using the angular settings of 25 automatically centered reflections in the range $23^\circ < 2\theta < 53^\circ$ (Table 2). Intensity data were recorded using a θ - 2θ scan up to $2\theta(\text{max}) = 124^\circ$. Three standard reflections monitored every 97 reflections showed less than 3% variation and no decay. Lorentz, polarization and Ψ -scan absorption corrections were applied using Crystal Logic software.

The structure was solved by direct methods using SHELXS-86 [4] and refined by full-matrix least-squares techniques on F^2 with SHELXL-93 [5]. The asymmetric unit contains two independent molecules. All hydrogen atoms except those of C7-C10 (for molecule **A**) and C1-C6 and C8 (for molecule **B**) which were introduced at calculated positions as riding on bonded atoms were located by difference maps and their positions were refined isotropically. All non-hydrogen atoms were refined anisotropically.

The positional parameters and the equivalent isotropic temperature factors for the non-hydrogen atoms are collected in Table 3. Hydrogen atomic coordinates and a list of structure factors can be obtained from the authors. A selection of bond distances and bond angles is given in Table 4.

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