

CRYSTAL STRUCTURES OF $(\eta^5\text{-C}_5\text{Me}_5)\text{TiCl}_3$ AND $(\eta^5\text{-C}_5\text{Me}_4\text{H})\text{TiCl}_3$

Andrej Pevec

Faculty of Chemistry and Chemical Technology, University of Ljubljana, Aškerčeva 5, P.O.Box 537, SI-1000 Ljubljana, Slovenia

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Abstract

Two organotitanium(IV) chloride complexes $(\eta^5\text{-C}_5\text{Me}_5)\text{TiCl}_3$ (**1**) and $(\eta^5\text{-C}_5\text{Me}_4\text{H})\text{TiCl}_3$ (**2**) have been structurally characterized. These compounds are a key entry for pentamethyl- and tetramethylcyclopentadienyl titanium chemistry. Both complexes adopt the familiar piano-stool geometry.

Introduction

Cyclopentadienyl ligands have played a major role in the development of organometallic chemistry since the discovery of ferrocene. The studies of compounds with alkylated cyclopentadienyl ligands have been an important area of research for a long period of time.¹ The alkylated cyclopentadienyl ligands offer several advantages over the unsubstituted ones including increased solubility and crystallizability.² Such ligands also significantly effect chemical reactivity of metal complexes.³ A numerous half-sandwich compounds with the general formula $(\eta^5\text{-C}_5\text{Me}_5)\text{ML}_3$ (M represents a transition metal and L a monodentate halogen or chalcogen ligand) have been synthesized and characterized. Among those $(\eta^5\text{-C}_5\text{Me}_5)\text{ReO}_3$ deserves special mention because of the versatile chemistry which has been appeared after its discovery.⁴ The extensive development of the chemistry of half-sandwich rhenium complexes in higher oxidation states exists after that.⁵ Moreover, the half-sandwich organotitanium chlorides are among the most common starting materials for the syntheses of titanium organometallic complexes.⁶

The geometry around the metal atom in those half-sandwich complexes can be described as a three-legged piano-stool configuration. Electron releasing ability of the substituents on the aromatic ring can effects catalytic reactivity of those compounds. The substituted trichloro(cyclopentadienyl)titanium complexes are more efficient catalysts for polymerization reactions than the unsubstituted ones.⁷ For example, the $(\eta^5\text{-$

C₅Me₅)TiCl₃/methylaluminumoxane catalytic system has been found to be highly active and syndiospecific in the polymerization of styrene.⁸

Herein the crystal structures of (η^5 -C₅Me₅)TiCl₃ (**1**) and (η^5 -C₅Me₄H)TiCl₃ (**2**), are reported. Although (η^5 -C₅H₅)TiCl₃,⁹ (η^5 -C₅H₄Me)TiCl₃¹⁰ and (η^5 -C₅Me₄Et)TiCl₃¹¹ have been structurally characterized and the synthesis of **1** has been reported already in 1962¹² to the best of our knowledge the structures of those two compounds have not been determined yet.

Results and discussion

The asymmetric unit of the complex **1** is depicted in Figure 1 and the complex of **2** in Figure 2. Selected bond lengths and angles for **1** and **2** are given in Table 1 and Table 2, respectively. The Ti-Cl bond distances in **1** range from 2.2423(5) to 2.2491(4) Å and those for **2** are from 2.2310(16) to 2.2378(10) Å. The distance between titanium and the centre of the ring is 2.021 Å and 2.010 Å, for **1** and **2** respectively. The Ti-C distances range from 2.3418(15) to 2.3616(15) Å for **1** and from 2.299(4) to 2.377(3) Å for **2**. The C atoms in the cyclopentadienyl ring lie in almost regular plane in both complexes with the similar distances C-C (from 1.419(2) to 1.426(2) Å for **1** and from 1.401(4) to 1.423(4) Å for **2**). The largest deviation from this plane of five C atoms of the cyclopentadienyl ring is 0.0077(9) Å for **1** and 0.001(3) Å for **2**.

The average Ti-Cl bond distance in **1** (2.2456 Å) is slightly longer than those in **2** (2.2344 Å). Both distances are shorter than in the unsubstituted compound (η^5 -C₅H₅)TiCl₃ (2.303 Å). The average Ti-C bond distance in **1** (2.356 Å) and **2** (2.338 Å) is longer than in (η^5 -C₅H₅)TiCl₃ (2.29 Å).¹¹ The molecule of **2** is more symmetrical than that of **1**, since Cl(2), Ti, C(3) and H(1) atoms in **2** lie on a mirror plane.

The methyl carbon atoms in the title compounds **1** and **2** are slightly moved out of the ring plane, away from the titanium and its chloride ligands. A view perpendicular to the ring (Figure 1b and 2b) provides a plausible rationalization for the different displacements of methyl carbons.

The two largest displacements in complex **1** (Figure 1b) are for C(7) (0.134(3) Å) and C(9) (0.111(3) Å) with the shortest methyl carbon - chlorine distances (Table 3). The two medium displacements are for C(6) (0.075(3) Å) and C(10) (0.058(3) Å), with the

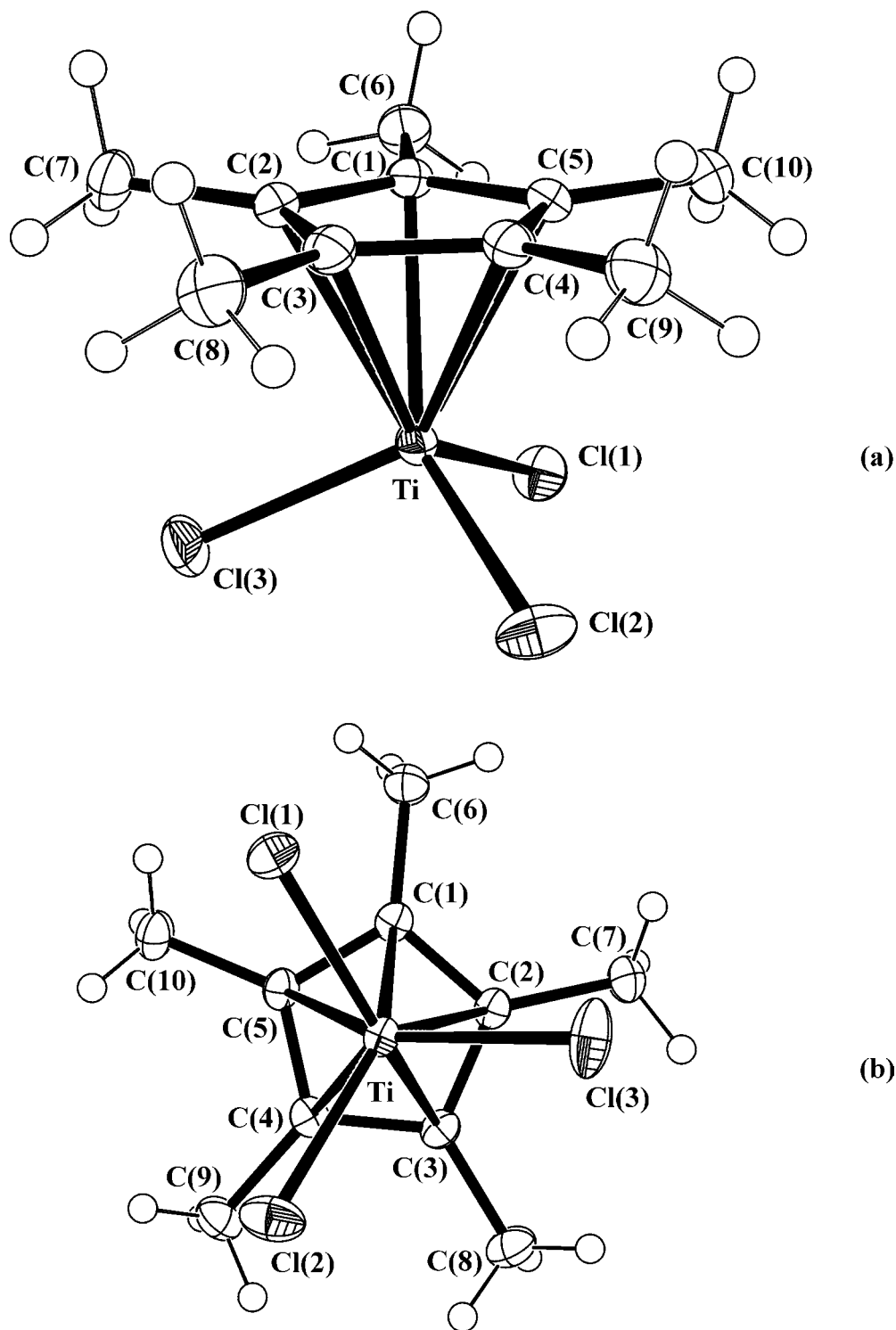


Figure 1. Ortep view of the asymmetric unit of **1** with labeling of nonhydrogen atoms (a) and a view along the Ti - (centre of the ring) direction (b). Ellipsoids are at 30% probability level.

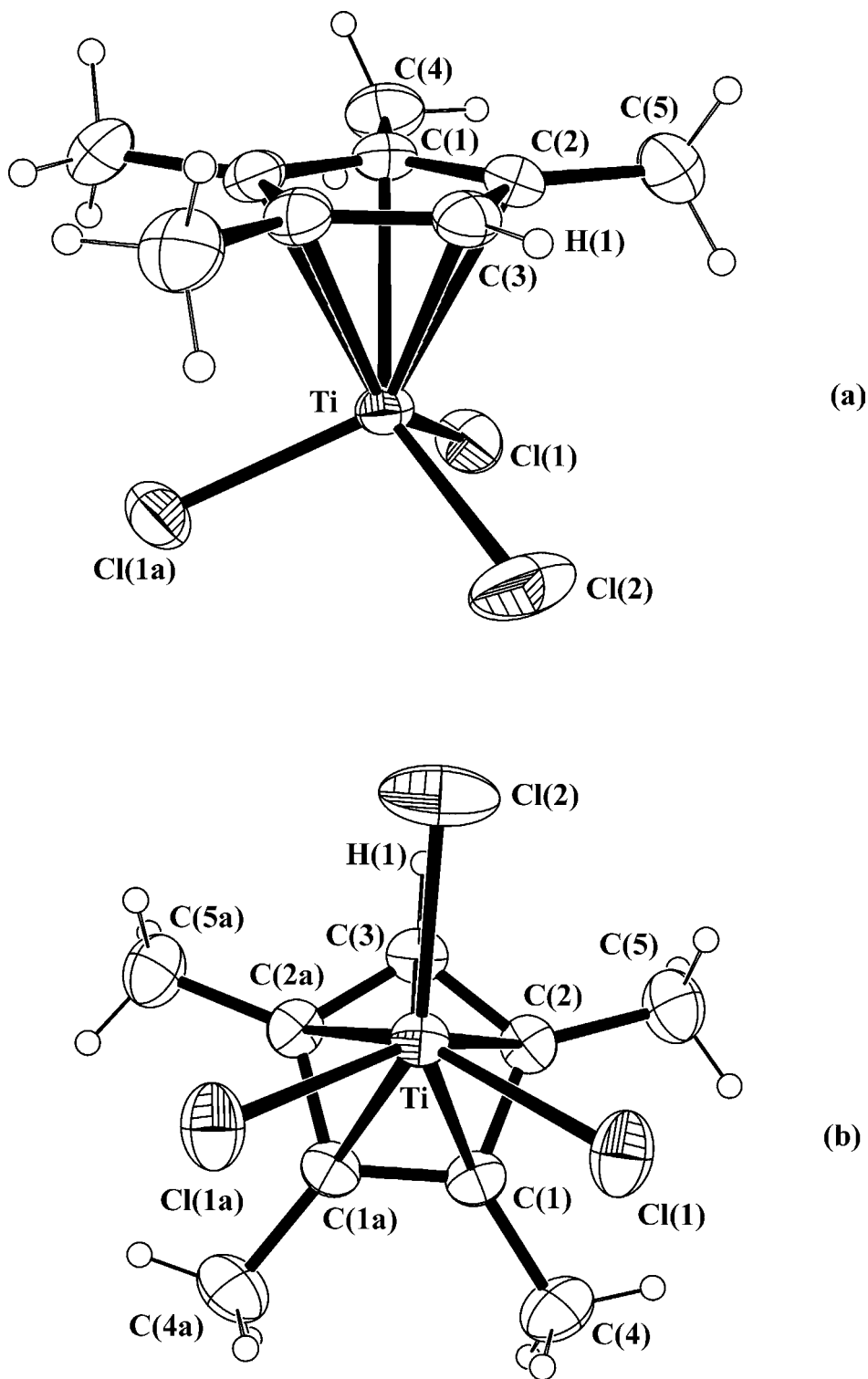


Figure 2. Ortep view of the complex of **2** (a) and a view along the Ti - (centre of the ring) direction (b). Ellipsoids are at 30% probability level.

larger methyl carbon - chlorine distances (Table 3). The smallest displacement is for C(8) (0.040(3) Å), which is the most remote and thus the less sterically hindered by chlorine atoms (Table 3).

The similar organization of the methyl carbon atoms is in the molecule of **2** (Figure 2b). The two large displacements (0.082(7) Å) are for the two symmetrically related methyl carbon atoms C(4) and C(4a) with the shortest distance (3.3111(41)) to the nearest chlorine atoms Cl1 and Cl1a. The smaller displacements are for C(5) and C(5a) (0.035(5) Å) with the larger distance to the chlorine atoms Cl(1) and Cl(1a) (3.5961(42)).

Table 1. Selected bond lengths (Å) and angles (°) for **1**.

Ti-Cl(1)	2.2491(4)	Ti-C(2)	2.3529(15)
Ti-Cl(2)	2.2423(5)	Ti-C(3)	2.3418(15)
Ti-Cl(3)	2.2455(5)	Ti-C(4)	2.3616(15)
Ti-C(1)	2.3596(15)	Ti-C(5)	2.3578(15)
Cl(1)-Ti-C(1)	88.67(4)	Cl(1)-Ti-C(5)	88.90(4)
Cl(1)-Ti-C(2)	119.84(4)	Cl(2)-Ti-Cl(1)	102.695(18)
Cl(1)-Ti-C(3)	145.56(4)	Cl(2)-Ti-Cl(3)	103.68(2)
Cl(1)-Ti-C(4)	120.12(4)	Cl(3)-Ti-Cl(1)	103.44(2)

Table 2. Selected bond lengths (Å) and angles (°) for **2**.

Ti-Cl(1)	2.2378(10)	Ti-C(2)	2.338(3)
Ti-Cl(2)	2.2310(16)	Ti-C(3)	2.299(4)
Ti-C(1)	2.377(3)		
Cl(1)-Ti-C(1)	86.19(8)	Cl(2)-Ti-C(2)	104.76(9)
Cl(1)-Ti-C(2)	92.58(9)	Cl(2)-Ti-C(3)	86.75(14)
Cl(1)-Ti-C(3)	126.39(4)	Cl(2)-Ti-Cl(1)	102.63(4)
Cl(2)-Ti-C(1)	139.80(9)	Cl(1)-Ti-Cl(1a)	103.13(6)

Table 3. Selected distances (Å) between methyl C and Cl atoms in **1**.

C(6)-Cl(1)	3.4306(18)	C(8)-Cl(3)	3.8669(19)
C(7)-Cl(3)	3.2380(19)	C(9)-Cl(2)	3.1818(19)
C(8)-Cl(2)	3.9007(19)	C(10)-Cl(1)	3.4297(19)

Table 4. Details on the crystal structure determination of **1** and **2**.

	1	2
Empirical formula	C ₁₀ H ₁₅ Cl ₃ Ti	C ₉ H ₁₃ Cl ₃ Ti
<i>M_r</i>	289.47	275.44
Crystal shape, colour	square prism, red	square prism, orange
Crystal dimensions / mm	0.20 x 0.10 x 0.10	0.35 x 0.25 x 0.10
Radiation Mo K α / Å	0.71073	0.71073
Crystal system	monoclinic	orthorhombic
Space group	P2 ₁ /n	Pbnm
<i>a</i> / Å	8.7393(2)	7.2031(2)
<i>b</i> / Å	12.9509(3)	12.2757(4)
<i>c</i> / Å	11.3683(2)	13.8748(5)
β / °	99.439(1)	90.00
<i>V</i> / Å ³	1269.26(5)	1226.85(7)
<i>Z</i>	4	4
<i>T</i> / K	110(2)	293(2)
No. of refl. for cell parameters	2958	1592
<i>D_x</i> / g cm ⁻³	1.515	1.491
μ / mm ⁻¹	1.266	1.306
θ Range (°)	2.40, 27.46	5.24, 27.00
Data measured, unique	15102, 2892	13583, 1382
<i>R</i> _{int}	0.026	0.069
<i>R</i> , <i>wR</i> 2 [<i>F</i> ² > 2 σ (<i>F</i> ²)]	0.0256, 0.0605	0.0448, 0.1014
<i>R</i> , <i>wR</i> 2 (all data)	0.0309, 0.0630	0.0686, 0.1133
Goodnes of fit, <i>S</i>	1.056	1.068
Refined parameters	187	67
(Δ/σ) _{max}	0.001	0.0001
Largest diff. peak, hole / e Å ⁻³	0.652, -0.572	0.258, -0.300
Diffractometer	Nonius Kappa CCD	Nonius Kappa CCD
Type of scan	ω scans at fixed $\chi = 55^\circ$	ω scans

Conclusions

The compounds **1** and **2** which have broad application in organotitanium chemistry and catalysis are now structurally characterized. Both complexes show piano-stool coordination geometry.

Experimental

The compound **1** was obtained by the reaction of TiCl_4 with $(\eta^1\text{-C}_5\text{Me}_5)\text{SiMe}_3$ in toluene, according to the previously described procedure.¹³ Recrystallization from pentane at 249 K afforded red crystals suitable for X-ray analysis. The compound **2** was obtained by analogous procedure as **1** by the reaction of TiCl_4 with $(\eta^1\text{-C}_5\text{Me}_4\text{H})\text{SiMe}_3$ in toluene. Recrystallization from hexane at 249 K afforded orange crystals suitable for X-ray analysis. The details of crystal data collection and refinement parameters for **1** and **2** are listed in Table 4. A red prism of compound **1** was greased and an orange prism of compound **2** was glued on a glass thread. Diffraction data were collected on a Nonius Kappa CCD diffractometer with area detector at 110(2) K for **1** and at room temperature for **2**. A Cryostream Cooler (Oxford Cryosystems) was used for cooling the sample. A graphite monochromated $\text{MoK}\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$) was employed in both measurements. Both structures were solved by direct methods implemented in SHELXS-97¹⁴ and refined by a full-matrix least-squares procedure based on F^2 using SHELXL-97.¹⁵ All non-hydrogen atoms were refined anisotropically. Hydrogen atoms in **1** were located from difference Fourier maps and were refined isotropically, with the C-H bond length from 0.90(3) to 0.99(2) \AA . The hydrogen atom H(1) in **2** was visible in the last stages of refinement and was refined freely (distance C(3)-H(1) = 0.93(5)) while the other methyl hydrogen atoms were included in the model at geometrically calculated positions and refined using a riding model. The figures were prepared with the aid of ORTEP-III.¹⁶ Additional crystallographic data for the structures reported in this paper have been deposited at the Cambridge Crystallographic Data Centre with quotation number CCDC 194086 for **1** and CCDC 207746 for **2**, respectively and are available free of charge on request.¹⁷

Acknowledgements

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Povzetek

Določeni sta bili kristalni strukturi dveh organotitanovih(IV) kompleksov (η^5 -C₅Me₅)TiCl₃ (**1**) in (η^5 -C₅Me₄H)TiCl₃ (**2**). Spojini **1** in **2** sta ključnega pomena za sinteze metiliranih ciklopentadieniltitanovih spojin. Kompleksa imata strukturo v obliki klavirskega stola z Ti-Cl veznimi razdaljami 2.2423(5) – 2.2491(4) Å pri **1** in 2.2310(16) – 2.2378(10) Å pri **2**.