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Organotitanoxanes $[C_5Me_5TiMe_2]_2(\mu\text{-O})$ and $[(C_5Me_5)_4Ti_4Me_2](\mu\text{-O})_5$: Synthesis and Crystal Structures

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Introduction

Polyoxotitanium compounds have drawn considerable attention with regard to their catalytic properties and as modeling systems for metal oxides in solution and precursors to organotitanoxane fluorides.[1] In most cases organotitanoxane compounds are prepared by the hydrolysis of $RTiCl_3$ (R = different cyclopentadienyl ligands) in appropriate stoichiometry to yield the corresponding systems.[2] As part of our research program on organotitanoxane fluorides, we recently reported on alkylation reactions of organotitanoxane fluoride with alkylaluminum compounds.[1e,3] In some instances stable polynuclear oxo-bridged species $[Cp^*TiMe(\mu\text{-O})]_3$, $[Cp^*TiMe(\mu\text{-O})]_4$, and $[Cp^*Ti]_4(\mu\text{-O})_6$ have been synthesized by the hydrolyses of Cp^*TiMe_3 and Cp^*TiCl_3[2d,4] ($Cp^* = C_5Me_5$); however, the crystal structure of the corresponding dimeric compound is not known to date. Though the structure of $[(Cp^*)_4Ti_4Me_2](\mu\text{-O})_5$ is known in the literature, the poor quality of the crystal gave only a limited number of reflections with poor crystallographic data.[5] In this note we report the synthesis of $[(Cp^*)_4Ti_4Me_2](\mu\text{-O})_5$ by an alternative method and the crystal structure of organotitanoxanes $[(Cp^*)_4Ti_4Me_2](\mu\text{-O})_5$ and $[Cp^*TiMe_2]_2(\mu\text{-O})$.

Experimental Section

All manipulations were carried out under nitrogen atmosphere, using Schlenk techniques. The samples for spectral measurements were prepared in a drybox. Solvents were dried over Na/K alloy and distilled freshly prior to use. ^{1}H, ^{13}C, and ^{19}F NMR spectra were measured on Bruker MSL-400, AM-250, and AM-200 instruments, respectively, using $SiMe_4$ and $CFCl_3$ as external standards. IR spectra were recorded on a Bio-Rad Digilab FTS 7 spectrometer. Mass spectra were obtained on a Finnigan MAT 8230 or a Varian MAT CH 5 spectrometer. Elemental analyses were performed at the Analytical Laboratory of the Institute of Inorganic Chemistry, University of Göttingen. The starting materials Cp^*TiCl_3 and Cp^*TiMe_3 were prepared according to the literature methods.[6,7]

Preparation of $[C_5Me_5TiMe_2]_2(\mu\text{-O})$ (1). This compound was prepared by the controlled hydrolysis of Cp^*TiMe_3. To a solution of Cp^*TiMe_3 (0.350 g, 1.53 mmol) in toluene (30 mL) distilled water (13.70 μL, 0.76 mmol) was added dropwise at room temperature. During this process gradual evolution of methane was noticed. The reaction mixture was stirred for 6 h, and the solvent was stripped off. The yellow solid obtained was recrystallized from toluene (10 mL) for 2 d at −20 °C to yield 82% (0.56 g, 1.26 mmol) of **1**. Mp: 154 °C. ^{1}H NMR (C_6D_6, 25 °C, δ): 1.91 (s, 30H, C_5Me_5), 0.68 (s, 12H, Ti-Me). $^{13}C\{^{1}H\}$ NMR (C_6D_6, 25 °C, δ): 11.66 (C_5Me_5), 52.70 (Ti-Me), 121.14 (C_5Me_5). IR (Nujol, cm^{-1}): 2910(s), 2880(s), 1450(s), 1340(m), 798(vs), 624(m). Anal. Calcd for $C_{24}H_{42}OTi_2$: C, 65.11; H, 9.49. Found: C, 64.6; H, 9.5.

Preparation of $[(C_5Me_5)_4Ti_4Cl_2](\mu\text{-O})_5$ (2a). To a stirred suspension of Cp^*TiCl_3 (0.625 g, 2.15 mmol) in *n*-hexane (50 mL) at 0 °C, distilled water (43 μL, 2.4 mmol) and triethylamine (0.670 mL, 4.8 mmol) were added by a syringe. The solution was allowed to warm to room temperature slowly. After it was stirred for 30 h, the triethylamine adduct formed was filtered through Celite. The solvent was removed in vacuo, and the yellow solid obtained was recrystallized from toluene (15 mL), affording **2a** in 45% (0.85 g) yield. Mp: 348 °C. ^{1}H NMR (C_6D_6, 25 °C, δ): 1.87 (s, 30H, C_5Me_5), 1.86 (s, 30H, C_5Me_5). MS (EI): m/z (%) 882[M$^+$], 747 [M$^+$ − C_5Me_5]. IR (Nujol, cm^{-1}): 2958(sh), 2912(vs), 2855 (sh), 1435(m), 1377(s), 1261(m), 1092(m), 1024(m), 784(s), 722(s), 624(m). Anal. Calcd for $C_{40}H_{60}Cl_2O_5Ti_4$: C, 54.39; H, 6.79; Cl, 8.04. Found: C, 53.9; H, 6.8; Cl, 7.8.

Preparation of $[(C_5Me_5)_4Ti_4F_2](\mu\text{-O})_5$ (2b). To a suspension of Me_3SnF (0.375 g, 2.05 mmol) in toluene (30 mL) a solution of **2a** (0.882 g, 1 mmol) in toluene (20 mL) was added. The reaction mixture was stirred under reflux for 6 h and then was allowed to cool to room temperature and was filtered. From the filtrate, the solvent was removed in vacuo, and the solid obtained was recrystallized from a minimum amount of toluene to obtain yellow crystals of **2b** in 79% (0.68 g) yield. Mp: >360 °C. ^{1}H NMR (C_6D_6, 25 °C, δ): 2.06 (s, 30H, C_5Me_5), 2.08 (s, 30H, C_5Me_5). ^{19}F NMR (C_6D_6, 25 °C, δ): 84, 74 (Ti-F). MS (EI): m/z (%) 850 [M$^+$], 715 [M$^+$ − C_5Me_5]. IR (Nujol, cm^{-1}): 2964(m), 2910(s), 2857(sh), 1435(s), 1376(s), 1262(s), 1096(s), 1023(s), 797(s), 722(s), 635(m), 608(s). Anal. Calcd for $C_{40}H_{60}F_2O_5Ti_4$: C, 56.43; H, 7.05; F, 4.46. Found: C, 55.7; H, 7.1; F, 4.2.

Preparation of $[(C_5Me_5)_4Ti_4Me_2](\mu\text{-O})_5$ (2c). To a solution of **2b** (1.00 g, 1.17 mmol) in toluene (50 mL), $AlMe_3$ (3.5 mL, 5 mmol, 1.4 M in hexane) was added dropwise with a syringe at 0 °C. The reaction mixture was slowly allowed to warm to room temperature over a period of 2 h. The resultant orange-yellow solution was stirred for an additional 2 h at room temperature. The solvent was removed under vacuum and the yellow solid obtained was recrystallized from toluene (10 mL) at −20 °C, which resulted in the isolation of **2c** in 81% (0.8 g) yield. Mp: 127 °C. ^{1}H NMR (C_6D_6, 25 °C, δ): 1.99 (s, 30H, C_5Me_5), 2.00 (s, 30H, C_5Me_5), 0.54 (s, 6H, TiMe). MS (EI): m/z (%) 827 [M$^+$ − Me]. IR (Nujol, cm^{-1}): 2947(sh), 2912(vs), 2859(sh), 1435(m), 1475(s), 1261(m), 1071(m), 908(m), 783(vs), 728(vs), 623(m). Anal. Calcd for $C_{42}H_{66}O_5Ti_4$: C, 59.82; H, 7.83. Found: C, 60.4; H, 7.7.

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Table 1. Crystal Data and Structure Refinement Details for **1** and **2c**

	1	**2c**
empirical formula	$C_{24}H_{42}OTi_2$	$C_{42}H_{66}O_5Ti_4 \cdot 0.5C_7H_8$
fw	442.38	888.61
cryst syst	monoclinic	monoclinic
space group	$P2_1/n$	$C2/m$
a (Å)	8.399(2)	18.149(4)
b (Å)	31.156(6)	16.458(3)
c (Å)	14.411(3)	15.358(3)
α (deg)	90	90
β (deg)	90.12(3)	100.33(3)
γ (deg)	90	90
V (Å^3)	3771(1)	4513(2)
Z	6	4
T (°C)	−73	−140
D_{calcd} (Mg cm^{-3})	1.169	1.308
μ (mm^{-1})	0.645	0.724
F(000)	1428	1884
cryst size (mm)	1.00 × 0.50 × 0.20	0.40 × 0.40 × 0.15
θ range (deg)	3.56−25.12	2.02−27.45
no. reflns collected	9803	34 250
no. independent reflns	6533	5321
R_{int}	0.0378	0.0460
no. data	6533	5321
no. params	388	361
no. restraints	0	473
GOF on F^2	1.049	1.085
R1 ^{a} [$I > 2\,\sigma(I)$]	0.0442	0.0354
wR2 ^{a} (all data)	0.1083	0.0921
largest diff peak and hole (e Å^{-3})	0.325, −0.362	0.398, −0.329

^{a} $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. $wR2 = [\Sigma w(|F_o^2| - |F_c^2|)^2/\Sigma w|F_o^2|^2]^{1/2}$.

X-ray Structure Determination. Crystals of **1** and **2c** were mounted with perfluoropolyether on a glass fiber and flash-cooled to 200(2) and 133(2) K, respectively, in a stream of nitrogen gas.[8] Diffraction data for **1** were collected on a Stoe-Siemens-AED four-circle diffractometer using a learned profile method. Data for **2c** were collected on a Stoe-Siemens-Huber four-circle diffractometer coupled to a Siemens 1K CCD area detector with graphite monochromated Mo Kα radiation (λ = 0.710 73 Å) using φ- and ω-scans. Both structures were solved by direct methods implemented in SHELXS-97[9] and refined against F^2 on all data by full-matrix least squares with SHELXL-97.[10] All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were then included on calculated positions and refined using a riding model. The disordered Cp* in **2c** was refined with the use of restraints on 1,2 and 1,3 distances, the sphericity and similarity of anisotropic displacement parameters, and rigid bond restraints for anisotropic displacement parameters. For the toluene molecule, distance and planarity restraints were used. The crystallographic data and structure refinement details for **1** and **2c** are given in Table 1.

Results and Discussion

Scheme 1

$$2Cp^*TiMe_3 + H_2O \rightarrow \underset{\mathbf{1}}{[C_5Me_5TiMe_2]_2(\mu\text{-O})} + 2CH_4 \qquad (1)$$

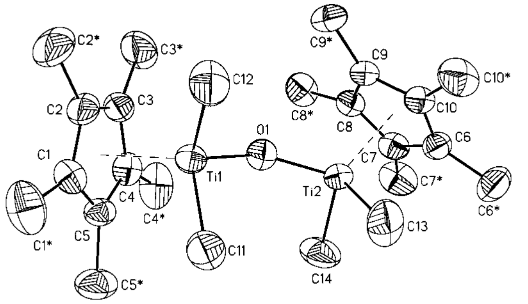

Figure 1. Molecular structure of $[C_5Me_5TiMe_2]_2(\mu\text{-O})$.

Under controlled conditions compound Cp^*TiMe_3 hydrolyzed in toluene at room temperature to the oxo-bridged dimeric species (**1**) as shown in Scheme 1. The progress of the reaction was indicated by the evolution of methane. The corresponding trimeric and tetrameric structures, known in the literature, are formed by adopting a similar synthetic procedure. The dimeric compound **1** is soluble in common organic solvents and has been characterized by X-ray diffraction techniques, elemental analysis, IR, and ^1H and ^{13}C NMR spectroscopy. The ^1H NMR spectrum of compound **1** shows two singlets assignable to pentamethylcyclopentadienyl protons (1.91 ppm) and methyl groups (0.68 ppm) attached to titanium centers. The IR spectrum indicates a very strong band at 800 cm^{-1}, which can be assigned as ν(Ti−O−Ti). Compound **1** crystallizes in the monoclinic space group $P2_1/n$ with one-and-a-half molecules in the asymmetric unit. The molecular structure of **1** depicted in Figure 1 shows a pseudotetrahedral arrangement about each titanium atom and comprises a pentamethylcyclopentadienyl ring, two methyl groups, and an oxo bridge. The Ti−O bond lengths fall in the range 1.800(2)−1.812(3) Å, which are slightly shorter than the average Ti−O distance in the corresponding trimeric structure $[Cp^*TiMe(\mu\text{-O})]_3$[4a] and in the same range of the values of $[Cp^*TiCl_2]_2(\mu\text{-O})$.[11] The two molecules in the asymmetric unit are significantly different. One of them lies on the inversion center so that the Ti−O−Ti angle is forced to be exactly 180°, while this angle is 153.4(1)° in the second molecule without crystallographic symmetry. In $[Cp^*TiCl_2]_2(\mu\text{-O})$ there are one and two half-molecules in the asymmetric unit. The Ti−O−Ti angle ranges from 154.4° to 159.1°. The flexibility of this angle is also shown in two different structures of $[Cp^*TiCl_2]_2(\mu\text{-O})$,[12,13] where the angles are 180°and 116.1°.

Reaction of Cp^*TiCl_3 with water in the presence of triethylamine afforded the isolation of **2a** in moderate yield. Compound **2a** is stable in air and has been characterized by ^1H NMR, IR, MS, and elemental analysis. In the ^1H NMR spectrum, two distinct signals (1.87 and 1.86 ppm range) were observed that are assignable to two different Ti−C_5Me_5 environments. The MS spectrum shows the molecular ion peak [M$^+$] at 882 (*m/z*) corresponding to **1**, and the fragment of the highest mass is observed at *m/z* 747 [M$^+$ − C_5Me_5]. The IR spectrum indicates two strong bands at 784 and 722 cm^{-1}, which arise from two different Ti−O−Ti linkages.

Scheme 2

$$[(C_5Me_5)_4Ti_4Cl_2](\mu\text{-O})_5 + 2Me_3SnF \rightarrow \underset{\mathbf{2b}}{[(C_5Me_5)_4Ti_4F_2](\mu\text{-O})_5} + 2Me_3SnCl \qquad (2)$$

A 1:2 reaction between **2a** and Me_3SnF in toluene leads to the isolation of **2b** (Scheme 2), which has been characterized by elemental analysis, MS, and ^1H and ^{19}F NMR spectroscopy. The ^1H NMR of **2b** demonstrates the presence of two different signals (2.06 and 2.08 ppm) for C_5Me_5, while its ^{19}F NMR spectrum shows two resonances at 74 and 84 ppm corresponding

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to Ti−F. However, the resonance that appeared at 84 ppm is less conspicuous; perhaps this is due to the existence of two kinds of fluorine, one above and the other below the plane of the titanoxane ring. The most intense peak in the mass spectrum of **2b** is at *m*/*z* 715 [$M^+ - C_5Me_5$], and the highest fragment observed is at *m*/*z* 850 [M^+], which corresponds to **2b**.

In a study of the reactivity of $AlMe_3$ toward organotitanoxane fluoride, **2b** at 0 °C leads to the isolation of **2c** in which one of the methyl groups is transferred from aluminum to titanium along with the elimination of Me_2AlF (Scheme 3). Similar studies on the akylation of organotitanoxane fluoride by $AlMe_3$ have been reported from this laboratory.[1d,3] The ^1H NMR spectrum of **2c** exhibits three signals assignable to two different C_5Me_5 (1.99 and 2.00 ppm range) and Ti−Me (0.54 ppm) protons. The mass spectrum shows the highest molecular mass at *m*/*z* 827 [$M^+ - Me$]. The molecular structure of **2c** is shown in Figure 2. The structure of **2c** does not differ significantly from the structure previously reported,[5] although the quality greatly improved. A root-mean-square fit of all titanium and oxygen atoms gave a weighted root-mean-square deviation of 0.030 Å. [$(Cp^*{}_4Ti_4Cl_2)(\mu\text{-}O)_5$], which is isostructural with **2c**, and [$(Cp^*{}_4Ti_4F_2)(\mu\text{-}O)_5$] show weighted rms deviations of 0.019 and 0.032 Å, respectively, for the same atoms.[1e]

Scheme 3

$$[(C_5Me_5)_4Ti_4F_2](\mu\text{-}O)_5 + 2AlMe_3 \rightarrow [(C_5Me_5)_4Ti_4Me_2](\mu\text{-}O)_5 + 2AlMe_2F \quad (3)$$

2c

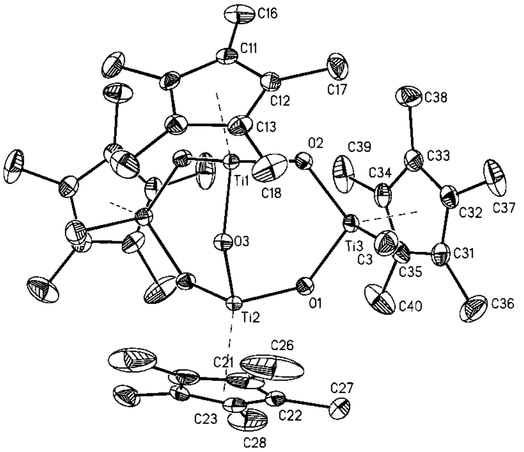

Figure 2. Molecular structure of $[(C_5Me_5)_4Ti_4Me_2](\mu\text{-}O)_5$.

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Supporting Information Available: Tables listing detailed crystallographic data, atomic positional parameters, and bond lengths and angles. This material is available free of charge via the Internet at http://pubs.acs.org.

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