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Synthesis of the Organotitanoxane Complexes $[(\eta^5\text{-C}_5\text{Me}_5)_4\text{Ti}_4\text{X}_2](\mu\text{-O})_5$. X-ray Structure of $[(\eta^5\text{-C}_5\text{Me}_5)_4\text{Ti}_4\text{Me}_2](\mu\text{-O})_5$

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Introduction

The family of the organotitanium oxoderivatives has been studied during the last years leading to the synthesis of several types of chain and ring organotitanoxanes. A great number of them have been prepared by hydrolysis of the precursors LTiCl$_3$, where L can be one of the different cyclopentadienyl ligands, giving organotitanium(IV) complexes with Ti$_2$O, Ti$_2$O$_2$, Ti$_3$O$_3$, Ti$_4$O$_4$, and Ti$_4$O$_6$ cages.[2]

In the hydrolytic processes of CpTiCl$_3$ (Cp = C$_5$H$_{5-n}$R$_n$), carried out by Floriani *et al.*, a missing compound with a Ti$_4$O$_5$ core was suggested from Cp$_4$Ti$_4$O$_4$ to Cp$_4$Ti$_4$O$_6$.[3] This intermediate had been previously isolated and characterized as [Cp*$_4$Ti$_4$O$_5$Cl$_2$] by Babcock and Klemperer via a "retrohydrolysis" performed on (Cp*$_4$Ti$_4$)O$_6$ with TiCl$_4$[4] and was formulated as a bicyclic structure (Figure 1B), although this had not been confirmed by X-ray crystallography.

Our work in this field has given several monopentamethylcyclopentadienyltitanium compounds with those kinds of cores[5] and now we are interested in their thermal behavior.[6] In this note, we report the synthesis and characterization of the novel tetranuclear complexes [Cp*$_4$Ti$_4$R$_2$](μ-O)$_5$ and the X-ray structure of the methyl derivative.

Experimental Section

All reactions were carried out under argon by Schlenk techniques or MBraun glovebox. Hexane and pentane were refluxed over Na/K amalgam, toluene over sodium, and THF over Na/benzophenone and all distilled under argon. Oven-dried glassware was repeatedly evacuated on a pumping system (~1 × 10^{-3} mmHg) and subsequently filled with inert gas. LiMe (1.6 M in diethyl ether) and EtMgCl (2 M in THF) were purchased from Aldrich, and LiPh was prepared in hexane from PhI and *n*-buthyllithium (1.6 M in hexane, from Aldrich). [Cp*$_3$Ti$_3$Cl$_2$(NMe$_2$)](μ-O)$_3$ was prepared by known procedures.[5b] IR spectra were measured on a Perkin-Elmer 883 spectrophotometer. ^{1}H and ^{13}C{^{1}H} NMR spectra were recorded on a Varian Unity 300 MHz spectrometer. Electron impact (EI) mass spectra were obtained at 70 eV with a Hewlett-Packard 5988 spectrometer. Satisfactory C and H analyses were obtained for all compounds and carried out with a Perkin-Elmer 240B and/or Heraeus CHN-O-Rapid microanalyzer.

Preparation of [Cp*$_4$Ti$_4$Cl$_2$](μ-O)$_5$ (1). A solution of [Cp*$_3$Ti$_3$Cl$_2$(NMe$_2$)](μ-O)$_3$ (0.60 g, 0.84 mmol) in toluene (50 mL) was transferred via cannula into a Carius tube (120 mL capacity) ready to be sealed by flame in vacuo. This solution was heated in an autoclave at 200 °C for 3 days. The Carius tube was opened in a glovebox and the solvent removed under vacuum. Adding 40 mL of pentane let us separate a red solution and the yellow product **1** (0.34 g, 91%). ^{1}H-NMR (C$_6$D$_6$, 20 °C, δ): 2.11 (s, 30H, C$_5$*Me*$_5$), 2.07 (s, 30H, C$_5$*Me*$_5$). ^{13}C{^{1}H}-NMR (C$_6$D$_6$, 20 °C, δ): 11.8, 12.5 (C$_5$*Me*$_5$), 125.29, 125.33 (*C*$_5$Me$_5$). MS *m/z* (assignment, rel intensity): 747 [(M − Cp*H)$^+$, 42]. IR(KBr, cm^{-1}): 2912 (s), 1490 (m), 1432 (m), 1375 (s), 1069 (w), 1024 (w), 787 (vs), 723 (vs), 622 (m), 431(s), 359 (s), 318 (s).

Preparation of [Cp*$_4$Ti$_4$Me$_2$](μ-O)$_5$ (2). LiMe (0.51 mL, 1.6 M, 0.81 mmol) diluted in 10 mL of THF was slowly added from a dropping funnel over a solution of **1** (0.30 g, 0.34 mmol) in THF (30 mL) at 0 °C. The reaction mixture was allowed to warm to room temperature and stirred for 2 days. The solvent was removed *in vacuo* and the solid extracted with 70 mL of hexane. The solution was filtered and the solvent removed to afford 0.25 g of **2** as a crystalline yellow solid in 87% yield. ^{1}H-NMR (C$_6$D$_6$, 20 °C, δ): 0.55 (s, 6H, Ti*Me*), 2.00 (s, 30H, C$_5$*Me*$_5$), 2.01 (s, 30H, C$_5$*Me*$_5$). ^{13}C{^{1}H}-NMR (CDCl$_3$, 20 °C, δ): 11.4, 11.7 (C$_5$*Me*$_5$), 41.0 (Ti-*Me*), 120.7, 122.6 (*C*$_5$Me$_5$). MS *m/z* (assignment, rel intensity): 827 [(M − Me)$^+$, 19], 812 [(M − 2Me)$^+$, 9], 677 [(M − 2Me − Cp*)$^+$, 29]. IR (KBr, cm^{-1}): 2912 (s), 1496 (w), 1436 (m), 1374 (m), 1070 (w), 1022 (w), 786 (vs), 730 (vs), 624 (m), 564 (m), 394 (s).

Preparation of [Cp*$_4$Ti$_4$Et$_2$](μ-O)$_5$ (3). In the same way as for **2**, from 0.35 g (0.40 mmol) of **1** and EtMgCl (0.59 mL, 2 M, 1.18 mmol) was obtained 0.29 g of yellow solid of **3** (83% yield). ^{1}H-NMR (C$_6$D$_6$, 20 °C, δ): 1.33 (q, 4H, ^3J = 7.5 Hz, TiC*H*$_2$Me), 1.63 (t, 6H, ^3J = 7.5 Hz, TiCH$_2$*Me*), 2.04 (s, 30H, C$_5$*Me*$_5$), 2.06 (s, 30H, C$_5$*Me*$_5$). ^{13}C{^{1}H}-NMR (C$_6$D$_6$, 20 °C, δ): 11.8, 12.1 (C$_5$*Me*$_5$), 17.3 (TiCH$_2$*Me*), 56.6 (Ti*C*H$_2$Me), 120.6, 122.7 (*C*$_5$Me$_5$). MS *m/z* (assignment, rel intensity): 406 [(Cp*Ti$_4$O$_5$)$^+$, 11]. IR (KBr, cm^{-1}): 2912 (s), 2858 (s), 1490 (w), 1436 (m), 1374 (m), 1066 (w), 1024 (w), 781 (vs), 720 (vs), 622 (m), 555 (m), 411 (s), 385 (s).

Preparation of [Cp*$_4$Ti$_4$Ph$_2$](μ-O)$_5$ (4). Similarly to **2**, the reaction of 0.38 g (0.43 mmol) of **1** and 0.10 g (1.19 mmol) of LiPh gave 0.34 g of **4** as a yellow solid (82%). ^{1}H-NMR (C$_6$D$_6$, 20 °C, δ): 1.88 (s, 30H, C$_5$*Me*$_5$), 2.04 (s, 30H, C$_5$*Me*$_5$), 7.23−7.81 (m, 10H, TiPh). ^{13}C{^{1}H}-NMR (C$_6$D$_6$, 20 °C, δ): 12.0, 12.8 (C$_5$*Me*$_5$), 122.9, 123.9 (*C*$_5$Me$_5$), 126.3, 126.5, 138.3 (*C*$_6$H$_5$), 190.0 (*ipso*-C$_6$H$_5$). MS *m/z* (assignment, rel intensity): 831 [(M − Cp*)$^+$, 9], 754 [(M − Cp* − Ph)$^+$, 5], 676 [(M − Cp* − 2Ph)$^+$, 7], 541 [(M − 2Cp* − 2Ph)$^+$, 21]. IR(KBr, cm^{-1}): 2911 (vs), 1439 (s), 1374 (s), 1260 (w), 1058 (m), 1022 (m), 781 (vs), 718 (vs), 620 (m), 557 (w), 386 (s).

Crystallography. A yellow crystal of [Cp*$_4$Ti$_4$Me$_2$](μ-O)$_5$ (**2**) was obtained from THF at −15 °C and mounted in a glass capillary in a random orientation. Preliminary examinations and data collection were performed at 20 °C using Mo Kα radiation (λ = 0.710 65 Å) and a graphite-orientated monochromator on an Enraf-Nonius CAD4 diffractometer. The poor quality of the crystals of **2** gave a limited number of observed reflections and prevented a more accurate structure determination.

The structure was solved by direct methods with SHELX-86[7] and refined by blocked full-matrix least-squares analysis on F^2 with SHELXL-93.[8] Non-hydrogen atoms were refined anisotropically, except carbon atoms from the methyl groups of the Cp* fragments, which were refined isotropically. Hydrogen atoms were inserted at calculated positions in the last cycles of refinement. Refinement converged with $R1 = 0.122$ and $wR2 = 0.327$ [for 1972 reflections with $I > 2\sigma(I)$], and for all data $R1 = 0.259$, $wR2 = 0.464$. Details of crystal data, measurements of intensities, and data processing are summarized in Table 1.

Results and Discussion

When a benzene-d_6 or toluene-d_8 solution of the complex [Cp*$_3$Ti$_3$Cl$_2$(NMe$_2$)](μ-O)$_3$ was heated, there was not change until the temperature reached 192 °C. Amine elimination was not detected, and instead of that, two signals (ratio 1:1) assignable to Cp* ligands of **1** were grown in addition to other resonances corresponding to residual nitrogen-containing fragments.

The preparation of the product **1** was performed by heating for 3 days at 200 °C a toluene solution of [Cp*$_3$Ti$_3$Cl$_2$(NMe$_2$)](μ-O)$_3$ (see Experimental Section). The solution was filtered and the solid washed with pentane to afford a yellow microcrystalline solid with the same spectroscopic properties as that reported by Klemperer.[4]

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(2) (a) Bottomley, F.; Sutin, L. *Adv. Organomet. Chem.* **1988**, *28*, 339. (b) Bottomley, F. *Polyhedron* **1992**, *11*, 1707. (c) King, R. B., Ed. *Encyclopedia of Inorganic Chemistry*; Wiley: Chichester, England, 1994; and references therein.

(3) Carofiglio, T.; Floriani, C.; Sgamellotti, A.; Rosi, M.; Chiesi-Villa, A.; Rizzoli, C. *J. Chem. Soc., Dalton Trans.* **1992**, 1081.

(4) Babcock, L. M.; Klemperer, W. G. *Inorg. Chem.* **1989**, *28*, 2003.

(5) (a) Gómez-Sal, M. P.; Mena, M.; Royo, P.; Serrano, R. *J. Organomet. Chem.* **1988**, *358*, 147. (b) Martín, A.; Mena, M.; Raithby, P. R.; Serrano, R.; Yélamos, C. *J. Organomet. Chem.* **1994**, *467*, 79.

(6) Andrés, R.; Galakhov, M.; Martín, A.; Mena, M.; Santamaría, C. *Organometallics* **1994**, *13*, 2159.

(7) Sheldrick, G. M.; *Acta Crystallogr.* **1990**, *A46*, 467.

(8) Sheldrick, G. M. SHELXL-93, *Program for the refinement of crystal structures,* VMS Version; Universität Göttingen, Göttingen, Germany, 1993.

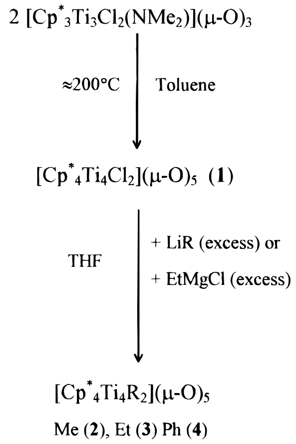
0020-1669/96/1335-0242$12.00/0

Table 1. Crystallographic Data for **2**

formula	$C_{42}H_{66}O_5Ti_4$
FW	842.55
crystal system	monoclinic
space group	$C2/m$
a (Å)	18.658(4)
b (Å)	16.388(3)
c (Å)	15.180(3)
β (deg)	99.86(3)
V (Å^3)	4573(2)
Z	4
density (calc) g/cm^3	1.224
θ range (deg)	2.27−41.45
absorptn coeff mm^{-1}	0.711
reflctns collctd	4222
data/restraints/params	3999/0/190
R [$I > 2\sigma(I)$]^a	$R1 = 0.122$, $wR2 = 0.327$
R (all data)^b	$R1 = 0.258$, $wR2 = 0.464$

[a] $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $wR2 = \{[\Sigma w(F_o^2 - F_c^2]/[\Sigma w(F_o^2)^2]\}^{1/2}$. $w^{-1} = 1/[\sigma^2(F_o^2) + (0.2307P)^2 + 121.8550P]$; $P = (F_o^2 + 2F_c^2)/3$.

Scheme 1



Although the structure proposed by Klemperer for complex **1** explains the observed spectroscopic data, we decided to study its chemical reactivity to confirm it. Complex **1** can be easily alkylated by a conventional method, adding excess of the corresponding organolithium or Grignard reagents in diethyl ether or THF to give the novel tetranuclear complexes $[Cp^*_4Ti_4R_2](\mu\text{-}O)_5$ in high yield. (See Scheme 1).

Alkyl derivatives **2**−**4** are air sensitive both in solution and in the solid state. They are soluble in organic solvents such as toluene, benzene, and THF, and such solutions are stable at room temperature under argon. These complexes were characterized by elemental analysis, IR, NMR spectroscopy, and mass spectrometry (see Experimental Section).

The ^{1}H- and ^{13}C-NMR spectra of the **2**−**4** complexes demonstrate the presence of two signals attributable to the Cp* groups in a 1:1 ratio and the typical resonances for the alkyl fragments, according to the complete substitution of the halogen atoms in **1**. IR spectra show bands assignable to the ν_{as}(Ti−O−Ti) (787−781 and 730−718 cm^{-1}), TiCp*, and TiR fragments in ranges similar to those that we have reported for similar compounds.[5,6]

The absence in the literature of crystallographic studies for this kind of structure prompted us to study by X-ray diffraction techniques the molecular disposition of **2**.

Selected bond lengths and angles can be observed in Table 2, and atomic coordinates and equivalent isotropic displacement coefficients are given in the supporting information. The cluster **2** takes the form of a "butterfly" structure (see Figure 1A) where the Ti(1) and Ti(2) atoms are located in a mirror plane. Both wings consist of three Cp*Ti units forming an isosceles triangle with each edge bridged by an oxide ligand. The methyl groups joined to the "terminal" titanium atoms are oriented to the outer direction instead of the inner one proposed by Klemperer for the analogous complex **1** (see Figure 1B).[4]

Table 2. Bond Lengths (Å) and Angles (deg) for $[Cp^*_4Ti_4Me_2][\mu\text{-}O]_5$ (**2**)^a

Ti−O(av)	1.830	Ti(1)···Ti(2)	3.230(5)
Ti(1)···Ti(3)	3.301(3)	Ti(2)···Ti(3)	3.295(3)
Ti(3)−C(1)	2.11(2)	Ti−Cp*(av)	2.06
O(13)−Ti(1)−O(13)A	105.0(6)	O(13)−Ti(1)−O(12)	101.6(4)
Ti(2)···Ti(1)···Ti(3)	60.6(1)	Ti(3)···Ti(1)···Ti(3)A	99.5(1)
O(12)−Ti(2)−O(23)	102.4(4)	O(23)−Ti(2)−O(23)A	105.1(6)
Ti(1)···Ti(2)···Ti(3)	60.8(8)	Ti(3)A···Ti(2)···Ti(3)	99.7(1)
O(13)−Ti(3)−O(23)	105.8(4)	O(13)−Ti(3)−C(1)	102.0(6)
O(23)−Ti(3)−C(1)	100.6(6)	Ti(2)···Ti(3)···Ti(1)	58.6(1)
Ti(2)−O(12)−Ti(1)	123.1(7)	Ti(3)−O(13)−Ti(1)	129.4(5)
Ti(3)−O(23)−Ti(2)	128.2(5)	Cp*−Ti−O(av)	116.1
Cp*(3)−Ti(3)−C(1)	111.5		

[a] Symmetry transformations used to generate equivalent atoms: $A = x, -y, z$; Cp* is the centroid of the C_5Me_5 ring.

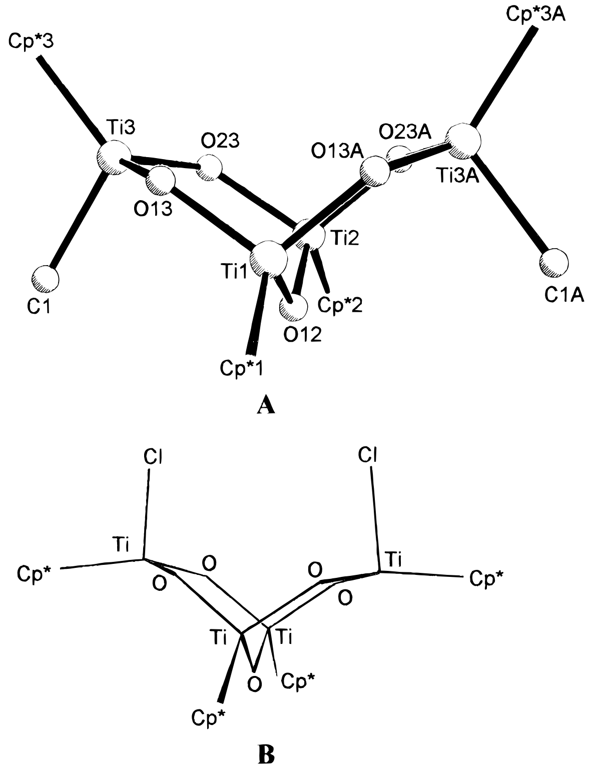


Figure 1. (A) View of the molecular structure of **2** without the Cp* rings. (B) Klemperer proposition for these complexes.

Both $Ti_3(\mu\text{-}O)_3$ units of the core are not planar with a pseudoboat conformation. Bond lengths corresponding to Ti−Cp*, Ti−O−Ti bridges, and the Ti(3)−O(13)−Ti(1) [129.4(5)°] and Ti(3)−O(23)−Ti(2) [128.2(5)°] angles are within the values reported for other structurally characterized oxotrimer titanium complexes,[3,5,9] while the Ti(2)−O(12)−Ti(1) [123.1(7)°] angle is smaller and equivalent to that found for the $[Cp^*_3Ti_3Cl(\mu\text{-}SO_4)](\mu\text{-}O)_3$[10] compound [122.2(4)°], where the μ-SO_4 ligand acts in a way similar to the "Cp*TiMe(O−)$_2$" moiety in the complex **2**.

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Supporting Information Available: ORTEP plot, crystallographic data, and listings of complete bond distances and angles, all positional and displacement parameters, and anisotropic thermal parameters for **2** (7 pages). Ordering information is given on any current masthead page.

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(9) Troyanov, S. I.; Varga, V.; Mach, K. *J. Organomet. Chem.* **1991**, *402*, 201.
(10) Abarca, A.; Martín, A.; Mena, M.; Raithby, P. R. *Inorg. Chem.*, in press.