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Organotitanoxanes with Unique Structure among Transition-Element Organometallic Oxide Derivatives

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The synthesis of novel titanoxane compounds, $[\{(\mathrm{TiCl})(\mathrm{Ti})[\mu\text{-}(\eta^5\text{-}\mathrm{C_5Me_4SiMe_2O}\text{-}\kappa\mathrm{O})]_2(\mu\text{-O})\}_2(\mu\text{-O})]$ (**4**) and $[\{\mathrm{Ti}[\mu\text{-}(\eta^5\text{-}\mathrm{C_5Me_4SiMe_2O}\text{-}\kappa\mathrm{O})](\mu\text{-O})\}_6]$ (**5**), by controlled hydrolysis of a dinuclear titanium/oxo complex is described. Complexes **4** and **5** show unprecedented structural features for organometallic oxide derivatives of transition elements and represent unique fully characterized examples of tetra- and hexanuclear organo-transition-metal oxide compounds with an open-chain and a monocyclic structure, respectively.

Since the discovery of organometallic oxides over 40 years ago,[1,2] this type of compound has drawn considerable attention because of their unexpected reactivities[3] and catalytic properties[4,5] and as hydrocarbon-soluble modeling systems for metal oxides.[6] A remarkable aspect of the chemistry of these kinds of compounds is their diversity of structural motifs.[7,8] Complexes containing an M_nO_m ($n \leq 4$) core constitute the more numerous group of organometaloxanes showing a rich variation in structural types. For di- and trinuclear compounds, open-chain examples containing a $M_2(\mu\text{-O})$[9,10] or $M_3(\mu\text{-O})_2$[11,12] motif as well as cyclic structures displaying $M_2(\mu\text{-O})_2$[13,14] or $M_3(\mu\text{-O})_3$[15–18] rings are known. However, tetranuclear compounds invariably display cyclic structures[8] such as square, $M_4(\mu\text{-O})_4$,[19–22] butterfly, $M_4(\mu\text{-O})_5$,[23–25] or adamantine-like dispositions, $M_4(\mu\text{-O})_6$.[26,27] Higher nuclearity organometallic oxides of transition metals (M_nO_m, $n \geq 5$) are scarce and, as a rule, feature cagelike structures.[8,28–34]

Among organometallic oxides of transition-metal derivatives, titanium complexes are one of the best-represented, exhibiting a high number and structural variety of metallic atom cores. Among the four general synthetic methods for

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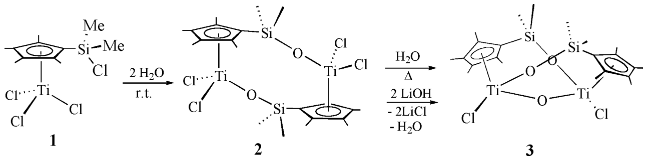
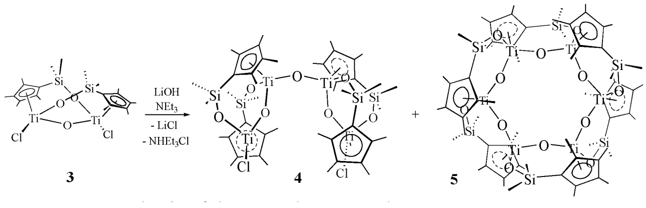
Scheme 1. Preparation of Dinuclear μ-Oxotitanium Complexes



Scheme 2. Synthesis of Complexes **4** and **5**

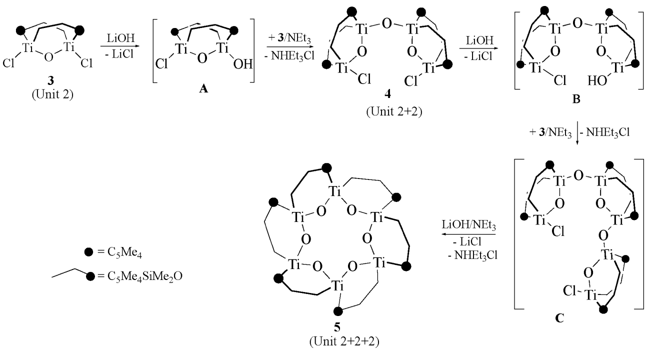


this kind of derivative,[35,36] the best route to prepare most of the organotitanoxane compounds is the controlled hydrolysis of the precursor $CpTiX_3$ (Cp being a cyclopentadienyl ligand and X a halogen or an alkyl group).[7]

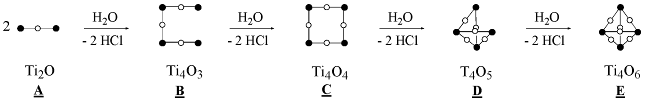
Recently, we have reported the synthesis of a dinuclear μ-oxotitanium complex, [{Ti[μ-(η^5-$C_5Me_4SiMe_2O$-κO)]Cl}$_2$(μ-O)] (**3**), in which the titanium atoms are triply bridged by an oxygen atom and two "CpSiO" moieties (Scheme 1).[37] Such a backbone (skeleton) imposes a high robustness and rigidity on the system, which could have a deciding influence on the chemical and structural behavior of the compound. With this idea in mind, we focused our interest toward investigating the reaction of **3** with different sources of oxo ligands, such as water and lithium hydroxide.

Scheme 2 summarizes the synthetic route to prepare the new compounds [{(TiCl)(Ti)[μ-(η^5-$C_5Me_4SiMe_2O$-κO)]$_2$(μ-O)}$_2$(μ-O)] (**4**) and [{Ti[μ-(η^5-$C_5Me_4SiMe_2O$-κO)](μ-O)}$_6$] (**5**) that have been fully characterized, including the determination of their molecular structures by single-crystal X-ray analysis. Compound **3** is obtained by treatment of **1** with H_2O or alternatively by reaction of **2** with LiOH (Scheme 1). However, all attempts to perform further hydrolysis of **3** were unsuccessful even under very energetic conditions, because of the decreased oxophilic character of the titanium center as chloride ligands are successively replaced by oxygen atoms in the coordination sphere, which hinders further hydrolysis of the remaining Ti−Cl bonds. However, **3** readily reacts with polar magnesium reagents to give the corresponding dialkyl derivatives [{Ti[μ-(η^5-$C_5Me_4SiMe_2O$-κO)]R}$_2$(μ-O)]. In view of these results, we proposed to investigate the reaction of **3** with a more nucleophilic source of the oxo group such as lithium hydroxide. Thus, a solution of **3** treated with anhydrous lithium hydroxide in the presence of triethylamine yielded a mixture of two new products. This mixture was separated by fractional recrystallization from a hexane solution, and the U-shaped open-chain titanoxane derivative **4** was obtained as the major product, with the wheel-shaped **5** obtained in a lower yield.

Scheme 3. Proposed Mechanism To Explain the Formation of **4** and **5**



Scheme 4. Filled and Open Spheres Representing Titanium and Oxygen Atoms, Respectively



Formation of **4** (unit 2 + 2) may be easily rationalized as the outcome of adding **3** (unit 2) to a molecule of the reasonable transient metal monohydroxide, [{[Ti{μ-(η^5-$C_5Me_4SiMe_2O$-κO)}]$_2$(Cl)(OH)}(μ-O)] (**A**; see Scheme 3). In fact, both building blocks, "{Ti{μ-(η^5-$C_5Me_4SiMe_2O$-κO)}$_2$", retain the basic structure found in the precursor **3**, where the bridges "μ-(η^5-$C_5Me_4SiMe_2O$-κO)" are arranged in a crossing manner inside this moiety. However, the formation of **5** (unit 2 + 2 + 2) cannot be straightforwardly explained because in this case the bridges "μ-(η^5-$C_5Me_4SiMe_2O$-κO)" are alternatively arranged along the molecular ring. The presence of **5** requires the formation of the monohydroxide species **B** with the addition of a new molecule of **3** to generate species **C**, from which a sequence of substitution and condensation processes with an internal rearrangement of the basic dinuclear unit formally gave the hexanuclear final disposition.

We propose that the formation of these unique open-chain and wheel-shaped[38–40] titanoxanes stems from the peculiarly rigid structure shown by **3**, which is retained in both dinuclear units that assemble to give **4**. The backbone of **4** forces the two remaining chloride ligands to be oriented in a relatively trans disposition (see the X-ray structure), with each placed far away from the other, therefore preventing the formation of a cycle under these conditions. Moreover, complex **4** is the only isolated tetrametaloxane compound containing a M_4O_3 core known to date and can be recognized as the last innovative disposition and not previously observed missing intermediate[3,23] (from Ti_2O to Ti_4O_4) in the proposed entire hydrolytic stepwise process of $CpTiX_3$ (Scheme 4).

The spectroscopic behavior observed for **4** and **5** confirms the structures proposed. The ^1H NMR spectrum of **4** shows eight and four signals with equal intensities for the methylcyclopentadienyl and methylsilyl protons, respectively, in agreement with the anticipated overall C_2 symmetry in

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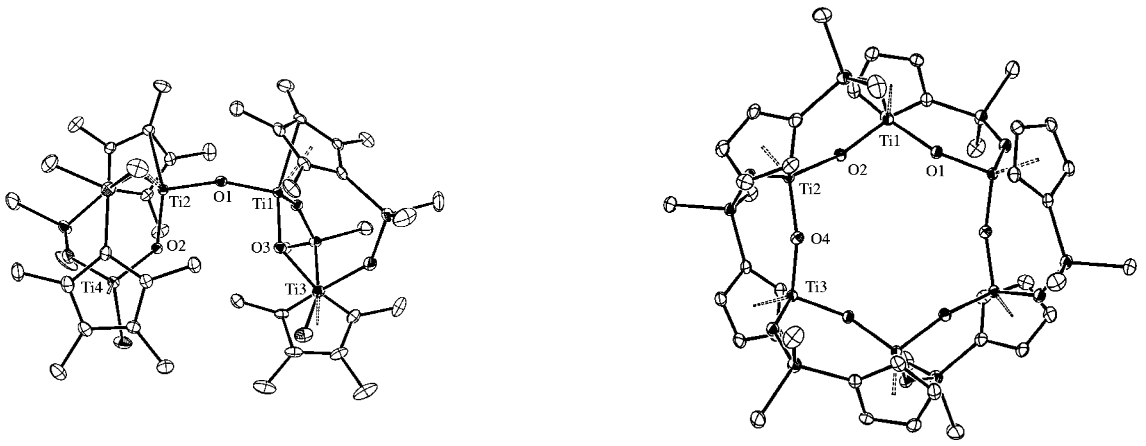

Figure 1. ORTEP view of **4** and **5** with 30% probability ellipsoids. Important bond lengths [Å] and angles [deg]. **4**·C_6H_{14}: Ti1−O1 = 1.835(3)/Ti1−O1 = 1.846(2), Ti1−O3 = 1.861(3)/Ti1−O7 = 1.862(3), Ti2−O1 = 1.853(3)/Ti2−O1 = 1.846(2), Ti2−O2 = 1.866(3)/Ti2−O4 = 1.869(3), Ti3−O3 = 1.804(3)/Ti3−O7 = 1.804(2), Ti4−O2 = 1.8043/Ti4−O4 = 1.798(3), Ti1−O1−Ti2 = 159.45(16)/Ti1−O1−Ti2 = 158.63(16), Ti4−O2−Ti2 = 132.24(15)/Ti4−O4−Ti2 = 131.92(13), Ti3−O3−Ti1 = 135.21(16)/Ti3−O7−Ti1 = 132.07(13). **5**·C_5H_{12}: Ti1−O2 = 1.843(2), Ti1−O1 = 1.843(2), Ti2−O4 = 1.838(2), Ti2−O2 = 1.838(2), Ti3−O4 = 1.843(2), Ti3−O1#1 = 1.842(2), Ti1−O2−Ti2 = 155.00(13), Ti2−O4−Ti3 = 155.57(13), Ti1−O1−Ti3#1 = 155.14(13).

solution, where the two "$\{Ti\{\mu\text{-}(\eta^5\text{-}C_5Me_4SiMe_2O\text{-}\kappa O)\}_2$" building blocks are related by a 2-fold symmetry axis but inside each one the internal and terminal metal fragments are not equivalent. The high symmetry of compound **5** (D_3 symmetry in solution) is reflected in the simplicity of its ^1H NMR spectrum, in which the six chiral molecular metal fragments "$Ti(\mu\text{-}\eta^5\text{-}C_5Me_4SiMe_2O\text{-}\kappa O)(O)\}$" are equivalent. Analogous spectroscopic features are observed in the ^{13}C NMR spectra.

Crystals of **4**[41] suitable for X-ray diffraction were obtained from hexane as two different polymorphs. The first retaining a hexane molecule shows a triclinic form (space group $P\bar{1}$) while the second hexane-free molecule exhibits a monoclinic symmetry (space group $P2_1/c$). Single crystal X-ray analysis (Figure 1) confirmed the open-chain structure with a U-shape. The molecular structure of **4** shows two dinuclear metallic fragments with a folded structure, similar to that found in **3**, related by a 2-fold axis passing through the linking O(1) atom and bisecting the Ti1−O1−Ti2 angle. The Cp rings lie alternately up and down with respect the plane defined by Ti1−O1−Ti2, which forces both chlorine atoms to be orientated in an antiperiplanar fashion.

The molecular structure of **5**,[42] depicted in Figure 1, consists of a 12-membered monocyclic compound with the adjacent titanium atoms linked by an oxygen bridge. In contrast to **4**, the hexanuclear titanoxane is formally the result of the assembling of six "$Ti(\mu\text{-}\eta^5\text{-}C_5Me_4SiMe_2O\text{-}\kappa O)(O)\}$" motifs, which are alternatively arranged to resemble a paddle-wheel shape. The molecular ring is not planar, and the titanium atoms define two equilateral triangles alternated and placed in two parallel planes separated by ≈0.5 Å. The six μ-oxo bridges are located on the inside, while the cyclopentadienyl ligands similarly appear oriented toward the outside edge of the ring, alternately above and below the ring plane. The diameter at the internal cavity, measured between opposite oxygen atoms, is in the range 5.665−5.889 Å.

In conclusion, we report herein the preparation and characterization of two novel titanoxane derivatives featuring structural properties previously unknown for organo-transition-metal oxide derivatives. An important aspect of our study is the demonstration that the choice of an appropriate ancillary ligand system can drive a reaction through unexpected pathways, resulting in unprecedented outcomes.

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Supporting Information Available: Experimental procedures and crystallographic data for **4** and **5** in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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(41) Crystal data for **4**: $C_{44}H_{72}Cl_2O_7Si_4Ti_4$, $M_r = 1087.88$, monoclinic, space group $P2_1/c$, $a = 12.911(3)$ Å, $b = 18.9580(17)$ Å, $c = 22.923(5)$ Å, $\beta = 105.610(10)°$, $V = 5403.8(18)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.337$ g cm^{-3}, $F(000) = 2280$, Mo Kα radiation ($\lambda = 0.710\,73$ Å), $\mu = 0.801$ mm^{-1}; crystal dimens 0.24 × 0.21 × 0.16 mm. $R1[F^2 > 2\sigma(F^2)] = 0.0587$, $wR2[F^2 > 2\sigma(F^2)] = 0.1275$, $R1(F^2) = 0.1327$, $wR2(F^2) = 0.1492$. Final difference Fourier maps showed no peaks higher than 0.529 or deeper than −0.531 e Å^{-3}. CCDC-672420. Crystal data for **4**·C_6H_{14}: $C_{44}H_{72}Cl_2O_7Si_4Ti_4\cdot C_6H_{14}$, $M_r = 1174.05$, triclinic, space group $P\bar{1}$, $a = 12.484(2)$ Å, $b = 15.7680(9)$ Å, $c = 17.217(4)$ Å, $\alpha = 65.561(7)°$, $\beta = 77.952(15)°$, $\gamma = 85.307(10)°$, $V = 3017.5(9)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.292$ g cm^{-3}, $F(000) = 1240$, Mo Kα radiation ($\lambda = 0.710\,73$ Å), $\mu = 0.722$ mm^{-1}; crystal dimens 0.451 × 0.29 × 0.246 mm. $R1[F^2 > 2\sigma(F^2)] = 0.0574$, $wR2[F^2 > 2\sigma(F^2)] = 0.1374$, $R1(F^2) = 0.1210$, $wR2(F^2) = 0.1617$. Final difference Fourier maps showed no peaks higher than 0.742 or deeper than −0.624 e Å^{-3}. CCDC-672421.

(42) Crystal data for **5**·C_5H_{12}: $C_{66}H_{108}O_{12}Si_6Ti_6\cdot C_5H_{12}$, $M_r = 1621$, monoclinic, space group $P2_1/n$, $a = 15.384(2)$ Å, $b = 14.826(2)$ Å, $c = 18.940(3)$ Å, $\beta = 104.140(10)°$, $V = 4189.1(4)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.286$ g cm^{-3}, $F(000) = 1716$, Mo Kα radiation ($\lambda = 0.710\,73$ Å), $\mu = 0.683$ mm^{-1}; crystal dimens 0.35 × 0.33 × 0.26 mm. Half a molecule of the hexanuclear complex and half a disordered pentane molecule are present in the asymmetric unit; the other halves are generated by the crystallographic inversion center. $R1[F^2 > 2\sigma(F^2)] = 0.0496$, $wR2[F^2 > 2\sigma(F^2)] = 0.1253$, $R1(F^2) = 0.0904$, $wR2(F^2) = 0.1460$. Final difference Fourier maps showed no peaks higher than 0.539 or deeper than −0.521 e Å^{-3}. CCDC-672422.