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Synthesis, Structures, and Solution Behavior of Di- and Trinuclear Titanium(IV)–Cyclophosphato Complexes

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The reaction of the cyclotetraphosphate ion ($P_4O_{12}{}^{4-}$) with [Cp*TiCl$_3$] (Cp* = η^5-C_5Me_5) gives $[(Cp^*Ti)_2(P_4O_{12})_2]^{2-}$ where the P_4O_{12} ligands adopt a saddle conformation, while that with $[(Cp^*TiCl)_3(\mu\text{-}O)_3]$ leads to $[(Cp^*Ti)_3(\mu\text{-}O)_3(P_4O_{12})]^-$ containing a crown form P_4O_{12} ligand; both products feature their unique cage structures. On the other hand, the reactions of the cyclotriphosphate ion ($P_3O_9{}^{3-}$) with $[(Cp^*TiCl_2)_2(\mu\text{-}O)]$ and $[(Cp^*TiCl)_3(\mu\text{-}O)_3]$ afford $[(Cp^*Ti)_2(\mu\text{-}O)(P_3O_9)_2]^{2-}$ and $[(Cp^*Ti)_3(\mu\text{-}O)_3Cl(P_3O_9)]^-$, respectively, and in both cases the P_3O_9 ligands bridge two titanium centers with an $\eta^2{:}\eta^1$ mode.

Organotransition metal complexes with O-donor ligands have recently been attracting considerable attention, because they serve as molecular models of metal species bound on oxo surfaces of heterogeneous catalysts.[1] They are also expected to provide effective single source precursors for structurally controlled inorganic materials.[2] In this context, a variety of three-dimensional coordination structures have successfully been constructed by using monophosphates,[3] monophosphonates,[4−6] and monophosphinates[6] as building blocks. In contrast, structural diversity of oxo-bridged inorganic−organometallic hybrids based on inorganic polyphosphates, especially that of oxophilic early transition metal derivarives, has been much less explored.[7,8] In this Communication, we disclose that the di- and trinuclear Ti(IV) complexes built up with Cp*Ti units and cyclophosphato ligand(s) possess unique three-dimensional structures, where the cyclophosphato ligands take coordination structures considerably different from those observed in late transition metal complexes.

When $(PPN)_4(P_4O_{12})\cdot 5H_2O$[7b] (PPN = $(PPh_3)_2N^+$) was allowed to react with 1 equiv of [Cp*TiCl$_3$] in CH_2Cl_2 at room temperature, the dianionic dinuclear complex $(PPN)_2[(Cp^*Ti)_2(P_4O_{12})_2]$ (**1**) was obtained as red crystals in 28% yield (Scheme 1).[9] The $^{31}P\{^1H\}$ NMR spectrum of **1** shows a singlet at δ −30.3 assignable to the P_4O_{12} ligand, while the ^1H NMR spectrum shows a Cp* signal at δ 2.17 (s), suggesting that the complex has a highly symmetric structure. The solid-state structure of **1**$\cdot 2C_2H_4Cl_2$ has been established by an X-ray diffraction study (Figure 1a).[10] The molecule has a crystallographic center of symmetry. The anionic part of **1** is composed of two Cp*Ti and two P_4O_{12} units, where

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(9) Although the formation of **1** and **2** seemed to be clean, difficulty in isolating them by recrystallization resulted in the significant loss of the yield.

10.1021/ic049206h CCC: $27.50

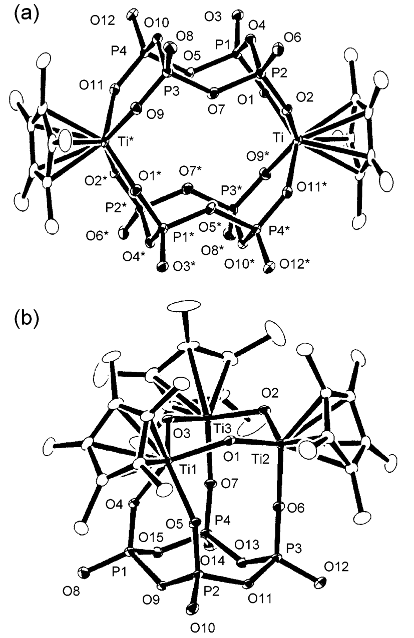
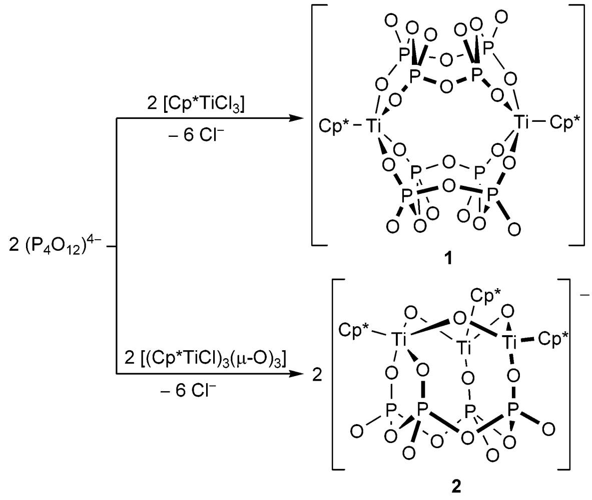


Figure 1. ORTEP drawings for the anionic parts of $\mathbf{1}\cdot 2C_2H_4Cl_2$ (a) and $\mathbf{2}\cdot 0.5C_6H_5CH_3$ (b). Thermal ellipsoids are drawn at the 30% probability level. Hydrogen atoms are omitted for clarity. Selected bond distances (Å) for $\mathbf{1}\cdot 2C_2H_4Cl_2$: Ti−O(1), 1.963(3); Ti−O(2), 1.980(3); Ti−O(9)*, 1.969(3); Ti−O(11)*, 1.995(2). For $\mathbf{2}\cdot 0.5C_6H_5CH_3$: Ti(1)−O(1), 1.921(2); Ti(1)−O(3), 1.906(2); Ti(1)−O(4), 2.011(2); Ti(1)−O(5), 2.023(2); Ti(2)−O(1), 1.774(2); Ti(2)−O(2), 1.833(2); Ti(2)−O(6), 1.927(2); Ti(3)−O(2), 1.834(2); Ti(3)−O(3), 1.780(2); Ti(3)−O(7), 1.916(2).

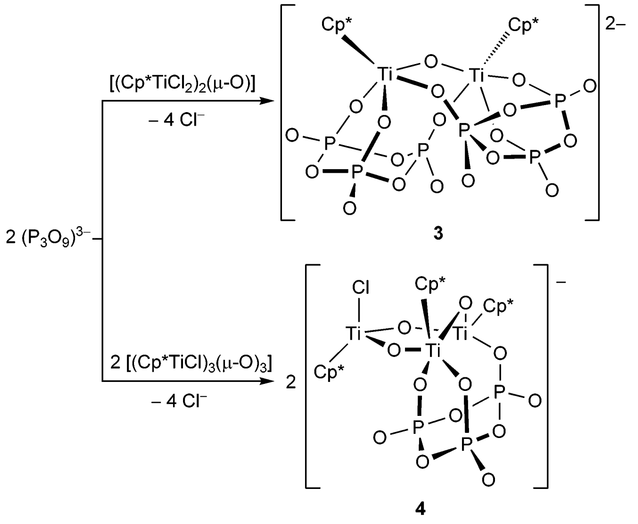
Scheme 1



each P_4O_{12} ligand takes a saddle conformation and bridges the two titanium atoms to form an unprecedented cage structure. Interestingly, the cage structure of **1** has a channel which penetrates the two side faces defined by the characteristic 12-membered $Ti_2P_4O_6$ rings. Considering the van der Waals radius of oxygen (1.4 Å) as well as the O(5)···O(7)*, O(1)···O(11), and Ti···Ti* interatomic distances at 3.683(4), 4.783(3), and 6.134(1) Å, respectively, the size of the rectangular entrance of the channel is estimated to be 0.9 Å × 2.0 Å.

On the other hand, the reaction of $(PPN)_4(P_4O_{12})\cdot 5H_2O$ with 1 equiv of the oxo-bridged trinuclear complex $[(Cp^*TiCl)_3(\mu\text{-}O)_3]$[11] afforded the monoanionic complex $(PPN)[(Cp^*Ti)_3(\mu\text{-}O)_3(P_4O_{12})]$ (**2**) as orange crystals in 28% yield (Scheme 1).[9] An X-ray diffraction study of $\mathbf{2}\cdot 0.5CH_2Cl_2$ has revealed that the core of complex **2** is a cage composed of a crown form P_4O_{12} ligand and a Ti_3O_3 six-membered ring (Figure 1b).[10] One of the three titanium centers (Ti(1)) adopts a four-legged piano stool geometry, while the geometry of the other two is a three-legged piano stool. It should be pointed out that **1** and **2** are rare examples of P_4O_{12} complexes,[7b] and to the best of our knowledge, **2** provides the first example of the coordination compound containing a crown conformation P_4O_{12} ligand.

Scheme 2



In the $^{31}P\{^1H\}$ and ^1H NMR spectra of **2** in CD_2Cl_2 at room temperature, only one broad signal at δ −33.6 (s) for the P_4O_{12} ligand and one singlet at δ 2.15 for the Cp* groups are observed, respectively. These spectral features, which are inconsistent with the local C_s symmetry of the anion of **2** in the solid state, indicate that the complex **2** is fluxional in solution. In fact, the broad $^{31}P\{^1H\}$ NMR signal coalesces at −20 °C and splits to two pseudodoublets (δ −30.3 (J = 32 Hz), −37.0 (J = 32 Hz)) at −80 °C in the variable temperature $^{31}P\{^1H\}$ NMR spectra (162 MHz), though there is no apparent change in the ^1H NMR over this temperature range. This fluxionality is rationalized by the rotation of the Ti_3O_3 unit on the P_4O_{12} platform, and the $\Delta G^\ddagger$ value for the

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(10) Crystal data for $\mathbf{1}\cdot 2C_2H_4Cl_2$ follow: formula $C_{96}H_{98}Cl_4N_2O_{24}P_{12}Ti_2$, M = 2273.17, triclinic, a = 12.28(1) Å, b = 14.16(2) Å, c = 15.65(2) Å, α = 87.08(4)°, β = 72.44(2)°, γ = 85.39(4)°, V = 2585(5) Å^3, $P\bar{1}$, Z = 1, μ = 5.15 cm^{-1}, D_c = 1.460 g cm^{-3}, 50474 reflections measured, 11675 unique (R_{int} = 0.041), R1 = 0.047, wR2 = 0.123. For $\mathbf{2}\cdot 0.5C_6H_5CH_3$: formula $C_{69.5}H_{79}NO_{15}P_6Ti_3$, M = 1497.93, triclinic, a = 11.2743(9) Å, b = 13.313(1) Å, c = 26.442(2) Å, α = 79.799(3)°, β = 89.912(5)°, γ = 65.218(2)°, V = 3534.6(5) Å^3, $P\bar{1}$, Z = 2, μ = 5.32 cm^{-1}, D_c = 1.407 g cm^{-3}, 31333 reflections measured, 15682 unique (R_{int} = 0.040), R1 = 0.055, wR2 = 0.121. For $\mathbf{3}\cdot CH_2Cl_2$: formula $C_{93}H_{92}Cl_2N_2O_{19}P_{10}Ti_2$, M = 2018.20, triclinic, a = 13.021(3) Å, b = 19.841(4) Å, c = 19.899(5) Å, α = 98.981(10)°, β = 105.971(13)°, γ = 105.740(11)°, V = 4607.0(17) Å^3, $P\bar{1}$, Z = 2, μ = 4.76 cm^{-1}, D_c = 1.455 g cm^{-3}, 68686 reflections measured, 19935 unique (R_{int} = 0.040), R1 = 0.050, wR2 = 0.098. For $\mathbf{4}\cdot 0.5C_2H_4Cl_2$: formula $C_{67}H_{77}Cl_2NO_{12}P_5Ti_3$, M = 1457.82, triclinic, a = 11.44(1) Å, b = 14.128(4) Å, c = 22.247(8) Å, α = 94.55(4)°, β = 97.81(4)°, γ = 92.84(4)°, V = 3544.6(4) Å^3, $P\bar{1}$, Z = 2, μ = 5.76 cm^{-1}, D_c = 1.366 g cm^{-3}, 16918 reflections measured, 16914 unique (R_{int} = 0.045), R = 0.051, R_w = 0.056 [7948 data $I > 3\sigma(I)$].

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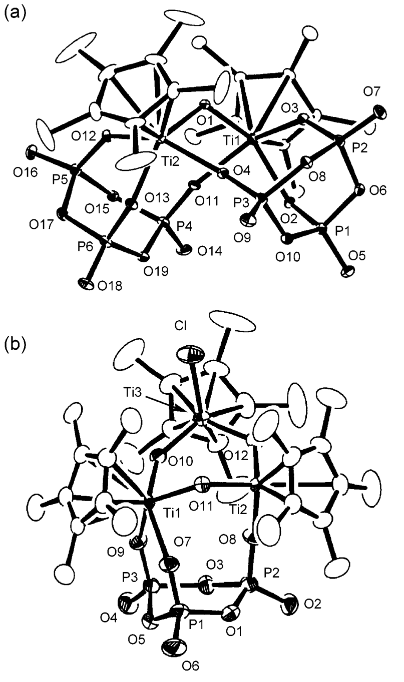
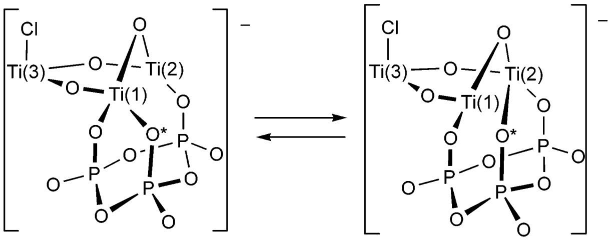


Figure 2. ORTEP drawings for the anionic parts of **3**·CH_2Cl_2 (a) and **4**·$0.5C_2H_4Cl_2$ (b). Thermal ellipsoids are drawn at the 30% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg) for **3**·CH_2Cl_2: Ti(1)−O(1), 1.859(3); Ti(1)−O(2), 2.046(2); Ti(1)−O(3), 2.028(3); Ti(1)−O(11), 2.061(3); Ti(2)−O(1), 1.819(2); Ti(2)−O(4), 2.044(2); Ti(2)−O(12), 2.025(2); Ti(2)−O(13), 2.041(2); Ti(1)···Ti(2), 3.120(1); Ti(1)−O(1)−Ti(2), 116.1(1). For **4**·$0.5C_2H_4Cl_2$: Ti(1)−O(7), 2.103(4); Ti(1)−O(9), 2.025(4); Ti(1)−O(10), 1.910(4); Ti(1)−O(11), 1.882(4); Ti(2)−O(8), 1.926(4); Ti(2)−O(11), 1.791(4); Ti(2)−O(12), 1.816(4); Ti(3)−Cl, 2.319(2); Ti(3)−O(10), 1.771(4); Ti(3)−O(12), 1.828(4).

rotation at the coalescence temperature (−20 °C) is estimated to be 45±2 kJ/mol (see Supporting Information).

The P_3O_9 ligand exhibited rather different coordination behavior. Although the reaction of $(PPN)_3(P_3O_9)\cdot H_2O$ with [Cp*$TiCl_3$] failed to give isolable products, that with 0.5 equiv of [(Cp*$TiCl_2$)$_2$(μ-O)][12] in CH_2Cl_2 at room temperature afforded the dianionic complex $(PPN)_2$[(Cp*Ti)$_2$(μ-O)(P_3O_9)$_2$] (**3**) as red crystals in 80% yield (Scheme 2). Its $^{31}P\{^1H\}$ NMR spectrum ($CDCl_3$) clearly shows the presence of three nonequivalent phosphorus atoms in the P_3O_9 ligand (δ −21.4 (dd, J = 14 Hz, J = 19 Hz), −24.4 (dd, J = 14 Hz, J = 24 Hz), −26.7 (dd, J = 19 Hz, J = 24 Hz)), while the ^1H NMR spectrum displays one singlet at δ 2.16 (s) assignable to the Cp* ligand. The molecular structure of **3**·CH_2Cl_2 has been confirmed by an X-ray study (Figure 2a).[10] In complex **3**, each P_3O_9 ligand bridges the two titanium atoms in a $\kappa^2 O,O'{:}\kappa O''$ fashion. It should be noted that in the P_3O_9 complexes reported so far only the monomeric κ^3- or κ^2-coordination mode has been observed; the above bridging coordination mode is unprecedented for the P_3O_9 ligand.

Scheme 3



Finally, treatment of $(PPN)_3(P_3O_9)\cdot H_2O$ with [(Cp*TiCl)$_3$(μ-O)$_3$] resulted in the formation of the monoanionic complex (PPN)[(Cp*Ti)$_3$(μ-O)$_3$Cl(P_3O_9)] (**4**) in 84% yield (Scheme 2). The structure of the anion is shown in Figure 2b. In contrast to the P_4O_{12} complex **2**, only two of the three titanium centers are bound to the terminal oxygen atoms of the P_3O_9 ligand in **4**, and the remaining titanium atom (Ti(3)) remains coordinated by a chloro ligand (Figure 2b).[10] Again, the P_3O_9 ligand adopts a $\kappa^2 O,O'{:}\kappa O''$ coordination mode, making the trititanium core unsymmetrical. Conversely, the $^{31}P\{^1H\}$ NMR spectra ($CDCl_3$) of **4** exhibit one triplet (δ −23.4, J = 15 Hz) and one doublet (δ −26.7, J = 15 Hz) assignable to the P_3O_9 ligand, and the ^1H NMR spectra display two Cp* singlets at δ 2.10 (30H) and 2.09 (15H), suggesting an apparent C_s symmetry of the complex in solution. Although no temperature dependence of the spectra was observed over the range 20 to −60 °C, these spectral features are explained by the fast migration of the specific oxygen atom (O*) between the titanium centers Ti(1) and Ti(2) (Scheme 3), but not by the rotation of the P_3O_9 ligand as observed in the P_4O_{12} complex **2**.

In summary, we have disclosed that cyclophosphate anions are versatile building blocks to construct organotitanium−phosphate hybrids with diversified structures, in which the P_4O_{12} and P_3O_9 ligands take unique coordination modes. The closed cage structures have been found for the P_4O_{12} complexes, while more open structures have been observed with the P_3O_9 ligands.

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Supporting Information Available: Experimental details describing the synthesis and characterization data; a table of crystal data for **1**−**4**; complete X-ray structural data for **1**−**4** in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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