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Article

Organic-Soluble Tri-, Tetra-, and Pentanuclear Titanium(IV) Phosphates

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Bulky 2,6-disubstituted aryl esters of phosphoric acid, 2,6-dimethylphenyl phosphate (dmppH$_2$), and 2,6-diisopropylphenyl phosphate (dippH$_2$) react differently with Cp*TiCl$_3$ (Cp* = C$_5$Me$_5$) under identical reaction conditions. While dippH$_2$ and Cp*TiCl$_3$ react in THF at 25 °C to yield air-stable trinuclear titanophosphate cage [(Ti$_3$Cp*Cl(μ_2-O)(dipp)$_2$(dippH)$_4$(THF)]·(toluene) (**1**), the similar reaction involving dmppH$_2$ yields the tetranuclear titanophosphate [Ti$_4$Cl$_2$(μ_2-O)$_2$(dmpp)$_2$(dmppH)$_6$(THF)$_2$]·(toluene)$_2$ (**2**). Interestingly, the change of titanium source to Ti(O*i*Pr)$_4$ in the reaction with dippH$_2$ produces a pentanuclear titanophosphate, [Ti$_5$(μ_3-O)(O*i*Pr)$_6$((dipp)$_6$(THF)] (**3**). Compounds **1**−**3** were the only products isolated as single crystals from the respective reaction mixtures in 59, 75, and 54% yield, respectively. The new clusters **1**−**3** have been characterized by elemental analysis, IR and NMR (^{1}H and ^{31}P) spectroscopy, and single crystal X-ray diffraction studies. The structural elucidation reveals that in the reactions leading to **1** and **2**, extensive Cp*-Ti bond cleavage occurs, leaving only one residual Cp*-ligand in cluster **1** and none in **2**. Closer analysis of the structures of **1**−**3** shows common structural features which in turn imply that the formation of all three products could have proceeded via a common Ti−O−Ti dimeric building block.

Introduction

Titanosilicates and titanophosphates have been under spotlight for the last few decades because of their varied technological applications including catalysis. Both extended and molecular titanosilicates have been well studied over the last few decades with the aim to develop new oxidation and epoxidation catalysts for organic transformations.[1–4] Interest in titanophosphates stem from the fact that alkali metal containing titanium phosphate materials are used in a variety of applications.[5,6] For example, lamellar titanium phosphates have been known to exhibit ion-exchange properties for numerous alkali- and alkaline-earth-metal ions.[5a,b] Similarly, Nasicon type phosphates (KTi$_2$(PO$_4$)$_3$) find applications as both fast ion conductors and low thermal expansion ceramics.[5c–e] KTP (KTiOPO$_4$) has been studied extensively as a NLO material.[6,7]

In contrast, the investigations on molecular titanium phosphonates (Chart 1)[8] and phosphates (Chart 2),[9] which could serve as both model compounds and precursors to solid-state phosphate materials, are very limited. Early work in this area afforded insoluble dialkyl phosphate titanium complexes that have been identified as polymeric materials.[10] Thorn and Harlow have reported the first well-defined molecular titanium phosphate complexes starting from either titanium halides, amides, or siloxides.[9a] More significantly, Tilley et al. have recently reported on the reaction of ditert-butyl phosphate with titanium precursors under a variety of conditions and isolated titanium phosphates of the type

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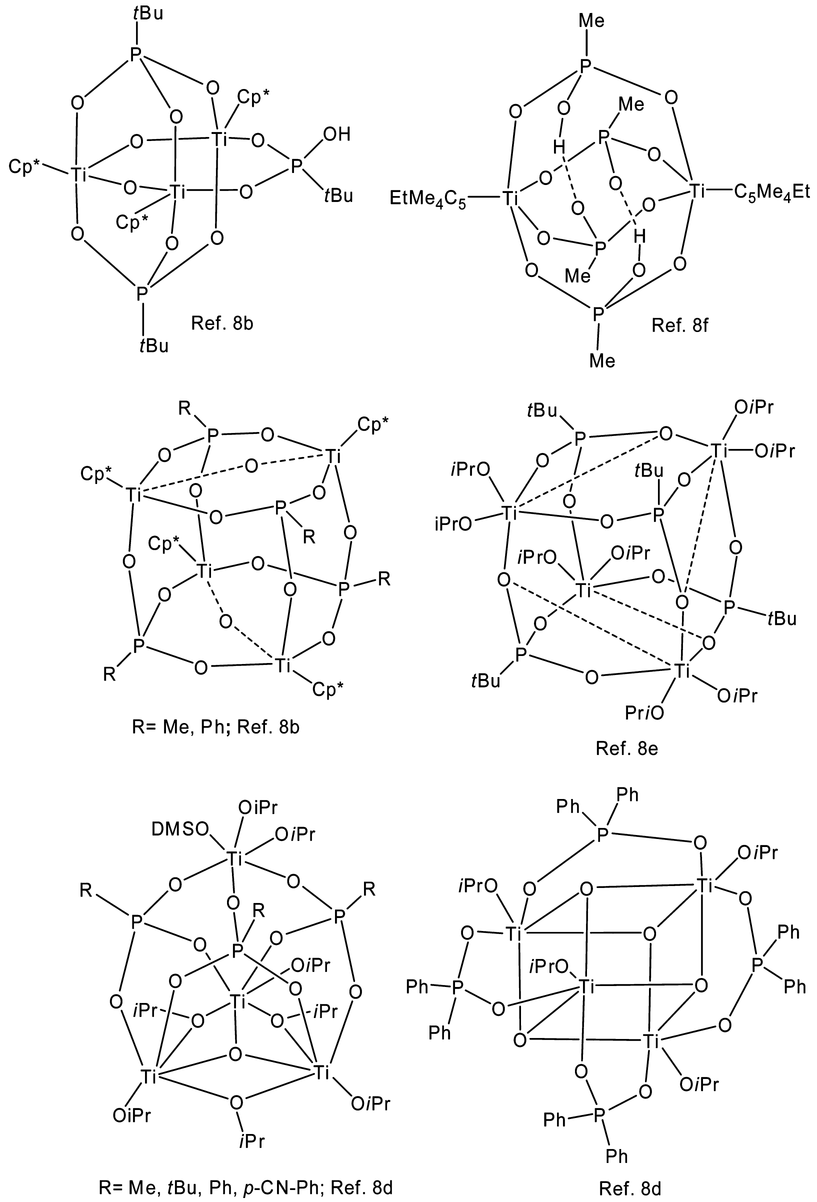
Chart 1. Molecular Titanium Phosphonates



Ref. 8b

Ref. 8f

R= Me, Ph; Ref. 8b

Ref. 8e

R= Me, *t*Bu, Ph, *p*-CN-Ph; Ref. 8d

Ref. 8d

$[Ti(OR)_3O_2P(OtBu)_2]_n$ (R = Et, *i*Pr) and $[Ti_2K(OEt)_8O_2P(OtBu)_2]_2$.[9b]

The examples shown in Chart 2, to the best of our knowledge, cover almost all the molecular titanium phosphates known in the literature to date[9] and thus reveal the paucity of suitable molecular models for complex titanophosphate framework materials. Further, all the molecules shown Chart 2 have been prepared from a dialkyl phosphate $(RO)_2P(O)(OH)$ (R = methyl, benzyl, tert-butyl) and there are no reports in the literature describing the synthesis of titanium phosphates starting from a mono alkyl or aryl ester

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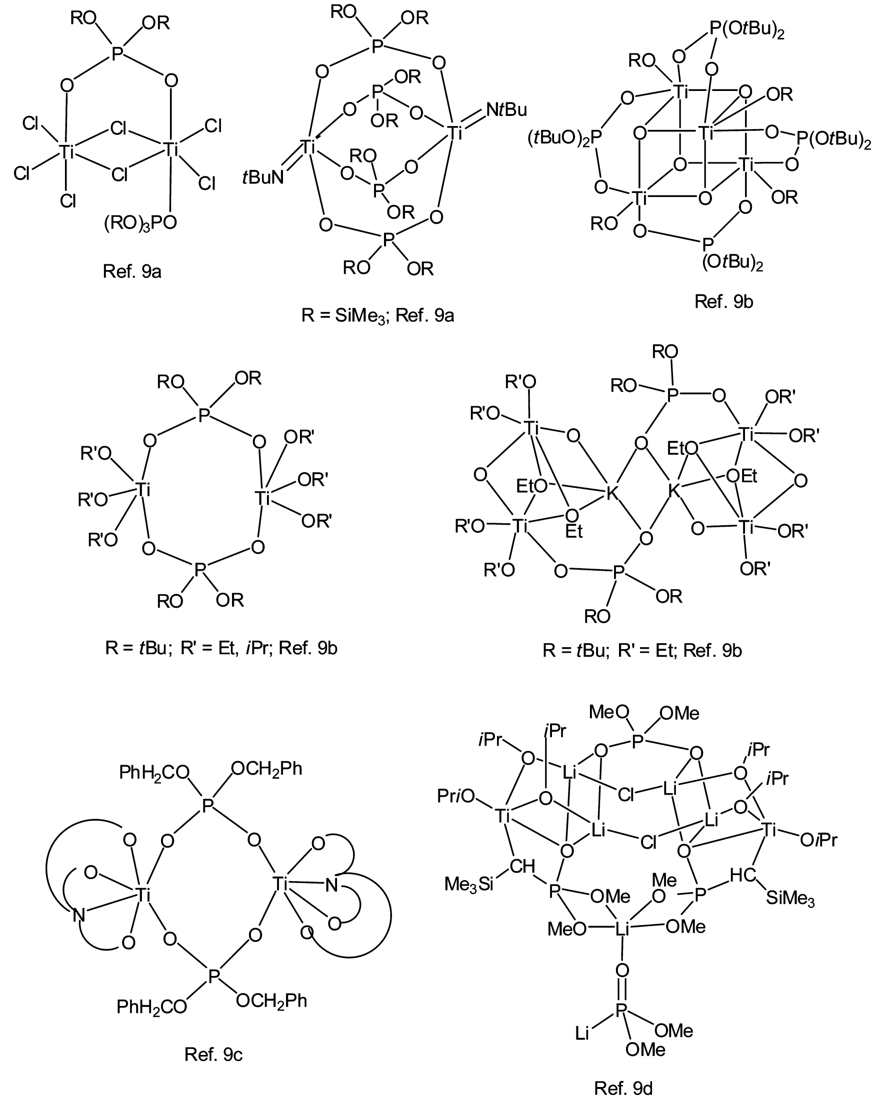
Chart 2. Molecular Titanium Phosphates



Ref. 9a

R = SiMe$_3$; Ref. 9a

Ref. 9b

R = *t*Bu; R' = Et, *i*Pr; Ref. 9b

R = *t*Bu; R' = Et; Ref. 9b

Ref. 9c

Ref. 9d

of phosphoric acid. We have shown in recent years that, compared to dialkyl phosphates,[11] mono esters of phosphoric acid (RO)P(O)(OH)$_2$[12] serve better to realize secondary building blocks of zeolite-like materials because of the presence of two acidic protons and a phosphoryl group. Continuing our recent investigations on the synthesis of both discrete and extended main group metal phosphates,[11,12] we have now studied the suitability of monoaryl phosphates (RO)P(O)(OH)$_2$ (R = 2,6-diisopropyl phenyl (dippH$_2$) and R = 2,6-dimethylphenyl (dmppH$_2$)) in preparing discrete cluster complexes of titanium starting from Cp*TiCl$_3$ or Ti(O*i*Pr)$_4$. The results of this investigation, reporting organic soluble tri-, tetra-, and pentanuclear titanium phosphate cages, are described in this contribution.

Results and Discussion

Synthesis. To obtain organic-soluble organotitanium phosphates, reactions of the titanium source Cp*TiCl$_3$ with monoaryl phosphates dippH$_2$ and dmppH$_2$ were carried out

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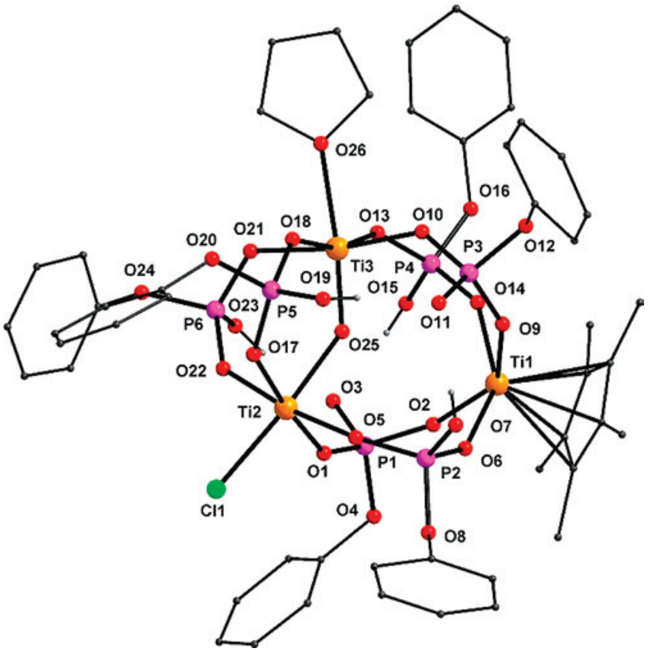

Figure 1. Molecular structure of **1** (lattice toluene molecules and the C−H hydrogen atoms have been omitted). Selected bond distances [Å]: Ti—O(P) 1.933(3)−2.026(3) (av. 1.965), Ti—Cl 2.252(1), Ti—O(Ti) 1.716(3), 2.019(3), Ti—O(THF) 2.191(3), Ti—C(Cp*) 2.360(4)−2.410(4) (av. 2.385), P—O(Ti) 1.506(3)−1.527(3) (av. 1.514), P—O(Ar) 1.563(3)−1.586(3) (av. 1.575), P—O(H) 1.536(3)−1.547(3) (av. 1.542). Bond angles [deg]: O—Ti1—O 83.2(1)−146.4(1), C—Ti1—O 75.9(1)−134.1(1), C—Ti1—C 34.1(1)−58.0(1), O—Ti2—O (cis) 84.2(1)−90.0(1), (trans) 172.6(1), 174.2(1), O—Ti2—Cl (cis) 90.27(8)−97.15(8), (trans) 174.47(9), O—Ti3—O (cis) 83.1(1)−100.5(1), (trans) 164.7(1), 171.2(1), 174.2(1), Ti—O—P 127.6(2)−151.2(2), Ti2—O—Ti3 139.2(1).

initially in the presence of Et_3N as the HCl scavenger. The removal of $Et_3N \cdot HCl$ from the reaction mixture and the subsequent spectroscopic analysis of the residue obtained revealed that the reaction yields a complex mixture of products. Attempts to isolate any analytically pure products from these mixtures or to obtain single crystals for X-ray diffraction studies were unsuccessful. The reactions were then repeated in the absence of Et_3N to rule out the role of its basicity/nucleophilicity in producing a complex mixture of products. Thus, the reaction of Cp^*TiCl_3 with dippH_2 in THF under dry dinitrogen (in absence of any HCl scavenger) over 24 h at room temperature leads to the formation of trinuclear titanophosphate complex $[(Ti_3\,Cp^*Cl(\mu_2\text{-}O)(dipp)_2(dippH)_4(THF)] \cdot (toluene)$ (**1**) as air-stable red single crystals, after the crystallization of crude product from toluene. When the same reaction was carried out under identical conditions, replacing dippH_2 by less bulky dmppH_2, the tetranuclear cage-shaped titanium phosphate complex $[Ti_4Cl_2(\mu_2\text{-}O)_2(dmpp)_2(dmppH)_6(THF)_2] \cdot (toluene)_2$ (**2**) was isolated. Formation of complexes **1** and **2** in the above reactions clearly indicates that the HCl produced in the reaction, in the absence of any acid scavenger, attacks the Ti-Cp* linkage and cleaves it. While the cleavage is total in the reaction leading to complex **2**, it is only partial in the case of the formation of **1**, leaving one of the three titanium atoms with a terminal Cp* ligand. It can be assumed that in the presence of the bulky dipp ligand, Ti-Cp* bond cleavage is not total.

To find out if any other types of cluster formation takes place in the presence of highly reactive metal precursors, $Ti(O\textit{i}Pr)_4$ was reacted with dippH_2 under an inert atmosphere. Subsequent crystallization of the reaction product from petroleum ether affords block shaped colorless single crystals of $[Ti_5(\mu_3\text{-}O)(O\textit{i}Pr)_6((dipp)_6(THF)]$ (**3**) in 54% yield.

Compounds **1**−**3** have been characterized by means of their analytical data, infrared, and multinuclear NMR spectroscopic techniques. All three compounds do not melt up to 250 °C; however, the onset of decomposition of the compounds is at 200 °C. Elemental analysis values obtained in each case revealed that the compounds are analytically pure. The infrared spectrum of **1** shows a broad vibration at 2329 cm^{-1} corresponding to the presence of a P−OH group. The strong bands observed at around 1171 and 1126 cm^{-1} are readily assignable to P=O and M−O−P vibrations, respectively.

In solution, compound **1** shows three single resonances in the ^{31}P NMR spectroscopy (δ −4.8, −9.4, −15.1 ppm) indicating that the six phosphate ligands in the complex exist in three different chemical environments. While the downfield signal at −4.8 ppm could be associated to the monodeprotonated phosphate ligands that bridge the two titanium centers without Cp* ligand, the upfield signal at −15.1 ppm is due to the doubly deprotonated ligands in the complex. The other two monodeprotonated phosphate ligands resonate at −9.4 ppm. The observed ^1H NMR spectral pattern and the ratio of the integrated intensities further lend evidence to the structure of **1**. The multiplets appearing in the range δ 7.14−7.28 ppm correspond to the aryl protons. As expected, the methine protons (C−H of the isopropyl group) appear as a septet centered at δ 3.43 ppm ($^3J_{HH} = 6.6$ Hz) and a broad-band at δ 3.18 ppm. The methyl protons (CH_3 of the isopropyl group) give rise to three overlapping doublets (δ 1.25, 1.07 and 1.02 ppm). Two singlets of similar intensity appearing at δ 2.38 and 2.35 ppm are assigned to the methyl groups of the pentamethylcyclopentadienyl ligand.

The infrared spectrum of **2** shows the presence of a P−OH group at 2294 cm^{-1} as a broad vibration. Compound **2** is poorly soluble in C_6D_6, and its ^{31}P NMR spectrum in $CDCl_3$ shows four single resonances at δ −4.2, −9.8, −14.9, and −20.3 ppm (vide infra). While the resonances at δ −4.2 and −9.8 ppm could be attributed to the mono deprotonated phosphate ligands existing in two different environments, the resonances appearing at δ −14.9 and −20.3 ppm are due to two different fully deprotonated phosphate ligands. The observed ^1H NMR spectral pattern and the ratio of integrated intensities are consistent with the structure of the compound.

Unlike **1** and **2**, compound **3** does not show any absorption at around 2300 cm^{-1} in the infrared spectrum indicating the complete deprotonation of the phosphate ligands in the molecule and hence the absence of free P−OH groups in the complex. The ^{31}P NMR spectrum of **3** shows two singlets at δ −12.0 and −18.6 ppm in a 2:1 ratio for the six phosphate ligands in the molecule. Although all the six phosphate ligands exist in a doubly deprotonated state in the complex, because of the difference in the coordination geometry and environment around the titanium centers to which they are attached, two different signals are obtained.

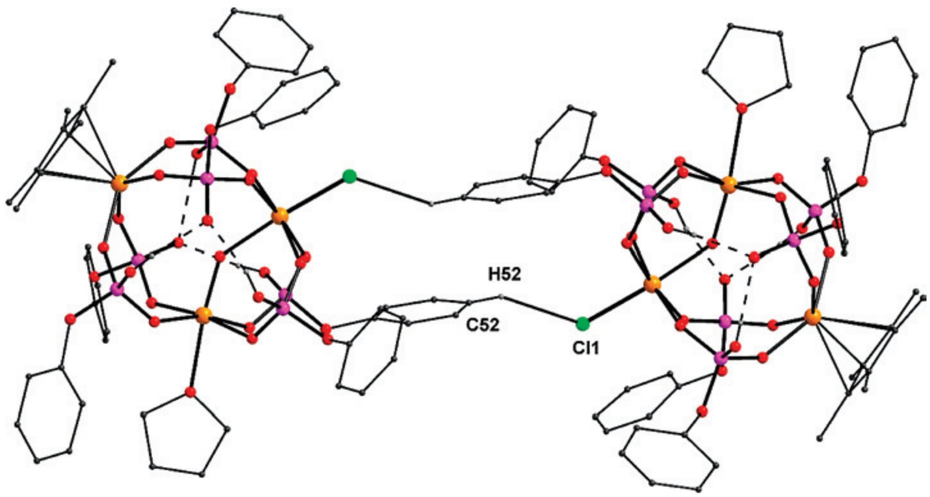

Figure 2. Intermolecular strong C−H···Cl hydrogen bonding interaction in **1**, leading to the formation of a dimeric assembly.

Molecular Structure of 1. To have a clear understanding of the new titanium phosphates synthesized in the present study, a single crystal X-ray diffraction study was carried out for each compound. A perspective view of the molecular structure of **1** is shown in Figure 1 along with selected bond length and angles. The compound is an asymmetric trinuclear titanophosphate cluster made up of three titanium(IV) centers, six phosphate ligands, and an μ-oxo group. An interesting feature of compound **1** is the asymmetry in terms of coordination geometry around the three titanium atoms. The three titanium ions exhibit three different coordination environments. While two of the titanium centers (Ti2 and Ti3) have lost the Cp* ligands (which were present in the starting material $\mathrm{Cp^*TiCl_3}$), the third titanium (Ti1) retains its Cp* ligand. The Ti2 and Ti3 centers are bridged by a μ-oxo ligand. The three titanium centers with three different coordination environments sit approximately at the three corners of an isosceles triangle. Each pair of Ti centers is bridged by two phosphate ligands existing either in the singly (dippH$^-$) or in the doubly deprotonated (dipp^{2-}) form. Out of the total six phosphate ligands in the molecule, only two have been completely deprotonated. Both types of phosphate ligands however bridge two Ti atoms and hence have the same Harris notation [2.110].[13] While the Ti2−Ti3 edge has been bridged by two dippH$^-$ ligands, the Ti1−Ti3 and Ti2−Ti3 edges have been bridged by one dippH$^-$ and one dipp^{2-} ligands.

A closer look at the Ti···Ti distances and metal coordination geometries reveals several interesting structural features. For example, as stated above, the three titanium ions differ from each other in terms of their coordination environment. While the oxo-bridged Ti-centers, Ti2 and Ti3, are octahedral, the third Ti-center (Ti1) exhibits a pseudosquare pyramidal geometry (highly distorted). The presence of bulky pentahapto Cp* ligand on Ti1 is the reason for this Ti atom being not bound to the central oxo-ligand which bridges the other two titanium centers (this is the major difference between the structure of **1** and that of the other two compounds **2** and **3** where the central oxo-ligand acts as a μ_3-bridge; vide infra). Thus, the core structure of **1** contains three nonplanar $Ti_2O_4P_2$ eight-membered rings, two Ti_2O_3P six-membered rings, and two $Ti_3O_5P_2$ ten-membered rings. The periphery of this core is surrounded by hydrophobic pentamethyl-cyclopentadienyl and phenoxy groups (in addition to that one chloride, one THF and two lattice toluene molecules), which explains the high solubility of **1** in common solvents. Thus, there are three types of Ti···Ti distances in **1** (Ti1···Ti2 4.573 Å, Ti1···Ti3 4.373 Å, and Ti2···Ti3 3.052 Å). Similarly, Ti···P distances also vary over a range (3.165−3.381 Å).

The electronegative chlorine in **1** is involved in strong intermolecular hydrogen bonding interactions with neighboring unit aryl protons, yielding a centro-symmetric dimeric structure (hydrogen bond parameters: C52···Cl1 = 3.642(5) Å, H52···Cl1 = 2.808(1) Å, C52−H52 = 0.950(5) Å, C52−H52···Cl1 = 147.1(3)°) (Figure 2), which is rare among titanium phosphate or phosphonate molecular clusters although similar interactions have been observed recently in late transition metal coordination compounds.[14] Several intramolecular hydrogen bonding interactions are also observed in between the phosphoryl oxygen and the undissociated P−OH hydroxyl protons in **1** as shown in Figure 2.

Molecular Structure of 2. The single crystal X-ray structural analysis of compound **2** shows that it is a tetranuclear centro-symmetric cluster composed of four titanium atoms and eight phosphate bridges (Figure 3). As described vide supra, tetranuclear clusters are uncommon among titanium phosphates, and only a very few structural motifs have been reported.[8] The structure of tetranuclear core in **2** is very different from the cubane-shaped core observed for the tetranuclear titanium phosphonates reported by

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(13) Harris notation describes the binding mode as [*X*. *Y*1*Y*2*Y*3. . *Yn*], where *X* is the overall number of metals bound by the whole ligand and each value of *Y* refers to the number of metal atoms attached to the different donor atoms. See Coxall, R. A.; Harris, S. G.; Henderson, D. K.; Parsons, S.; Tasker, P. A.; Winpenny, R. E. P. *J. Chem. Soc., Dalton Trans.* **2000**, 2349.

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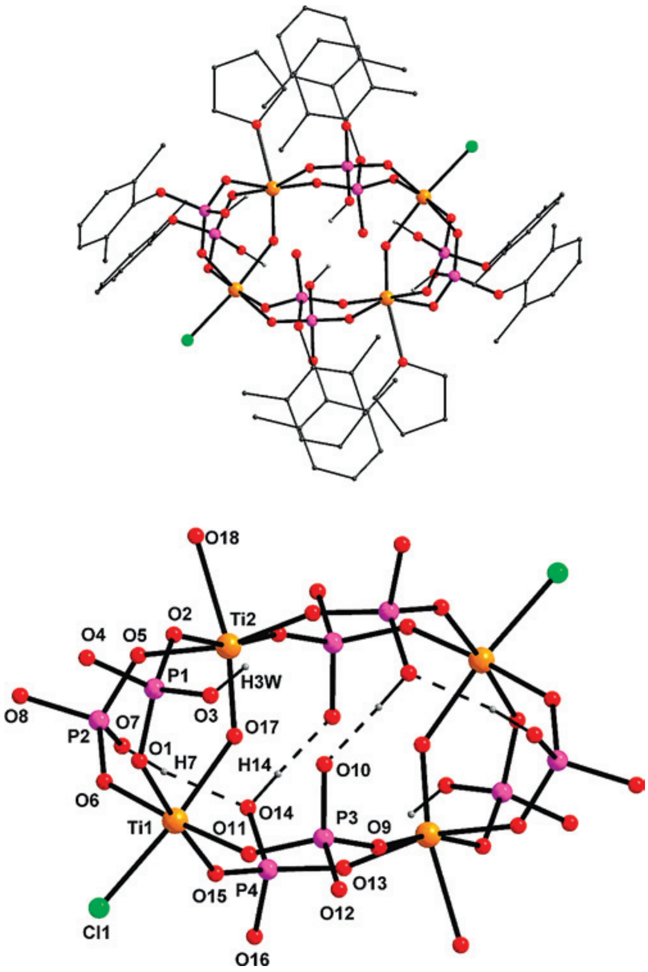


Figure 3. Molecular structure of **2** (the C−H hydrogen atoms have been omitted). Selected bond distances [Å]: Ti−O(P) 1.903(3)−1.993(3) (av. 1.956), Ti−Cl 2.266(1), Ti1−O17 2.011(3), Ti2−O17 1.720(3), Ti−O(THF) 2.177(3), P−O(Ti) 1.504(4)−1.527(3) (av. 1.514), P−O(H) 1.520(4)−1.553(4) (av. 1.541), P−O(Ar) 1.565(3)−1.575(4) (av. 1.571). Bond angles [deg]: O−Ti1−O (cis) 85.2(1)−90.6(2), (trans) 175.4(2), 175.9(2), O−Cl (cis) 90.4(1)−94.1(1), (trans) 174.2(1), O−Ti2−O (cis) 78.4(2)−101.4(2), (trans) 166.5(2), 166.8(2), 167.1(1), Ti−O−P 130.0(2)−160.1(2), Ti1−O−Ti2 141.2(2).

Roesky et al.[8b] and Mehring et al.[8e] or the tetrameric zinc phosphates prepared by us.[12c] The core structure of **2**, however, somewhat resembles the *tert*-butylphosphonate tin clusters [nBu$_4$Sn$_4$(μ-OH)$_2$(μ-dippH)$_6$(μ-dipp)$_2$],[12e] [(nBuSn)$_4$(O)$_2$(tBuPO$_3$H)$_8$],[15a] or [(PhCH$_2$Sn)$_4$(O)$_2$(tBuPO$_3$H)$_8$][15b] and the niobium phosphonate [Bu$^n{}_4$N]$_2$[{Nb(OMe)$_3$(O$_3$PPh)}$_2$(μ-O)].[15c] The molecule of **2** is centrosymmetric and contains four titanium ions and eight phosphate ligands and two oxo ligands. The four titanium ions exist in the molecule as two μ-oxo bridged Ti−O−Ti units that are held together by eight phosphate ligands. Any two adjacent titanium atoms in the molecule are bridged by a pair of phosphate ligands as shown in Figure 3. Among the eight phosphate ligands, only two are doubly deprotonated (dmpp^{2-}) while the rest exist in the mono deprotonated (dmppH$^-$) form. All the phosphate ligands however show a [2.110] type of coordination.

The core structure of **2** contains Ti$_4$O$_8$P$_4$ sixteen-membered rings, four nonplanar Ti$_2$O$_4$P$_2$ eight-membered rings, four Ti$_2$O$_3$P six-membered rings, and two Ti$_4$O$_6$P$_2$ twelve-membered rings. The two sixteen-membered Ti$_4$O$_8$P$_4$ rings which are connected at the Ti centers are clearly shown in Figure 4 (the central bridging-oxo ligands have been removed from the core structure for clarity). All four titanium centers adopt six-coordinated octahedral geometry. Four of the coordination sites around each metal are occupied by phosphate oxygen atoms; the fifth coordination site is accounted by the μ-oxo oxygen atom. The sixth coordination is completed either by an anionic chloride (Ti1) or by a neutral THF ligand (Ti2). All the four titanium centers lie on a plane and exhibit three different types of Ti···Ti nonbonded distances. The distance between oxo-bridged Ti atoms is the shortest (3.520 Å), while the diagonal Ti···Ti′ distance is the longest (6.787 Å). The Ti···Ti distance between Ti1 and Ti2 along the side of the rectangle is 4.917 Å. The Ti−O distances vary in the range 1.903(3)−1.993(3) Å and are comparable to those found in **1** and other titanophosphate molecules.[8,9]

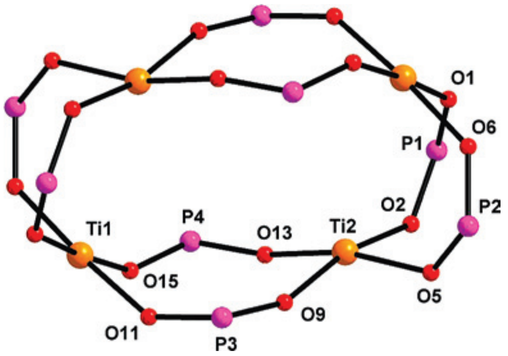


Figure 4. View of Ti$_2$O$_4$P$_2$ eight-membered and Ti$_4$O$_8$P$_4$ sixteen-membered rings in **2**.

Because six of the phosphate ligands are not fully deprotonated, they are involved in intramolecular H-bonding interactions with phosphoryl oxygen atoms (hydrogen bond parameters: O7···O14 = 2.650(5) Å, H7···O14 = 1.728(3) Å, O7−H7 = 0.928(4) Å, O7−H7···O14 = 171.7(2)°; O14···O10 = 2.431(5) Å, H14···O10 = 1.551(3) Å, O14−H14 = 0.880(4) Å, O14−H14···O10 = 177.8(3)°; Figure 3 bottom). In the recently reported dimeric titanium-phosphonate cage such nondeprotonated hydroxyl protons are involved in strong intramolecular hydrogen bonding interactions (Chart 1).[8f]

Molecular Structure of 3. A perspective view of the molecule of **3** with the core structure of **3** is shown in Figure 5. The molecule is a pentanuclear titanophosphate cluster composed of six phosphates, six isopropoxides, one THF, and also a μ_3-oxygen as ligands. The oxo-group bridges three central titanium centers in a μ_3-fashion. On either side of this trinuclear unit one peripheral titanium atom is present. The central and peripheral titanium ions are joined together by six dipp^{2-} phosphate ligands, each with a [3.111] mode of coordination to three different titanium centers. Thus, the central titanium ions are bound by four phosphate oxygen atoms while the terminal ones are surrounded by three phosphate oxygen atoms. The titanium ions in the trinuclear unit (Ti1, Ti2, and Ti3), which are tethered by μ_3-O, adopt a six coordinate octahedral geometry, whereas the peripheral terminal titanium centers (Ti4 and Ti5) adopt a five

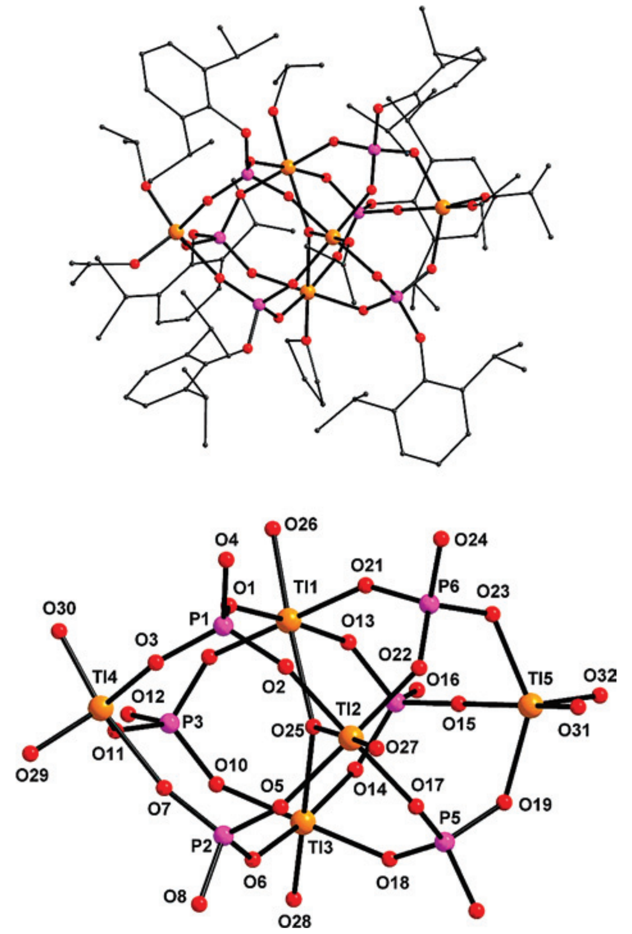
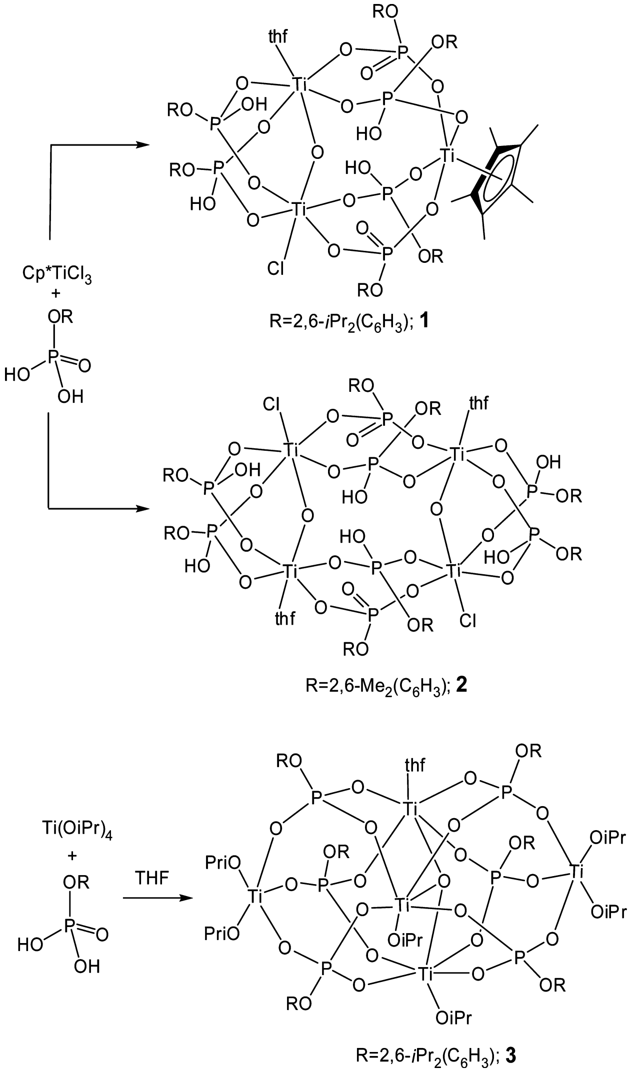


Figure 5. Molecular structure of **3** (all the hydrogen atoms have been omitted). Selected bond distances [Å]: Ti−O(P) 1.913(4)−1.996(4) (av. 1.943), Ti−O(^{i}Pr) 1.746(5)−1.960(4) (av. 1.803), Ti−O(Ti) 2.254(4), 2.279(4), 2.364(4), Ti−O(THF) 1.852(4), P−O(Ti) 1.479(4)−1.517(4) (av. 1.501), P−O(Ar) 1.569(4)−1.590(4) (av. 1.578). Bond angles [deg]: O−Ti1−O (cis) 87.2(2)−95.1(2), (trans) 175.9(2), 176.0(2), 177.5(2), O−Ti2−O (cis) 85.0(2)−96.0(2), (trans) 171.2(2), 173.3(2), 177.4(2), O−Ti3−O (cis) 84.4(2)−95.7(2), (trans) 169.3(2), 179.1(2), 179.3(2), O−Ti4−O (basal) 111.9(2), 111.9(2), 134.8(2), (cis) 84.1(2)−99.2(3), (trans) 169.5(2), O−Ti5−O (basal) 109.1(2), 111.5(2), 138.1(2), (cis) 83.3(2)−98.7(2), (trans) 167.7(2), Ti−O−P 123.4(3)−168.3(2), Ti2−Ti3 119.0(2), 120.0(2), 121.1(2).

coordinate distorted trigonal bipyramidal (tbp) geometry. The sixth coordination site in the octahedral ions is completed either by a isopropoxide (Ti1 and Ti2) or by a coordinated THF (Ti3). The peripheral titanium centers are coordinated to two isopropoxide ligands to complete the tbp geometry.

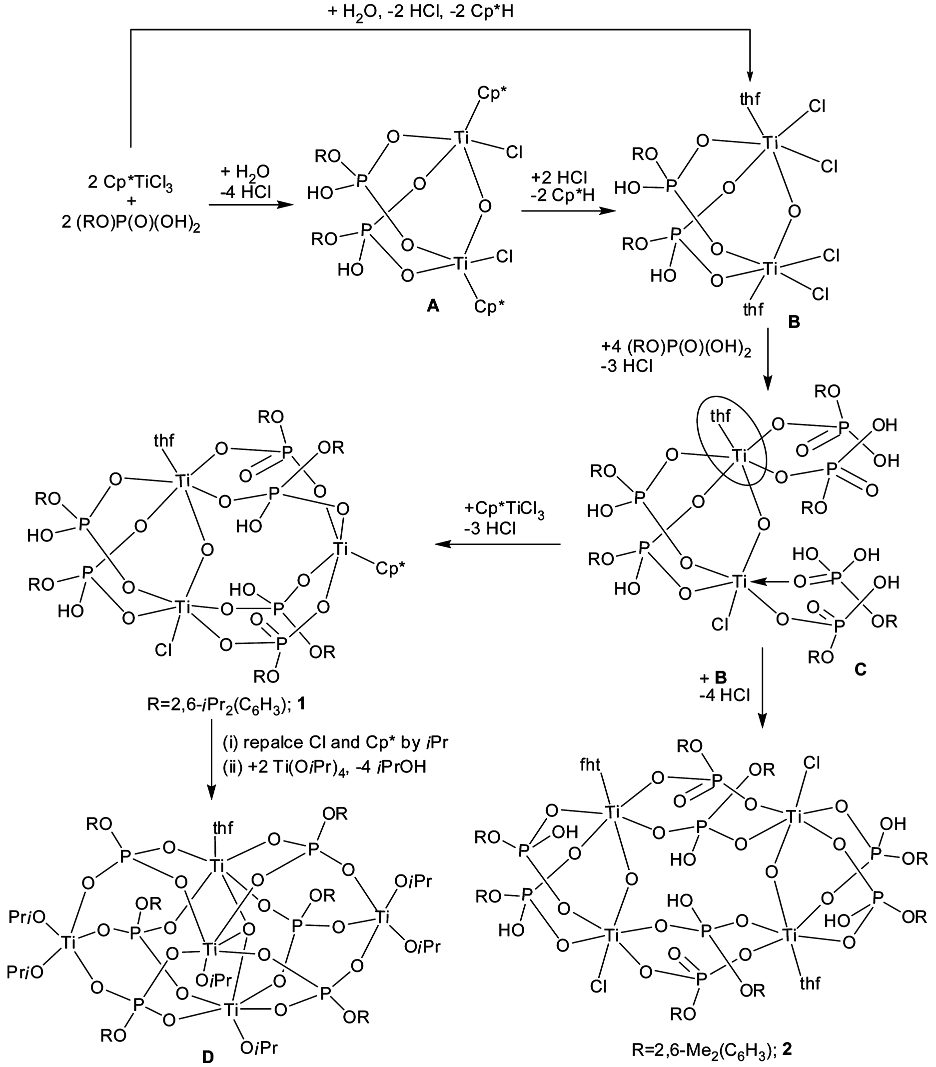
The average Ti−O(phosphate) and Ti−O(alkoxide) bond distances in **3** are comparable to similar distances found in the molecular titanium phosphonates and phosphates reported in the literature.[8,9] There are small variations in the three Ti−μ_3-O distances in the molecule (2.254(4), 2.279(4), 2.364(4) Å) which is reflected in three different Ti···Ti distances in the central core (Ti1···Ti2, Ti1···Ti3, and Ti2···Ti3 distances are 3.977 Å, 3.945 Å, and 4.019 Å, respectively). Similarly, the Ti···P distances also vary over a wide range (3.071−3.457 Å).Scheme 1

Scheme 1. Synthesis of Titanium Phosphates **1**−**3**



Comparison of Structures of 1−3. Although compounds **1**−**3** represent tri-, tetra-, and pentanuclear forms of molecular titanium phosphates synthesized from different starting materials, they share some common structural features. For example, all the compounds are built around Ti−O−Ti units which are bridged by phosphate ligands. It is likely that the formation of all the three compounds have essentially followed a similar reaction pathway. The cluster growth, however, in each case terminates at different stages in different cases, yielding different nuclearities. A possible pathway to the formation of these clusters is shown in Scheme 2, albeit with no proof for existence of the intermediate species shown. It is likely that the initial reaction is either a HCl or *i*PrOH elimination to form an eight-membered titanophosphate which then undergoes hydrolysis to form an oxo-bridged species **A** from which Cp*H elimination takes place to produce **B.** The subsequent steps involve stepwise addition of two phosphate ligands and one titanium precursor to produce the trinuclear cluster **1** via **C**. The intermediate **C** can also condense with **B** to produce the tetranuclear species **2**. The addition of **B** to **C** versus addition of Cp*TiCl$_3$ to **C** appears to depend on the steric bulkiness of the phosphate ligand. The addition of **B** to **C** seems to be an unlikely process with a diisopropylphenyl substituted phosphate ligand. In the case of the dimethylphenyl phosphate, this is the preferred reaction. The formation of **3** can also be conceived from **1** just by the addition of

Scheme 2. Suggested Pathway Which Connects the Formation of All Three Products, Involving Common Intermediates



two equivalents of titanium precursor, since the numbers of phosphate ligands are same in both **1** and **3**. The presence of an -O*i*Pr terminal ligand in the reaction leading to **3** would have induced the deprotonation of all the acidic protons of the phosphate ligands compared to the presence of Cp* or Cl ligands in the reaction leading to **1**. Although one may argue that such a mechanism is highly speculative, it is important to note that this sequence of events explain the formation of all the three products on the basis of both the steric bulkiness of the ligand and the electronic modification of the metal by other terminal ligands such as Cp*, Cl, and O*i*Pr.

Conclusions

In conclusion, we have shown that it is possible to build hierarchical titanium phosphate clusters by a proper choice of titanium metal precursors and the organophosphate esters. Although compounds **1**−**3** represent the first examples for mono-organophosphate complexes of titanium, it appears that these three complexes are not the only possible compounds that could be isolated from organophosphate esters. If the formation of these clusters indeed takes places in a stepwise manner as shown in Scheme 2, it is likely that it would be possible to obtain even higher nuclearity structural motifs by a careful variation of the starting materials. We are currently investigating these possibilities. Further, the new clusters with hydrolyzable surface functionalities could find applications as precursors for titanophosphate and related hybrid materials through either sol−gel or other appropriate processes.

Experimental Section

All operations were carried out under an inert atmosphere using standard vacuum or Schlenck line techniques. Solvents were purified according to standard procedures prior to use.[16] Cp^*TiCl_3 and $Ti(OiPr)_4$ were procured from Aldrich. Diisopropylphenyl phosphate ($dippH_2$) and dimethylphenyl phosphate ($dmppH_2$) were prepared according to literature procedures.[17] Infrared spectra were obtained

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Table 1. Crystal Data and Structure Refinement Details for **1**−**3**

compound	1	2	3
identification code	newrm160	newrm178	newrm171
formula	$C_{100}H_{145}ClO_{26}P_6Ti_3$	$C_{93}H_{118}Cl_2O_{36}P_8Ti_4$	$C_{94}H_{152}O_{32}P_6Ti_5$
fw	2128.13	2322.13	2219.48
temp, [K]	150(2)	150(2)	150(2)
λ(Mo Kα), [Å]	0.71073	0.71073	0.71073
crystal system	monoclinic	monoclinic	monoclinic
space group	$P2_1/c$	$P2_1/n$	$P2_1/c$
a, [Å]	25.581(3)	13.9814(2)	25.7498(6)
b, [Å]	26.3082(10)	19.0606(3)	15.2049(4)
c, [Å]	16.3269(5)	20.0920(4)	28.9126(9)
β, [deg.]	99.682(5)	96.544(2)	99.845(3)
V, [Å^3]	10831.3(13)	5319.51(15)	11153.3(5)
Z	4	2	4
D(calcd), [Mg/m^3]	1.305	1.450	1.322
μ, [mm^{-1}]	0.399	0.541	0.501
cryst size, [mm^3]	0.32 × 0.27 × 0.22	0.24 × 0.21 × 0.19	0.35 × 0.32 × 0.27
θ range, [deg.]	3.02 to 28.00	2.96 to 28.00	2.91 to 28.00
no. of rflns collected	82131	62374	112051
no. of obsd rflns ($I > 2\sigma(I_0)$)	26066	12826	26813
goodness-of-fit on F^2	0.930	1.033	1.019
R1($I > 2\sigma(I_0)$)	0.0598	0.0700	0.0939
wR2 (all data)	0.1630	0.2227	0.2431
largest hole and peak [e Å^{-3}]	−1.040, 1.235	−1.872, 1.748	−1.203, 1.648

on a Perkin-Elmer Spectrum One FT-IR spectrometer as KBr diluted discs. Microanalyses were performed on a Thermo Finnigan (FLASH EA 1112) microanalyzer. The ^{1}H (Me_4Si internal standard) and ^{31}P (85% H_3PO_4 external standard) NMR spectra were recorded on a Varian VXR 300S spectrometer. Thermogravimetric analysis was carried out on a Perkin-Elmer thermal analysis system, under a stream of nitrogen gas at the heating rate of 10 °C/min.

Synthesis of 1. Phosphate ester dippH$_2$ (516 mg, 2 mmol) in THF (20 mL) was added dropwise to Cp*TiCl$_3$ (290 mg, 1 mmol) in THF (30 mL) and stirred for 24 h at 25 °C. The solvent was removed in vacuo, and the residue was dissolved in toluene (10 mL), filtered, and left for crystallization. Red single crystals of **1** were obtained after 7 days. Yield: 0.4 g (59%, based on the dippH$_2$). Mp > 200 °C (decomp). Anal. Calcd for $C_{93}ClH_{137}O_{26}P_6Ti_3$. (2036.8): C, 54.86; H, 6.78. Found: C, 54.71; H, 7.05. IR (KBr, cm^{-1}): 3065(w), 2965(s), 2929(w), 2869(w), 2329(br), 1629(br), 1465(m), 1440(m), 1383(w), 1362(w), 1334(w), 1258(m), 1171(vs), 1126(vs), 1094(w), 1048(w), 992(vs), 938(m), 797(m), 769(m). ^{1}H NMR (benzene-d_6, 300 MHz): δ 1.02(d, CH$_3$; $^3J_{HH} = 6.6$ Hz), 1.07(d, CH$_3$; $^3J_{HH} = 6.6$ Hz), 1.25(dd), 1.84(br), 2.35(s), 2.38(s), 2.50(s), 3.18(br), 3.42(sept, CH; $^3J_{HH} = 6.6$ Hz), 3.73−3.82(br), 7.14−7.28(br) ppm. ^{31}P NMR (benzene-d_6, 121 MHz): δ −4.8, −9.4, −15.1 ppm. TGA: Temp. range °C (% weight loss): 75−160 (8.7); 160−300 (19.3); 300−600 (38.0).

Synthesis of 2. Phosphate ester dmppH$_2$ (404 mg, 2 mmol) in THF (20 mL) was added dropwise to Cp*TiCl$_3$ (290 mg, 1 mmol) in THF (30 mL) and stirred for 24 h at 25 °C. The solvent was removed in vacuo, and the residue was dissolved in toluene (10 mL), filtered, and left for crystallization. Red single crystals of **2** were obtained after 10−15 days. Yield: 0.42 g (75%, based on the dmppH$_2$). Mp > 200 °C (decomp). Anal. Calcd for $C_{86}Cl_2H_{110}O_{36}P_8Ti_4$. (2230.0): C, 46.32; H, 4.97. Found: C, 45.79; H, 5.21. IR (KBr, cm^{-1}): 3025(w), 2964(m), 2928(m), 2858(w), 2294(br), 2202(br), 1637(m), 1617(m), 1480(s), 1443(w), 1381(w), 1269(m), 1168(vs), 1095(vs), 999(vs), 779(s). ^{1}H NMR (CDCl$_3$, 300 MHz): δ 1.82(br), 2.13−2.27(m), 2.30−2.46(m), 3.72−3.75(br), 6.83−7.00(m), 7.12−7.22(m) ppm. ^{31}P NMR (CDCl$_3$, 121 MHz): δ −4.2, −9.8, −14.9, −20.3 ppm. TGA: Temp. range °C (% weight loss): 40−150 (6.1); 150−380 (43.0); 380−500 (7.3).

Synthesis of 3. Ti(O*i*Pr)$_4$ (568 mg, 2 mmol) was added dropwise to dippH$_2$ (516 mg, 2 mmol) in THF (50 mL) and stirred for 24 h at 25 °C. The solvent was removed in vacuo, and the residue was dissolved in petroleum ether (10 mL), filtered, and left for crystallization. Block shaped colorless single crystals of **3** were obtained after 5−7 days. Yield: 0.4 g (54%, based on the dippH$_2$). Mp > 275 °C. Anal. Calcd for $C_{94}H_{152}O_{32}P_6Ti_5$ (2219.5): C, 50.87; H, 6.90. Found: C, 49.96; H, 7.25. IR (KBr, cm^{-1}): 3067(w), 2967(s), 2930(w), 2869(w), 1633(br), 1465(m), 1441(m), 1336(w), 1257(m), 1160(s), 1101(s), 1049(w), 1024(vs), 954(w), 772(m). ^{1}H NMR (benzene-d_6, 300 MHz) δ: 0.72−1.36(m), 1.82(s), 2.01(s), 2.16(s), 3.52−3.61(m), 3.81(s), 4.08(br), 4.23−4.31(m), 4.41−4.51(m), 4.59−4.71(m), 4.89−5.01(m), 5.06−5.21(m), 5.25−5.43(m), 6.91−7.09 (m) ppm. ^{31}P NMR (benzene-d_6, 121 MHz): δ −12.0, −18.6 ppm. TGA: Temp. range °C (% weight loss): 65−270 (15.7); 270−350 (13.7); 350−600 (29.8).

Single Crystal X-ray Diffraction Studies. Intensity data for all the three compounds were collected on a Oxford XCalibur CCD diffractrometer at 150 K. All calculations were carried out using the programs in WinGX module.[18] The structure solution was achieved by direct methods in each case using SIR-92 as implemented in WinGX.[19] The final refinement of the structure was carried out using full least-squares methods on F^2 using SHELXL-97.[20] Selected crystal data are given Table 1, and the detailed crystallographic data for all the structures are provided in the Supporting Information. The level-A alerts showed by check cif software are mainly due to the large thermal vibrations of disordered toluene solvent molecules and the peripheral isopropyl groups.

Acknowledgment. This work was supported by DST, New Delhi. We thank the DST funded National Single Crystal Diffraction Facility at IIT-Bombay for the diffraction data and SAIF, IIT-Bombay for the spectral data.

Supporting Information Available: Details of X-ray structure investigations (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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