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Syntheses, Characterizations, and Single-Crystal X-ray Structures of Soluble Titanium Alkoxide Phosphonates

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Reactions of $Ti(O^iPr)_4$ with different phosphonic acids RPO_3H_2 (R = Ph, 4-CNPh, Me, ^tBu) in organic solvents have been investigated. In the presence of small amounts of water, the new molecular titanium oxide alkoxide phosphonates $[Ti_4(\mu_3\text{-}O)(O^iPr)_5(\mu\text{-}O^iPr)_3(RPO_3)_3]\cdot DMSO$ [R = Ph (**1**), Me (**2**), ^tBu (**3**), 4-CNPh (**4**)] were isolated. The single-crystal X-ray structure analyses of **1** and **2** revealed hexacoordinated titanium atoms and a connectivity of (111) for each phosphonate. Under rigorous exclusion of water, the reaction of $Ti(O^iPr)_4$ with *tert*-butylphosphonic acid in toluene gave the titanium phosphonate tetramer $[Ti(O^iPr)_2(^tBuPO_3)]_4$ (**5**). A single-crystal X-ray structure analysis of **5** revealed a 5 + 1 coordination of the titanium atoms as a result of the (112) connectivity of each phosphonate; such a coordination mode has never been reported for a titanium phosphate, phosphonate, or phosphinate. Compounds **1**−**5** were characterized by FT-IR, ^{31}P MAS NMR, and solution multinuclear NMR (^1H, $^{13}C\{^1H\}$, $^{31}P\{^1H\}$) spectroscopies. ^{13}C CP MAS NMR experiments were carried out on arylphosphonates **1** and **4**. Solution NMR experiments were also used to investigate the exchange reaction between **1** and **2** and the conversion of **5** to $[Ti_4(\mu_3\text{-}O)(O^iPr)_5(\mu\text{-}O^iPr)_3(^tBuPO_3)_3]\cdot {}^iPrOH$ by partial hydrolysis in the presence of $Ti(O^iPr)_4$. The phosphonate clusters **1**−**5** are soluble in organic solvents and are likely intermediates in the sol−gel processing of inorganic−organic hybrids based on titanium oxide and phosphonate groups that we are currently developing.

Introduction

Metal alkoxides play an important role as precursors to metal oxide materials prepared by sol−gel processing or metal−organic chemical vapor deposition (MOCVD).[1−4] In the sol−gel process, chemical modifiers such as β-diketonate or carboxylate ligands are usually allowed to react with the metal alkoxides prior to hydrolysis:[5−8] the partial replacement of alkoxy groups by these ligands decreases the reactivity and thus permits control of the formation of sols and gels. Furthermore, it allows the introduction of organic functionalities for organic−inorganic hybrid materials applications.[2,9]

Partial hydrolysis and condensation reactions of (modified) transition metal alkoxides lead to the formation of oxide alkoxides, which serve as models for the initial stages in the sol−gel process as well as molecular building blocks for novel advanced materials.[10−13] Several molecular titanium oxide alkoxide clusters have been prepared by reactions of titanium alkoxides with bidentate carboxylic acids.[14−19] However, the use of bidentate diorganophosphinic acids (R_2PO_2H) or tridentate organophosphonic acids (RPO_3H_2) to prepare molecular titanium (oxide) alkoxide clusters remains mainly unexplored,[20,21] although phosphato, phosphonato, and phosphinato ligands have been widely used to prepare polynuclear oxo anions such as vanadates and molybdates,[22−24] layered titanium phosphates and phosphonates,[25] and polymeric titanium alkoxide phosphinates.[26] To date, the only crystallographically characterized molecular titanium phosphonates are the titanium alkoxo anion in

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$[Ti_2(OMe)_6(O_3PPh)_2][^nBu_4N]_2$[20] and the partially hydrolyzed complexes $[(Cp^*TiO_3PR)_4(\mu\text{-}O)_2]$ (R = Me, Ph) and $[(Cp^*Ti)_3(^tBuPO_3)_2\{^tBuPO_2(OH)\}(\mu\text{-}O)_2]$.[27]

The condensation of titanium alkoxides with carboxylic acids as well as with phosphinic and phosphonic acids results in the formation of alcohols. In the case of carboxylic acids, esterification of unreacted acids by the liberated alcohols leads to the formation of water. Under the same conditions, the esterification of phosphonic or phosphinic acids by the liberated alcohols does not take place; hence, no water forms, which allows a better control of the formation of oxo bridges.

We recently reported a promising sol−gel route to novel inorganic−organic hybrids based on metal oxide and phosphonate groups. This sol−gel route involves the nonhydrolytic condensation between a metal alkoxide and an organophosphorus acid, followed by a controlled hydrolysis−condensation of the remaining alkoxy groups.[28]

The present contribution deals with the reaction of $Ti(O^iPr)_4$ with different phosphonic acids (phenylphosphonic acid, (4-cyanophenyl)phosphonic acid, methylphosphonic acid, and *tert*-butylphosphonic acid), resulting in the formation of novel, organic-soluble molecular titanium phosphonates. The syntheses and characterizations of the titanium oxide alkoxide phosphonates $[Ti_4(\mu_3\text{-}O)(O^iPr)_5(\mu\text{-}O^iPr)_3(RPO_3)_3]\cdot DMSO$ [R = Ph (**1**), Me (**2**), ^{t}Bu (**3**), 4-CNPh (**4**)] and the titanium alkoxide phosphonate $[Ti(O^iPr)_2(^tBuPO_3)]_4$ (**5**) are presented. In a preliminary communication, the X-ray single-crystal structure of **1** was reported.[21] In this work, we present the X-ray single-crystal structures of the methyl analogue **2** and of the first example of a molecular phosphonate-bridged titanium alkoxide **5**. We also present the characterizations of compounds **1**−**5** by IR spectroscopy, variable-temperature multinuclear NMR spectroscopy (^{1}H, ^{13}C, ^{31}P) in solution, and ^{31}P solid-state NMR spectroscopy, which shows **3** and **4** to be analogues of **1** and **2**.

Experimental Section

General Methods. All manipulations were carried out under an atmosphere of dry argon using standard Schlenk and glovebox techniques. Solvents were purified by conventional procedures and distilled prior to use. DMSO was distilled two times from CaH_2 and stored over molecular sieve (4 Å). Elemental analyses were performed by the microanalysis laboratory of the CNRS in Vernaison. The melting points were measured under argon in sealed capillaries on a Büchi B 450 melting point apparatus and are reported uncorrected. All manipulations were carried out under an inert atmosphere. $Ti(O^iPr)_4$ (Aldrich) was distilled prior to use. Methylphosphonic and phenylphosphonic acids (Aldrich), *tert*-butylphosphonic acid (Lancaster), and 4-(cyanophenyl)phosphonic acid[29,30] were dried under high vacuum prior to use.

Spectroscopies. Solution ^{1}H and ^{31}P NMR experiments were performed using a Bruker DPX200 spectrometer. When THF was used as the solvent for NMR experiments, samples were transferred under an argon atmosphere into a 5 mm NMR tube and an acetone-d_6 capillary was used as a lock standard. ^{1}H NMR chemical shifts are referenced to Me_4Si and ^{31}P NMR chemical shifts to H_3PO_4 (85% in water). Solid-state NMR spectra were obtained with a Bruker Avance DPX300 spectrometer, using magic angle spinning (MAS) (spinning rate 10 kHz) and high-power proton decoupling. ^{31}P MAS NMR spectra were recorded without cross-polarization (CP) using a 45° flip angle and a 10 s recycling delay; chemical shifts are referenced to H_3PO_4 (85% in water). ^{13}C CP-MAS NMR spectra were recorded using cross-polarization (CP) with a 5 s recycling delay; chemical shifts are referenced to Me_4Si. FT-IR spectra were obtained on a Perkin-Elmer Spectrum 2000 spectrophotometer with the KBr pellet technique.

Table 1. Crystallographic Collection Data for $[Ti(\mu_3\text{-}O)(O^iPr)_5(\mu\text{-}O^iPr)_3(MePO_3)_3]\cdot DMSO$ (**2**) and $[Ti(O^iPr)_2(^tBuPO_3)]_4$ (**5**)

	2	**5**
empirical formula	$C_{29}H_{71}O_{19}P_3STi_4$	$C_{40}H_{92}O_{20}P_4Ti_4$
fw	1040.43	1208.62
space group	$P2_1/c$ (No. 14)	$P\bar{1}$ (No. 2)
a, Å	19.743(3)	14.1115(17)
b, Å	12.6777(11)	19.819(2)
c, Å	19.896(3)	21.784(3)
α, deg	90	92.677(16)
β, deg	91.019(15)	92.369(16)
γ, deg	90	92.074(14)
V, Å^3	4979.1(10)	6076.1(14)
Z	4	4
λ, Å	0.710 73	0.710 73
T, K	160 ± 2	160 ± 2
ρ_{calcd}, Mg/m^3	1.388	1.321
μ(Mo Kα), mm^{-1}	0.819	0.675
R:[a] obsd, all	0.0218, 0.0344	0.0304, 0.0569
R_w:[b] obsd, all	0.0451, 0.0488	0.0548, 0.0601

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $R_w = [\sum w(|F_o^2| - |F_c^2|)^2/\sum w|F_o^2|^2]^{1/2}$.

X-ray Data Collections and Structure Determinations for 2 and 5. The data were collected[31] on a Stoe imaging plate diffractometer system (IPDS), equipped with an Oxford Cryosystems cooler device, at 160 K using Mo Kα radiation with a graphite monochromator (λ = 0.710 73 Å). In both cases, the data were collected with a crystal-to-detector distance of 80 mm, in the 2θ range 2.9−48.4° with a φ rotation movement (φ = 0.0−249.6° and $\Delta\varphi$ = 1.3° for **2;** φ = 0.0−250.5° and $\Delta\varphi$ = 1.5° for **5**). No absorption corrections were made. The structures were solved using direct methods[32] and refined[33] by full-matrix least-squares techniques based on F^2. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were found on difference Fourier maps and introduced into calculations with riding models, where U_{iso} was equal to 1.1 times U_{iso} of the atom of attachment. The atomic scattering factors and anomalous dispersion terms were taken from the standard compilation.[34] The crystallographic data are summarized in Table 1, and the non-carbon fractional coordinates for **2** and **5** are listed in Tables 2 and 3, respectively.

$[Ti_4(\mu_3\text{-}O)(O^iPr)_5(\mu\text{-}O^iPr)_3(PhPO_3)_3]\cdot DMSO$ (1). This compound was prepared as described previously.[21] Anal. Calcd for $C_{44}H_{77}O_{19}P_3STi_4$: C, 43.08; H, 6.32. Found: C, 42.85; H, 6.52. ^{1}H NMR (200.1 MHz, THF, 23 °C), δ (ppm): 0.33 (d, 12H, Me_{O^iPr}), 0.71 (d, 18H, Me_{O^iPr}), 0.80 (d, 18H, Me_{O^iPr}), 1.83 (s, 6H, Me_{DMSO}), 4.03 (sep, 3H, CH_{O^iPr}), 4.26 (sep, 2H, CH_{O^iPr}), 4.40 (sep, 3H, CH_{O^iPr}), 6.60−6.71 (complex pattern, 12H, H_{aryl}), 7.16−7.28 (complex pattern, 6H, H_{aryl}). $^{13}C\{^1H\}$ NMR (50.3 MHz, THF, 23 °C), δ (ppm): 24.0, 24.2 (Me_{O^iPr}), 38.8 (Me_{DMSO}), 77.6, 78.4 (CH_{O^iPr}), 126.9 (d, $^3J(^{13}C-^{31}P)$ = 15 Hz, $C_{aryl/meta}$), 129.0 (d, $^4J(^{13}C-^{31}P)$ = 3 Hz, $C_{aryl/para}$), 130.6 (d, $^2J(^{13}C-^{31}P)$ = 9 Hz, $C_{aryl/ortho}$), 135.5 (d, $^1J(^{13}C-^{31}P)$ = 203 Hz, $C_{aryl/ipso}$). $^{31}P\{^1H\}$ NMR (101.3 MHz, THF, 23 °C), δ (ppm): 6.8. $^{31}P\{^1H\}$ NMR (101.3 MHz, THF, −40 °C), δ (ppm): 6.7, 6.5 (2:1). $^{31}P\{^1H\}$ MAS NMR (solid state, 121.5 MHz), δ (ppm): 5.84, 6.20, 7.25 (1:1:1). $^{13}C\{^1H\}$ MAS NMR (solid state, 75.5 MHz), δ (ppm): 24.0, 25.1, 25.7,

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Table 2. Selected Positional and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^2$) and Their Esd's for $[Ti(\mu_3\text{-}O)(O^iPr)_5(\mu\text{-}O^iPr)_3(MePO_3)_3]\cdot DMSO$ (**2**)

	x	*y*	*z*	U_{eq}[a]
Ti(1)	0.25164(2)	0.33956(3)	0.11894(2)	2.62(1)
Ti(2)	0.30721(2)	0.56442(3)	0.09055(2)	2.60(1)
Ti(3)	0.32514(2)	0.46501(3)	0.23228(2)	2.69(1)
Ti(4)	0.09730(2)	0.60588(3)	0.21244(2)	2.16(1)
S(1)	−0.00852(3)	0.41890(4)	0.22391(2)	3.09(1)
P(1)	0.15666(3)	0.51395(4)	0.05957(2)	2.58(1)
P(2)	0.18158(2)	0.37147(4)	0.25523(2)	2.57(1)
P(3)	0.26186(3)	0.68918(4)	0.21728(2)	3.11(1)
O(1)	0.17379(7)	0.3962(1)	0.06800(6)	3.14(3)
O(2)	0.19208(6)	0.3033(1)	0.19250(6)	2.94(3)
O(3)	0.18687(7)	0.6718(1)	0.22113(7)	3.61(3)
O(4)	0.00680(7)	0.5280(1)	0.19543(7)	3.25(3)
O(5)	0.26087(6)	0.4814(1)	0.15828(6)	2.64(3)
O(6)	0.31354(6)	0.4144(1)	0.05497(6)	2.99(3)
O(7)	0.33079(7)	0.3247(1)	0.18433(6)	3.10(3)
O(8)	0.25046(7)	0.2136(1)	0.07960(7)	3.59(3)
O(9)	0.22060(7)	0.5779(1)	0.04339(6)	3.41(3)
O(10)	0.35642(7)	0.6320(1)	0.03074(7)	3.73(3)
O(11)	0.28751(7)	0.6903(1)	0.14511(7)	3.87(4)
O(12)	0.38143(7)	0.5286(1)	0.15815(7)	3.24(3)
O(13)	0.30275(7)	0.6091(1)	0.26046(7)	3.68(3)
O(14)	0.38835(7)	0.4394(1)	0.29518(7)	3.40(3)
O(15)	0.24982(6)	0.4081(1)	0.28468(6)	2.85(3)
O(16)	0.13256(6)	0.4608(1)	0.24150(6)	2.62(3)
O(17)	0.11846(7)	0.5587(1)	0.11764(6)	2.80(3)
O(18)	0.05553(6)	0.72315(9)	0.18192(6)	2.42(3)
O(19)	0.07822(7)	0.6274(1)	0.30058(6)	3.11(3)

[a] U_{eq} = one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

Table 3. Selected Positional and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^2$) and Their Esd's for $[Ti(O^iPr)_2(^tBuPO_3)]_4$ (**5**)

	x	*y*	*z*	U_{eq}[a]
Ti(1A)	0.87566(3)	0.53824(2)	0.34760(2)	1.66(1)
Ti(2A)	0.83416(3)	0.35688(2)	0.24889(2)	1.45(1)
Ti(3A)	0.79120(3)	0.49948(2)	0.11874(2)	1.95(1)
Ti(4A)	0.61346(3)	0.55461(2)	0.25781(2)	1.87(1)
P(1A)	0.95297(5)	0.46107(3)	0.21287(3)	1.42(1)
P(2A)	0.72813(5)	0.44118(3)	0.34979(3)	1.58(1)
P(3A)	0.78773(5)	0.61990(3)	0.23969(3)	1.99(2)
P(4A)	0.64422(5)	0.42679(3)	0.16949(3)	1.80(2)
O(1A)	0.9014(1)	0.46827(7)	0.27400(7)	1.28(4)
O(2A)	0.9349(1)	0.38583(7)	0.19416(7)	1.62(4)
O(3A)	0.9148(1)	0.50634(7)	0.16317(7)	1.68(4)
O(4A)	0.7111(1)	0.50575(7)	0.31574(7)	1.81(4)
O(5A)	0.8229(1)	0.45789(8)	0.38624(7)	1.78(4)
O(6A)	0.7360(1)	0.37895(8)	0.30667(7)	1.79(4)
O(7A)	0.8710(1)	0.60196(8)	0.28180(7)	1.94(4)
O(8A)	0.7508(1)	0.56160(7)	0.19447(7)	1.76(4)
O(9A)	0.6994(1)	0.63449(8)	0.27683(7)	2.33(4)
O(10A)	0.7476(1)	0.41232(8)	0.18749(7)	1.79(4)
O(11A)	0.6555(1)	0.47229(8)	0.11397(7)	2.28(4)
O(12A)	0.5915(1)	0.46259(8)	0.22091(7)	1.99(4)
O(13A)	0.9974(1)	0.53821(8)	0.37325(7)	2.25(4)
O(14A)	0.8369(1)	0.59971(8)	0.40189(7)	2.58(4)
O(15A)	0.9106(1)	0.32237(8)	0.30414(7)	1.97(4)
O(16A)	0.7885(1)	0.28002(8)	0.21142(7)	2.23(4)
O(17A)	0.8301(1)	0.43856(9)	0.06473(7)	2.71(4)
O(18A)	0.7883(1)	0.56974(9)	0.07066(8)	2.99(5)
O(19A)	0.5339(1)	0.56049(8)	0.31934(8)	2.49(4)
O(20A)	0.5422(1)	0.59058(9)	0.20047(8)	2.76(4)
Ti(1B)	0.21336(3)	1.12488(2)	0.26890(2)	2.09(1)
Ti(2B)	0.25293(4)	0.95891(2)	0.37502(2)	3.10(1)
Ti(3B)	0.42685(4)	0.92619(2)	0.23021(2)	3.22(1)
Ti(4B)	0.16535(4)	0.95869(2)	0.14636(2)	2.59(1)
P(1B)	0.40180(6)	1.03903(4)	0.33465(3)	3.05(2)
P(2B)	0.09118(5)	1.01517(3)	0.28911(3)	2.12(2)
P(3B)	0.31436(5)	1.05626(3)	0.15683(3)	2.42(2)
P(4B)	0.25200(6)	0.85923(3)	0.23978(4)	3.03(2)
O(1B)	0.2991(1)	1.05880(9)	0.31993(8)	2.76(4)
O(2B)	0.3891(1)	0.98398(9)	0.38136(8)	3.62(5)
O(3B)	0.4515(1)	1.01139(9)	0.27773(9)	3.44(5)
O(4B)	0.1398(1)	1.01730(8)	0.22747(7)	2.14(4)
O(5B)	0.1122(1)	1.08745(8)	0.31751(7)	2.21(4)
O(6B)	0.1297(1)	0.96219(8)	0.33092(8)	2.83(4)
O(7B)	0.3086(1)	1.11098(8)	0.20781(8)	2.50(4)
O(8B)	0.3305(1)	0.98603(8)	0.18017(8)	2.82(4)
O(9B)	0.2186(1)	1.04584(8)	0.11950(8)	2.73(4)
O(10B)	0.2904(1)	0.90882(9)	0.29201(8)	3.17(5)
O(11B)	0.3386(1)	0.85101(9)	0.20036(9)	3.55(5)
O(12B)	0.1682(1)	0.88569(8)	0.20286(8)	2.89(4)
O(13B)	0.2587(1)	1.19667(8)	0.31534(8)	2.70(4)
O(14B)	0.1391(1)	1.16725(8)	0.21656(8)	2.56(4)
O(15B)	0.2210(2)	1.0133(1)	0.43630(9)	4.02(5)
O(16B)	0.2476(2)	0.8808(1)	0.41339(9)	4.47(6)
O(17B)	0.4963(2)	0.8797(1)	0.2810(1)	4.22(5)
O(18B)	0.5063(2)	0.9278(1)	0.16845(9)	4.05(5)
O(19B)	0.0435(1)	0.95830(9)	0.12167(8)	3.41(5)
O(20B)	0.2083(2)	0.90876(9)	0.08502(9)	3.99(5)

[a] U_{eq} = one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

26.3, 26.9 (Me_{O^iPr}), 37.7, 38.9 (Me_{DMSO}), 78.5, 79.0, 79.1, 82.8 (CH_{O^iPr}), 125.6−134.9 (broad, C_{aryl}), 136.5 (d, $^1J(^{13}C-^{31}P)$ = 201 Hz, $C_{aryl/ipso}$), 137.2 (d, $^1J(^{13}C-^{31}P)$ = 208 Hz, $C_{aryl/ipso}$). FT-IR (Nujol), cm^{-1}: 602 (m), 623 (m), 618 (m), 697 (m), 719 (w), 750 (m), 838 (m), 854 (m), 958 (s), 972 (s), 1003 (sh), 1010 (vs), 1035 (m), 1068 (w), 1094 (s), 1137 (vs), 1164 (sh), 1194 (s), 1316 (w), 1327 (w).

$[Ti_4(\mu_3\text{-}O)(O^iPr)_5(\mu\text{-}O^iPr)_3(MePO_3)_3]\cdot DMSO$ (2). To a solution of methylphosphonic acid (270 mg, 2.81 mmol) in 3.5 mL of DMSO was added $Ti(O^iPr)_4$ (1.60 g, 5.63 mmol), giving a colorless precipitate. Addition of water (17 μL, 0.94 mmol) in 3 mL of THF and stirring for 10 min at room temperature gave a cloudy solution. A 5 mL portion of THF was added, and the reaction mixture was heated until a clear solution was observed. The solvent was evaporated until a cloudy solution was obtained. Colorless crystals appeared in this solution after several days at 0 °C. These crystals were filtered off, washed with two 5 mL portions of Et_2O, and dried in vacuo, giving 593 mg (61% yield) of **2**. Mp: 140−142 °C. Anal. Calcd for $C_{29}H_{71}O_{19}P_3STi_4$: C, 33.48; H, 6.83. Found: C, 33.38; H, 6.81. ^1H NMR (200.1 MHz, THF, 23 °C), δ (ppm): 0.42−0.64 (broad complex pattern, 21H, Me_{PMe}, Me_{OiPr}), 0.68 (d, 18H, Me_{O^iPr}), 0.81 (d, broad, 18H, Me_{O^iPr}), 1.92 (s, 6H, Me_{DMSO}), 4.00 (sep, 3H, CH_{O^iPr}), 4.23−4.45 (broad complex pattern, 5H, CH_{O^iPr}). $^{13}C\{^1H\}$ NMR (50.3 MHz, THF, 23 °C), δ (ppm): 12.1 (d, $^1J(^{13}C-^{31}P)$ = 158 Hz, Me_{PMe}), 23.7, 24.0 (Me_{O^iPr}), 39.3 (Me_{DMSO}), 76.9, 77.2, 77.8 (CH_{O^iPr}). $^{31}P\{^1H\}$ NMR (81.0 MHz, THF, 23 °C), δ (ppm): 17.2, 19.2 (1:2). $^{31}P\{^1H\}$ NMR (81.0 MHz, CH_2Cl_2/CD_2Cl_2, 23 °C), δ (ppm): 20.7, 21.5 (1:2). $^{31}P\{^1H\}$ MAS NMR (solid state, 121.5 MHz), δ (ppm): 14.7, 16.7, 17.6 (1:1:1). FT-IR (Nujol), cm^{-1}: 608 (m), 769 (w), 776 (w), 798 (w), 835 (w), 854 (w), 890 (vw), 954 (m), 1008 (vs), 1036 (w), 1066 (s), 1104 (s), 1132 (s), 1164 (sh), 1195 (sh), 1303 (w), 1327 (vw).

Reaction of 1 with 2. Crystals of **1** (118 mg, 0.096 mmol) and **2** (100 mg, 0.096 mmol) were mixed in 1.5 mL of THF at room temperature. A cloudy solution formed, and the ^{31}P NMR analysis showed signals at 20.8 (1%), 20.1 (8%), 19.6 (12%), 17.7 (20%), 8.5 (6%), and 7.3 ppm (53%). No assignment was made.

$[Ti_4(\mu_3\text{-}O)(O^iPr)_5(\mu\text{-}O^iPr)_3(^tBuPO_3)_3]\cdot DMSO$ (3). To a solution of *tert*-butylphosphonic acid (450 mg, 3.25 mmol) in 5 mL of DMSO was added $Ti(O^iPr)_4$ (1.80 g, 6.33 mmol), giving two liquid phases. Addition of water (20 μL, 1.11 mmol) in 3 mL of THF and heating gave a clear yellow solution. Colorless crystals were obtained from this solution after several days. These crystals were filtered off and dried under high vacuum, giving 670 mg (53% yield) of **3** as an amorphous powder. Mp: 187−190 °C. No satisfactory elemental analysis was obtained for **3**, probably as a result of the high sensitivity of this fine, amorphous powder to hydrolysis. ^1H NMR (200.1 MHz, CD_2Cl_2, 23 °C), δ (ppm): 1.20 (d, $^3J(^1H-^{31}P)$ = 15 Hz, 27H, Me_{PtBu}), 1.23 (d, 12H, Me_{O^iPr}), 1.37 (d, 18H, Me_{O^iPr}), 1.48 (d, 18H, Me_{O^iPr}), 2.61 (s, 6H, Me_{DMSO}), 4.65 (sep, 3H, CH_{O^iPr}), 4.87 (sep, 3H, CH_{O^iPr}), 5.15 (m, 2H, CH_{O^iPr}). $^{13}C\{^1H\}$ NMR (50.3 MHz, CD_2Cl_2, 23 °C), δ (ppm): 25.1, 26.0, 26.1 (Me_{O^iPr}), 26.7 (d, $^2J(^{13}C-^{31}P)$ = 2 Hz, Me_{PtBu}), 31.3 (d, $^1J(^{13}C-^{31}P)$ = 153 Hz, C_{PtBu}), 41.5 (Me_{DMSO}), 77.7, 79.8 (CH_{O^iPr}), 80.3 (broad, CH_{O^iPr}). $^{31}P\{^1H\}$ NMR (81.0 MHz, THF, 23 °C), δ (ppm): 28.8. $^{31}P\{^1H\}$ NMR (101.3 MHz, CD_2Cl_2, 23 °C), δ (ppm): 27.3. $^{31}P\{^1H\}$ NMR (101.3 MHz, CD_2Cl_2, −70 °C), δ (ppm): 24.3, 25.0 (1:2). $^{31}P\{^1H\}$ MAS NMR (solid state, 121.5 MHz), δ (ppm): 23.6, 24.5 (1:2) (from the deconvolution of overlapping signals). FT-IR (Nujol), cm^{-1}: 606 (s), 694 (w), 827 (sh), 835 (m), 853 (m), 954 (s), 1004 (vs), 1044 (s), 1056 (m), 1070 (m), 1104 (s), 1127 (s), 1164 (sh), 1204 (vw), 1233 (vw), 1308 (w), 1326 (w).

[$Ti_4(\mu_3$-O)($O^iPr)_5(\mu$-$O^iPr)_3$(4-$CNPhPO_3)_3$]·DMSO (4). Water (30 μL, 1.67 mmol) was added to a solution of (4-cyanophenyl)phosphonic acid (771 mg, 9.85 mmol) in 3 mL of DMSO. The addition of Ti($O^iPr)_4$ (2.80 g, 9.85 mmol) gave a clear yellow solution. Colorless crystals were obtained from this solution after several days. These crystals were filtered off, washed with two 4 mL portions of Et_2O, and dried in vacuo, giving 1.05 g (57% yield) of **4**. Mp: >240 °C dec. Anal. Calcd for $C_{47}H_{74}N_3O_{19}P_3STi_4$: C, 43.37; H, 5.73; N, 3.22. Found: C, 43.18; H, 5.93; N, 3.11. ^1H NMR (200.1 MHz, THF, 23 °C), δ (ppm): 0.33 (d, 12H, Me_{O^iPr}), 0.71 (d, 18H, Me_{O^iPr}), 0.79 (d, 18H, Me_{O^iPr}), 1.84 (s, 6H, Me_{DMSO}), 4.02 (sep, 3H, CH_{O^iPr}), 4.22 (sep, 2H, CH_{O^iPr}), 4.41 (sep, 3H, CH_{O^iPr}), 7.01−7.08 (complex pattern, 6H, H_{aryl}), 7.27−7.38 (complex pattern, 6H, H_{aryl}). $^{13}C\{^1H\}$ NMR (50.3 MHz, THF, 23 °C), δ (ppm): 23.8, 23.9, 24.0 (Me_{O^iPr}), 39.1 (Me_{DMSO}), 78.3, 79.2 (CH_{O^iPr}), 113.3 (d, $^4J(^{13}C-^{31}P) = 3.4$ Hz, $C_{aryl/para}$), 117.7 (d, $^5J(^{13}C-^{31}P) = 1.6$ Hz, CN), 130.9 (d, $^3J(^{13}C-^{31}P) = 15$ Hz, $C_{aryl/meta}$), 131.1 (d, $^2J(^{13}C-^{31}P) = 10$ Hz, $C_{aryl/ortho}$), 140.6 (d, $^1J(^{13}C-^{31}P) = 200$ Hz, $C_{aryl/ipso}$). $^{31}P\{^1H\}$ NMR (101.3 MHz, THF, 23 °C), δ (ppm): 4.5. $^{31}P\{^1H\}$ NMR (101.3 MHz, THF, −40 °C), δ (ppm): 4.6, 4.3 (2:1). $^{31}P\{^1H\}$ MAS NMR (solid state, 121.5 MHz), δ (ppm): 3.1, 4.4 (1:2). FT-IR (Nujol), cm^{-1}: 606 (s), 631 (s), 778 (vw), 795 (vw), 834 (s), 854 (s), 952 (s), 982 (s), 1005 (vs), 1049 (s), 1090 (s), 1129 (vs), 1160 (s), 1181 (w), 1205 (s), 1298 (vw), 1321 (w), 1328 (w) 2229 (m).

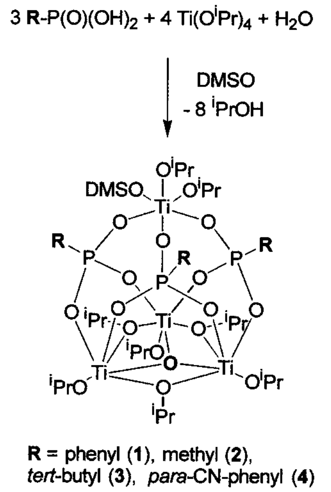
[Ti($O^iPr)_2(^tBuPO_3)]_4$ (5). Ti($O^iPr)_4$ (3.64 g, 12.81 mmol) was added dropwise to a suspension of *tert*-butylphosphonic acid (910 mg, 6.59 mmol) in 60 mL of toluene, giving a clear solution. This solution was heated at 80 °C for 2 h, and 45 mL of toluene was distilled off. Colorless crystals were isolated from this solution after 2 weeks at 0 °C. The crystals were dried in vacuo, giving 0.60 g (30% yield) of **5**. Mp: >260 °C dec. Anal. Calcd for $C_{40}H_{92}O_{20}P_4Ti_4$: C, 39.77; H, 7.62. Found: C, 39.31; H, 7.57. ^1H NMR (200.1 MHz, CD_2Cl_2, 23 °C), δ (ppm): 1.30 (d, 12H, Me_{O^iPr}), 1.36 (d, $^3J(^1H-^{31}P) = 17$ Hz, 9H, Me_{PtBu}), 5.35 (sep, 2H, CH_{O^iPr}). $^{13}C\{^1H\}$ NMR (50.3 MHz, CD_2Cl_2, 23 °C), δ (ppm): 25.8 (Me_{O^iPr}), 25.9 (Me_{PtBu}), 32.3 (d, $^1J(^{13}C-^{31}P) = 137$ Hz, C_{PtBu}), 83.0 (CH_{O^iPr}). $^{31}P\{^1H\}$ NMR (101.3 MHz, CD_2Cl_2, 23 °C), δ (ppm): 40.2. $^{31}P\{^1H\}$ NMR (101.3 MHz, THF, 23 °C), δ (ppm): 39.3. $^{31}P\{^1H\}$ MAS NMR (solid state, 121.5 MHz), δ (ppm): 36.9, 37.9, 38.0, 38.7, 39.0, 39.1. FT-IR (Nujol), cm^{-1}: 605 (m), 668 (vw), 834 (w), 854 (w), 1002 (vs), 1010 (s), 1075 (sh), 1096 (m), 1126 (m), 1162 (w), 1204 (vw), 1235 (vw), 1224 (w).

Reaction of 5 with H_2O in the Presence of Ti($O^iPr)_4$. Pure [Ti($O^iPr)_2(^tBuPO_3)]_4$ (**5**) (320 mg, 0.265 mmol) was dissolved in 0.6 mL of CD_2Cl_2, and Ti($O^iPr)_4$ (115 mg, 0.405 mmol) was added. To this solution was added water (6 μL, 0.33 mmol) in three steps, leading to a cloudy solution after the addition of the third portion of water. After each addition, the ^{31}P and ^1H NMR spectra were recorded. The initial signal of **5** disappeared, and the ^{31}P and ^1H NMR spectra showed the formation of [$Ti_4(\mu_3$-O)($O^iPr)_5(\mu$-$O^iPr)_3(^tBuPO_3)_3$]·HO^iPr and 2-propanol, together with minor, unidentified phosphonate products.

Results

Syntheses. The titanium oxide alkoxide phosphonates [$Ti_4(\mu_3$-O)($O^iPr)_5(\mu$-$O^iPr)_3(RPO_3)_3$]·DMSO [R = Ph (**1**), Me (**2**), ^{t}Bu (**3**), 4-CNPh (**4**)] were each prepared by adding Ti($O^iPr)_4$ and small amounts of water to a DMSO solution of the appropriate organophosphonic acid (Scheme 1). In the case of the phenyl- and methylphosphonic acids, an amorphous precipitate was formed first, which was dissolved by adding small amounts of THF followed by a slight warming of the reaction mixture. Crystallization of colorless needles of **1** and **2** from the light yellow solution was observed after several days, depending on the amount of THF added.

Scheme 1



When THF was used as the solvent instead of DMSO, the reaction of phenylphosphonic acid, water, and Ti($O^iPr)_4$ gave a clear solution. The ^{31}P NMR and ^1H NMR data of the crude reaction mixture indicated the formation of [Ti(μ_3-O)($O^iPr)_5(\mu$-$O^iPr)_3(PhPO_3)_3$]·THF.

The reaction of Ti($O^iPr)_4$ with a DMSO solution of *tert*-butylphosphonic acid gave two liquid phases. Upon addition of THF and water, a yellow solution was obtained and crystallization began after several hours. When (4-cyanophenyl)-phosphonic acid, water, and Ti($O^iPr)_4$ were allowed to react in DMSO, no precipitate was observed, in contrast to what was observed with phenylphosphonic acid. Compound **4** crystallized after several days from a concentrated DMSO solution.

Attempts to isolate a nonhydrolyzed titanium alkoxide phosphonate from DMSO or THF solutions failed, and the addition of water was required to prepare the partially hydrolyzed compounds **1**−**4** in significant yields. If an insufficient amount of water was used for the preparation of **1**, the ^{31}P NMR spectrum of the crude reaction mixture was indicative of a complex mixture containing several products. Further addition of water gave a ^{31}P NMR spectrum showing one main signal for the cluster at δ 6.8 ppm (ca. 70−80%) and two signals in the region of δ 16 ppm (ca. 30−20%) (unidentified compounds). When the ratio of Ti($O^iPr)_4$ to phenylphosphonic acid was varied between 1.33 and 10, the ^{31}P NMR spectra of the crude reaction mixtures did not vary significantly and **1** was always obtained as the main product.

Despite a certain sensitivity to hydrolysis, the arylphosphonates **1** and **4** may be handled in air for short periods of time without notable decomposition: the ^{31}P MAS NMR spectra of **1** and **4** recorded after exposure to atmospheric moisture for 2 h were unchanged compared to the initial ^{31}P MAS NMR spectra. This was not the case for the alkylphosphonates **2** and **3**, which showed much higher sensitivity to hydrolysis.

The titanium alkoxide phosphonate [Ti($O^iPr)_2(^tBuPO_3)]_4$ (**5**) (Scheme 2) was prepared by adding Ti($O^iPr)_4$ to a suspension of *tert*-butylphosphonic acid in toluene, giving a clear solution. After heating, the ^{31}P NMR spectrum of the crude reaction mixture showed one main signal at δ 39.4 ppm corresponding to **5** and several signals of minor intensity in the region of δ 20−40 ppm. **5** was crystallized from this solution on standing at 0 °C for several days.

Single-Crystal X-ray Structures of [$Ti_4(\mu_3$-O)($O^iPr)_5(\mu$-$O^iPr)_3(MePO_3)_3$]·DMSO (2) and [Ti($O^iPr)_2(^tBuPO_3)]_4$ (5). The structures of **2** (Figure 1) and **5** (Figure 2) are molecular

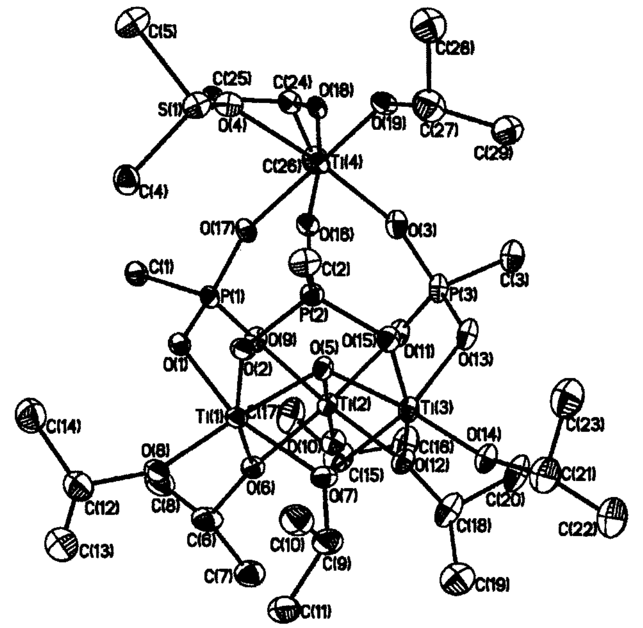
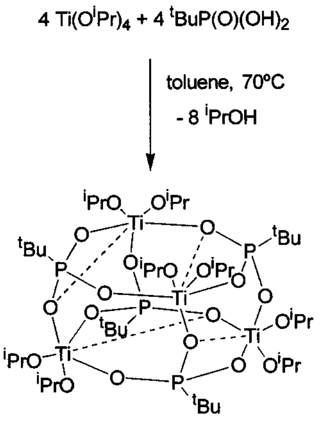


Figure 1. ORTEP view of **2**. Hydrogen atoms have been omitted for clarity. Thermal allipsoids are drawn at 50% probability.

Scheme 2



5

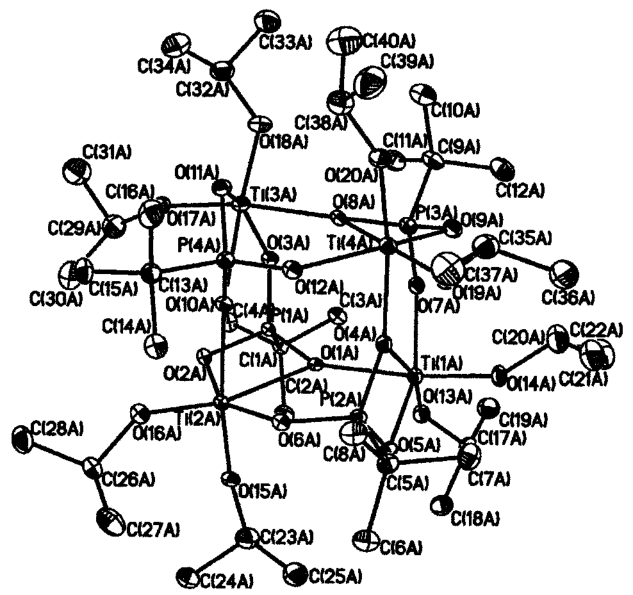


Figure 2. ORTEP view of one molecule of **5** (A). Hydrogen atoms have been omitted for clarity. Thermal ellipsoids are drawn at 50% probability. The geometry of the other molecule is essentially the same.

Table 4. Selected Bond Lengths (Å) and Angles (deg) for [Ti$_4$(μ_3-O)(O^{i}Pr)$_5$(μ-O^{i}Pr)$_3$(MePO$_3$)$_3$]·DMSO (**2**)

Bond Lengths			
Ti(1)−O(1)	1.962(1)	Ti(4)−O(16)	2.047(1)
Ti(1)−O(2)	1.949(1)	Ti(4)−O(17)	2.029(1)
Ti(1)−O(5)	1.968(1)	Ti(4)−O(18)	1.800(1)
Ti(1)−O(6)	2.017(1)	Ti(4)−O(19)	1.821(1)
Ti(1)−O(7)	2.024(1)	P(1)−O(1)	1.539(2)
Ti(1)−O(8)	1.778(1)	P(1)−O(9)	1.539(1)
Ti(4)−O(3)	1.961(1)	P(1)−O(17)	1.502(1)
Ti(4)−O(4)	2.064(1)	S(1)−O(4)	1.527(1)

Bond Angles			
O(1)−Ti(1)−O(2)	89.81(6)	O(3)−Ti(4)−O(17)	90.41(6)
O(1)−Ti(1)−O(5)	86.40(5)	O(3)−Ti(4)−O(18)	94.88(6)
O(1)−Ti(1)−O(6)	88.84(6)	O(3)−Ti(4)−O(19)	93.05(6)
O(1)−Ti(1)−O(7)	162.70(6)	O(4)−Ti(4)−O(16)	84.57(5)
O(1)−Ti(1)−O(8)	95.59(6)	O(4)−Ti(4)−O(17)	84.17(5)
O(2)−Ti(1)−O(5)	88.26(5)	O(4)−Ti(4)−O(18)	87.12(6)
O(2)−Ti(1)−O(6)	164.88(6)	O(4)−Ti(4)−O(19)	92.08(6)
O(2)−Ti(1)−O(7)	87.97(5)	O(16)−Ti(4)−O(17)	85.58(5)
O(2)−Ti(1)−O(8)	96.63(6)	O(16)−Ti(4)−O(18)	171.48(6)
O(5)−Ti(1)−O(6)	76.63(5)	O(16)−Ti(4)−O(19)	86.42(5)
O(5)−Ti(1)−O(7)	76.39(5)	O(17)−Ti(4)−O(18)	91.75(5)
O(5)−Ti(1)−O(8)	174.72(6)	O(17)−Ti(4)−O(19)	171.45(6)
O(6)−Ti(1)−O(7)	88.85(5)	O(18)−Ti(4)−O(19)	95.74(6)
O(6)−Ti(1)−O(8)	98.49(6)	O(1)−P(1)−O(9)	110.74(8)
O(7)−Ti(1)−O(8)	101.71(6)	O(1)−P(1)−O(17)	113.26(7)
O(3)−Ti(4)−O(4)	174.28(6)	O(9)−P(1)−O(17)	112.76(8)
O(3)−Ti(4)−O(16)	93.23(6)		

with no significant intermolecular contacts in their respective crystal lattices. The molecular structure of **2** is similar to that of the phenylphosphonate analogue **1**, with the four Ti atoms forming a trigonal pyramid (Scheme 1). Selected bond lengths and angles for **2** are displayed in Table 4. The three titanium atoms of the base, Ti(1), Ti(2), and Ti(3), have similar coordination geometries, formed by two oxygen atoms of two different phosphonato groups [Ti−O 1.943(1)−1.973(2) Å], one terminal isopropoxy group [Ti−O 1.771(1)−1.781(2) Å], two bridging isopropoxy groups [Ti−O 2.017(1)−2.035(2) Å], and the μ_3-oxygen atom [Ti−O 1.938(1)−1.968(1) Å]. The Ti−O(^{i}Pr) and the Ti−O(P) bond distances compare well with those reported for titanium oxide alkoxides[13] and titanium phosphonates,[20,27] respectively. The distorted octahedral geometry of Ti(1)−Ti(3) is demonstrated by the O−Ti−O trans angles in the range 162.70(6)−174.72(6)° and the O−Ti−O cis angles in the range 76.26(5)−101.71(6)°. The μ_3-oxygen atom symmetrically bridges the titanium centers Ti(1), Ti(2), and Ti(3), and the Ti−μ_3-O−Ti angles are almost identical [105.03(6)−105.89°]. The six-coordinate titanium atom Ti(4) of the apex is bonded to the Ti$_3$O(O^{i}Pr)$_6$ fragment of the base by three bridging phosphonato groups. Two of the phosphonato oxygen atoms are trans to terminal isopropoxy groups [Ti−O 1.800(1)−1.821(1) Å], and the corresponding Ti−O(P) bonds are slightly shorter [Ti−O 2.047(1)/2.029(1) Å] than the Ti(4)−O(3)(P) bond [Ti−O 1.961(1) Å], which is trans to the coordinated DMSO molecule. The distortion of the octahedral coordination geometry of Ti(4) is shown by the O−Ti−O trans and cis angles in the ranges 171.45(6)−174.28(6) and 84.17(5)−95.74(6)°, respectively. In this cluster, the phosphonate groups act as tridentate bridging ligands. Each of the phosphonate units is bonded to three different titanium atoms, and the connectivity is noted (111).[35] Nevertheless, two groups of distinct O−P−O angles are found. Those bridging the titanium atoms of the central Ti$_3$O unit

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(35) Massiot, D.; Drumel, S.; Janvier, P.; Bujoli-Doeuff, M.; Bujoli, B. *Chem. Mater.* **1997**, *9*, 6−7.

Table 5. Selected Bond Lengths (Å) and Angles (deg) for $[Ti(O^iPr)_2(^tBuPO_3)]_4$ (**5**) (Molecule **A**)

Bond Distances			
Ti(1)−O(1)	2.122(2)	Ti(1)−O(14)	1.775(2)
Ti(1)−O(4)	2.450(2)	P(1)−O(1)	1.547(2)
Ti(1)−O(5)	1.972(2)	P(1)−O(2)	1.537(2)
Ti(1)−O(7)	1.955(2)	P(1)−O(3)	1.531(2)
Ti(1)−O(13)	1.784(2)		

Bond Angles			
O(1)−Ti(1)−O(4)	80.96(6)	O(4)−Ti(1)−O(14)	90.96(7)
O(1)−Ti(1)−O(5)	83.89(6)	O(5)−Ti(1)−O(7)	149.94(7)
O(1)−Ti(1)−O(7)	82.77(6)	O(5)−Ti(1)−O(13)	101.62(7)
O(1)−Ti(1)−O(13)	90.65(7)	O(5)−Ti(1)−O(14)	97.24(7)
O(1)−Ti(1)−O(14)	170.51(8)	O(7)−Ti(1)−O(13)	105.35(8)
O(4)−Ti(1)−O(5)	64.89(6)	O(7)−Ti(1)−O(14)	91.82(7)
O(4)−Ti(1)−O(7)	86.44(7)	O(13)−Ti(1)−O(14)	98.31(8)
O(4)−Ti(1)−O(13)	164.65(7)		

[O−P−O average 110.6°] are slightly smaller than those connecting Ti(4) to the Ti_3O unit [O−P−O average 112.8°]. In the same way, the P−O bonds that are directed toward Ti(1), Ti(2), and Ti(3) [P−O average 1.537 Å] are slightly longer than the P−O bonds which are directed toward Ti(4) [P−O average 1.504 Å].

The asymmetric unit of $[Ti(O^iPr)_2(^tBuPO_3)]_4$ (**5**) contains two independent molecules, **5A** and **5B**, which are chemically identical in composition and do not differ significantly in structure. The central $Ti_4O_{12}P_4$ core of **5** is formed by four titanium and four phosphorus atoms that occupy the alternate vertexes of a highly distorted cube (Scheme 2). This three-dimensional Ti−O−P core is surrounded by eight terminal isopropoxy groups and four *tert*-butyl groups, making the organic−inorganic cluster compound highly soluble in common organic solvents. Selected bond lengths and angles for **5** are given in Table 5. The Ti−O bond distances of the terminal isopropoxy groups [Ti−O 1.760(2)−1.794(2) Å] are comparable to those reported for titanium (oxide) alkoxides.[13]

The phosphonato groups in **5** present a (112) connectivity.[35] Thus, two of the oxygens of the phosphonate units are bonded to one titanium atom only; the corresponding Ti−O(P) bond distances [Ti−O(P) 1.948(2)−1.982(2) Å] are comparable to those found for **2** or for other titanium phosphonates where the phosphonato groups are in a (111) connectivity.[21,27] The third oxygen of the phosphonate units is bonded to two titanium atoms on the same face of the distorted $Ti_4O_{12}P_4$ cube; the corresponding Ti−O(P) bond distances are in the ranges 2.120(2)−2.141(2) and 2.401(2)−2.454(2) Å, respectively. Note that the longest Ti−O(P) bonds are across a face of the $Ti_4O_{12}P_4$ cube. The P−O bond distances (P−O(Ti) 1.523(2)−1.552(2) Å) are comparable to those of previously reported molecular titanium phosphonates and show no particularities. On the other hand, the O−P−O angles are significantly larger in the bridging coordination mode (average 112.4°) than in the chelating coordination mode (average 102.6°).

Owing to the (112) connectivity of the phosphonate groups, the titanium atoms are hexacoordinated: they are bonded to three different phosphonate groups via four Ti−O(P) bonds and to two terminal alkoxy groups. The resulting coordination polyhedron is a highly distorted TiO_6 octahedron, as shown by the O−Ti−O cis angle range (64.55(7)−05.68(9))° and the O−Ti−O trans angle range (149.11(7)−171.99(7)°).

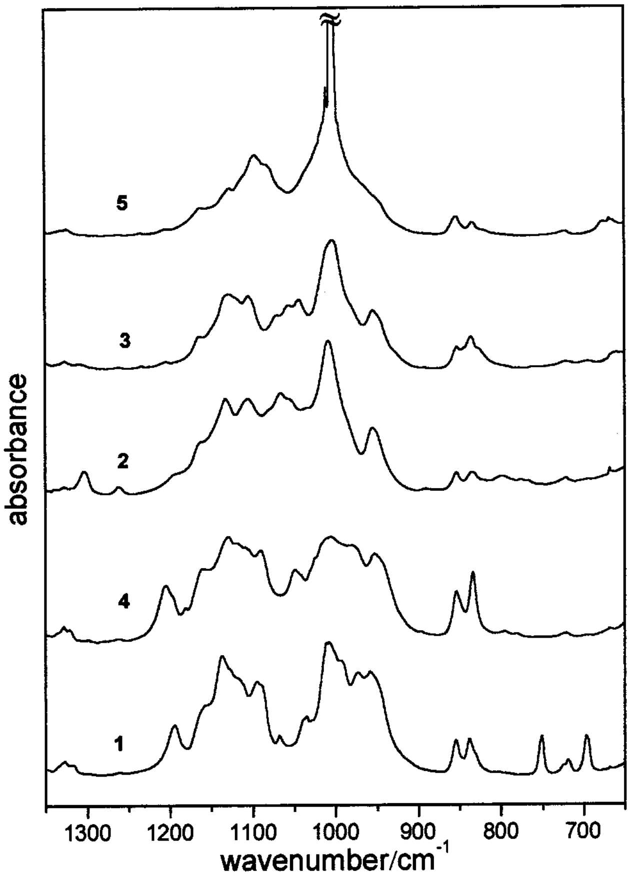

Figure 3. FT-IR spectra of compounds **1**−**5**.

Spectroscopic Characterizations. (a) Infrared Spectroscopy. The FT-IR spectra of the titanium alkylphosphonates **2** and **3** as well as the FT-IR spectra of the arylphosphonates **1** and **4** do not differ significantly in the region 900−1300 cm^{-1}, which is ascribed to their similar Ti−O−P frameworks (Figure 3). For all of the titanium phosphonates **1**−**5**, the FT-IR spectra showed no absorptions corresponding to P−OH or P═O groups, suggesting $RP(O-Ti)_3$ units in all cases.[36−39] The ν(Ti−O) absorption frequencies of **1**−**5** are observed in the 602−608 cm^{-1} range. Furthermore, all compounds show characteristic absorptions at 1126−1137 and 1162−1164 cm^{-1} assigned to the iso-branching vibrations of the isopropoxy groups.[40] Another general spectral feature of compounds **1**−**5** is a strong band observed in the range 1090−1104 cm^{-1} which may be ascribed to a ν(P−O) absorption frequency. The IR spectra of the arylphosphonates **1** and **4** also exhibit strong ν(P−O) absorption bands at 972 and 982 cm^{-1}, respectively, which are well separated from the ν(C−O) bands at 1010 cm^{-1} (**1**) and 1005 cm^{-1} (**4**). In the IR spectra of **2**, **3**, and **5**, these P−O absorption bands overlap with the ν(C−O) bands in the range 1002−1008 cm^{-1}; the resulting ν(P−O)/ν(C−O) overlap bands are very intense, especially for **5**. The characteristic absorption of the CN group in $[Ti_4(\mu_3\text{-}O)(O^iPr)_5(\mu\text{-}O^iPr)_3(4\text{-}CNPhPO_3)_3]\cdot DMSO$ (**4**) is observed as a sharp band at 2229 cm^{-1}.

(b) Solid-State NMR. ^{31}P MAS NMR experiments for the cluster compounds **1**−**5** and ^{13}C CP-MAS NMR experiments on the arylphosphonates **1** and **4** were undertaken to obtain further structural information. The crystal structures of **1** and **2**

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reveal a different chemical environment for each of the three phosphonate groups due to different bond distances and angles and to the coordinated DMSO molecule. Indeed, three sharp signals are observed in the ^{31}P MAS NMR spectra of well-crystallized samples of **1** and **2**, at δ 5.8, 6.2, 7.3 ppm and δ 14.7, 16.7, 17.0 ppm, respectively. For less crystalline powders of **1** and **2**, the line widths of the signals increase slightly and the signals at δ 5.8 and 6.2 ppm for **1** and at δ 16.7 and 17.0 ppm for **2** are no longer separated, leading to broader resonances with double the intensity. The same effect is observed in the ^{31}P MAS NMR spectra of **3** and **4**: two signals with a 1:2 integral ratio are observed at δ 23.6 and 24.5 ppm for **3** and at δ 3.1 and 4.4 ppm for **4**.

The ^{31}P MAS NMR chemical shifts of the molecular titanium phosphonates **1** and **2** are low-field-shifted compared to those of layered titanium phenyl- and methylphosphonates (δ −4.0 and 9.0 ppm, respectively).[36] These low-field shifts are probably the result of different O−P−O bond angles, since the RPO_3 connectivity is (111) in all cases.

The ^{31}P MAS NMRspectrum of **5** shows several overlapping resonances in the range δ 36.9−39.1 ppm as a result of the presence of two independent molecules in its crystal structure which both contain slighlty inequivalent phosphonate groups. The ^{31}P NMR resonance of $[Ti(O^iPr)_2(^tBuPO_3)]_4$ (**5**) is significantly low-field-shifted ($\Delta\delta \cong 14$ ppm) compared to that of $[Ti_4(O)(O^iPr)_8(^tBuPO_3)_3]\cdot DMSO$ (**3**). This is ascribed to the different coordination modes of the phosphonate groups which are (111) in **3** and (112) in **5**. A similar effect was previously reported for zinc phosphonates.[38]

^{13}C CP-MAS NMR experiments were performed on a well-crystallized sample of **1** and an amorphous powder of **4**. The spectrum of **1** exhibits five well-resolved ^{13}C NMR signals around δ 25 ppm for Me_{O^iPr} whereas the spectrum of **4** shows only one broad signal at δ 25.8 ppm. The corresponding resonances of the CH_{O^iPr} groups are located around δ 80 ppm. In both spectra, the signals of the aromatic ipso carbons are well separated from those in the broad aromatic region around δ 125−135 ppm. In the spectrum of **1**, two distinct doublets are observed at δ 136.5 and δ 137.2 ppm, the former being of double intensity. As a result of the lower crystallinity of **4**, overlapping signals are observed in the δ 140−145 ppm region for the ipso carbons. Furthermore, the signals of the aromatic para carbons overlap with the CN resonances at δ 113.3−115.3 ppm. Interestingly, the methyl groups of the coordinated DMSO in **1** give rise to two separated resonances at δ 37.6 and 38.9 ppm, reflecting the different chemical environment of Me_{DMSO} found in the crystal structure; on the other hand, only one broad signal at δ 40 ppm is observed in the case of **4**.

(c) Multinuclear NMR Experiments in Solution. $^{31}P\{^1H\}$, ^{1}H, and $^{13}C\{^1H\}$ NMR studies in solution were performed on all compounds. In contrast to the solid state ^{31}P MAS NMR spectrum, the $^{31}P\{^1H\}$ NMR spectrum of **1** in THF (room temperature) displays only one single resonance at δ 6.8 ppm, which we ascribe to a fast exchange of coordinated solvent molecules. A variable-temperature $^{31}P\{^1H\}$ NMR experiment showed the single resonance to split into two well-separated signals at δ 6.7 and 6.5 ppm as a result of a slower exchange process of coordinated solvent molecules. These chemical shifts are comparable to those previously reported for titanium phenylphosphonates: $[Ti_2(OMe)_6(O_3PPh)_2][^nBu_4N]_2$,[20] δ 8.2 ppm; $[(Cp^*TiO_3PPh)_4(\mu\text{-}O)_2]$,[27] δ 7.4 ppm. A similar coordination behavior in solution is observed for compounds **3** and **4**: At room temperature, their $^{31}P\{^1H\}$ NMR spectra each show only one sharp resonance at δ 28.8 and 4.3 ppm, respectively. At −40 °C, in the $^{31}P\{^1H\}$ NMR spectrum of **4**, two signals at δ 4.6 and 4.3 ppm (2:1) are observed, whereas the $^{31}P\{^1H\}$ NMR spectrum of **3** at −70 °C shows a broad signal at δ 24.3 ppm with a shoulder centered at 25.0 ppm. Surprisingly, the methylphosphonate **2** exhibits the expected two signals at δ 17.2 (broad) and δ 19.2 ppm with an integral ratio of 1:2 at room temperature, indicating a slower exchange process.

The ^{31}P NMR chemical shift of **5** in solution is similar to the one observed in the solid state, which shows that the (112) connectivity of the phosphonate groups is maintained in solution.

In the pyramidal clusters **1**−**4**, three different types of isopropoxo ligands are expected: three bridging and three terminal ones bonded to the three Ti atoms of the base and two terminal ones bonded to the Ti atom of the apex. In the ^{1}H NMR spectra of phosphonates **1**−**4**, the three expected doublets of Me_{O^iPr} can easily be distinguished (see Experimental Section), although for methylphosphonate **2** the doublets overlap with the signals of the methyl groups of P_{PMe}. In the ^{13}C NMR spectra of *tert*-butylphosphonate **3** and (4-cyanophenyl)phosphonate **4**, three resonances of Me_{O^iPr} are observed at δ 25.1, 26.0 (broad), and 26.1 ppm (**3**) and at δ 23.8, 23.9, and 24.0 ppm (**4**), whereas only two signals can be distinguished for **1** (δ 24.0, 24.2 ppm) and **2** (δ 23.7, 24.0 ppm). The ^{13}C NMR signals of CH_{O^iPr} (**1**−**4**) are also found in a narrow range and partially overlap. For the arylphosphonates **1** and **4**, only two signals are observed at δ 77.6, 78.4 ppm and at δ 78.3, 79.2 ppm, respectively, whereas three signals are found in the ^{13}C NMR spectra of the alkylphosphonates **2** and **3** (**2** δ 76.9, 77.2, 77.8 ppm; **3** δ 77.7, 79.8, 80.3 ppm). However, the CH_{O^iPr} resonances at δ 77.2 ppm for **2** and at δ 79.8 ppm for **3** associated with the isopropoxo ligands bonded to the apex of the pyramid are broadened, which suggests that these ligands are involved in an exchange process.

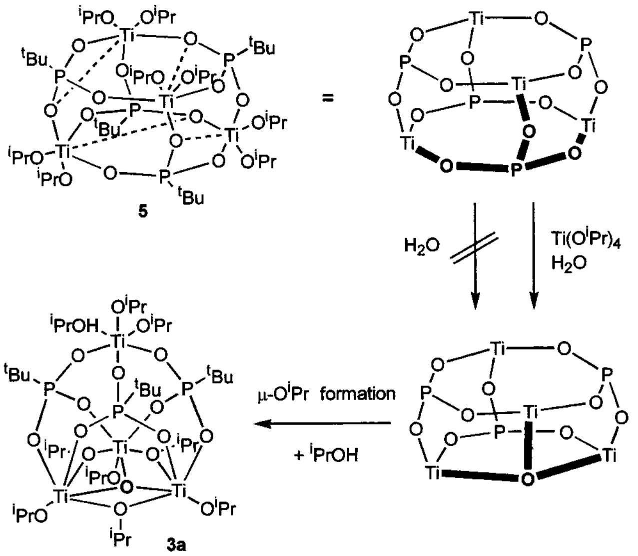
This exchange is probably the result of a trace amount of ^{i}PrOH in the NMR solution. Upon the addition of a small amount of ^{i}PrOH to the ^{1}H NMR solution of **1**, the signals assigned to the terminal isopropxy ligands (CH_{O^iPr} δ 4.26 ppm; Me_{O^iPr} δ 0.33 ppm) bonded to the apex of the pyramid disappear, whereas the resonances attributed to the isopropoxy groups bonded to the Ti_3O base (CH_{O^iPr} δ 4.03, 4.40 ppm; Me_{O^iPr} δ 0.71, 0.80 ppm) are unaffected. This behavior shows that ^{i}PrOH exchanges rapidly only with the terminal O^{i}Pr ligands of the titanium atom of the apex.

For $[Ti(O^iPr)_2(^tBuPO_3)]_4$ (**5**), only one type of isopropoxy group is observed in the ^{1}H NMR spectrum (Me_{O^iPr} δ 1.30 ppm; CH_{O^iPr} δ 5.35 ppm) as well as in the $^{13}C\{^1H\}$ NMR spectrum (Me_{O^iPr} δ 25.8 ppm; CH_{O^iPr} δ 83.0 ppm). The addition of a small amount of ^{i}PrOH does not affect the signals of **5**, which indicates that no isoproxide ligand exchange occurs.

Reactivity of the Clusters. (a) Exchange Reaction of 1 with 2. We were intrigued by a possible scrambling reaction between the phenylphosphonate **1** and the methylphosphonate **2**, which present similar structures. A mixture of **1** and **2** in THF gave a cloudy solution. Nevertheless, in the ^{31}P NMR spectrum of the reaction mixture, six signals at 20.8 (1%), 20.1 (8%), 19.6 (12%), 17.7 (20%), 8.5 (6%), and 7.3 ppm (52%) were observed. Although no assignment of the NMR signals was made, this experiment suggests that exchange processes involving Ti−O−P bond cleavage are operative.

(b) Reaction of 5 with Water and Titanium Isopropoxide. We were also interested in the possible conversion of **5** into cluster **3a** (having the same structure as **3** but coordinated by ^{i}PrOH instead of DMSO). Indeed, the Ti−O−P frameworks of both clusters are related: the replacement of one tridentate

Scheme 3



phosphonate group in **5** by one μ_3-oxygen atom leads to the framework of **3a** (Scheme 3).

According to the ^{31}P and ^{1}H NMR spectra, the addition of 1 equiv of water to a solution of **5** gave 2-propanol and several unidentified hydrolysis products, but the formation of cluster **3a** was not observed. On the other hand, addition of 1 equiv of water to a solution of **5** *and* Ti(O^{i}Pr)$_4$ gave 2-propanol and compound **3a** as the major product (65% based on ^{31}P NMR), as indicated by the ^{1}H and ^{31}P NMR spectra. Note that after the addition of 0.66 equiv of water, both the starting material **5** and cluster **3a** were present.

Discussion and Conclusion

The reactions of Ti(O^{i}Pr)$_4$ with different organophosphonic acids RPO$_3$H$_2$ (R = Ph, 4-CNPh, Me, ^{t}Bu) gave two novel types of molecular titanium phosphonates which are highly soluble in organic solvents. Interestingly, under the same reaction conditions the same cluster framework, [Ti$_4$(μ_3-O)(O^{i}Pr)$_2$(O^{i}Pr)$_3$(μ-O^{i}Pr)$_3$(RPO$_3$)$_3$], formed regardless of the organic group R bonded to phosphorus [R = Ph (**1**), Me (**2**), ^{t}Bu (**3**), 4-CNPh (**4**)]. The main driving forces for the cluster geometry seem to be the tendency of titanium to be hexacoordinated, the stability of the Ti$_3$(μ_3-O)(μ_2-OR)$_3$ fragment which is present in several titanium oxoalkoxides,[13,15] and the (111) coordination mode of the phosphonato ligands found in most titanium phosphonates. In contrast, the reactions of Cp*TiMe$_3$ with RPO$_3$H$_2$ led to two different structures, depending on the organic group R (R = Me, Ph; R = ^{t}Bu).[27] As already reported for other titanophosphonate clusters,[27] the average Ti−O and P−O bond lengths in clusters **1** and **2** are in good agreement with the lengths predicted by the bond valence method[41] (Table 6).

A novel type of titanium phosphonate cluster, [Ti(O^{i}Pr)$_2$(^{t}BuPO$_3$)]$_4$ (**5**), was isolated by reacting *tert*-butylphosphonic acid and Ti(O^{i}Pr)$_4$ in toluene under strictly anhydrous conditions. Single-crystal X-ray analysis revealed that **5** consists of an M$_4$P$_4$O$_{12}$ framework. This fragment is often found for typically tetracoordinated metals, for instance in group 13 metal phosphonates,[42,43] but is unexpected for a typically hexacoordinated metal. A similar structural arrangement involving pentacoordinated titanium atoms was previously described for [(Cp*TiO$_3$PR)$_4$(μ-O)$_2$] (R = Me, Ph)[27] although two opposite faces of the cubic core were capped by two μ_2-oxygen atoms. In compound **5**, the sixth coordination to the Ti atoms comes from the (112) connectivity of the phosphonate groups, unusual for a titanium phosphonate. This connectivity leads to three sets of Ti−O(P) bond lengths: the phosphonato oxygens bonded to one titanium atom give "short" (average 1.97 Å) Ti−O(P) bonds, and the phosphonato oxygen bonded to two titanium atoms gives one "medium" (average 2.13 Å) and one "long" (average 2.43 Å) Ti−O(P) bond. These Ti−O(P) bond lengths are in good agreement with the lengths predicted by the bond valence method, assuming apparent bond valences of 0.667−0.2 and of 0.2 for the "medium" and "long" Ti−O(P) bonds, respectively (Table 6).

Table 6. Comparison between Bond Lengths Predicted by the Bond Valence Method (d_{BV}) and Observed Average Bond Lengths (d_{obsd})

compd	bond	v^a	d_{BV},^{b} Å	$\bar{d}_{obsd}$, Å
1	Ti−O(Ti)	0.667	2.00	1.96
	Ti−O(P)	0.667	2.00	1.99
	P−O(Ti)	1.333	1.53	1.53
2	Ti−O(Ti)	0.667	2.00	1.98
	Ti−O(P)	0.667	2.00	1.53
	P−O(Ti)	1.333	1.53	
5	Ti−O(P)(short)	0.667	2.00	1.97
	Ti−O(P)(medium)	0.467	2.13	2.13
	Ti−O(P)(long)	0.200	2.45	2.43
	P−O(Ti)	1.333	1.53	1.54

[a] Bond order. [b] Bond length calculated by the formula $d = d_0 - b \ln(v)$ where $b = 0.37$ Å, $d_0 = 1.85$ Å for Ti−O, and $d_0 = 1.64$ Å for P−O.[27]

The (112) connectivity of the phosphonate groups in **5** accounts for the significant difference between the ^{31}P NMR chemical shift of **5** and the chemical shifts of **3** and other molecular *tert*-butylphosphonates of titanium[27] and group 13 metals[42] which all present a (111) connectivity.

Interestingly, in the presence of water and Ti(O^{i}Pr)$_4$, compound **5** was converted into the titanium oxide alkoxide phosphonate **3a**, with the same Ti−O−P framework as that of compounds **1**−**4**. This conversion probably involves Ti−O−P/Ti−O−Ti bond exchanges between the titanium alkoxide phosphonate **5** and titanium oxide alkoxide species formed by partial hydrolysis−condensation of Ti(O^{i}Pr)$_4$. The formation of clusters **1**−**4** could follow a similar mechanism.

The reported titanium phosphonate clusters are major intermediates in the sol−gel processing of titanium oxide/phosphonate hybrid materials.[28] Furthermore, they are promising single-source sol−gel precursors for the preparation of organic−inorganic hybrids, as they are well-defined compounds, soluble in common organic solvents, and can be condensed by hydrolysis−condensation of the remaining Ti−O^{i}Pr groups. The isolation of the cyanophenyl derivative **4** illustrates the possibility of introducing functional organic groups for hybrid materials applications and for the design of self-assembled nanostructured materials.

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Supporting Information Available: X-ray crystallographic files, in CIF format, for **2** and **5**. This material is available free of charge via the Internet at http://pubs.acs.org.

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