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Novel Organic-Soluble Molecular Titanophosphonates with Cage Structures Comparable to Titanium-Containing Silicates[†]

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Reactions of Cp^*TiMe_3 ($Cp^* = C_5Me_5$) with methyl-, phenyl- and *tert*-butylphosphonic acids $[RP(O)(OH)_2]$ (R = Me, Ph, *t*-Bu) yield the air-stable titanophosphonates $[(Cp^*TiO_3PR)_4(\mu\text{-}O)_2]$ (R = Me (**1**), Ph (**2**)) and $[(Cp^*Ti)_3(t\text{-}BuPO_3)_2\{t\text{-}BuPO_2(OH)\}(\mu\text{-}O)_2]$ (**3**), which are freely soluble in organic solvents. Alternatively, the reaction between Cp^*TiCl_3 and methylphosphonic acid was also found to produce **1**. The titanophosphonates mentioned are the first examples of organic-soluble molecular transition metal phosphonate cages.

Introduction

In the search for new highly specific and selective catalytic materials, one of the main objectives has been anchoring catalytically active centers on solid-state surfaces. In recent years, this has been achieved by anchoring catalytically active centers inside zeolite-like matrixes by means of various chemical techniques. Efforts to incorporate titanium centers inside zeolite matrixes are of particular importance in view of the proven utility of Ti-doped zeolite materials as catalysts in many commercially important organic transformations, including the alkene to epoxide conversion.[1−5] In the past few years, Thomas et al.[3,4] and others[1,2] have succeeded in stabilizing titanium centers in several different coordination states (coordination numbers 4, 5, and 6) and site environments inside zeolite-like matrixes and have used them as catalysts in many organic transformations.

Phosphate-based molecular sieves are analogous to many zeolites in terms of their structures, properties, and catalytic activity. Hence, the synthetic efforts in this area of zeolite matrixes were also extended recently to the preparation of micro- and mesoporous phosphate and phosphonate materials.[6] Most of the above-mentioned compounds have been prepared as heterogeneous micro- and mesoporous materials,[7]and the synthesis of such materials is normally carried out by hydrothermal routes or by using structure-directing templating agents. Our aim in this area has been to synthesize molecular and soluble titanosilicates and titanophosphonates that could serve as models for many of these heterogeneous Ti-doped catalytic materials. Our recent experience in the synthesis of titanosilicate molecules (displaying tetrahedral, trigonal-bipyramidal, and octahedral coordination environments around Ti)[8] prompted us to explore the possibility of synthesizing molecular titanophosphonates that could model a Ti-containing zeolite-like matrix.

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[†] Dedicated to Professor Edgar Niecke on the occasion of his 60th birthday.

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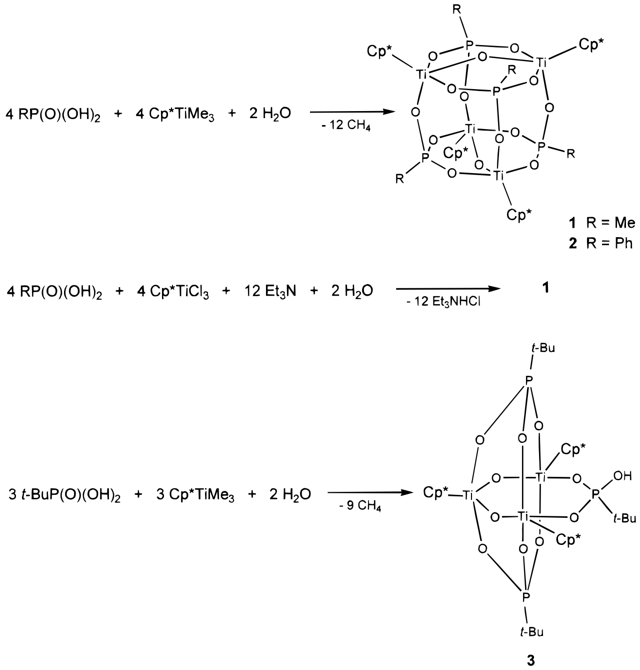
Scheme 1



Results and Discussion

The synthesis of the titanophosphonates **1**−**3** has been achieved by reactions between Cp^*TiMe_3 and a series of phosphonic acids $RP(O)(OH)_2$ (R = Me, Ph, or *t*-Bu). A reaction of Cp^*TiCl_3 with $MeP(O)(OH)_2$ was also found to be a source for the synthesis of **1** (Scheme 1). Compounds **1**−**3** have been fully characterized by means of analytical and spectroscopic techniques, as well as in each case by a single-crystal X-ray diffraction study. The IR spectra of phosphonates **1** and **2** are devoid of any absorptions in the region 3000−3500 cm^{-1}, suggesting complete reaction of all P−OH groups. The IR spectrum of **3** reveals the presence of a weak absorption (3400 cm^{-1}) corresponding to a residual P−OH group present in the molecule.

The EI-MS spectra of compounds **1** and **2** reveal peaks due to $[M^+ - O]$ (*m/e* 1124) and $[M^+ - Me]$ (*m/e* 1373) fragments, respectively. The most prominent fragment in the case of **3** is due to the $[M^+ - BuPO_2(OH)]$ (*m/e* 853) moiety, although the molecular ion is observed (*m/e* 990) with a very low intensity (2%). The ^1H NMR spectra of **1**−**3** reveal that there are no methyl groups remaining on titanium. The ^{31}P NMR spectrum displays a single resonance for **1** (16.4 ppm) and **2** (7.4 ppm), respectively, indicating that all the phosphorus centers in each molecule are in a similar environment. In the case of **3**, three signals of equal intensity are observed, indicating that all the phosphorus atoms in this molecule have different environments. While two rather close chemical shifts (35.9 and 35.6 ppm) could be assigned to the two triply bridging $t\text{-}BuPO_3$ moieties, the resonance observed at 31.9 ppm could be attributed to the $t\text{-}BuPO_2OH$ group (Scheme 1).

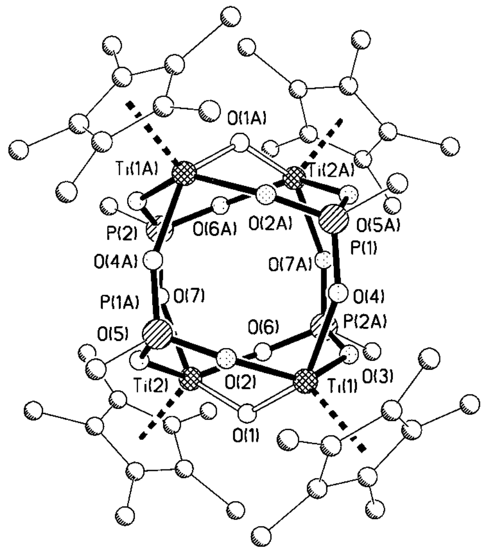


Figure 1. Molecular structure of $[(Cp^*TiO_3PMe)_4(\mu\text{-}O)_2]$ (**1**).

The source of water in the reaction system could be attributed to trace amounts present in the commercially available phosphonic acids. Our experience has been that even a sample of these acids dried under high vacuum for 12 h shows the presence of water in the NMR spectrum.[7a]

Moreover, on addition of concentrated H_2SO_4, the ^{31}P NMR in THF for phenylphosphonic acid shows a shift of ca. 6 ppm and in addition a new signal appeared (2 ppm) which we tentatively assign to a dehydrated phosphorus acid. The dehydration process might also occur using phosphonic acid and organometallic reagents. This is obviously the source of water or oxygen in the products.

As can be seen from Scheme 1, compounds **1** and **2** are made up of very similar Ti−O−P three-dimensional frameworks. Compound **1** crystallizes in the centrosymmetric tetragonal space group $4_1/acd$ with 16 molecules in the unit cell (Figure 1). The central $Ti_4O_{14}P_4$ core contains four titanium and four phosphorus atoms that occupy the alternate vertexes of a distorted cube. Each of the Ti- - -P edges of this polyhedron is bridged by an oxygen atom in a μ_2-fashion (Ti−O−P), resulting in six nonplanar $Ti_2O_4P_2$ eight-membered rings that form the six sides of the cube. In addition, on two opposite faces, the titanium atoms of the $Ti_2O_4P_2$ rings are joined by a μ_2-oxygen atom (Ti−O−Ti). The $Ti_4O_{14}P_4$ central polyhedron (Figures 1 and 2) can be described as a highly distorted bicapped cube with $\bar{4}2m$ (D_{2d}) molecular symmetry.

The periphery of this central $Ti_4O_{14}P_4$ polyhedron is surrounded by hydrophobic pentamethylcyclopentadienyl and methyl (in **1**, that additionally contains $^1/_2$ THF molecule) or phenyl (in **2**) groups, which explains the high solubility of these compounds in common organic solvents.

As shown in Table 1, the bond lengths in compounds **1**−**3** are in good agreement with the bond-valence

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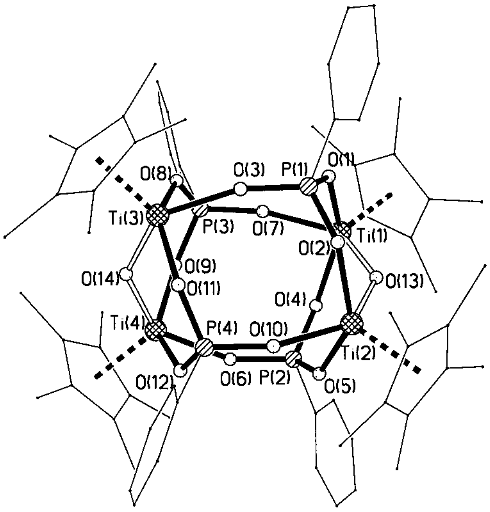

Figure 2. Molecular structure of $[(Cp^*TiO_3PPh)_4(\mu\text{-}O)_2]$ (**2**).

Table 1. Independent Symmetry-Averaged Bond Lengths Calculated with the Bond-Valence Method in Comparison with Observed Values[a]

compd	bond	ν	d_{BV}, Å	$\bar{d}_{obs}$, Å
1	Ti−O(Ti)	1.000	1.85	1.84
1	Ti−O(P)	0.667	2.00	1.99
1	P−O	1.333	1.53	1.52
2	Ti−O(Ti)	1.000	1.85	1.84
2	Ti−O(P)	0.667	2.00	2.01
2	P−O	1.333	1.53	1.52
3	Ti2−O1(Ti)	0.833	1.92	1.86
3	Ti2−O7(P)	0.667	2.00	2.07
3	Ti1−O1(Ti)	1.167	1.79	1.81
3	Ti1−O4(P)	0.500	2.11	2.08
3	Ti1−O5(P)	0.667	2.00	2.02
3	P1−O7(Ti)	1.333	1.53	1.53
3	P1−O5(Ti)	1.333	1.53	1.54
3	P2−O4(Ti)	1.500	1.49	1.53

[a] ν is the bond order, d_{BV} was calculated as explained in the text, and $\bar{d}_{obs}$ is the mean observed distance.

formula $d = d_0 - b \ln(\nu)$[9] when d_0 is taken to be 1.85 Å for Ti−O and 1.64 Å for P−O, $b = 0.37$ Å, and ν is the bond order. These single bond lengths are a little greater than those observed for minerals (Ti−O 1.815 Å, for P−O 1.604 Å).[10] For compound **3** (Figure 3), it was necessary to assume that the P1−O bond orders are the same in order to solve for the bond orders given in Table 1.

We have thus demonstrated the use of the organometallic precursors Cp^*TiMe_3 and Cp^*TiCl_3 and commonly available phosphonic acids as starting materials for organic-soluble titanophosphonates with different polyhedral frameworks, complementing our recent results in titanosilicate chemistry. To our surprise, the titanium atoms in compounds **1**−**3**, respectively, have distorted trigonal-bipyramidal coordination spheres, in contrast to the known titanosilicates.

Experimental Section

General Information. All experimental manipulations were carried out under a dry, prepurified nitrogen atmosphere, using Schlenk techniques and rigorously excluding moisture and air.[11] The samples for spectral measurements were prepared in a drybox. Solvents were purified by conventional procedures and were freshly distilled prior to use. All ^1H and ^{31}P NMR spectra were recorded on a Bruker AS 400 instrument. The chemical shifts are reported in ppm with reference to $SiMe_4$ (external) for ^1H and to 85% H_3PO_4 (external) for ^{31}P nuclei. The upfield shifts from the reference are negative. IR spectra were recorded on a Bio-Rad Digilab FTS 7 spectrometer. Mass spectra were obtained on a Finnigan MAT 8230 or a Varian MAT CH 5 mass spectrometer. Melting points were obtained on a HWS-SG 3000 instrument and are reported uncorrected. Elemental analyses were performed at the analytical laboratory of the Institute of Inorganic Chemistry, University of Göttingen.

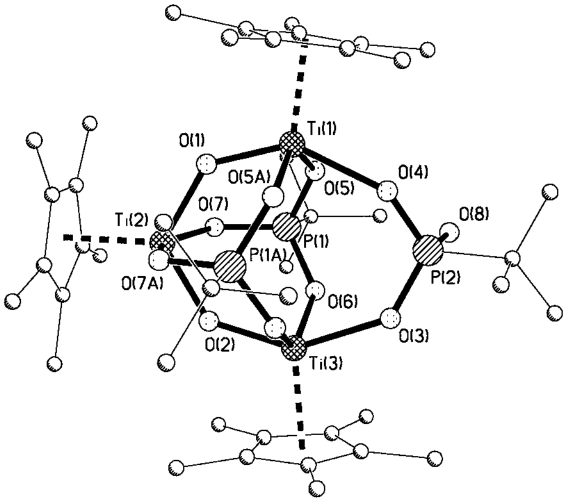

Figure 3. $[(Cp^*Ti)_3(t\text{-}BuPO_3)_2\{t\text{-}BuPO_2(OH)\}(\mu\text{-}O)_2]$ (**3**).

Starting Materials. Cp^*TiCl_3 and Cp^*TiMe_3 were prepared using literature procedures.[12,13] Methylphosphonic acid, phenylphosphonic acid and *tert*-butylphosphonic acid (Aldrich) were dried under high vacuum prior to use.

Preparation of $[(Cp^*TiO_3PMe)_4(\mu\text{-}O)_2]$ (1). Method 1. To a solution of Cp^*TiMe_3 (4 mmol, 910 mg) in THF (25 mL) was added dropwise at 0 °C a solution of methylphosphonic acid (4 mmol, 388 mg) in THF (25 mL). The onset of the reaction was marked by the evolution of methane gas. The reaction mixture was allowed to warm to room temperature and stirred for an additional 4 h period. After removal of the solvent in vacuo, the resulting orange solid was recrystallized from *n*-hexane over a period of 15 d at room temperature to obtain analytically pure **1**. Yield: 570 mg (50%, 0.5 mmol). Mp: 270 °C dec. Anal. Calcd for $C_{44}H_{72}O_{14}P_4Ti_4$ (M_r = 1140.5): C, 46.0; H, 6.3. Found: C, 45.9; H, 6.2. MS (EI, 70 eV): *m*/*e* 1124 (12%, $M^+ - O$). IR (Nujol): 1296, 1261, 1150, 1102, 1035, 1018, 797, 765 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 1.25 (d, 12H, $^2J_{P-H}$ = 17.7 Hz, PCH_3), 1.97 (s, 60H, $C_5(CH_3)_5$).^{31}P NMR (101 MHz, $CDCl_3$): δ 16.4 (s).

Method 2. To a solution containing methylphosphonic acid (1.70 mmol, 330 mg) and Et_3N (3.46 mmol, 350 mg) in THF (25 mL) was added dropwise a solution containing Cp^*TiCl_3 (1.13 mmol, 330 mg) in THF (25 mL). The solution was allowed to stir overnight. After removal of the solvent in vacuo, the residue was extracted with diethyl ether (50 mL). The ether extract was pumped to dryness, and the orange solid obtained was recrystallized from benzene to yield analytically

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Table 2. Crystal Data and Structure Refinement Details for 1−3

	1	2	3
empirical formula	$C_{44}H_{72}O_{14}P_4Ti_4$ ($\cdot{}^1/_2$THF)	$C_{64}H_{80}O_{14}P_4Ti_4$	$C_{42}H_{73}O_{11}P_3Ti_3$
fw	1176.55	1388.76	990.61
temp, K	133(2)	210(2)	150(2)
wavelength, Å	0.710 73	0.710 73	0.710 73
cryst system	tetragonal	monoclinic	orthorhombic
space group	$I4_1/acd$	$P2_1/c$	$Pnma$
a, Å	22.889(3)	23.239(5)	23.850(5)
b, Å	22.889(3)	26.899(5)	14.829(3)
c, Å	42.345(9)	24.155(5)	13.574(3)
α, deg	90	90	90
β, deg	90	118.12(3)	90
γ, deg	90	90	90
V, Å^3	22186(6)	13317(5)	4801(2)
Z	16	8	4
D_{calcd}, g·cm^{-3}	1.409	1.385	1.371
μ, mm^{-1}	0.730	0.620	0.641
F(000)	9856	5792	2096
cryst size, mm	0.4 × 0.2 × 0.2	0.7 × 0.5 × 0.5	0.5 × 0.5 × 0.5
θ range, deg	2−23.25	3.51−24.56	3.57−22.54
index ranges	$0 \le h \le 17$	$-24 \le h \le 24$	$-25 \le h \le 25$
	$0 \le k \le 25$	$-24 \le k \le 27$	$-15 \le k \le 15$
	$0 \le l \le 46$	$-24 \le l \le 24$	$-14 \le l \le 14$
no. of tot. reflcns	97 508	18 564	9999
no. of indepdt reflcns	3977 [R(int) = 0.0831]	15 191 [R(int) = 0.0338]	3283 [R(int) = 0.0353]
refinement method	full-matrix, least-squares on F^2		
data/restraints/params	3977/814/451	15190/0/1588	3282/3/320
goodness-of-fit on F2	1.165	1.002	0.931
R_1, wR_2 [$I > 2\sigma(I)$]	0.0449, 0.0898	0.0527, 0.1173	0.0325, 0.0845
R_1, wR_2 (all data)	0.0531, 0.0932	0.0969, 0.1491	0.0393, 0.0918
largest diff peak and hole, e·Å^{-3}	0.739, −0.262	0.338, −0.331	0.321, −0.257

pure [$(Cp^*TiO_3PMe)_4(\mu\text{-}O)_2$]. Yield: 75 mg (58.6%). MS (EI, 70 eV): *m/e* 1124 (12%, $M^+ - O$).

Preparation of [$(Cp^*TiO_3PPh)_4(\mu\text{-}O)_2$] (2). To a solution of Cp^*TiMe_3 (1 mmol, 228 mg) in THF (25 mL) was added dropwise at room temperature a solution of phenylphosphonic acid (1 mmol, 159 mg) in THF (10 mL). The onset of the reaction was marked by the evolution of methane gas. The reaction mixture was allowed to stir for 12 h. After removal of the solvent in vacuo, the resulting orange solid was recrystallized from a CH_2Cl_2/*n*-hexane (1:1) mixture over a period of 10 d to obtain analytically pure **2**. Yield: 243 mg (70%, 0.18 mmol). Mp: >260 °C dec. Anal. Calcd for $C_{64}H_{80}O_{14}P_4Ti_4$ (M_r = 1388.7): C, 55.4; H, 5.8. Found: C, 55.0; H, 5.7. MS (EI, 70 eV): *m/e* 1373 (18%, $M^+ - Me$). IR (Nujol): 1402, 1136, 1109, 1006, 993, 746, 709, 659 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 1.75 (s, 60H, $C_5(CH_3)_5$), 7.40 and 8.02 (m, 20H, aromatic CH). ^{31}P NMR (101 MHz, $CDCl_3$): δ 7.4 (s).

Preparation of [$(Cp^*Ti)_3(t\text{-}BuPO_3)_2\{t\text{-}BuPO_2(OH)\}(\mu\text{-}O)_2$] (3). To a solution of Cp^*TiMe_3 (1 mmol, 228 mg) in THF (25 mL) was added dropwise at room temperature a solution of *tert*-butylphosphonic acid (1 mmol, 138 mg) in THF (10 mL). The reaction mixture was allowed to stir for 12 h, and the solvent was removed in vacuo. The resulting orange solid was recrystallized from a CH_2Cl_2/*n*-hexane (1:1) mixture at −10 °C over 30 d to obtain analytically pure **3** as single crystals. Yield: 65 mg (20%, 0.06 mmol). Examination of the mother liquor by NMR showed the presence of a large number of noncharacterizable products. Mp: >300 °C dec. Anal. Calcd for $C_{42}H_{73}O_{11}P_3Ti_3$ (M_r = 990.6): C, 50.9; H, 7.4. Found: C, 50.3; H, 7.7. MS (EI, 70 eV): *m/e* 990 (2%, M^+), 853 (60%, $M^+ - BuPO_2(OH)$), 135 (100%, Cp*). IR (Nujol): 3420, 1261, 1153, 1079, 1056, 1021, 973, 946, 800, 723, 622 cm^{-1}. ^1H NMR (250 MHz, $CDCl_3$): δ 1.15−1.25 (many signals, 27H, $C(CH_3)_3$), 1.99, 2.10 (2:1, s, 45H, $C_5(CH_3)_5$). ^{31}P NMR (101 MHz, $CDCl_3$): 31.9, 35.6, 35.9 (s, 1:1:1).

X-ray Structure Determinations. Crystal data for **1** were collected on a Stoe-Siemens-Huber four-circle diffractometer equipped with a Siemens CCD area detector using the ψ-scan mode. The data for **2** and **3** were collected on a Stoe-Siemens-AED four-circle diffractometer using a learnt-profile method.[14] The structures were solved by direct methods (SHELXS-90/96)[15] and refined on all data by full-matrix least-squares (**1** and **3**) or by block-matrix least squares (**2**) procedures on F^2.[16] All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were added in idealized positions and refined using a riding model. The crystal data and structure refinement details for **1**−**3** are given in Table 2.

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Supporting Information Available: Tables of the X-ray crystal structure determination data, atomic coordinates, anisotropic thermal parameters, and bond lengths and angles for **1**−**3** (27 pages). Ordering information is given on any current masthead page.

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