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Formic Acid Modified $Ti(OCHMe_2)_4$. Syntheses, Characterization, and X-ray Structures of $Ti_4(\mu_4\text{-}O)(\mu\text{-}O)(OFc)_2(\mu\text{-}OR)_4(OR)_6$ and $Ti_6(\mu_3\text{-}O)_6(OFc)_6(OR)_6$ (OFc = O_2CH; OR = $OCHMe_2$)

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Novel structural arrangements for carboxylic acid modified titanium alkoxides were obtained from stoichiometric reactions between titanium isopropoxide ($Ti(OPr^i)_4$) and formic acid (HOFc). The 1:1 reaction in toluene forms the tetranuclear species $Ti_4O_2(OFc)_2(OPr^i)_{10}$, **1**. The structure of **1** was solved in the triclinic space group $P\bar{1}$ with $a = 13.034(3)$ Å, $b = 13.467(2)$ Å, $c = 13.996(2)$ Å, $\alpha = 98.79(1)°$, $\beta = 104.68(2)°$, and $\gamma = 97.82(2)°$ for $Z = 2$. The general structure of **1** resembles two face-shared $[Ti-O]_4$ cubes with one set of mirror-related titanium atoms removed. The oxygen atoms are represented by one μ_4-O, one μ-O, and four μ-OR ligands, with the remaining sites filled by two OFc ligands and six terminal alkoxides. Increasing the stoichiometry to 1:2 (Ti/HOFc) leads to the isolation of $Ti_6O_6(OFc)_6(OR)_6$, **2**. The structure of **2** was solved in the monoclinic space group $P2_1/c$ with $a = 8.968(2)$ Å, $b = 26.520(4)$ Å, $c = 20.046(2)$ Å, and $\beta = 93.19(1)°$ for $Z = 4$. The structure of **2** consists of two offset six-membered $[Ti-(\mu_3\text{-}O)]_3$ rings joined through Ti−O bonds. The OFc ligands are arranged externally around the central hexagon-prism, oscillating between the top and bottom rings. Compound **1** adopts a very symmetrical arrangement in solution due to the labile OFc ligands and was found to undergo "aging" by a trans-esterification mechanism, the rate of which is enhanced by heating. Compound **2** maintains its solid-state structure in solution.

Introduction

Early transition metal alkoxide complexes are of interest for a wide variety of uses, including metal oxide ceramic precursors.[1−9] Titanium alkoxides ($Ti(OR)_4$) are often used as precursors to titanium-containing ceramics due to their relatively low decomposition/crystallization temperatures. In an effort to tailor hydrolysis and condensation rates, these precursors are often modified through the addition of multidentate ligands such as acetic acid (HO_2CMe = HOAc).[10,11] When $Ti(OR)_4$ is reacted with *n*HOAc, compounds of the general formula $Ti_6O_4(OAc)_{4n}(OR)_{16-4n}$ [OAc = O_2CMe; OR = OEt (OCH_2Me, $n = 1$),[12] OPr^i ($OCHMe_2$, $n = 1$ or 2),[13,14] OBu^n ($O(CH_2)_3Me$, $n = 2$)[15]] have been isolated and characterized. Figure 1a shows the basic structural skeleton of these compounds, which are best described as corner-removed, inversion-related $[Ti-O]_4$ cubes with face-linked oxide bridges. Even when the steric bulk of the alkoxides and/or carboxylic acid was increased, the same general structure was isolated.[16] For example, the reaction of $Ti(OPr^i)_2(1,2\text{-}O_2C_6H_4)_2$ and the cluster-substituted acid, $HO_2C(\mu_3\text{-}C)[Co_3(CO)_9]$ ($HOAcCo_3$), yielded the isostructural (Figure 1a) product $Ti_6O_4(OAcCo_3)_4(O_2C_6H_4)_4(OPr^i)_4$.[16]

Only two other geometries shown in Figure 1 parts b and c have been reported for carboxylic acid (HORc) modified $Ti(OR)_4$. Figure 1b represents the basic structural arrangement of $Ti_6O_4(OPr^i)_{12}(ONc)_4$ isolated from the reaction between $Ti(OPr^i)_4$ and $HO_2CCH_2CMe_3$ (HONc).[1] This new structural arrangement was described as two inversion-related, edge-shared

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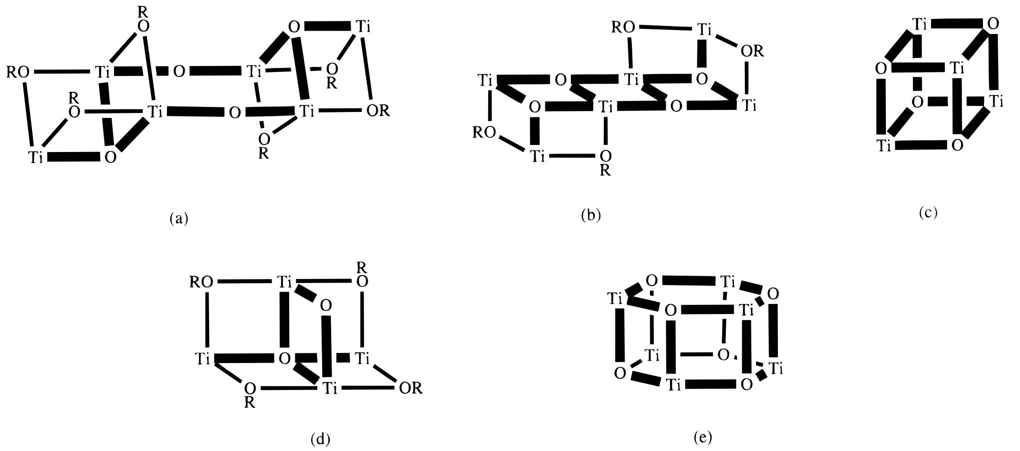

(a) (b) (c) (d) (e)

Figure 1. Schematic representations of the skeletal arrangements of titanium oxo-, alkoxy, acetate compounds: (a) corner-removed, inversion-related, oxide-bridge cube; (b) inversion-related, corner-removed, edge-shared cube; (c) cube; (d) face-shared, mirror corner-removed cube; (e) hexagon-prism.

$[Ti-O]_4$ cubes with inversion-related corners missing. A similar structure was found for the reaction product of $Ti(OEt)_4$ and the $HOAcCo_3$, which was characterized as $Ti_6O_4(OEt)_{12}(OAcCo_3)_4$.[17] The only other arrangement noted in the literature is the cubane structure (Figure 1c) reported for $Ti_4O_4(OC(Me)_3)_4(O_2CCHMe_2)_4$[17] and $Ti_4O_4(OR)_4(OAcCo_3)_4$ (OR = Pr^i, Bu^n, OC_6H_5, $O(2,6\text{-}(Me)_2)C_6H_3)$).[16] From these results, it is apparent that various forms of linked $[Ti-O]_4$ cubelike arrangements are favored for HORc-modified $Ti(OR)_4$ complexes.

We are interested in both large and small oligomers of metallo-organic titanium compounds. It was thought that if the steric bulk of the modifying HORc was reduced while its acidity was increased, significantly altered products should be formed. Formic acid (HO_2CH = HOFc) appeared to satisfy these requirements (1.0 M HOFc had a pH of 1.73; 1.0 M HOAc had a pH of 2.29). This paper reports the synthesis and novel structure types adopted by HOFc-modified $Ti(OPr^i)_4$ compounds.

Experimental Section

All compounds described below were handled with rigorous exclusion of air and water using standard Schlenk line and glovebox techniques. Analytical data were obtained and solvents were dried as previously described.[18] $Ti(OPr^i)_4$ (Aldrich) and HOFc (96%, ACS reagent Aldrich) were freshly distilled immediately prior to use.

$Ti_4(\mu_4\text{-}O)(\mu\text{-}O)(OFc)_2(\mu\text{-}OR)_4(OR)_6$ (1). In a vial, $Ti(OPr^i)_4$ (1.00 g, 3.52 mmol) was added to a solution of HOFc (0.16 g, 3.52 mmol) in toluene (3 mL). A white precipitate immediately formed but dissolves during 12 h of stirring. Crystals were grown by slow evaporation of the volatile component of the reaction mixture under glovebox atmosphere conditions. Crystalline yield: 0.34 g (42.7%). ^1H NMR (tol-d_8, 400.1 MHz, sample prep time = 30s): δ 8.16 (1H, s, O_2CH), 5.20 (1.2H, sept., $OCHMe_2$, J_{H-H} = 6.4 Hz), 5.04 (3.6H, sept., $OCHMe_2$, J_{H-H} = 6.4 Hz), 4.75 (1.1H, sept., $OCHMe_2$, J_{H-H} = 6.0 Hz), 1.58 (10.6H, d, $OCHMe_2$, J_{H-H} = 6.0), 1.35 (22.0H, mult., $OCHMe_2$, J_{H-H} = 6.8), 1.26 (9.8H, mult., $OCHMe_2$, J_{H-H} = 6.8). $^{13}C\{^1H\}$ NMR (tol-d_8, 100.6 MHz, sample prep time = 30s): δ 168.4 (O_2CH), 79.8, 79.7, 78.5, 76.1 ($OCHMe_2$), 26.2, 26.1, 25.7, 25.5, 25.3, 25.0, 24.8, 24.7 ($OCHMe_2$). FT-IR (KBr, cm^{-1}): 2968 (m), 2930 (m), 2863 (m), 2615 (w), 1582 (m), 1467 (w), 1443 (w), 1381 (m), 1362 (m), 1328 (w), 1164 (sh, s), 1132 (s), 1016 (s), 952 (m), 855 (m), 770 (w), 668 (sh, m), 603 (s), 530 (sh, w), 474 (w) cm^{-1}. Anal. Calcd for $C_{32}H_{72}O_{16}Ti_4$: C, 42.49; H, 8.02. Found: C, 42.66; H, 7.97.

$Ti_6(\mu_3\text{-}O)_6(\mu\text{-}OFc)_6(OR)_6$ (2). In a vial, HOFc (0.32 g, 7.04 mmol) was added via syringe to a stirring solution of $Ti(OPr^i)_4$ (1.00 g, 3.52 mmol) in toluene (3 mL), which immediately formed a white precipitate. The mixture was allowed to stir for 12 h. The soluble fraction was separated from the precipitate by centrifugation and allowed to stand at glovebox temperatures until crystals formed. Crystalline yield: 0.39 g (60.5%). ^1H NMR (toluene-d_8, 400.1 MHz): δ 7.86 (5.0H, s, O_2CH), 5.11 (9.8H, sept., $OCHMe_2$, J_{H-H} = 6.0 Hz), 1.51 (71H, d, $OCHMe_2$, J_{H-H} = 6.0 Hz). $^{13}C\{^1H\}$ NMR (toluene-d_8, 100.6 MHz): δ 168.2 (O_2CH), 83.6 ($OCHMe_2$), 25.4 ($OCHMe_2$). FT-IR (KBr, cm^{-1}): 2966 (m), 2926 (m), 2873 (m), 1627 (s), 1547 (s), 1381 (s), 1322 (w), 1262 (w), 1131 (sh), 1129 (s), 1010 (s),864 (w), 705 (s), 625 (m), 493 (m). Anal. Calcd for $C_{31}H_{56}O_{24}Ti_6$: C, 33.84; H, 5.13. Found: C, 33.58; H, 4.94.

X-ray Collection, Structure Determination, and Refinement. Colorless rectangular block crystals of **1** or **2** were mounted, from a pool of mineral oil under an argon gas flow, onto a thin glass fiber and then placed under a liquid nitrogen stream on a Siemens P4/PC diffractometer. The radiation used was graphite-monochromatized Mo Kα radiation (λ = 0.710 69 Å). The lattice parameters were optimized from a least-squares calculation on 25 carefully centered reflections of high Bragg angle. The data were collected using ω scans with a 0.94° and 1.18° scan range for **1** and **2**, respectively. Three check reflections monitored every 97 reflections showed no systematic variation of intensities. No extinction corrections were made for either crystal. Transmission factors were equal to 0.74/0.88. Lattice determination and data collection were carried out using XSCANS version 2.10b software.[19] All data reduction, including Lorentz and polarization corrections and structure solution and graphics were performed using SHELXTL PC version 4.2/360 software.[19] The structure refinement was performed using SHELX 93 software.[19] The data were not corrected for absorption due to the low absorption coefficient. Data collection parameters are given in Table 1.

The heavy atoms and carbon atoms of the structure of **1** were located in the space group $P\bar{1}$ using Patterson and difference Fourier techniques. The hydrogen atoms were fixed in positions of ideal geometry with C−H distances of 0.98, 0.93, and 0.96 Å for the isopropyl, formate ion, and methyl hydrogens, respectively. The hydrogen atoms were refined using a riding model. These idealized hydrogen atoms had their isotropic temperature factors fixed at 1.2 times (isopropyl and formate) or 1.5 times (methyl) the equivalent isotropic U of the C atoms they were bonded to. The final refinement included anisotropic thermal parameters on all non-hydrogen atoms and converged to R1 = 0.0462 and wR2 = 0.1168.

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Table 1. Data Collection for: $Ti_4(\mu_4\text{-}O)(\mu\text{-}O)(\mu\text{-}O_2CH)_2(\mu\text{-}OR)_4(OR)_8$ (**1**) and $Ti_6(\mu_3\text{-}O)_6(\mu\text{-}O_2CH)_6(OR)_6$ (**2**)$\cdot C_7H_8$

compound	**1**	**2**$\cdot C_7H_8$
chemical formula	$C_{32}H_{72}O_{16}Ti_4$	$C_{31}H_{56}O_{24}Ti_6$
fw	904.50	1100.16
temp (K)	183	198
space group	$P\bar{1}$, triclinic	$P2_1/c$, monoclinic
a (Å)	13.034(3)	8.968(2)
b (Å)	13.467(2)	26.520(4)
c (Å)	13.996(2)	20.046(2)
α (deg)	98.79(1)	
β (deg)	104.68(2)	93.19(1)
γ (deg)	97.82(2)	
V (Å^3)	2309(1)	4760(1)
Z	2	4
D_{calcd} (Mg/m^3)	1.301	1.535
μ, (Mo Kα) (mm^{-1})	0.725	1.036
R1[a] (%)	4.62	5.23
wR2[b](%)	11.68[c]	10.78[d]
R1[a] (%, all data)	6.35	10.36
wR2[b] (%, all data)	15.20[c]	13.21[d]

[a] $R1 = \sum||F_o| - |F_c||/\sum|F_o| \times 100$. [b] $wR2 = [\sum w(F_o^2 - F_c^2)^2/\sum(w|F_o|^2)^2]^{1/2} \times 100$. [c] Final weighting scheme calculated using $w = 1/[\alpha^2(F_o^2) + (0.0526P)^2 + 3.7866P]$, where $P = (F_o^2 + 2F_c^2)/3$. [d] Final weighting scheme calculated using $w = 1/[\alpha^2(F_o^2) + (0.0442P)^2 + 0.0395P]$, where $P = (F_o^2 + 2F_c^2)/3$.

The titanium, carbon, and oxygen atom positions of **2** were solved in space group $P2_1/c$ using Patterson and difference Fourier techniques. Subsequent Fourier synthesis gave all remaining non-hydrogen atom positions. A lattice toluene molecule was found and refined at full occupancy. All hydrogen atoms were fixed in positions of ideal geometry, with C−H distances of 0.97 Å for methylene hydrogens, 0.96 Å for methyl hydrogens, and 0.93 Å for aromatic hydrogens and refined using the riding model in the HFIX facility in SHELXL 93. These idealized hydrogen atoms had their isotropic temperature factors fixed at 1.2 times (methylene and aromatic) or 1.5 times (methyl) the equivalent isotropic *U* of the carbon atom they were bonded to. The final refinement included anisotropic thermal parameters on all non-hydrogen atoms and converged to R1= 0.0523 and wR2 = 0.1078.

Results and Discussion

Several $Ti(OR)_4$ modified by HORc have been structurally characterized and found to adopt similar skeletal arrangements (Figure 1a−c) independent of the pendant hydrocarbons of the alkoxide and/or carboxylic acid.[12−17] Crystals of these compounds were typically obtained from neat mixtures of the various components by allowing them to sit at glovebox temperatures for several days. We initiated studies of HOFc-modified $Ti(OPr^i)_4$ to determine the structural properties of these less sterically demanding acids. As a result of the propensity of these reagents to precipitate out of solution when reacted, toluene was used as the solvent.

Synthesis. To a stirring solution of HOFc in toluene 1 equiv of $Ti(OPr^i)_4$ was added, which immediately resulted in the formation of a white precipitate. After being stirred for 4 h, the precipitate began to dissolve, and after 12 h, no precipitate was present. (Note: the order of addition of the reagents is critical; if HOFc is added to $Ti(OPr^i)_4$, the precipitate does not redissolve!) Crystals were grown by slow evaporation of the solvent and proved to be $Ti_4(\mu_4\text{-}O)(\mu\text{-}O)(\mu\text{-}OFc)_2(\mu\text{-}OPr^i)_4(OPr^i)_6$ (**1**), eq 1. A thermal ellipsoid plot of **1** is shown in Figure 2. A higher yield of **1** was realized by drastically reducing the volume of the reaction mixture and cooling it to −35 °C; however, the crystals were significantly smaller. The elemental and thermal data of the bulk powder were consistent with the solid-state structure. Compound **1** was found to be soluble in aromatic solvents and sublimed below 150 °C at 10^{-3} Torr. Increasing the ratio of the Ti/HOFc to 2:1 did not result in the formation of a new complex but instead led to the isolation of **1** and $Ti(OPr^i)_4$.

$$4Ti(OPr^i)_4 + 4HOFc \xrightarrow{\text{toluene}} Ti_4O_2(OFc)_2(OPr^i)_{10} + 4HOPr^i + 2Pr^iOFc \quad (1)$$

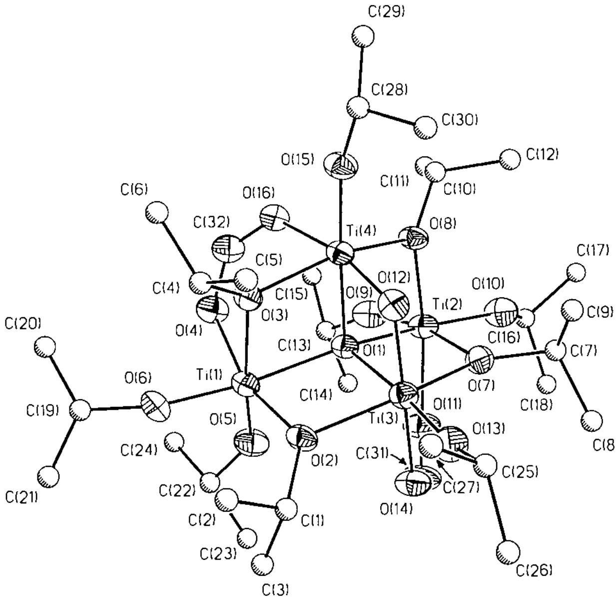


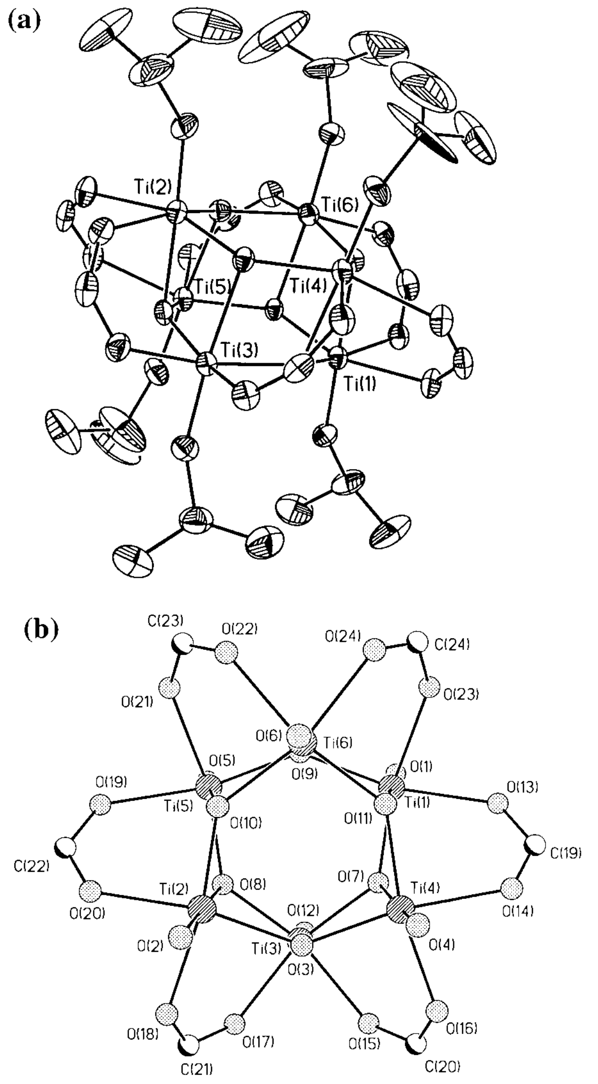
Figure 2. Thermal ellipsoid plot of $Ti_4(\mu_4\text{-}O)(\mu\text{-}O)(OFc)_2(\mu\text{-}OR)_4(OR)_6$, **1**. Thermal ellipsoids are drawn at 50% probability.

Decreasing the ratio of Ti/HOFc to 1:2, under similar conditions (toluene), produced a white precipitate, which did not redissolve (even with the application of heat). The soluble fraction of an unheated suspension was separated from the precipitate and allowed to sit for several days at glovebox temperatures. Long needlelike crystals were isolated and were found to be $Ti_6(\mu_3\text{-}O)_6(\mu\text{-}OFc)_6(OPr^i)_6$ (**2**), eq 2. A thermal ellipsoid plot is shown in Figure 3 (the lattice toluene molecule is not shown for clarity). The insoluble material has not been identified, as of yet, but was found to be soluble in pyridine, and further characterization is underway. The thermal and elemental data of the bulk powder of **2** were consistent with the solid-state structure, with the inclusion of the toluene molecule. Compound **2** was found to be soluble in aromatic solvents and readily sublimed intact at 150 °C at 10^{-3} Torr.

$$6Ti(OPr^i)_4 + 12HOFc \xrightarrow{\text{toluene}} Ti_6O_6(OFc)_6(OPr^i)_6 + 12HOPr^i + 6Pr^iOFc \quad (2)$$

Solid State. a. X-ray Crystallographic Structures. Table 1 lists the data collection parameters for compounds **1** and **2**. Tables 2 and 3 display the heavier atom positional parameters for **1** and **2**, respectively. Tables 4 and 5 give selected bond distances and angles for **1** and **2**, respectively. The structures of **1** and **2** are shown in Figures 2 and 3, respectively. Only the general cubelike structures shown in Figure 1a−c have been previously reported as structures adopted by HORc-modified $Ti(OR)_4$.[12−14,17]

The structure of **1** is the first OFc-modified $Ti(OR)_4$ derivative reported. Figure 2 is the thermal ellipsoid plot of **1** with the appropriate labeling scheme for **1**. The basic skeletal arrange-



Isopropyl groups omitted for clarity

Figure 3. Thermal ellipsoid plot of (a) $Ti_6(\mu_3\text{-}O)_6(OFc)_6(OR)_6$, **2**, and (b) the central core where the isopropyl groups have been removed for clarity. Thermal ellipsoids are drawn at 50% probability.

ment is illustrated in Figure 1d. The structure is best described as two face-shared $[Ti-O]_4$ cubes, which have one of the nonshared, mirror-related titanium atoms removed from each cube. The four six-coordinated titanium metal centers are joined by bridging alkoxide ligands and a single μ_4-O. Two of the opposing titaniums [Ti(4) and Ti(3)] are further bound to a single μ-O and possess a terminal OR. The OFc ligands bridge from Ti(4) to Ti(1) and from Ti(3) to Ti(2). Ti(1) and Ti(2) both fill their coordination sphere with two terminal OPr^i. Only two other crystallographically characterized tetranuclear complexes observed for an alkoxy, oxo, acetate, titanium complex are noted in the literature, $Ti_4O_4(OPr^i)_4[OAcCo_3]_4$ and an unpublished structure of $Ti_4O_4(OPc)_4(OBu^t)_4)$.[16] Both of these adopt the opposing edge-shared partial Ti_4O_4 cube structure shown in Figure 1b. Surprisingly, **1** has only two oxo ligands versus the four oxo ligands of the other tetranuclear compounds.

Figure 3 shows the structure of **2** with the basic skeletal arrangement shown in Figure 1d. Compound **2** is the first hexagon-prismatic shaped alkoxy, oxo, acetate, titanium complex isolated and only the second OFc titanium derivative characterized (vide supra); however, other carboxylate derivatives have been found to adopt structures similar to that observed for **2**.[20−25] The structure of this compound consists of two six-membered rings of alternating Ti and O atoms $[Ti-(\mu_3\text{-}O)]_3$ that are stacked, offset to each other. Each titanium atom possesses a terminal alkoxide and two OFc ligands, forming an up−down chain of OFc ligands. This new structural

Table 2. Select Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) for **1**

atoms	*x*	*y*	*z*	*U*(eq)[a]
Ti(1)	2944 (1)	2540 (1)	1078 (1)	28 (1)
Ti(2)	1936 (1)	2609 (1)	3528 (1)	29 (1)
Ti(3)	4205 (1)	2260 (1)	3266 (1)	28 (1)
Ti(4)	2321 (1)	685 (1)	2086 (1)	25 (1)
O(1)	2671 (2)	2269 (2)	2392 (2)	24 (1)
O(2)	4443 (2)	2618 (2)	1976 (2)	29 (1)
O(3)	2831 (2)	944 (2)	927 (2)	28 (1)
O(4)	1307 (2)	2106 (2)	401 (2)	36 (1)
O(5)	2808 (2)	3863 (2)	1293 (2)	39 (1)
O(6)	3243 (2)	2499 (2)	−106 (2)	40 (1)
O(7)	3438 (2)	2361 (2)	4306 (2)	32 (1)
O(8)	1541 (2)	1078 (2)	3125 (2)	28 (1)
O(9)	807 (2)	2989 (2)	2760 (2)	37 (1)
O(10)	1581 (2)	2796 (2)	4704 (2)	41 (1)
O(11)	2764 (2)	4078 (2)	3773 (2)	39 (1)
O(12)	3704 (2)	876 (2)	2891 (2)	31 (1)
O(13)	5565 (2)	2256 (2)	3911 (2)	39 (1)
O(14)	4426 (2)	3893 (2)	3668 (2)	37 (1)
O(15)	1953 (2)	−675 (2)	1882 (2)	33 (1)
O(16)	809 (2)	781 (2)	1086 (2)	32 (1)

[a] *U*(eq) is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Table 3. Select Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) for **2**

atoms	*x*	*y*	*z*	*U*(eq)[a]
Ti(1)	2649 (1)	3024 (1)	5196 (1)	20(1)
Ti(2)	4349 (1)	1917 (1)	3604 (1)	21(1)
Ti(3)	5099 (1)	3039 (1)	3908 (1)	20(1)
Ti(4)	5523 (1)	2366 (1)	5187 (1)	21(1)
Ti(5)	1479 (1)	2573 (1)	3623 (1)	22(1)
Ti(6)	1912 (1)	1900 (1)	4902 (1)	21(1)
O(1)	1939 (5)	3639 (2)	5081 (2)	26(1)
O(2)	5073 (5)	1299 (2)	3690 (2)	30(1)
O(3)	4647 (5)	3664 (2)	3699 (2)	27(1)
O(4)	6174 (5)	1785 (2)	5493 (2)	31(1)
O(5)	821 (5)	3157 (2)	3337 (2)	32(1)
O(6)	2323 (5)	1273 (2)	5131 (2)	30(1)
O(7)	4497 (4)	3053 (1)	4810 (2)	19(1)
O(8)	3550 (5)	2670 (2)	3467 (2)	22(1)
O(9)	1453 (4)	2653 (2)	4555 (2)	18(1)
O(10)	2517 (5)	1882 (2)	4003 (2)	22(1)
O(11)	3451 (5)	2267 (2)	5344 (2)	20(1)
O(12)	5548 (4)	2277 (2)	4253 (2)	20(1)
O(13)	3706 (5)	3203 (2)	6098 (2)	28(1)
O(14)	5749 (5)	2715 (2)	6113 (2)	27(1)
O(15)	7229 (5)	3230 (2)	4287 (2)	25(1)
O(16)	7577 (5)	2702 (2)	5150 (2)	25(1)
O(17)	6377 (5)	2906 (2)	3114 (2)	29(1)
O(18)	6015 (5)	2081 (2)	2944 (2)	26(1)
O(19)	1222 (5)	2235 (2)	2692 (2)	30(1)
O(20)	3285 (5)	1752 (2)	2695 (2)	27(1)
O(21)	−590 (5)	2231 (2)	3659 (2)	27(1)
O(22)	−205 (5)	1703 (2)	4522 (2)	29(1)
O(23)	1003 (5)	2869 (2)	5859 (2)	25(1)
O(24)	602 (5)	2040 (2)	5697 (2)	26(1)

[a] *U*(eq) is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

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Table 4. Interatomic Distances (Å) and Angles (deg) for **1**

distances (Å)			angles (deg)		
Ti−(μ-OR)	Ti(1)−O(2)	2.017 (2)	Ti−(μ-OR)−Ti	Ti(1)−O(2)−Ti(3)	104.35 (9)
	Ti(1)−O(3)	2.108 (2)		Ti(1)−O(3)−Ti(4)	101.83 (9)
	Ti(2)−O(7)	2.083 (2)		Ti(2)−O(7)−Ti(3)	102.58 (10)
	Ti(2)−O(8)	2.010 (2)		Ti(2)−O(8)−Ti(4)	105.51 (9)
	Ti(3)−O(2)	2.025 (2)			
	Ti(3)−O(7)	1.962 (2)			
	Ti(4)−O(3)	1.962 (2)			
	Ti(4)−O(8)	2.024 (2)			
Ti−(OFc)	Ti(4)−O(16)	2.142 (2)	(O)−C−(O)	O(4)−C(32)−O(16)	127.6 (3)
	Ti(2)−O(11)	2.146 (2)		O(11)−C(31)−O(14)	128.0 (3)
	Ti(3)−O(14)	2.054 (2)			
	Ti(1)−O(4)	2.064 (2)			
Ti−(μ-O)	Ti(4)−O(12)	1.827 (2)	Ti−(μ-O)−Ti	Ti(4)−O(12)−Ti(3)	107.33 (11)
	Ti(3)−O(12)	1.836 (2)			
Ti−(μ_4-O)	Ti(1)−O(1)	2.036 (2)	Ti−(μ_4-O)−Ti	Ti(1)−O(1)−Ti(2)	148.82 (11)
	Ti(2)−O(1)	2.078 (2)		Ti(1)−O(1)−Ti(3)	102.24 (9)
	Ti(3)−O(1)	2.065 (2)		Ti(1)−O(1)−Ti(4)	91.00 (8)
	Ti(4)−O(1)	2.073 (2)		Ti(2)−O(1)−Ti(3)	99.28 (9)
				Ti(2)−O(1)−Ti(4)	101.33 (9)
				Ti(3)−O(1)−Ti(4)	91.00 (8)
Ti−OR	Ti(1)−O(5)	1.802 (2)			
	Ti(1)−O(6)	1.791 (2)			
	Ti(2)−O(9)	1.776 (2)			
	Ti(2)−(10)	1.810 (2)			
	Ti(3)−O(13)	1.775 (2)			
	Ti(4)−O(15)	1.788 (2)			
Ti···Ti	Ti(3)−Ti(4)	2.952 (1)			
	Ti(2)−Ti(3)	3.158 (1)			
	Ti(1)−Ti(4)	3.161 (1)			
	Ti(1)−Ti(3)	3.193 (1)			
	Ti(2)−Ti(4)	3.211 (1)			

arrangement is the first noncubelike geometry that these types of molecules have been shown to adopt. The center of the molecule is empty, generating a hole ~3.72 Å in diameter (Ti(6)···O(3) = 3.72 Å; Ti(4)···O(10) = 3.72 Å; Ti(2)···O(11) = 3.74 Å). The molecules were found by analysis of the packing diagram to be slightly offset from each other, and channels are not formed.

The bond distances and angles observed for **1** and **2** are consistent with literature values.[12−15] The Ti−(μ-O), Ti−(μ_3-O), and Ti···Ti distances [**1** (av 3.14 Å) and **2** (av 3.12 Å)] and the Ti−OFc distances of **1** and **2** [**1** (2.10 Å) and **2** (2.07 Å)] are similar to the metrical data reported for the Ti−OAc compounds.[10,11] The Ti−(μ_4-O) distances of **1** (av 2.06 Å) are slightly longer than the Ti−(μ_3-O) (av 1.93 Å) distances of **2**, in agreement with what is typically observed for these compounds (i.e., the bond length increases with the degree of bonding). The bite angles of the OFc ligands for **1** (av 127°) and **2** (av 127°) are similar to those reported for the OAc compounds of $n = 1$ (126°) and $n = 2$ (125°). The $[\mathrm{Ti{-}O}]_3$ rings of **2** are distorted hexagons, which have alternating angles of 135° and 100°. The top ring is bound to the lower ring by roughly 90° Ti−(μ_3-O)−Ti angles. The unusual structures adopted by **1** and **2**, in comparison to the previously reported cubelike structures of other acid-modified $\mathrm{Ti(OR)_4}$, must be due to the characteristics of the OFc ligand. The faster esterification (hydrolysis) caused by the increased acidity of the formic acid, coupled with its reduced steric bulk, allows for highly condensed species to form.

b. FT-IR. Since both **1** and **2** possess OFc and $\mathrm{OPr^i}$ ligands, the FT-IR spectra of these compounds are very similar. However, there is a significant difference in the intensity of the stretches, which is consistent with the observed solid-state structures. For **1**, there is only one broad stretch observed at 1582 $\mathrm{cm^{-1}}$, which was assigned to the OFc ligands, whereas **2** has two strong stretches associated with the OFc ligand at 1627 and 1547 $\mathrm{cm^{-1}}$. The M−O region for **1** consists of a number of broad stretches centered around 600 $\mathrm{cm^{-1}}$ indicative of the many types of Ti−O bonds present, whereas for **2**, this region has one strong (705 $\mathrm{cm^{-1}}$) and two medium sharp stretches (625 and 493 $\mathrm{cm^{-1}}$) indicative of the three types of Ti−O bonds present in the structure of **2**.

Solution State. The degree of condensation for alkoxy, oxo, titanium species as defined by the ratio of y/x [y = the number of $\mathrm{O^{2-}}$ anions; x = the number of $\mathrm{Ti^{4+}}$ cations {i.e., $\mathrm{Ti}_x\mathrm{O}_y(\mathrm{OR})_{4x-2y}$}] has been suggested as a method for indicating the stability of a complex in solution.[26] For **1**, the y/x value would be 0.5, indicative of a rather unstable complex, whereas the degree of condensation for **2** ($y/x = 1$) would be considered to be stable in solution. Fehlner and co-workers have also pointed out that the degree of "free space" in a specific molecule may be equally important in determining stability.[16] Investigation of these compounds in solution using molecular weight determinations and NMR solution studies was undertaken to determine their solution stability.

a. NMR. NMR information on metal alkoxide compounds is often complicated by rapid ligand exchange and multinuclear equilibria.[2−5,27,28] In an effort to minimize these effects, only saturated samples were investigated.

As a result of the asymmetry of **1**, 10 unique $\mathrm{OPr^i}$ and 2 OFc ligands should exist for the static molecule in solution. A

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Table 5. Interatomic Distances (Å) and Angles (deg) for **2**

distances (Å)			angles (deg)		
Ti−(OFc)	Ti(1)−O(13)	2.049 (4)	(O)−C−(O)	O(13)−C(19)−O(14)	126.9 (6)
	Ti(4)−O(14)	2.076 (4)		O(15)−C(20)−O(16)	126.3 (6)
	Ti(3)−O(15)	2.079 (4)		O(17)−C(21)−O(18)	127.3 (6)
	Ti(4)−O(16)	2.052 (5)		O(19)−C(22)−O(20)	127.7 (6)
	Ti(3)−O(17)	2.042 (5)		O(21)−C(23)−O(22)	127.7 (7)
	Ti(2)−O(18)	2.095 (4)		O(23)−C(24)−O(24)	127.9 (6)
	Ti(5)−O(19)	2.071 (4)			
	Ti(2)−O(20)	2.057 (4)			
	Ti(5)−O(21)	2.071 (4)			
	TI(6)−O(22)	2.072 (5)			
	Ti(1)−O(23)	2.081 (4)			
	Ti(6)−O(24)	2.066 (5)			
Ti−(μ_3-O)	Ti(1)−O(7)	1.870 (4)	Ti−(μ_3-O)−Ti	Ti(1)−O(7)−Ti(3)	133.9 (2)
	Ti(3)−O(7)	1.915 (4)		Ti(1)−O(7)−Ti(4)	101.0 (2)
	Ti(4)−O(7)	2.158 (4)		Ti(1)−O(9)−Ti(6)	99.9 (2)
	Ti(2)−O(8)	2.133 (4)		Ti(2)−O(10)−Ti(6)	134.8 (2)
	Ti(3)−O(8)	1.880 (4)		Ti(2)−O(10)−Ti(5)	100.2 (2)
	Ti(5)−O(8)	2.071 (4)		Ti(2)−O(12)−Ti(3)	99.3 (2)
	Ti(1)−O(9)	1.902 (4)		Ti(3)−O(7)−Ti(4)	100.2 (2)
	Ti(5)−O(9)	1.883 (4)		Ti(3)−O(8)−Ti(2)	101.1 (2)
	Ti(6)−O(9)	2.148 (4)		Ti(3)−O(8)−Ti(5)	133.6 (2)
	Ti(2)−O(10)	1.869 (4)		Ti(4)−O(11)−Ti(1)	99.8 (2)
	Ti(5)−O(10)	2.173 (4)		Ti(4)−O(12)−Ti(2)	134.8 (2)
	Ti(6)−O(10)	1.912 (4)		Ti(4)−O(12)−Ti(3)	100.8 (2)
	Ti(1)−O(11)	2.146 (4)		Ti(5)−O(8)−Ti(2)	100.1 (2)
	Ti(4)−O(11)	1.920 (4)		Ti(5)−O(9)−Ti(1)	133.7 (2)
	Ti(6)−O(11)	1.872 (4)		Ti(5)−O(9)−Ti(6)	101.8 (2)
	Ti(2)−O(12)	1.898 (4)		Ti(6)−O(10)−Ti(5)	99.9 (2)
	Ti(3)−O(12)	2.167 (4)		Ti(6)−O(11)−Ti(1)	100.9 (2)
	Ti(4)−O(12)	1.887 (4)		Ti(6)−O(11)−Ti(4)	133.5 (2)
Ti−OR	Ti(1)−O(1)	1.762 (4)			
	Ti(2)−O(2)	1.768 (4)			
	Ti(3)−O(3)	1.751 (4)			
	Ti(4)−O(4)	1.747 (4)			
	Ti(5)−O(5)	1.743 (4)			
	Ti(6)−O(6)	1.757 (4)			
Ti⋯Ti	Ti(1)−Ti(4)	3.112 (2)			
	Ti(1)−Ti(6)	3.103 (2)			
	Ti(2)−Ti(5)	3.108 (2)			
	Ti(3)−Ti(4)	3.129 (2)			
	Ti(5)−Ti(6)	3.132 (2)			

sample of **1**, dissolved immediately before analysis, reveals a simple spectrum that consists of one OFc resonance and three types of OPr^i resonances (methine region has three resonances at δ 5.20, 5.04, and 4.75 in a 1:3:1 ratio). This simple NMR pattern indicates that a highly symmetric molecule exists in solution, which can be explained if the OFc ligands are rapidly exchanging among each of the four Ti metal centers or if the OFc ligands become monodentate. If either condition exists, a mirror plane is created through the $\overline{\mathrm{Ti(4)-O(12)-Ti(3)-O(1)}}$ plane, thereby generating two pairs of equivalent μ-OPr^i ligands and equating four of the terminal OPr^i ligands. The remaining terminal OPr^i ligands must then be coincidentally overlapped with the other terminal OPr^i ligands. The $^{13}C\{^1H\}$ NMR spectrum obtained on a freshly dissolved sample of **1** revealed carbon resonances consistent with one type of OFc, four types of methine, and multiple methyl ligands, which is consistent with the symmetric molecule generated by labile OFc ligands noted previously.

To further elucidate the solution behavior of **1**, variable temperature NMR (VT NMR) spectra were obtained on a freshly dissolved sample of **1** using cooled (0 °C) toluene-d_8 as the solvent. The sample was immediately placed into a cooled (−30 °C) probe. The low-temperature ^1H NMR spectra of **1** showed no change in the number of OFc or methine regions versus the room temperature spectrum; however, the OFc peak shifts slightly from 8.21 ppm at room temperature to 8.25 ppm at −30 °C. The methyl peaks do reveal a sharpening of several of the methyl resonances; however, due to overlapping peaks, this region is still very complex. Low-temperature $^{13}C\{^1H\}$ NMR (−35 °C) spectroscopy revealed a sharpening of the four methine resonances and a simplification of the multiplet of methyl resonances to eight distinct methyl resonances, but the region is still congested. The rate of dynamic exchange of the ligands of **1** was not significantly lowered at this temperature; however, colder temperature investigations were not performed due to preferential crystallization of **1**.

A 2D heteronuclear multiple quantum correlation (HMQC) VT NMR experiment was undertaken at −35 °C to aid in the interpretation of the methine region. From the HMQC studies, the δ 5.04 ^1H methine resonance is clearly associated with three different ^{13}C resonances (δ 79.8, 79.7, 76.1 ppm). The other two ^1H methine resonance (δ 5.20 and 4.75) are associated with the ^{13}C resonance at δ 78.5. This suggests that the 5.04 ppm resonance results from a coincidental overlap of three terminal OPr^i ligands, whereas the 78.5 ppm $^{13}C\{^1H\}$ resonance represents the coincidental overlap of the other two μ-OPr^i ligands. The HMQC data suggest that a symmetric structure is adopted in solution with coincidental overlapping of several resonances. As was inferred from the ^1H and $^{13}C\{^1H\}$ interpretation, the OFc ligands must be labile to realize this effect. The initial stability of **1** in solution is not predicted by the y/x computation, but due to the high degree of condensation (lack of “openness”)

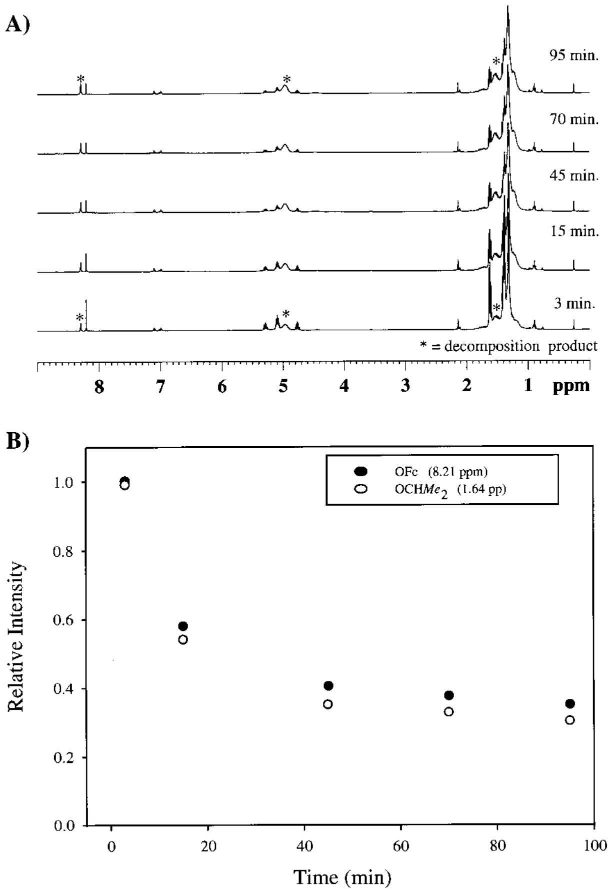

Figure 4. High-temperature (35 °C) aging of **1**. (a) Stack plot of ^{1}H NMR spectra at listed minutes. (b) Plot of decomposition of **1** versus time (min) based on peak integration.

retention of the solid-state structure appears to occur in solution at room and low temperature.

A sample of **1** sealed under vacuum and stored at room temperature was monitored over time. Over a 2 week period of time (~310 h), the sample of **1** underwent more than 50% conversion (the majority of which occurs within the first 120 min) with the ingrowth of three broad peaks around the OFc, methine, and methyl resonances. The high-temperature ^{1}H NMR spectra (up to 60 °C) of **1** also reveal the ingrowth of the same three broad peaks; however, upon cooling this sample to room temperature, the original spectrum was not obtained. The new peaks observed for **1** (either due to extended "aging" over time or after high-temperature treatment) are consistent with the "ester" reaction product between HOFc and HOPr^{i}. This indicates that **1** undergoes a trans-esterification decomposition, which has been reported for other acid alkoxy systems.[27] If the OFc ligands are labile (vide supra), then the rapidity of esterification is easily visualized. Heating the sample to 35 °C and following the decomposition (Figure 4) by monitoring the ingrowth of these new peaks indicate that the sample was ~50% decomposed within 30 min. Analysis of these data concerning the order of reaction based on the amount of "ester" generated was inconclusive.

For **2**, there are only three resonances in the ^{1}H NMR spectrum (δ 7.86, 5.11, 1.51) and the ^{13}C{^{1}H} NMR spectrum (δ 168.2, 83.6, 25.4), which have been assigned as the OFc resonances, the methine, and the methyl moiety of the OPr^{i} ligand, respectively. This indicates that a highly symmetrical molecule exists in solution, which is in agreement with the solid-state structure of **2**. On the basis of the high degree of condensation ($y/x = 1$) as well as the condensed nature of this molecule, it is expected that this compound would remain intact in solution. It is also possible that due to rapid ligand exchange the resonances appear equivalent, so ^{1}H VT NMR spectra were collected. On the basis of these data, there was no evidence for ligand exchange at either high or low temperature.

b. Molecular Weight Determination. Isopiestic molecular weight (MW) studies (Signer method)[29] of **1** found the MW to be av 860 ± 14. This value is lower than the solid-state structure would predict (MW = 904.50) and indicates some disruption of the solid-state structure. As a result of the extended period of time required to obtain the MW values and the trans-esterification decomposition noted above, it is not unreasonable that this value is not consistent with the solid-state structure. **2** was not soluble enough to allow a MW determination to be realized at the standard 0.1 M concentration.

Conclusion

$Ti(OPr^{i})_4$ modified by HOFc has resulted in two novel compounds, $Ti_4(\mu_4\text{-}O)(\mu\text{-}O)(OFc)_2(\mu\text{-}OPr^{i})_4(OPr^{i})_6$, **1**, and $Ti_6(\mu_3\text{-}O)_6(OFc)_6(OPr^{i})_6$, **2**. These molecules expand the structural arrangements known for this family of compounds. The steric decongestion and increased acidity characteristics of the OFc ligand versus other ORc ligands allow for highly condensed species to form. For **1**, a symmetric molecule was found to exist in solution. This was interpreted as being a result of labile OFc ligands, which also allow for facile decomposition of **1** by a trans-esterification mechanism. Elevated temperatures increased the observed rate of decomposition of **1**. The structure of **2** was also retained in solution, which is consistent with the highly condensed nature of the compound.

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Supporting Information Available: A complete listing of crystal data collection, positional and thermal parameters, additional figures, and bond distances and angles for **1** and **2** are available (30 pages). Ordering information is given on any current masthead page.

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