

# Titanium(IV) Neopentoxides. X-ray Structures of $\text{Ti}_3(\mu_3\text{-O})(\mu_3\text{-Cl})(\mu\text{-OCH}_2\text{CMe}_3)_3(\text{OCH}_2\text{CMe}_3)_6$ and $[\text{Ti}(\mu\text{-OCH}_2\text{CMe}_3)(\text{OCH}_2\text{CMe}_3)_3]_2$

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Attempts to synthesize titanium(IV) neopentoxide led to two unique products which were crystallographically characterized. A metathesis reaction between  $\text{TiCl}_4$  and  $\text{NaOCH}_2\text{CMe}_3$  ( $\text{NaONp}$ ) yielded  $\text{Ti}_3(\text{O})(\text{Cl})(\text{ONp})_9 \cdot \text{C}_7\text{H}_8$ , **1**, which adopts a standard  $\text{M}_3(\mu_3\text{-X})_2(\mu\text{-X})_3\text{X}_6$  structure. The  $\mu_3$  ligands are a Cl and an O atom, with the rest of ligands represented by bridging and terminal ONp ligands.  $[\text{Ti}(\text{ONp})_4]_2$ , **2**, was isolated in high yield by an alcoholysis exchange between  $\text{Ti}(\text{OPr}^i)_4$  and HONp. **2** adopts a typical  $\text{M}_2(\mu\text{-X})_2(\text{X})_6$  fused axial–equatorial edge-shared geometry, wherein each metal center is 5 coordinated. On the basis of molecular weight solution studies and  $^1\text{H}$ ,  $^{13}\text{C}$ ,  $^{17}\text{O}$  (natural abundance), and  $^{47,49}\text{Ti}$  solution and solid-state NMR investigations, **2** was determined to be a monomer in solution.

## Introduction

Titanium(IV) alkoxides have been studied and successfully used for a wide range of applications including complex ceramic synthesis,<sup>1–5</sup> catalysts for Ziegler–Natta polymerization of olefins,<sup>6–8</sup> and stereoselective and asymmetric organic synthesis reagents.<sup>9–12</sup> The most investigated and utilized member of this group is titanium isopropoxide,  $[\text{Ti}(\text{OPr}^i)_4]$ . This compound is an oil; hence, the actual solid state structure has not been determined.<sup>1,13</sup> Reportedly, the solution state of most  $\text{Ti}(\text{OR})_4$  ( $\text{R} = \text{Me}$ ,  $\text{Et}$ , and  $\text{Bu}^n$ , which stand for methyl, ethyl, and *n*-butyl, respectively) in benzene appears to be an equilibrium between mono-, di-, and trinuclear species, favoring the trinuclear species at room temperature.<sup>14,15</sup> When the steric bulk

of the alkoxide is increased ( $\text{OR} = \text{OPr}^i$  or  $\text{OBu}^t$ , which stand respectively for isopropyl and *tert*-butyl), roughly monomeric species are reported,<sup>13,14</sup>  $\text{Ti}(\text{OPr}^i)_4$  has an aggregation of 1.4, indicating some degree of oligomerization occurs in solution.<sup>1</sup> This fluctuation in the actual solution structures along with a dependence on temperature of solution and solvent makes it difficult to predict the characteristics that  $\text{Ti}(\text{OPr}^i)_4$  will impart to a given system. Therefore, well-characterized, highly soluble homoleptic titanium alkoxide complexes are of interest to a wide range of investigators.

The only homoleptic compounds that have been structurally characterized are the methoxide and ethoxide derivatives,  $[\text{Ti}(\text{OMe})_4]_4$ <sup>16</sup> and  $[\text{Ti}(\text{OEt})_4]_4$ ,<sup>17</sup> respectively. Both of these possess a typical fused  $\text{M}_3(\text{OR})_{12}$  geometry<sup>16–18</sup> but exhibit poor solubility in standard organic solvents. We became interested in the neopentoxide ( $\text{OCH}_2\text{CMe}_3 = \text{ONp}$ ) ligands for materials applications due to the combination of favorable characteristics from both the  $\text{OPr}^i$  and  $\text{OBu}^t$  moieties. The  $\beta$ -hydrogens present in the  $\text{OPr}^i$  and  $\text{ONp}$  ligands are easily eliminated upon hydrolysis, allowing for rapid organic decomposition, vital for production of uniform materials at low temperature. The  $\text{OBu}^t$  moiety of the  $\text{ONp}$  ligand greatly increases the solubility of the alkoxide ligands by introducing steric bulk around the metal center, inhibiting oligomerization. The combination of these

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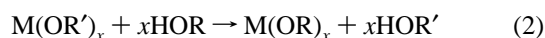
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two attributes made the ONp ligand a potential candidate for production of a well-characterized highly soluble titanium alkoxide.

The two general synthetic pathways that were chosen for preparation of "Ti(ONp)<sub>4</sub>" are shown below (eqs 1 and 2) with



$x = 4^{1-5}$  and were based upon the simplicity of synthesis and availability of starting materials. The third reaction pathway (eq 3) was undertaken to produce "Ti(ONp)<sub>4</sub>" without Ti(OPr<sup>i</sup>)<sub>4</sub> contamination. It is of note that there are a number of alternative routes for production of metal alkoxides;<sup>1-5</sup> however, the majority of these require even more complex handling/synthesis than eq 1 or 2 which would be prohibitive for larger scale studies.

In this report, we describe two novel titanium neopentoxide complexes: Ti<sub>3</sub>(μ<sub>3</sub>-O)(μ<sub>3</sub>-Cl)(μ-ONp)<sub>3</sub>(ONp)<sub>6</sub>·C<sub>7</sub>H<sub>8</sub>, **1**, which was isolated from the metathesis reaction similar to eq 1, and [Ti(μ-ONp)(ONp)<sub>3</sub>]<sub>2</sub>, **2**, which was synthesized by an alcoholysis exchange (eq 2) or an amide-alcohol exchange (eq 3). The solid- and solution state properties of **2** are reported.

## Experimental Section

All reactions were performed under a dry nitrogen or argon atmosphere, using standard Schlenk, vacuum line, and glovebox techniques. Solvents were dried, as previously described.<sup>18</sup> Ti(OPr<sup>i</sup>)<sub>4</sub> (Aldrich) was vacuum distilled immediately prior to use, whereas TiCl<sub>4</sub> (Aldrich) and HONp (Aldrich) were used as received. Ti(N(SiMe<sub>3</sub>)<sub>2</sub>)<sub>4</sub> (purified by sublimation) was isolated from the reaction between LiN(SiMe<sub>3</sub>)<sub>2</sub> (Aldrich) and TiCl<sub>4</sub> in hexanes. NaONp (purified by vacuum sublimation) was isolated from a reaction between Na metal and HONp in toluene.

Solution- and solid-state NMR and variable-temperature NMR spectra were obtained using a 5 mm BB solution probe or a 7 mm MAS probe on an AMX 400 spectrometer: <sup>1</sup>H (400.1 MHz), <sup>13</sup>C (100.6 MHz), <sup>17</sup>O (54.3 MHz; external reference distilled H<sub>2</sub>O, δ 0.0), and <sup>47,49</sup>Ti (22.6 MHz; external reference TiCl<sub>4</sub> (neat), δ 0.0). <sup>1</sup>H and <sup>13</sup>C (including the APT and DEPT <sup>13</sup>C) experiments were obtained using standard pulse sequences and are referenced to residual solution resonances. The natural abundance <sup>17</sup>O{<sup>1</sup>H} was obtained at 298 K using 48K averages, 100 ms recycle delay. Both the <sup>17</sup>O and the <sup>47,49</sup>-Ti NMR spectra were obtained using a composite pulse 90 sequence to reduce acoustic ring. For MAS NMR experiments the carbonyl of glycine was referenced at δ 176.0 for <sup>13</sup>C experiments and an external reference of TiCl<sub>4</sub> at δ = 0.0 for <sup>47,49</sup>Ti. All experiments were performed at 298 K. The <sup>13</sup>C cross polarized (CP) spectra were obtained using a contact time 1 ms, 5 s recycle delay with 4.75 μs π/2 pulses. The solid-state Ti experiments were attempted using a one-pulse high-power decoupling sequence.

**Ti<sub>3</sub>(μ<sub>3</sub>-O)(μ<sub>3</sub>-Cl)(μ-ONp)<sub>3</sub>(ONp)<sub>6</sub>·C<sub>7</sub>H<sub>8</sub>, **1**.** A Schlenk flask charged with NaONp (5.24 g, 47.6 mmol) and toluene (50 mL) was cooled to 0 °C in an ice bath. TiCl<sub>4</sub> (2.26 g, 11.9 mmol) was added slowly to this mixture via a syringe, whereupon the solution immediately turned orange, followed by the formation of a white precipitate. The reaction mixture was stirred for several hours, as the ice bath was allowed to warm to room temperature and then warmed (~100 °C) for 5 min. After being cooled to room temperature, all of the volatile material was removed *in vacuo* (without heating for 12 h), resulting in an off-white powder. The powder was washed with hexanes and extracted with toluene. The solvent was drastically reduced and after several days at glovebox temperature, crystals were isolated. One of these crystals proved to be **1**. A high-yield synthesis of this material has not been determined to date.

**Table 1.** Crystallographic Collection Data for Ti<sub>3</sub>(O)(Cl)(ONp)<sub>9</sub>, **1**, and [Ti(ONp)<sub>4</sub>]<sub>2</sub>, **2**

	<b>1</b>	<b>2</b>
chem formula	C <sub>52</sub> H <sub>107</sub> ClO <sub>10</sub> Ti <sub>3</sub>	C <sub>40</sub> H <sub>88</sub> O <sub>8</sub> Ti <sub>2</sub>
fw	1071.53	792.90
temp (K)	158	188
space group	Pn, monoclinic	P $\bar{1}$ , triclinic
<i>a</i> (Å)	15.252(5)	11.608(3)
<i>b</i> (Å)	13.471(4)	12.308(7)
<i>c</i> (Å)	15.429 (5)	19.752(4)
α (deg)		83.36
β (deg)	97.42	76.34
γ (deg)		62.14
<i>V</i> (Å <sup>3</sup> )	3144(2)	2424(2)
<i>Z</i>	2	2
λ(Mo Kα radiation) (Å)	0.710 73	0.710 69
<i>D</i> <sub>calcd</sub> (Mg/m <sup>3</sup> )	1.132	1.086
μ(Mo, Kα) (mm <sup>-1</sup> )	0.461	0.371
R1 <sup>a</sup> (%)	7.61 <sup>b</sup>	7.56 <sup>c</sup>
R1 <sup>a</sup> (all data) (%)	11.54 <sup>b</sup>	16.29 <sup>c</sup>
wR2 <sup>d</sup> (%)	19.04 <sup>e</sup>	14.16 <sup>f</sup>
wR2 <sup>d</sup> (all data)	22.11 <sup>e</sup>	18.27 <sup>f</sup>

<sup>a</sup> R1 = Σ|F<sub>o</sub> - |F<sub>c</sub>||/Σ|F<sub>o</sub>|. <sup>b</sup> [I > 2σ(I)]. <sup>c</sup> 3372F<sub>o</sub>[F<sub>o</sub> > 4σ(F<sub>o</sub>)]. <sup>d</sup> wR2 = [Σ{w(F<sub>o</sub><sup>2</sup> - F<sub>c</sub><sup>2</sup>)<sup>2</sup>}/Σ{w(F<sub>o</sub><sup>2</sup>)<sup>2</sup>}]<sup>1/2</sup>. <sup>e</sup> w = 1/[σ<sup>2</sup>(F<sub>o</sub><sup>2</sup>) + (0.1204P)<sup>2</sup> + 6.1386P]. <sup>f</sup> w = 1/[σ<sup>2</sup>(F<sub>o</sub><sup>2</sup>) + (0.0548P)<sup>2</sup> + 3.897P].

**[Ti(μ-ONp)(ONp)<sub>3</sub>]<sub>2</sub>, **2**. Method A.** To a mixture of Ti(OPr<sup>i</sup>)<sub>4</sub> (20.0 g, 70.4 mmol) and toluene (250 mL) in a Schlenk flask was added HONp (27.8 g, 316 mmol) via a funnel. The reaction mixture was stirred for 12 h in an oil bath at 50–60 °C, after which the volatile material was removed *in vacuo*, followed by extraction with toluene. The resultant solution was cooled to –35 °C which yielded crystals of **2**. Crystalline yield: 72.0% (20.0 g). FT-IR (KBr, cm<sup>-1</sup>): 2954 (s), 2908 (m), 2868 (s), 2841 (m), 2693 (w), 1481 (s), 1464 (m), 1394 (s), 1361 (s), 1296 (w), 1261 (w), 1217 (w), 1125 (s), 1070 (s), 1041 (m), 1021 (s), 937 (w), 804 (w), 752 (w), 704 (s), 679 (s), 608 (w), 570 (w), 521 (m), 484 (m). <sup>1</sup>H NMR (400.1 MHz, C<sub>7</sub>D<sub>8</sub>): δ 4.01 (s, 2H, OCH<sub>2</sub>CMe<sub>3</sub>), 0.97 (s, 9H, OCH<sub>2</sub>CMe<sub>3</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (100.6 MHz, C<sub>7</sub>D<sub>8</sub>): δ 86.0 (OCH<sub>2</sub>CMe<sub>3</sub>), 33.8 (OCH<sub>2</sub>CMe<sub>3</sub>), 26.1 (OCH<sub>2</sub>CMe<sub>3</sub>). <sup>17</sup>O NMR (54.3 MHz, toluene-*d*<sub>8</sub>): δ 253.9. <sup>47,49</sup>Ti NMR (22.6, toluene-*d*<sub>8</sub>): –865 (<sup>47</sup>Ti), –1133 (<sup>49</sup>Ti).

**Method B.** HONp (0.29 g, 3.30 mmol) was added to a stirring mixture of Ti(N(SiMe<sub>3</sub>)<sub>2</sub>)<sub>4</sub> (0.50 g, 0.73 mmol) and toluene (5 mL) in a vial. The reaction mixture stirred for 12 h at ambient temperature during which the initial red color faded to pale green. The volatile material was removed by rotary evaporation, resulting in a pale green powder. Extraction with hexanes, followed by rotary evaporation, and sublimation at 80 °C at 10<sup>-3</sup> Torr yielded a clear crystalline material. Crystalline yield: 28% (0.080 g). The analytical data of the crystals were consistent with that of **2**.

**X-ray Collection, Structure Determination, and Refinement.** **Ti<sub>3</sub>(μ<sub>3</sub>-O)(μ<sub>3</sub>-Cl)(μ-OCH<sub>2</sub>CMe<sub>3</sub>)<sub>3</sub>(OCH<sub>2</sub>CMe<sub>3</sub>)<sub>6</sub>·C<sub>7</sub>H<sub>8</sub>, **1**.** A colorless crystal was oil-mounted on a glass fiber and transferred to the Siemens P4 rotating-anode diffractometer. The determination of Laue symmetry, crystal class, unit cell parameters, and the crystal's orientation matrix were carried out according to standard procedures.<sup>19</sup> The raw data were processed with a local version of CARESS<sup>20</sup> which employs a modified version of the Lehman–Larsen algorithm to obtain intensities and standard deviation from the measured 96-step peak profiles. All 5752 data were corrected for Lorentz and polarization effects and were placed on an approximately absolute scale. The diffraction symmetry was 2/*m* with the systematic absence *h*0*l* for *h* + *l* = 2*n* + 1. Of the two possible monoclinic space groups (*Pn* and *P2*/*n*), the noncentrosymmetric space group *Pn* was found to be correct by successful refinement of the model. Data collection parameters are given in Table 1.

(19) XSCANS Software Users Guide, Version 2.1; Siemens Industrial Automation, Inc.: Madison, WI, 1994.

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All calculations were carried out using the SHELXL program.<sup>21</sup> The analytical scattering factors for neutral atoms were used throughout the analysis.<sup>22</sup> The structure was solved by direct methods and refined on  $F^2$  by full-matrix least-squares techniques. Hydrogen atoms were included using a riding model. There is one molecule of toluene present per formula unit. Carbon atom C(36) is disordered and was included in the refinement with two components, C(36A) and C(36B), each with site occupancy = 0.50. At convergence,  $wR2 = 0.2211$  and  $GOF = 1.023$  for 524 variables refined against all 5686 unique data. As a comparison for refinement on  $F$ ,  $RI = 0.0761$  for those 3972 data with  $F > 4.0\sigma(F)$ .

The esd's of distances and angles involving the ONp ligands are larger than expected. This is most likely due to the fact that these groups can be quite fluctional even in the crystalline state at low temperatures (158 K data collection). The group defined by atoms O(9)–C(40) is disordered. It is possible that the high thermal parameters observed for some of the other ONp ligands arise from disorder as well. Suitable disordered models for these groups could not be determined, and full anisotropic refinement of these ligands was not possible. Since better quality crystals of compound **1** were not available, this refinement is the best that can be expected with the current diffraction data.

**[Ti( $\mu$ -OCH<sub>2</sub>CMe<sub>3</sub>)(OCH<sub>2</sub>CMe<sub>3</sub>)<sub>3</sub>]<sub>2</sub>, **2**.** From a pool of mineral oil bathed in argon, a colorless, rectangular crystal was mounted onto a thin glass fiber using silicone grease and placed under a liquid-N<sub>2</sub> stream on a Siemens P4/PC diffractometer. The lattice parameters were optimized from a least-squares calculation on 25 carefully centered reflections of high Bragg angle. Three check reflections monitored every 97 reflections showed no systematic variation of intensities. Lattice determination and data collection were carried out using XSCANS Version 2.10b software. All data reduction, including Lorentz and polarization corrections and structure solution and graphics, were performed using SHELXTL PC Version 4.2/360 software. The structure refinement was performed using SHELXL-93 software.<sup>21</sup> The data were not corrected for absorption due to the low absorption coefficient (3.71 cm<sup>-1</sup>). Data collection parameters are given in Table 1.

The structure was solved in space group  $P\bar{1}$  using direct methods. This solution yielded the titanium and oxygen atom positions. Subsequent synthesis gave the carbon positions. The hydrogen atoms were fixed in positions of ideal geometry, with a C–H distance of 0.97 Å for ethyl hydrogens and 0.96 Å for methyl 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 (ethyl) 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  $R1 = 0.0756$  and  $R2_w = 0.1416$ .

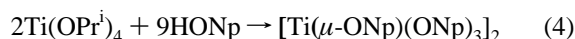
## Results and Discussion

**Synthesis.** Several routes were undertaken to generate “Ti(ONp)<sub>4</sub>”: alkali metal metathesis (eq 1), alcoholysis exchange (eq 2), and alcohol–amide substitution (eq 3).<sup>1–5</sup>

The first experiment attempted was an exchange between TiCl<sub>4</sub> and NaONp at 0 °C in toluene which yielded an orange solution with a white precipitate. Removal of the solvent, followed by extraction of the resultant powder with toluene and subsequent cooling, yielded a crystal of Ti<sub>3</sub>( $\mu_3$ -O)( $\mu_3$ -Cl)( $\mu$ -ONp)<sub>3</sub>(ONp)<sub>6</sub>·C<sub>7</sub>H<sub>8</sub>, **1**. Analysis of the bulk sample by <sup>1</sup>H and FT-IR spectroscopy indicated that more than one product had been formed. Halide retention and/or alkali metal incorporation is not uncommon in the synthesis of other early transition metal

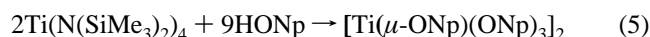
alkoxide systems.<sup>23–27</sup> Due to the complex product mixture generated by eq 1 and the potential for an undesired halide contamination, an alternative method was sought for the synthesis of “Ti(ONp)<sub>4</sub>”. A high-yield synthesis to **1** has yet to be determined, and further characterization was not pursued.

An alcoholysis exchange reaction was undertaken by mixing Ti(OPr<sup>*i*</sup>)<sub>4</sub> with an excess of HONp (eq 4). This solution was



warmed at ~60 °C overnight to ensure complete exchange. Crystals of [Ti( $\mu$ -ONp)(ONp)<sub>3</sub>]<sub>2</sub>, **2**, were easily isolated from cooled solutions of hexanes or toluene. Compound **2** is very soluble in hexanes, toluene, or chloroform at concentrations > 2.5 M; the maximum concentration in these solvents was not determined. **2** is frequently isolated with small contaminant of Ti(OPr<sup>*i*</sup>)<sub>4</sub> which can be significantly reduced by washing with cold hexanes, successive crystallizations, or through sublimation (<100 °C at 10<sup>-3</sup> Torr). TGA/DTA data shows that independent of the atmosphere (oxygen or argon), the material completely volatilized before pyrolysis of the organic moieties could be initiated, at ~150 °C. This indicates that **2** is less susceptible to hydrolysis than Ti(OPr<sup>*i*</sup>)<sub>4</sub> (thermal data are readily obtained on Ti(OPr<sup>*i*</sup>)<sub>4</sub> since it is rapidly oligomerized due to hydrolysis by ambient humidity).<sup>18</sup> The high volatility and low melting point of **2** make it an ideal candidate for MOCVD applications.

An alternative route which avoids any Ti(OPr<sup>*i*</sup>)<sub>4</sub> contamination was also undertaken to generate **2**. A reaction between a titanium amide [Ti(N(SiMe<sub>3</sub>)<sub>2</sub>)<sub>4</sub>] and HONp (eq 5) in toluene



was stirred for 12 h. The initial red solution turned pale green over this time frame. After removal of all volatile material, extraction with hexanes, and sublimation, crystalline material were isolated. The analytical data obtained on these crystals was consistent with that previously collected for **2**. However, the synthetic route of eq 5 is more complex and produces significantly more products (hence, reduced yield of **2**) in comparison to eq 4. Therefore, studies of the solution behavior of **2** were pursued with materials generated by the alcohol metathesis (eq 4) route.

**Solid State.** Both **1** and **2** were crystallographically characterized, and the collection data are summarized in Table 1. Tables 2 and 3 list the positional parameters of selected atoms for **1** and **2**, respectively. Table 4 lists selected bond distances and angles for **1** and **2**. Figures 1 and 2 show thermal ellipsoid plots of **1** and **2**, respectively.

**Ti<sub>3</sub>(Cl)(O)(ONp)<sub>9</sub>, **1**.** The structure of **1** is another member of the well-known M<sub>3</sub>( $\mu_3$ -X)<sub>2</sub>( $\mu$ -X)<sub>3</sub>X<sub>6</sub> class of compounds.<sup>23–30</sup> The basic trimetallic framework of **1** is consistent with other well-characterized compounds, including U<sub>3</sub>(OBu<sup>*t*</sup>)<sub>10</sub>O,<sup>28</sup> Mo-(OPr<sup>*i*</sup>)<sub>10</sub>O,<sup>29,30</sup> and lanthanide OBU<sup>*t*</sup> complexes M<sub>3</sub>(OR)<sub>8</sub>(X)(S)<sub>2</sub> (M = Y or La; X = Br, Cl; S = solvent).<sup>23–27</sup> For **1**, there is

- (21) (a) Sheldrick, G. M.; Program for Crystal Structure Refinement, Univ. of Gottingen, Germany, 1993. (b) Sheldrick, G. M. Siemens Analytical X-ray Instruments, Inc., 1994. (c) The SAME instruction restrains the bonds of the listed atoms to be the same length (with an esd) as those of the model atoms.  
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**Table 2.** Select Atomic Coordinates ( $\times 10^4$ ) and Equivalent Isotropic Displacement Parameters ( $\text{\AA}^2 \times 10^3$ ) for  $\text{Ti}_3(\text{O})(\text{Cl})(\text{ONp})_9$ , **1**

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{eq}}^a$
Ti(1)	1870(1)	8178(1)	5(1)	29(1)
Ti(2)	1358(1)	6010(1)	-296(1)	30(1)
Ti(3)	2149(1)	7161(1)	-1699(1)	29(1)
Cl(1)	493(2)	7549(2)	-1268(2)	31(1)
O(1)	1256(5)	7096(5)	607(5)	30(2)
O(2)	1631(5)	5796(5)	-1548(4)	30(2)
O(3)	2267(5)	8551(5)	-1159(4)	27(2)
O(4)	2285(4)	6948(5)	-452(5)	26(2)
O(5)	2794(5)	8527(6)	774(5)	37(2)
O(6)	1143(5)	9192(5)	128(4)	33(2)
O(7)	1986(5)	5065(5)	299(5)	39(2)
O(8)	274(5)	5482(6)	-381(5)	37(2)
O(9)	3247(5)	6850(7)	-1898(6)	47(2)
O(10)	1668(5)	7481(5)	-2791(5)	34(2)

<sup>a</sup>  $U_{\text{eq}}$  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 ( $\text{\AA}^2 \times 10^3$ ) for  $[\text{Ti}(\text{ONp})_4]_2$ , **2**

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{eq}}^a$
Ti(1)	51(1)	4861(1)	2269(1)	30(1)
Ti(2)	-2238(1)	7663(1)	2255(1)	30(1)
O(1)	-1800(4)	5999(3)	1996(2)	28(1)
O(2)	-154(4)	6529(4)	2056(2)	30(1)
O(3)	-800(5)	4257(4)	2960(2)	48(1)
O(4)	1450(5)	4502(4)	2661(2)	45(1)
O(5)	772(4)	3786(4)	1576(2)	40(1)
O(6)	-2081(5)	8207(5)	3014(3)	53(2)
O(7)	-3968(4)	8012(4)	2538(2)	44(1)
O(8)	-2257(5)	8757(4)	1583(2)	44(1)

<sup>a</sup>  $U_{\text{eq}}$  is defined as one third of the trace of the orthogonalized  $U_{ij}$  tensor.

no solvent coordination as observed for the lanthanide compounds; however, toluene is found in the unit cell as a cocrystallized species. The three titanium metal centers of **1** each possess an octahedral geometry linked together by bridging ONp ligands. Triply bridging chloride and oxygen atoms cap on opposite sides of the planar arrangement of titanium atoms. The final coordination sites for each metal are filled by two terminal ONp ligands. Titanium complexes containing  $\mu_3$ -O are ubiquitous in the literature,<sup>16-18,31-51</sup> however, species containing a  $\mu_3$ -Cl are surprisingly sparse.<sup>51-54</sup> Therefore, a

titanium complex containing both atoms is quite rare. In fact, the only complexes reported that contain both  $\mu_3$ -Cl and  $\mu_3$ -O are the Ti(III)/Ti(IV) complexes,  $(\eta^5\text{-C}_5\text{Me}_5)_6\text{Ti}_6(\mu_3\text{-Cl})_4(\mu_3\text{-O})_6$  and  $(\eta^5\text{-C}_5\text{H}_5)_6\text{Ti}_6(\mu_3\text{-Cl})_2(\mu_3\text{-O})_4\text{C}_7\text{H}_8$ .<sup>51</sup> However, in these compounds the  $\mu_3$ -atoms do not bridge between the same three metals (cap) as observed for **1**. Interestingly, this is the first structural report of a group IV compound that adopts this  $\text{M}_3(\mu_3\text{-X})_2(\mu\text{-X})_3\text{X}_6$  structure type.

As Table 4 shows, there is a relatively small range of bond distances and angles for the various ONp ligands of **1**. This is due to the symmetrical constraints induced by the two capping ligands. The average Ti-ONp, Ti-( $\mu$ -ONp), and Ti---Ti distances of 1.78, 2.03, and 3.04  $\text{\AA}$ , respectively, fall within the ranges reported for other Ti alkoxides.<sup>16-18,31-51</sup> The Ti-( $\mu_3$ -Cl) distances of **1** (average 2.78  $\text{\AA}$ ) is the longest observed, 2.470(5)–2.684(2)  $\text{\AA}$ ,<sup>51-54</sup> whereas the Ti-( $\mu_3$ -O) distance of 1.93  $\text{\AA}$  (average) is one of the shortest distances reported for  $\mu_3$ -oxo ligands, 1.962(4)–2.088(8)  $\text{\AA}$ .<sup>16-18,31-51</sup> The angles adopted around the various metal centers of **1** are consistent with a slightly distorted octahedral geometry. The Ti-( $\mu_3$ -OR)-Ti angle of 103.6° is consistent with other  $\mu_3$ -O ligated compounds.<sup>31,49,51</sup> The Ti-( $\mu$ -OR)-Ti angles of 96.6° (average) and the Ti-( $\mu_3$ -Cl)-Ti angles of 66.2° (average) are the smallest angles reported for titanium alkoxides which range from 104 to 112° and 73.7(1) to 114.3(1)°, respectively.<sup>16,18,55,56</sup>

**[Ti( $\mu$ -ONp)(ONp)<sub>3</sub>]<sub>2</sub>, 2.** Compound **2** adopts a typical  $\text{M}_2(\mu\text{-X})_2(\text{X})_6$  fused axial-equatorial edge-shared structure which has been observed for a wide range of other metal alkoxides.<sup>57</sup> **2** possesses only 5-coordinated metal centers (reports of 5-coordinated titanium alkoxides are becoming more abundant).<sup>55</sup> Other homo- and heteroalkoxide titanium species, which had been previously characterized, adopted multinuclear geometries (> 3 Ti).<sup>16-18</sup> It is unusual that even with the excess alcohol in solution **2** does not adopt an octahedral geometry by coordination of free alcohol as was noted for the aryloxide derivative,  $[\text{Ti}(\mu\text{-OPh})(\text{OPh})_3\text{HOPh}]_2$ ,<sup>58</sup> where OPh =  $\text{OC}_6\text{H}_5$ , or the group IV congener,  $[\text{Zr}(\mu\text{-OPr}^i)(\text{OPr}^i)_3\text{HOPr}^i]_2$ .<sup>59</sup> For a five-coordinated metal center there are two possible geometries, trigonal bipyramidal (TBP) and square pyramidal (SP).<sup>15</sup> The titaniums can be said to adopt an extremely distorted TBP geometry with the O(4)-Ti(1)-O(1) (155.4(2)°) and O(7)-Ti(2)-O(2) (156.1(2)°) significantly deviated from the idealized 180° angle. The Ti-( $\mu$ -OR)-Ti distance (average 104.7°) of **2** is substantially shorter than the angle of 112(1)° for [Ti-

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**Table 4.** Select Bond Distances (Å) and Angles (deg) for  $Ti_5(O)(Cl)(ONp)_9$ , **1**, and  $[Ti(ONp)_4]_2$ , **2**

Distances (Å)					
		<b>1</b>		<b>2</b>	
Ti---Ti	Ti(1)---Ti(2)	3.044(3)	Ti(1)---Ti(2)	3.225(2)	
	Ti(1)---Ti(3)	3.042(3)			
	Ti(2)---Ti(3)	3.037(3)			
Ti-(OR) <sup>a</sup>	Ti(1)-O(5)	1.783(7)	Ti(1)-O(3)	1.790(5)	
	Ti(1)-O(6)	1.786(7)	Ti(1)-O(4)	1.811(5)	
	Ti(2)-O(7)	1.776(7)	Ti(1)-O(5)	1.780(4)	
	Ti(2)-O(8)	1.788(8)	Ti(2)-O(6)	1.789(5)	
	Ti(3)-O(9)	1.792(8)	Ti(2)-O(7)	1.803(5)	
	Ti(3)-O(10)	1.802(7)	Ti(2)-O(8)	1.775(5)	
Ti-(μ-OR)	Ti(1)-O(1)	2.023(7)	Ti(1)-O(1)	2.104(4)	
	Ti(1)-O(3)	2.030(7)	Ti(1)-O(2)	1.960(4)	
	Ti(2)-O(1)	2.010(7)	Ti(2)-O(1)	1.965(4)	
	Ti(2)-O(2)	2.048(7)	Ti(2)-O(2)	2.116(4)	
	Ti(3)-O(2)	2.027(7)			
	Ti(3)-O(3)	2.048(7)			
Ti-(μ <sub>3</sub> -O)	Ti(1)-O(4)	1.939(7)			
	Ti(2)-O(4)	1.935(7)			
	Ti(3)-O(4)	1.929(7)			
Ti-(μ <sub>3</sub> -Cl)	Ti(1)-Cl(1)	2.815(3)			
	Ti(2)-Cl(1)	2.788(3)			
	Ti(3)-Cl(1)	2.744(3)			
Angles (deg)					
		<b>1</b>		<b>2</b>	
Ti-(μ-OR)-Ti	Ti(1)-O(1)-Ti(2)	96.4(3)	Ti(1)-O(1)-Ti(2)	104.8(2)	
	Ti(1)-O(3)-Ti(3)	96.5(3)	Ti(1)-O(2)-Ti(2)	104.6(2)	
	Ti(2)-O(2)-Ti(3)	97.0(3)			
Ti-(μ <sub>3</sub> -O)-Ti	Ti(1)-O(4)-Ti(2)	103.6(3)			
	Ti(1)-O(4)-Ti(3)	103.7(3)			
	Ti(2)-O(4)-Ti(3)	103.6(3)			
Ti-(μ <sub>3</sub> -Cl)-Ti	Ti(1)-Cl(1)-Ti(2)	65.81(8)			
	Ti(1)-Cl(1)-Ti(3)	66.35(8)			
	Ti(2)-Cl(1)-Ti(3)	66.58(8)			
RO-Ti-OR	O(5)-Ti(1)-O(6)	100.1(4)	O(3)-Ti(1)-O(4)	96.6(2)	
	O(7)-Ti(2)-O(8)	100.7(4)	O(3)-Ti(1)-O(5)	106.3(2)	
	O(9)-Ti(3)-O(10)	99.9(4)	O(4)-Ti(1)-O(5)	102.8(2)	
(μ-OR)-Ti-OR	O(1)-Ti(1)-O(5)	104.9(3)	O(1)-Ti(1)-O(3)	87.8(2)	
	O(3)-Ti(1)-O(6)	99.5(3)	O(1)-Ti(1)-O(4)	155.4(2)	
	O(1)-Ti(2)-O(7)	104.2(3)	O(1)-Ti(1)-O(5)	99.1(2)	
	O(2)-Ti(2)-O(8)	100.0(3)	O(2)-Ti(1)-O(3)	132.0(2)	
	O(2)-Ti(3)-O(9)	101.3(4)	O(2)-Ti(1)-O(4)	90.2(2)	
	O(3)-Ti(3)-O(10)	99.5(3)	O(2)-Ti(1)-O(5)	118.4(2)	
(μ-OR)-Ti-(μ-OR)	O(1)-Ti(1)-O(3)	142.5(3)	O(1)-Ti(1)-O(2)	69.5(2)	
	O(1)-Ti(2)-O(2)	141.9(3)	O(1)-Ti(2)-O(2)	69.2(2)	
	O(2)-Ti(3)-O(3)	142.9(3)			
(μ <sub>3</sub> -Cl)-Ti-O	Cl(1)-Ti(1)-O(5)	176.1(3)			
	Cl(1)-Ti(2)-O(7)	175.6(3)			
	Cl(1)-Ti(3)-O(9)	175.3(3)			

<sup>a</sup> R = CH<sub>2</sub>CMe<sub>3</sub>.

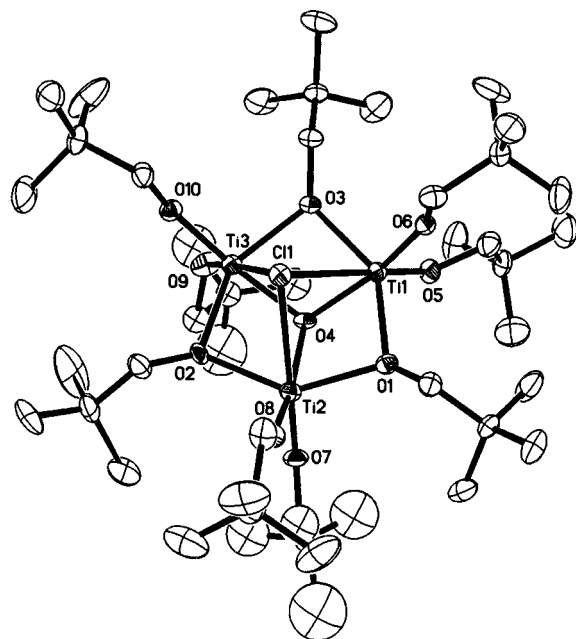
(OMe)<sub>4</sub>]<sub>4</sub>.<sup>16</sup> It is of note that compound **2** is the lowest nuclearity that a homoleptic alkoxy titanium complex has been shown to adopt in the solid state,<sup>16,17</sup> which helps to explain the high solubility and volatility previously noted.

Once again, all the bond lengths and angles for **2** are within literature reported values and follow standard trends, wherein, bond lengths increase with increased binding (Ti-OR, 1.79 Å (average), < Ti-(μ-OR), 2.04 Å (average)).<sup>18</sup> The center Ti<sub>2</sub>O<sub>2</sub> unit is asymmetrically bound with Ti-O distances of the axial oxygen [Ti(1)-O(1) and Ti(2)-O(2)] being ~0.15 Å longer than the equatorial atoms [Ti(1)-O(2) and Ti(2)-O(1)]. These distances, along with the five coordination of the metal centers, which are separated by 3.23 Å (average), are in agreement with those characteristics of Ti(OPr<sup>i</sup>)<sub>4</sub> inferred by Sanchez et al.<sup>13</sup> and other literature values.<sup>16,18,56</sup> For comparison the Ti-Ti distance of the (THMR)<sub>2</sub>Ti<sub>4</sub>(OPr<sup>i</sup>)<sub>10</sub> compounds range from 3.319(1) to 3.337(1) Å (R = E (tris(hydroxymethyl)ethane) and P (tris(hydroxymethyl)propane)) and [Ti(OMe)<sub>4</sub>]<sub>4</sub> has metal-

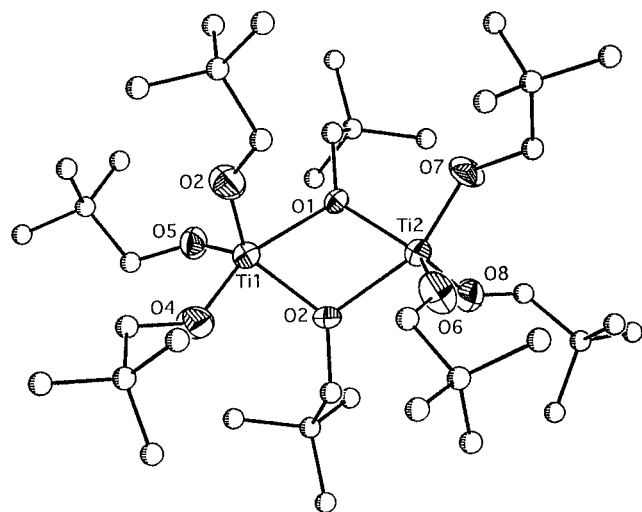
metal distances of 3.351-3.353 Å.<sup>16,18,55</sup> The five-coordinate geometry leaves both titanium metal centers coordinately unsaturated. Molecular weight and NMR studies were undertaken to elucidate solution characteristics of **2**.

**Solution State.** On the basis of the reduced nuclearity of **2** in the solid state, it was assumed **2** would either remain a dinuclear species in solution or be cleaved to form a monomer. We undertook several experiments using molecular weight determinations and NMR studies to verify solution nuclearity. Trace amounts of Ti(OPr<sup>i</sup>)<sub>4</sub> for single crystallized samples of **2** were observed in solution at lower temperatures (see Supporting Information for spectra); therefore, all samples of **2** were crystallized 3 times before analyses were undertaken. Investigation of this ultrapurified material showed no Ti(OPr<sup>i</sup>)<sub>4</sub>.

**Molecular Weight.** Isopiestic molecular weight studies (Signer method)<sup>60</sup> indicate that **2** exists as a monomer in solution



**Figure 1.** Thermal ellipsoid plot of  $\text{Ti}_3(\mu_3\text{-O})(\mu_3\text{-Cl})(\mu\text{-OCH}_2\text{-CMe}_3)_3(\text{OCH}_2\text{CMe}_3)_6$ , **1**. Ellipsoids are shown at the 50% level. Toluene is omitted for clarity.



**Figure 2.** Thermal ellipsoid plot of  $[\text{Ti}(\mu\text{-OCH}_2\text{CMe}_3)(\text{OCH}_2\text{CMe}_3)_2]_2$ , **2**. Ellipsoids are shown at the 50% level. Carbon atoms are drawn as ball and stick atoms for clarity.

( $375 \pm 38$  in  $\text{CHCl}_3$  or  $346 \pm 35$  in toluene).<sup>61</sup> Early molecular weight determinations reported by Bradley on “ $\text{Ti}(\text{ONp})_4$ ” reported that the complex was roughly monomeric in solution (a 1.3 degree of aggregation in benzene for “ $\text{Ti}(\text{ONp})_4$ ”).<sup>1,62</sup> The potential equilibrium Bradley reported for the assumed “ $\text{Ti}(\text{ONp})_4$ ” complex was not observed in analyses of **2**.<sup>63</sup> A monomer in solution explains the “simple”  $^1\text{H}$ ,  $^{13}\text{C}$ ,  $^{17}\text{O}$ , and  $^{47,49}\text{Ti}$  NMR signals observed (*vide infra*) for **2** and would be consistent with the reported XANES and EXAFS results reported by Sanchez *et al.* for longer, highly branched alkoxides [ $\text{OR} = \text{OPr}^i$ ,  $\text{OBu}^t$ ,  $\text{OAm}^t$  (*tert*-amyl oxide)].<sup>13</sup> The disruption of the asymmetrically bound dinuclear complex of **2** to form a

(61) The solid-state molecular weight of **2** is 792.90. Molecular weight determinations in toluene (0.1 M solutions) yielded a molecular weight of  $346 \pm 35$ . An identical determination in  $\text{CDCl}_3$  yielded a value of  $375 \pm 38$ . This is approximately  $1/2$  the solid-state molecular weight (396.45) and indicates a monomer exists in solution at these concentrations.

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**Table 5.** NMR Data for (a)  $\text{Ti}(\text{OEt})_4$ , (b)  $\text{Ti}(\text{OPr}^i)_4$ , and (c)  $[\text{Ti}(\mu\text{-ONp})(\text{ONp})_3]_2$ , **2**

compd	$\delta(^1\text{H})$ (Hz)	$\delta(^{17}\text{O})$ (Hz)	$^{47,49}\text{Ti}$		ref
			$\delta$ (Hz)	hwp <sup>d</sup> (Hz)	
$\text{Ti}(\text{OEt})_4^a$		251	-858	4200	65
$\text{Ti}(\text{OPr}^i)_4^a$			-854	180	13,65,76,77
			-1120	720	
$\text{Ti}(\text{OPr}^i)_4^b$	4.48 (sept)	295	-863	76.0	c
	1.24(d)		-1128	174	
<b>2</b> <sup>b</sup>	4.01 (s)	254	-865	81.5	c
	0.97 (s)		-1133	212	

<sup>a</sup> Neat. <sup>b</sup> Toluene-*d*<sub>8</sub>. <sup>c</sup> This work. <sup>d</sup> hpw = half-height peak width.

tetrahedrally bound monomer is easily envisioned from the asymmetrical core of the solid-state structure noted previously.

**$^1\text{H}$  and  $^{13}\text{C}$  NMR.** The solution  $^1\text{H}$  NMR ( $\text{CDCl}_3$  or  $\text{C}_7\text{D}_8$ ) of **2** is quite simple with only two resonances present, representative of the methylene and methyl resonances for the ONp ligand (see Table 5). For the  $^{13}\text{C}\{^1\text{H}\}$  spectrum there are three singlets, representative of the quaternary, methylene, and methyl carbon resonances. These spectra are consistent with a mononuclear compound or a species that is exhibiting rapid, dynamic exchange between bridging and terminal ONp ligands.

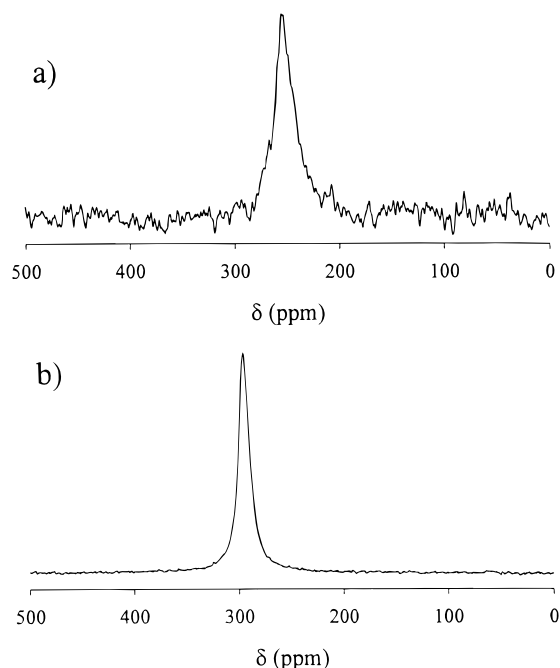
To further elucidate the solution behavior of **2**, variable-temperature NMR studies were initiated. At high temperatures there is no change in the observed spectra. At low temperatures, **2** preferentially crystallizes out of solution with no observed decoalescence of the initial peaks. Unfortunately, the reduced solubility of **2** at lower temperatures does not allow for a differentiation between the dinuclear species or rapid exchange. In an effort to further determine solution behavior, a number of alternative nuclei were investigated.

**$^{17}\text{O}$  NMR.** Studies involving  $^{17}\text{O}$  NMR nuclei typically benefit from enriched samples due to the low natural abundance; however, the high solubility of **2** allowed us to make a sufficiently concentrated sample so that we could obtain a  $^{17}\text{O}$  signal quickly (32 K scans). The resultant spectrum has a resonance at  $\delta$  254 with a line width of 1260 Hz. This spectra is similar to that observed for  $\text{Ti}(\text{OPr}^i)_4$  and  $\text{Ti}(\text{OEt})_4$  which had resonances at  $\delta$  295 and 251, respectively.<sup>13</sup> Figure 3a,b shows the  $^{17}\text{O}$  NMR spectra of **2** and  $\text{Ti}(\text{OPr}^i)_4$ ,<sup>64</sup> respectively, in toluene-*d*<sub>8</sub>, with metrics listed in Table 5. Once again the single peak can be accounted for by either a monomer in solution or a rapid exchange between  $\mu$ - and terminal ONp ligands of a dinuclear complex. The lack of a  $^1\text{H}$ ,  $^{13}\text{C}$ , and  $^{17}\text{O}$  resonance for  $\text{Ti}(\text{OPr}^i)_4$  in the spectra of **2** is significant in realizing that there is little contamination present in these samples of **2**.

**$^{47,49}\text{Ti}$  NMR.** The ability to perform  $^{47,49}\text{Ti}$  NMR reportedly requires compounds with a high degree of symmetry around the metal center so that large-field gradients which yield broad resonances are reduced.  $^{47,49}\text{Ti}$  NMR resonances have only been reported for tetrahedral and octahedral compounds with cyclo-

(63) The differences in solution molecular weight determinations may be explained by the synthetic route Bradley used for production of “ $\text{Ti}(\text{ONp})_4$ ”, wherein a  $\text{Ti}(\text{OR})_4$  was reacted with 4 equiv of HONp for 1 h at benzene reflux temperatures. This time frame may not be sufficient to completely exchange all of the OR groups with ONp ligands. A mixed ligated Ti species is more likely to undergo an equilibrium between mononuclear and dinuclear species due to the reduced steric bulk; thus, a higher molecularity would be recorded. We have observed a lack of complete exchange between  $\text{Nb}(\text{OEt})_5$  for HONp at elevated temperatures for extended times, yielding only  $[\text{Nb}(\mu\text{-OEt})(\text{ONp})_4]_2$  (manuscript in preparation).

(64)  $\text{Ti}(\text{OPr}^i)_4$  was prepared by the repeated mixing and vacuum distillation of  $\text{Ti}(\text{OPr}^i)_4$  and a 1:1 mixture of (20%)  $\text{H}^{17}\text{OPr}^i/\text{HOPr}^i$ .

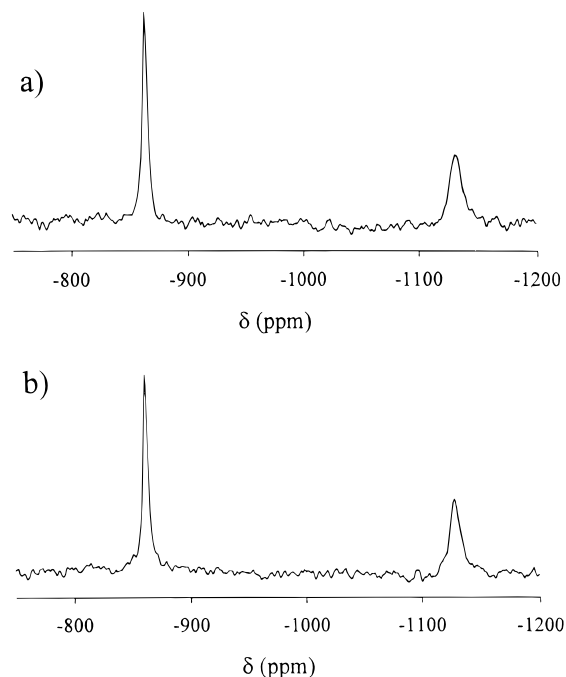


**Figure 3.**  $^{17}\text{O}$  (natural abundance) NMR spectrum (toluene- $d_8$ ) of (a)  $[\text{Ti}(\mu\text{-OCH}_2\text{CMe}_3)(\text{OCH}_2\text{CMe}_3)_3]_2$ , **2**, and (b)  $\text{Ti}(\text{OPr}^i)_4$ .

pentadienyl halide,<sup>65–71</sup> carbonyl,<sup>72</sup> halide,<sup>65,66,71,73–75</sup> and alkoxide<sup>13,65,76</sup> ligands. It appears that even slightly perturbed octahedrally bound titanium metal centers are not amenable to Ti NMR nuclei studies due to the reduced symmetry of the axial ligands. This explains why most of the  $\text{Ti}(\text{OR})_4$ 's, which are oligomeric in solution with octahedrally bound metal centers, do not show  $^{47,49}\text{Ti}$  NMR signals.

Few titanium alkoxide ligated species have yielded  $^{47,49}\text{Ti}$  NMR signals. One of those that has is the assumed mononuclear  $\text{Ti}(\text{OPr}^i)_4$  species.<sup>13,65,76</sup> It is of note that a  $^{49}\text{Ti}$  NMR signal was observed for (neat)  $\text{Ti}(\text{OEt})_4$ ; however, the peak was extremely broad [h<sub>pw</sub> (half-height peak width) = ~4200 Hz].<sup>65</sup> Observation of this signal was reportedly critically dependent on the use of a transverse probe (transmit/receive coils are orthogonal to the magnetic field).<sup>65</sup> We were unable to observe any signal for a pure sample of  $\text{Ti}(\text{OEt})_4$  through standard methods. Dire and Babonneau report the spectrum of a mixed  $\text{Ti}(\text{OPr}^i)_4/\text{Ti}(\text{OEt})_4$  solution; wherein, the titanium metal center was reportedly 5 coordinated.<sup>76</sup>

**2** possesses five-coordinated metal centers in the solid state. The likelihood that these unsymmetrically ligated metal centers would be accessible for Ti NMR study is remote, based on the majority of literature reports. However, since our solution



**Figure 4.**  $^{47,49}\text{Ti}$  NMR spectrum (toluene- $d_8$ ) of (a)  $[\text{Ti}(\mu\text{-OCH}_2\text{CMe}_3)(\text{OCH}_2\text{CMe}_3)_3]_2$ , **2**, and (b)  $\text{Ti}(\text{OPr}^i)_4$ .

studies indicated that **2** may be mononuclear in solution and a wide variety of titanium compounds have been accessible by this nuclei,  $^{47,49}\text{Ti}$  NMR studies were attempted.

The  $^{47,49}\text{Ti}$  NMR spectrum obtained on crystalline material of **2** redissolved in toluene- $d_8$  is shown in Figure 4a, whereas Figure 4b shows the spectrum obtained on  $\text{Ti}(\text{OPr}^i)_4$  in toluene- $d_8$ . Table 5 presents a listing of the  $^{47,49}\text{Ti}$  NMR data. The sample of **2** used in our study was significantly diluted in comparison to the previously reported  $^{47,49}\text{Ti}$  NMR spectrum of (neat)  $\text{Ti}(\text{OPr}^i)_4$ .<sup>76,77</sup> Solution-state Ti NMR studies of **2** showed resonances in toluene- $d_8$  at  $\delta$  -865  $^{49}\text{Ti}$  (h<sub>pw</sub> = 81.5 Hz) and -1133  $^{47}\text{Ti}$  (212 Hz). Slight shifts are noted for different solvents. In  $\text{CDCl}_3$ , resonances were recorded at -855 ppm for (165 Hz) and -1119 (330 Hz). Not surprisingly, the resonances recorded for **2** are nearly identical to what was reported for (neat)  $\text{Ti}(\text{OPr}^i)_4$  ( $\delta$  -854 and -1120).<sup>13,65,76,77</sup> (compared to our observed values of -863 and -1128 in toluene- $d_8$ ) and (neat)  $\text{Ti}(\text{OEt})_4$  ( $\delta$  -858).<sup>65</sup> Since the  $\alpha$  and  $\beta$  atoms of the OEt, OPr<sup>i</sup>, and ONp ligands are nearly identical, the environments of these compounds around the metal center should be similar yielding a small range of  $^{47,49}\text{Ti}$  NMR signals. It is of note that while these metal centers are similar as evidenced by the similarity of  $^{47,49}\text{Ti}$  NMR shifts, the oxygen environments are significantly varied by the pendant hydrocarbon moiety.

**Further Characterization.** Since the  $^{47,49}\text{Ti}$  NMR resonances of **2** and  $\text{Ti}(\text{OPr}^i)_4$  were so similar, it was necessary to prove we were not merely observing a signal from a trace impurity of  $\text{Ti}(\text{OPr}^i)_4$ . Three experiments were undertaken to accomplish this: (i) an alternative synthesis to eliminate  $\text{Ti}(\text{OPr}^i)_4$ , (ii) signal integration of equimolar NMR samples, and (iii) solid-state NMR investigations.

**Amide Synthesis.** The crystalline product isolated from eq 5 proved to have an identical FT-IR spectrum and  $^1\text{H}$  NMR resonances recorded for **2**. Furthermore, the  $^{47,49}\text{Ti}$  NMR spectrum of this compound was also identical to that of **2**. We were not able to observe a  $^{47,49}\text{Ti}$  signal for  $\text{Ti}(\text{N}(\text{SiMe}_3)_2)_4$ .

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Since there is absolutely no possibility of this signal being from any titanium impurity, both this and the original  $^{47,49}\text{Ti}$  NMR signals recorded must be representative of **2**.

**Signal Integration.** To further verify that the signal observed was not an impurity, signal intensities for equimolar samples of **2** and  $\text{Ti}(\text{OPr}^i)_4$  were compared. First, a  $^{47,49}\text{Ti}$  signal for a sample of **2** (40 mg/0.5 mL;  $\sim 0.20$  M in toluene- $d_8$ ) was obtained (shown in Figure 4a). The integration of the  $^{47}\text{Ti}$  resonance at  $-865$  was set to 1.0, and all following spectra were scaled to this spectrum (i.e., the relative scale was not changed). Next, the signal for a sample of  $\text{Ti}(\text{OPr}^i)_4$  (29  $\mu\text{L}$ /0.5 mL;  $\sim 0.20$  M in toluene- $d_8$ ) at identical concentration was obtained. The integration of this sample (with the sample of **2** being 1.0) was 1.08. Both samples of equal molarity gave the same intensity. Therefore, if the signal observed for the 0.20 M solution of **2** was due to an impurity of  $\text{Ti}(\text{OPr}^i)_4$ , the sample would have had to have  $\sim 30$  mg of  $\text{Ti}(\text{OPr}^i)_4$  (i.e.,  $\sim 75\%$  impurity by weight) since both had the same integral signal intensity. This amount of impurity would be readily observable in the analytical data obtained for **2**, which is not the case.

**Solid-State NMR.** Solid-state spectra of the multicrystallized powder of **2** were obtained for  $^{13}\text{C}$  and  $^{47,49}\text{Ti}$  nuclei.  $^1\text{H}$  and  $^{17}\text{O}$  solid-state NMR spectra were not attempted due to the extremely broad spectra typically recorded and the lack of  $^{17}\text{O}$ -enriched samples available. The  $^{13}\text{C}$  MAS NMR spectra revealed 4 methyl and methylene resonances and over 6 peaks in the quaternary carbon region. The large number of quaternary carbons is indicative of a completely unsymmetrical molecule due to the large distortion of the TBP geometry of **2** in the solid state. The reduced number of methyl and methylene resonances must be due to resonance overlap.

No signal was observed for the solid-state  $^{47,49}\text{Ti}$  spectra of the multicrystallized **2** isolated from eq 4. This strongly suggests that the 5-coordinated metal centers of **2** in the solid state are not readily amenable to  $^{47,49}\text{Ti}$  NMR due to their large quadrupolar moment. The absence of a signal further indicates the lack of any  $\text{Ti}(\text{OPr}^i)_4$  contamination. The observation of a strong, relatively narrow resonance for **2** in solution would also suggest that a tetrahedrally coordinated monomer structure for **2** is likely. Larger oligomers, like  $\text{Ti}(\text{OEt})_4$ , are not amenable to solution  $^{47,49}\text{Ti}$  NMR studies unless special probe setups are utilized.<sup>65</sup>

## Conclusion

Attempts to make a highly solubilized group IV homoalkoxide yielded two unique structure types for titanium compounds:  $\text{Ti}_3(\mu\text{-Cl})(\mu_3\text{-O})(\text{ONp})_3(\text{ONp})_6$ , **1**, and  $[\text{Ti}(\mu\text{-ONp})(\text{ONp})_3]_2$ , **2**. The isolation of **1** extends the family of  $\text{M}_3(\mu_3\text{-X})_2(\mu\text{-X})_3(\text{X})_6$  structural types to include titanium compounds. Compound **2** is an unusual crystallographically characterized titanium alkoxide that is highly soluble and easily volatilized due to its reduced oligomerization.

Compound **2** is the first structurally characterized titanium alkoxide which can be tracked by solution-state  $^{47,49}\text{Ti}$  NMR.<sup>65</sup> The readily obtained solution-state  $^{47,49}\text{Ti}$  NMR signal and molecular weight determination indicate that **2** exists as a monomer in solution. This was further supported by the lack of an observable solid-state  $^{47,49}\text{Ti}$  NMR signal. Compound **2** shows striking solution similarities to the  $\text{Ti}(\text{OPr}^i)_4$  and may be used as a well-characterized alternative to this ubiquitous reagent.

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**Supporting Information Available:** Complete listings of crystal collection data, positional and thermal parameters, and bond distances and angles for **1** and **2** and low-temperature spectra (30 pages). Ordering information is given on any current masthead page.

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