

Titanatranes Derailed: Static and Dynamic Triethanolamine Slippage Induced by Polyphenoxide Chelation<sup>†</sup>

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Aryloxytitanatranes  $[\text{N}(\text{CH}_2\text{CH}_2\text{O})_3\text{Ti}[\text{OC}_6\text{H}_2-2,4\text{-}^i\text{Bu}_2-6\text{-CHPh}_{3-n}(\text{C}_6\text{H}_2-3,5\text{-}^i\text{Bu}_2-2\text{-OH})_{n-1}]]$  (**1**,  $n = 1$ ; **2**,  $n = 2$ ; **3**,  $n = 3$ ) containing aryloxides derived from substituted triphenylmethanes are formed in high yield in the reactions of the corresponding phenols with *tert*-butoxytitanatranes  $[\text{N}(\text{CH}_2\text{CH}_2\text{O})_3\text{Ti}(\text{O}^i\text{Bu})]$ . The aryloxytitanatranes adopt monomeric, trigonal bipyramidal structures, as confirmed by X-ray crystallography for **1** and **2**. The compounds with pendant phenol groups display fluxional behavior due to interchange of the bound phenoxide with the free phenol groups, most likely via a mechanism involving displacement of one arm of the nitrilotriethoxide by the dangling phenol group. The amidotitanatranes  $\{[\text{N}(\text{CH}_2\text{CH}_2\text{O})_3\text{Ti}(\text{NEt}_2)]_2\}$  reacts with the bisphenol  $\text{PhCH}(\text{C}_6\text{H}_2-3,5\text{-}^i\text{Bu}_2-2\text{-OH})_2$  to give a crystallographically characterized fully metalated cyclic octatitanium complex of the formula  $\{\text{PhCH}(\text{C}_6\text{H}_2-3,5\text{-}^i\text{Bu}_2-2\text{-O})_2\text{Ti}_2[(\text{OCH}_2\text{CH}_2)_3\text{N}]_2\}_4$  (**4**). The structure of **4** reveals a metallamacrocycle (minimum ring size = 28 members) consisting of four repeating unsymmetrical dititanium units. In each dititanium unit, there is an unprecedented slippage of the nitrilotriethoxide ligand such that both triethanolamine nitrogens coordinate to only one of the two titaniums, while the bisphenoxide is coordinated only to the other titanium. The propensity of the polyphenoxide ligands to chelate is attributed to favorable  $\pi$ -bonding interactions attainable in the eight-membered chelate rings.

## Introduction

Triply deprotonated triethanolamine,  $[\text{N}(\text{CH}_2\text{CH}_2\text{O})_3]^{3-}$ , forms an extensive series of so-called atrane complexes with main group and transition metals.<sup>1</sup> While these complexes are most commonly monomeric and five-coordinate, a wide variety of other structures are known, including examples of four-,<sup>2</sup> six-,<sup>3</sup> and seven-coordinate<sup>4,5</sup> complexes and alkoxide-bridged dimers,<sup>6</sup> trimers,<sup>7</sup> and higher oligomers.<sup>8,9</sup>

One feature is constant across this set of complexes, though: the aminetriethoxide moiety always serves as a tetradentate chelating ligand. The high propensity of the aminetriethoxide group to chelate is reflected in the great stability of atrane complexes; for example, triethanolamine has even been used to solubilize titanium dioxide.<sup>10</sup>

We recently set out to explore the effects of bringing one, two, or three titanium centers into close proximity using the

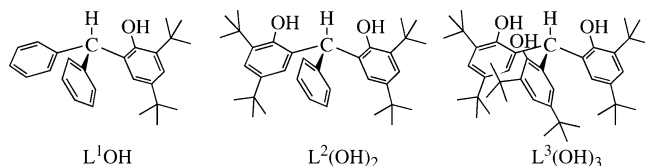
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<sup>†</sup> Dedicated in memory of Ian P. Rothwell, a trailblazer in the study of early metal aryloxides.

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hydroxylated triphenylmethane scaffolds  $L^1OH$ ,  $L^2(OH)_2$  and  $L^3(OH)_3$  illustrated below. Scott and co-workers have reported that the deprotonated tris(phenoxy)methanes such as  $L^3(OH)_3$  form polymeric complexes with alkali metals and zinc, where the aryloxides bridge between the bound metal atoms.<sup>11</sup> We find, however, that when bound to  $[N(CH_2CH_2O)_3Ti]$ , these deprotonated hydroxytriphenylmethanes do not form complexes with bridging aryloxide ligands. Complexes of the monodeprotonated ligands form monomeric five-coordinate titanatrane, but polydeprotonation leads, at least in one case, to the formation of a complex with a chelated bis(phenoxide) and an unprecedented *de*-chelated aminetriethoxide ligand.



## Experimental Section

All reactions were carried out under argon at room temperature using vacuum-line techniques or in a nitrogen-filled Innovative Technologies drybox, unless otherwise stated. Dry tetrahydrofuran was vacuum-transferred from sodium benzophenone ketyl, and toluene, benzene, and pentane from sodium. Methylene chloride and chloroform were vacuum-transferred from calcium hydride. Triethanolamine was distilled under vacuum and stored in the drybox.  $HCPPh(2-OH-3,5-tBu_2C_6H_2)_2$  ( $L^2(OH)_2$ ),<sup>12</sup>  $[N(CH_2CH_2O)_3]TiO^tBu$ ,<sup>13</sup> and  $\{[N(CH_2CH_2O)]Ti(NEt_2)_2\}_2$ <sup>14</sup> were prepared using literature procedures. The trisphenol  $HC(2-OH-3,5-tBu_2C_6H_2)_3$  ( $L^3(OH)_3$ ) was prepared in 55% yield from 2,4-di-*tert*-butylphenol, isopropylmagnesium bromide, and triethylorthoformate as described by Casnati and co-workers;<sup>15</sup> a similar procedure has also been described by Dinger and Scott.<sup>16</sup> All other reagents were commercially available and used without further purification.

NMR spectra were measured on a Varian-300 FT-NMR spectrometer in  $CDCl_3$ ,  $CD_2Cl_2$ , or  $C_7D_8$ , using the proton impurity of the solvents as an internal reference for the  $^1H$  spectra (300 MHz) and the  $^{13}C$  resonance of the solvents as an internal reference for  $^{13}C\{^1H\}$  spectra (75.5 MHz). In the assignments, the unsubstituted phenyl groups are noted as Ph, while the di-*tert*-butylphenoxy aryl rings are abbreviated Ar. Unless otherwise noted, spectra were obtained at 22 °C. IR spectra were recorded on a Perkin-Elmer PARAGON 1000 FT-IR spectrophotometer as Nujol mulls; frequencies are reported in wavenumbers. Elemental analyses of air-sensitive compounds were performed by Canadian Microanalytical Service, Ltd. (Vancouver, BC), and those of air-stable compounds by M-H-W Laboratories (Phoenix, AZ).

**2-(Diphenylmethyl)-4,6-*tert*-butylphenol, 2-Ph<sub>2</sub>CH-4,6-*t*-Bu<sub>2</sub>-C<sub>6</sub>H<sub>2</sub>OH ( $L^1OH$ ).** To a 100-mL round-bottom flask were added a

magnetic stir bar, 2,4-di-*tert*-butylphenol (1.578 g, 7.65 mmol), and diphenylbromomethane (1.90 g, 7.60 mmol). The flask was heated, open to the air, in a 155 °C silicone oil bath; the reaction turned blood red after 10 min of heating. The progress of the reaction was monitored by holding moistened pH paper above the neck of the flask to detect the evolution of HBr, which continued for 4 h. The reaction was heated for 1 h after the evolution of HBr ceased and then the red oil was allowed to cool to room temperature, layered with 50 mL pentane, and stored for 3 days at -20 °C. The off-white solid was collected on a glass frit, washed with 5 × 40 mL cold pentane, and air-dried to yield 1.86 g of  $L^1OH$  (55%).  $^1H$  NMR ( $CDCl_3$ ):  $\delta$  1.17 (s, 9H; *t*-Bu), 1.39 (s, 9H; *t*-Bu), 4.55 (s, 1H; OH), 5.61 (s, 1H; Ph<sub>2</sub>CH), 6.61 (d, 2.5 Hz, 1H; ArH), 7.16 (d, 7.5 Hz, 4H; *ortho*-Ph), 7.24 (d, 2.4 Hz, 1H; ArH), 7.30 (t, 7.5 Hz, 4H; *meta*-Ph), 7.31 (t, 7.2 Hz, 2H; *para*-Ph).  $^{13}C\{^1H\}$  NMR ( $CDCl_3$ ):  $\delta$  30.2, 31.7 (C[CH<sub>3</sub>]<sub>3</sub>), 34.5, 35.0 (C[CH<sub>3</sub>]<sub>3</sub>), 52.3 (ArPh<sub>2</sub>CH), 122.6, 125.4, 130.2, 136.4, 142.3, 150.3 (ArOH); 127.2, 128.9, 129.6, 142.4 (Ph). Anal. Calcd for  $C_{27}H_{32}O$ : C, 87.05; H, 8.66. Found: C, 86.80; H, 8.63.

**2-(Diphenylmethyl)-4,6-*tert*-butylphenoxytitanatrane,  $[N(CH_2CH_2O)_3]TiOL^1$  (**1**).** In the drybox,  $L^1OH$  (0.168 g, 0.432 mmol), (*tert*-butoxy)titanatrane (0.116 g, 0.434 mmol), and dichloromethane (2.5 mL) were added to a 20-mL screw-cap vial. The yellow solution was stirred for 30 min, then layered with 10 mL of pentane, and stored at -40 °C. After 48 h, pale yellow crystals suitable for X-ray analysis appeared. The yellow solid was filtered off onto a glass frit and the filtrate recrystallized from  $CH_2Cl_2$ /pentane. The combined yellow solids were collected on a glass frit in the drybox and washed twice with cold pentane to yield 150.2 mg of **1** (60%).  $^1H$  NMR ( $CDCl_3$ ):  $\delta$  1.15 (s, 9H; *t*-Bu), 1.47 (s, 9H; *t*-Bu), 3.16 (t, 6 Hz, 6H; NCH<sub>2</sub>), 4.37 (t, 6 Hz, 6H; OCH<sub>2</sub>), 6.60 (s, 1H; Ph<sub>2</sub>CH), 6.70 (d, 2.5 Hz, 1H; ArH), 7.14 (m, 7H; *o*-Ph, *p*-Ph, ArH), 7.21 (t, 7.5 Hz, 4H; *m*-Ph).  $^{13}C\{^1H\}$  NMR ( $CD_2Cl_2$ ):  $\delta$  30.6, 31.8 (C[CH<sub>3</sub>]<sub>3</sub>), 34.8, 35.5 (C[CH<sub>3</sub>]<sub>3</sub>), 49.7 (ArPh<sub>2</sub>CH), 57.2 (NCH<sub>2</sub>), 71.9 (OCH<sub>2</sub>), 121.8, 126.3, 134.2, 137.6, 142.0, 160.3 (ArOTi); 126.1, 128.2, 130.4, 146.2 (Ph). IR: 1558 (s), 1300 (s), 1259 (s), 1101 (s), 1063 (s), 1033 (s), 926 (s), 881 (s), 768 (s), 758 (s), 696 (s), 568 (s). Anal. Calcd for  $C_{33}H_{43}NO_4Ti$ : C, 70.08; H, 7.66; N, 2.48. Found: C, 69.99; H, 7.46; N, 2.54.

**2-( $\alpha$ -(2-hydroxy-3,5-di-*tert*-butylphenyl)benzyl)-4,6-di-*tert*-butylphenoxytitanatrane,  $L^2(OH)(OTi[(OCH_2CH_2)_3N])$  (**2**).** To a 20-mL vial in the drybox were added  $L^2(OH)_2$  (0.106 g, 0.217 mmol),  $\{[N(CH_2CH_2O)_3]Ti(NEt_2)_2\}_2$  (0.058 g, 0.109 mmol of dimer), and  $CH_2Cl_2$  (2 mL). The yellow solution was swirled for a few minutes and then allowed to stand for 15 min. The mixture was layered with pentane (10 mL) and stored at -40 °C for 48 h. The pale yellow crystals were collected on a glass frit and the filtrate was recrystallized from  $CH_2Cl_2$ /pentane and then filtered. The combined solid was washed with 2 × 40 mL cold pentane and allowed to dry in the glovebox to yield 89.1 mg **2** (58%).  $^1H$  NMR ( $CDCl_3$ ):  $\delta$  1.15 (s, 18H; *t*-Bu), 1.38 (s, 9H; *t*-Bu), 1.46 (s, 9H; *t*-Bu), 3.25 (apparent td, 5.5, 1.2 Hz, 6H; NCH<sub>2</sub>), 4.47 (apparent q, 5.5 Hz, 6H; OCH<sub>2</sub>), 6.55 (s, 1H; PhCH), 6.65 (sl br, 1H; 3,5-ArH), 6.72 (sl br, 1H; 3,5-ArH), 6.77 (s, 1H; OH), 7.03 (d, 8 Hz, 2H; *o*-Ph), 7.18 (m, 5H; *m*-Ph, *p*-Ph, 2 ArH).  $^{13}C\{^1H\}$  NMR ( $CDCl_3$ ):  $\delta$  30.2 (ArOH C[CH<sub>3</sub>]<sub>3</sub>), 30.6 (ArOTi C[CH<sub>3</sub>]<sub>3</sub>), 31.8 (coalesced ArOH and ArOTi C[CH<sub>3</sub>]<sub>3</sub>), 34.5 (coalesced ArOH and ArOTi C[CH<sub>3</sub>]<sub>3</sub>), 35.3 (coalesced ArOH and ArOTi C[CH<sub>3</sub>]<sub>3</sub>), 44.2 (Ar<sub>2</sub>-PhCH), 56.9 (NCH<sub>2</sub>), 71.3 (OCH<sub>2</sub>), 121.4, 125.6, 131.1, 136.2, 141.1, 151.2 (ArOH); 121.6, 126.0, 132.9, 137.3, 142.0, 160.3 (ArOTi); 125.8, 127.8, 129.7, 144.9 (Ph). IR: 3176 (m,  $\nu_{OH}$ ), 1298 (s), 1244 (s), 1201 (s), 1159 (m), 1125 (s), 1075 (s), 1062 (s), 923 (s), 906 (s), 886 (s), 765 (s), 722 (s), 702 (s), 623 (s). Anal. Calcd

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for  $C_{41}H_{59}NO_5Ti$ : C, 70.78; H, 8.57; N, 2.02. Found: C, 70.39; H, 8.60; N, 2.06.

**2-(Bis-(2-hydroxy-3,5-di-*tert*-butylphenyl)methyl)-4,6-di-*tert*-butylphenoxytitanatran,  $L^3(OH)_2(O\text{Ti}[(OCH_2CH_2)_3N])$  (**3**).** To a 100-mL round-bottom flask in the drybox were added  $L^3(OH)_3$  (0.091 g, 0.145 mmol), *tert*-butoxytitanatran (0.038 g, 0.144 mmol), and a magnetic stir bar. The flask was attached to a swivel frit and taken to the vacuum line. Ten milliliters of  $CH_2Cl_2$  was vacuum-transferred to the flask and the yellow solution stirred for 30 min. The volume was reduced to 2 mL and then pentane (10 mL) was vacuum-transferred to the flask. Pale yellow crystals grew overnight, were isolated on the swivel frit, and were dried in vacuo to yield 62 mg **3** (52%).  $^1H$  NMR ( $CD_2Cl_2$ ):  $\delta$  1.09 (s, 18H; 'Bu), 1.13 (s, 9H; 'Bu), 1.38 (s, 18H; 'Bu), 1.45 (s, 9H; 'Bu), 3.33 (t, 6 Hz, 6H;  $NCH_2$ ), 4.57 (t, 6 Hz, 6H;  $OCH_2$ ), 6.30 (s, 1H;  $Ar_3CH$ ), 6.35 (d, 2.5 Hz, 2H;  $ArH$ ), 6.57 (s, 2H;  $OH$ ), 6.64 (d, 2.5 Hz, 1H;  $ArH$ ), 7.18 (d, 2.5 Hz, 2H;  $ArH$ ), 7.21 (d, 2.5 Hz, 1H;  $ArH$ ).  $^{13}C\{-^1H\}$  NMR ( $CD_2Cl_2$ ):  $\delta$  30.4 (ArOH  $C[CH_3]_3$ ), 30.7 (ArOTi  $C[CH_3]_3$ ), 31.8 (coalesced ArOH and ArOTi  $C[CH_3]_3$ ), 34.7 (ArOH  $C[CH_3]_3$ ), 34.8 (ArOTi  $C[CH_3]_3$ ), 35.5 (coalesced ArOH and ArOTi  $C[CH_3]_3$ ), 40.1 ( $Ar_3CH$ ), 57.3 ( $NCH_2$ ), 72.0 ( $OCH_2$ ), 122.2, 125.4, 130.8, 137.2, 142.3, 151.2 (ArOH); 122.3, 126.0, 131.6, 137.4, 143.0, 160.7 (ArOTi). IR: 3179 (m,  $\nu_{OH}$ ), 1298 (s), 1244 (s), 1201 (s), 1159 (m), 1125 (s), 1075 (s), 1062 (s), 923 (s), 906 (s), 886 (s), 765 (s), 722 (s), 702 (s), 623 (s). Anal. Calcd for  $C_{49}H_{75}NO_6Ti$ : C, 71.59; H, 9.20; N, 1.70. Found: C, 71.60; H, 9.25; N, 1.63.

**$\{L^2(O)_2Ti_2[(OCH_2CH_2)_3N]_2\}_4$  (**4**).** To a 20-mL vial in the drybox were added  $\{[N(CH_2CH_2O)_3]TiNEt_2\}_2$  (0.102 g, 0.192 mmol),  $L^2(OH)_2$  (0.096 g, 0.192 mmol), and  $CH_2Cl_2$  (2 mL). The solution was swirled for a few minutes and then allowed to stand for 15 min. Pentane was carefully layered on the solution and allowed to mix over 60 h into the  $CH_2Cl_2$  at  $-40^\circ C$ , depositing orange blocks of X-ray quality. The solid was then isolated by gravity filtration onto a glass frit, washed with  $3 \times 30$  mL pentane, and allowed to dry. Yield of the orange powdery solid was 45 mg (42%). IR: 1259 (m), 1233 (w), 1156 (w), 1125 (m), 1098 (m), 1074 (m), 1062 (s), 1026 (w), 1014 (w), 922 (m), 906 (w), 881 (m), 839 (w), 764 (w), 730 (s), 621 (s), 600 (s).

**Variable-Temperature NMR Studies of **2** and **3**.** In a typical procedure, a 5-mm NMR tube sealed to a ground glass joint was charged with 0.012 g (0.017 mmol) of **2** and toluene- $d_8$  (0.7 mL) in a drybox under an  $N_2$  atmosphere. The tube was flame-sealed while cooled in liquid nitrogen under dynamic vacuum and the seal checked for integrity. The tube was transferred to the NMR probe, and  $^1H$  NMR spectra were recorded between 25 and  $100^\circ C$ . At  $25^\circ C$  the *o-tert*-butyl resonances are observed at  $\delta$  1.75 and 1.65. Upon warming, the *tert*-butyl resonances broaden, coalescing at  $70^\circ C$ . The dynamic process was modeled as an AB exchange using the program gNMR<sup>17</sup> to obtain rate constants. The NMR spectra of **3** were analyzed analogously, except that they were modeled as an  $AB_2$  exchange.

**X-ray Crystal Structure Determinations of **1**, **2**, and **4**.**  **$2C_2H_5 \cdot 8.5CH_2Cl_2$ .** Crystals of compound **1** were grown as described above. A small yellow plate ( $0.08 \times 0.19 \times 0.28$  mm) was placed in inert oil and transferred to the tip of a glass fiber in the cold  $N_2$  stream of a Bruker Apex CCD diffractometer ( $T = -103^\circ C$ ). Data were reduced, correcting for absorption and decay, using the program SADABS. The crystal was triclinic. The titanium atom was located on a Patterson map, and remaining nonhydrogen atoms were found on difference Fourier syntheses. Hydrogens were

placed in calculated positions. Final full-matrix least-squares refinement on  $F^2$  converged at  $R = 0.0500$  for 5252 reflections with  $F_o > 4\sigma(F_o)$ ,  $R = 0.0652$  for all 6831 unique reflections ( $wR_2 = 0.1270, 0.1390$ , respectively.). All the calculations used SHELXTL (Bruker Analytical X-ray Systems), with scattering factors and anomalous dispersion terms taken from the literature.<sup>18</sup>

Crystals of compound **2** were grown as described above. A yellow prism ( $0.33 \times 0.37 \times 0.43$  mm) was placed in inert oil and transferred to the tip of a glass fiber in the cold  $N_2$  stream of a Bruker Apex CCD diffractometer ( $T = -103^\circ C$ ). Data were analyzed as described for **1**, except that the O–H hydrogen was found on the difference Fourier map and refined isotropically. Final full-matrix least-squares refinement on  $F^2$  converged at  $R = 0.0605$  for 7349 reflections with  $F_o > 4\sigma(F_o)$ ,  $R = 0.0715$  for all 8898 unique reflections ( $wR_2 = 0.1702, 0.1835$ , respectively.).

Yellow-orange blocks of octatitanium complex **4** were deposited after slow diffusion of pentane into a freshly generated solution of the complex in methylene chloride. A crystal of approximate dimensions  $0.35 \times 0.45 \times 0.50$  mm was rapidly covered in oil and placed on the tip of a glass fiber in the cold  $N_2$  stream of a Bruker Apex CCD diffractometer ( $T = -103^\circ C$ ). Once removed from the mother liquor, the crystals showed a marked tendency to lose solvent and become opaque, so rapid handling was essential. The structure was solved by direct methods, and remaining nonhydrogen atoms were found on difference Fourier syntheses. Hydrogens were placed in calculated positions. Two *tert*-butyl groups (with central carbons C250 and C254) were disordered and were modeled in two sites; the occupancy of the major sites was refined to 0.700(6) and 0.741(10), respectively. One triethanolamine group was also disordered over two possible helical twists and was modeled with two sites occupied by C44, C45, and C46 (major site occupancy 0.780(6)). All nonhydrogen atoms except those of two methylene chloride molecules (which showed electron density characteristic of partial occupancy and were arbitrarily refined at 1/2 occupancy) were refined anisotropically. Hydrogens were placed in calculated positions. Final full-matrix least-squares refinement on  $F^2$  converged at  $R = 0.0759$  for 17366 reflections with  $F_o > 4\sigma(F_o)$ ,  $R = 0.1171$  for all 28593 unique data ( $wR_2 = 0.2330, 0.2639$ , respectively.).

## Results

**Preparation and Characterization of Monometalated Hydroxylated Triphenylmethanes.** To compare the bonding of mono-, di-, and trititanium complexes, we sought a series of analogous hydroxylated triphenylmethanes,  $HCP_h_{3-n}(2-OH-3,5-tBu_2C_6H_2)_n$  ( $n = 1, L^1OH$ ;  $n = 2, L^2(OH)_2$ ;  $n = 3, L^3(OH)_3$ ). The triphenol  $L^3(OH)_3$  was prepared from the bromomagnesium salt of 2,4-di-*tert*-butylphenol and triethylorthoformate;<sup>15,16</sup> it has also been prepared by an alternate route<sup>16</sup> and studied as a ligand<sup>11</sup> by Scott and co-workers. The bisphenol ligand  $L^2(OH)_2$  was also available, by acid-catalyzed condensation of 2,4-di-*tert*-butylphenol with benzaldehyde,<sup>12</sup> but  $L^1OH$  had not been prepared previously. It was synthesized in 55% yield by heating 2,4-di-*tert*-butylphenol with neat benzhydryl bromide (eq 1).

Complexes in which one phenoxide of a polyphenol is ligated to titanium can be readily prepared via protonolysis of the polyphenols. Thus, *tert*-butoxytitanatran  $[N(CH_2-$

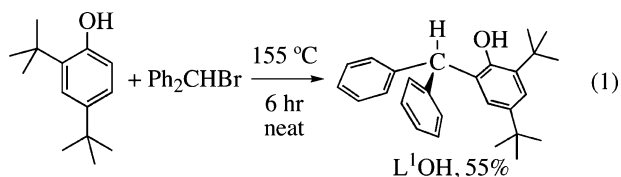
(17) Budzelaar, P. H. M. *gNMR* v.3.6.5. Cherwell Scientific Publishing: Oxford, 1996.

(18) *International Tables of Crystallography*; Kluwer Academic Publishers: Dordrecht, The Netherlands, 1992; Vol. C.

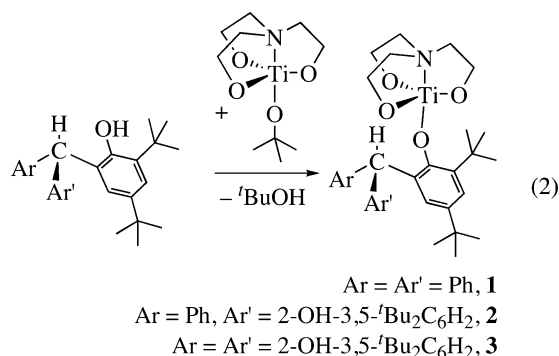
**Table 1.** Crystallographic Details for  $[\text{N}(\text{CH}_2\text{CH}_2\text{O})_3]\text{TiOL}^1$  (**1**),  $\text{L}^2(\text{OH})(\text{OTi}[\text{N}(\text{CH}_2\text{CH}_2\text{O})_3])$  (**2**), and  $\{\text{L}^2(\text{OTi}[\text{N}(\text{CH}_2\text{CH}_2\text{O})_3])_2\}_4 \cdot 2\text{C}_5\text{H}_{12} \cdot 8.5\text{CH}_2\text{Cl}_2$  ( $4 \cdot 2\text{C}_5\text{H}_{12} \cdot 8.5\text{CH}_2\text{Cl}_2$ )

	<b>1</b>	<b>2</b>	$4 \cdot 2\text{C}_5\text{H}_{12} \cdot 8.5\text{CH}_2\text{Cl}_2$
empirical formula	$\text{C}_{33}\text{H}_{43}\text{NO}_4\text{Ti}$	$\text{C}_{41}\text{H}_{59}\text{NO}_5\text{Ti}$	$\text{C}_{206.5}\text{H}_{321}\text{Cl}_{17}\text{N}_8\text{O}_{32}\text{Ti}_8$
fw	565.58	693.79	4413.56
temp (K)	170(2)	170(2)	170(2)
$\lambda$ , Å	0.71073 (Mo K $\alpha$ )	0.71073 (Mo K $\alpha$ )	0.71073 (Mo K $\alpha$ )
space group	$P\bar{1}$	$P\bar{1}$	$I2/a$
total data collected	9696	17541	77317
no. of indep. reflns	6831	8898	28593
$R_{\text{int}}$	0.0162	0.0364	0.0381
obsd reflns [ $I > 2\sigma(I)$ ]	5252	7349	17366
$a$ (Å)	10.4044(7)	10.9755(11)	27.581(2)
$b$ (Å)	10.5516(7)	11.3514(11)	30.981(2)
$c$ (Å)	14.9791(10)	16.730(2)	28.825(2)
$\alpha$ (deg)	90.9430(10)	80.299(2)	90
$\beta$ (deg)	102.2840(10)	74.070(2)	95.7410(10)
$\gamma$ (deg)	104.3430(10)	79.102(2)	90
$V$ (Å <sup>3</sup> )	1552.6(2)	1953.1(3)	24507.3(29)
$Z$	2	2	4
calcd $\rho$ (g/cm <sup>3</sup> )	1.210	1.180	1.196
cryst size (mm)	$0.08 \times 0.19 \times 0.28$	$0.33 \times 0.37 \times 0.43$	$0.35 \times 0.45 \times 0.50$
$\mu$ (mm <sup>-1</sup> )	0.311	0.261	0.493
no. refined params	488	633	1270
$R$ indices [ $I > 2\sigma(I)$ ] <sup>a</sup>	$R1 = 0.0500$ $wR2 = 0.1270$	$R1 = 0.0605$ $wR2 = 0.1702$	$R1 = 0.0759$ $wR2 = 0.2330$
$R$ indices (all data) <sup>a</sup>	$R1 = 0.0652$ $wR2 = 0.1390$	$R1 = 0.0715$ $wR2 = 0.1835$	$R1 = 0.1171$ $wR2 = 0.2639$
GOF	0.984	0.998	1.000

$$^a R1 = \sum |F_o| - |F_c| / \sum |F_o|; wR2 = (\sum [w(F_o^2 - F_c^2)^2] / \sum w(F_o^2)^2)^{1/2}.$$



$\text{CH}_2\text{O})_3]\text{Ti}(\text{O}^t\text{Bu})^{13}$  reacts with the ligands  $\text{L}^1\text{OH}$ ,  $\text{L}^2(\text{OH})_2$ , and  $\text{L}^3(\text{OH})_3$  to produce the monometalated complexes  $[\text{N}(\text{CH}_2\text{CH}_2\text{O})_3]\text{Ti}(\text{OL}^1)$  (**1**),  $[\text{N}(\text{CH}_2\text{CH}_2\text{O})_3]\text{Ti}[\text{OL}^2(\text{OH})]$  (**2**), and  $[\text{N}(\text{CH}_2\text{CH}_2\text{O})_3]\text{Ti}[\text{OL}^3(\text{OH})_2]$  (**3**), respectively (eq 2). In all cases yields are quantitative by NMR, though some



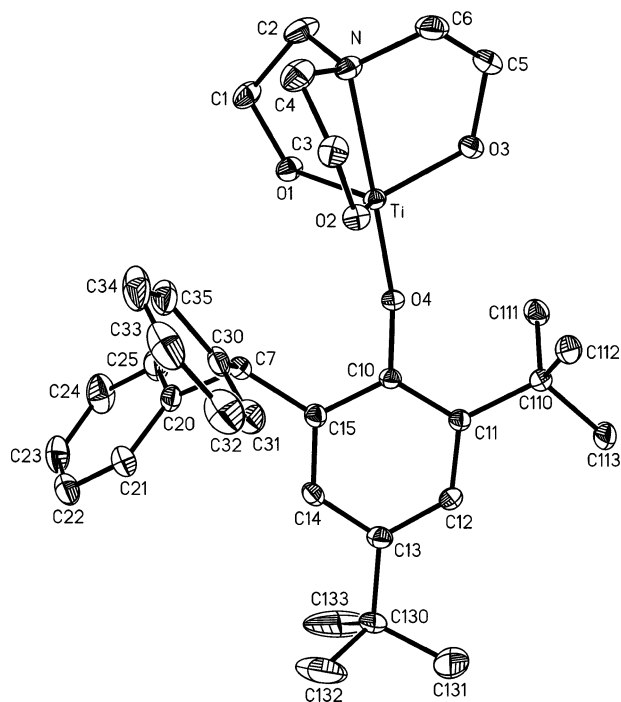
material is lost on isolation. These protonolysis reactions can also be carried out using the diethylamido complex  $\{[\text{N}(\text{CH}_2\text{CH}_2\text{O})_3]\text{Ti}(\text{NEt}_2)\}_2$  in a titanium:polyphenol ratio of 1:1, and this method produced somewhat higher isolated yields in the preparation of **2** than did the use of the *tert*-butoxide. The complexes are yellow crystalline materials that are stable indefinitely in the solid or in solution in the absence of air and moisture, but decompose within hours in solution when

exposed to air.  $^1\text{H}$  NMR spectra clearly indicate that the complexes contain only one  $[\text{N}(\text{CH}_2\text{CH}_2\text{O})_3]\text{Ti}$  unit per polyphenol. For example, spectra of **2** and **3** at room temperature show distinct aryl and *tert*-butyl resonances for bound phenoxide and free phenol groups, and IR spectra of **2** and **3** (but not **1**) show the retention of free O–H groups (e.g.,  $\nu_{\text{OH}} = 3176 \text{ cm}^{-1}$  in **2**).

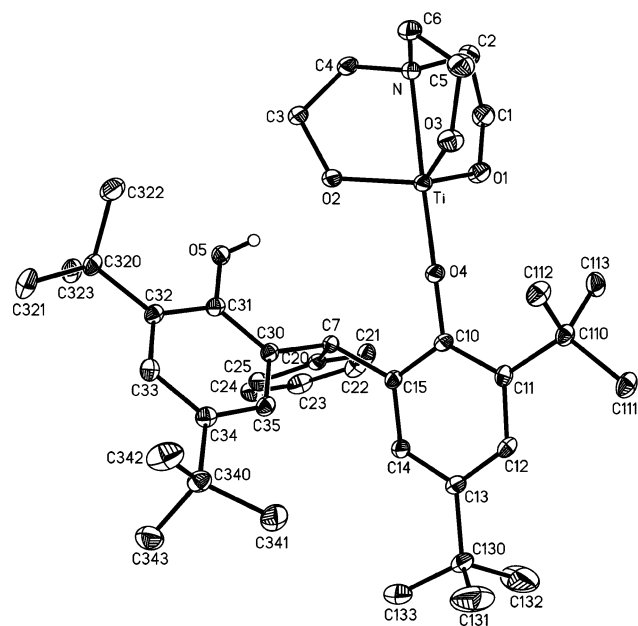
The structures of **1** and **2** were confirmed by single-crystal X-ray structure determinations (Table 1). Both complexes have generally similar overall structures (Figures 1 and 2) and metrical data (Table 2). The aryl groups of the phenoxide ligands are arranged in a propeller-like fashion around the central methine carbon. The titanium centers are trigonal bipyramidal, with Ti–O<sub>eq</sub> distances averaging 1.836 Å in **1** and 1.839 Å in **2** and Ti–N bond distances of 2.263(2) Å in **1** and 2.280(2) Å in **2**. These distances are typical of those seen in other five-coordinate titanatranes such as  $[\text{N}(\text{CH}_2\text{CH}_2\text{O})_3]\text{TiOSiPh}_3^{13}$  and  $[\text{N}(\text{CH}_2\text{CH}_2\text{O})_3]\text{TiOCMe}_2\text{CMe}_2\text{OTi}[(\text{OCH}_2\text{CH}_2)_3\text{N}]^{14}$ . The Ti–O<sub>aryloxide</sub> distances of 1.8231(14) in **1** and 1.8183(14) in **2** are similar to those observed in recently reported five-coordinate complexes with 2,6-diisopropylphenoxide,  $[\text{N}(\text{CH}_2\text{C}_6\text{H}_2\text{Me}_2\text{O})_3]\text{Ti}(\text{OAr})$  and  $[\text{N}(\text{CH}_2\text{C}_6\text{H}_2\text{Me}_2\text{O})_2(\text{CH}_2\text{CH}_2\text{O})]\text{Ti}(\text{OAr})$  (1.834(2) and 1.828(3) Å, respectively).<sup>19</sup> Presumably **1** and **2** adopt monomeric, rather than alkoxide-bridged dimeric structures, due to the steric bulk of the 2,6-disubstituted aryloxides. For example, (triphenylsiloxy)titanatranes is monomeric in the crystal,<sup>13</sup> while the isopropoxide complex is dimeric.<sup>6a</sup>

There are significant differences between the two structures, which stem from the formation of a hydrogen bond between the unmetalated phenol O–H group and the

(19) Kim, Y.; Verkade, J. G. *Organometallics* **2002**, *21*, 2395–2399.



**Figure 1.** SHELXTL plot (30% thermal ellipsoids) of  $[N(CH_2CH_2O)_3]TiOL^1$  (**1**).

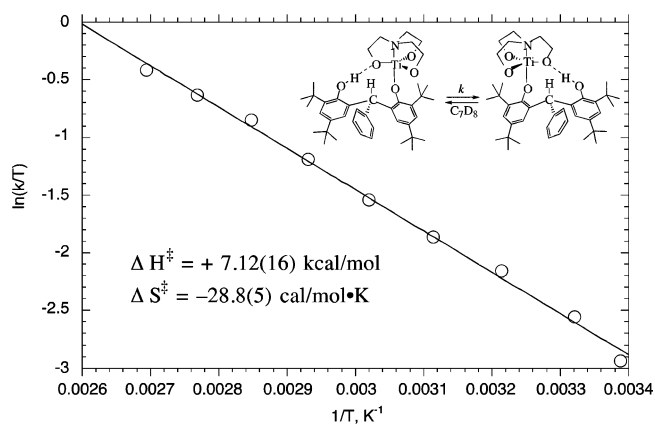


**Figure 2.** SHELXTL plot (30% thermal ellipsoids) of  $L^2(OH)(OTi[N(CH_2CH_2O)_3])$  (**2**).

equatorial oxygen O2 (O2–O5 distance of 2.751 Å). This interaction results in elongation of the bond from O2 to titanium (1.875(2) Å compared with Ti–O1 and Ti–O3 bonds of 1.823(2) and 1.818(2) Å, respectively), consistent with a decrease in electron density on O2 upon formation of a hydrogen bond. The hydrogen bond is presumably also responsible for the difference in conformation of the  $[N(CH_2CH_2O)_3]Ti$  moiety in the two structures. In **1**, the bond to the methine group from the aryloxy bisects an O–Ti–O group, while in **2** it approximately eclipses the Ti–O2 bond to allow hydrogen bonding to the phenol.

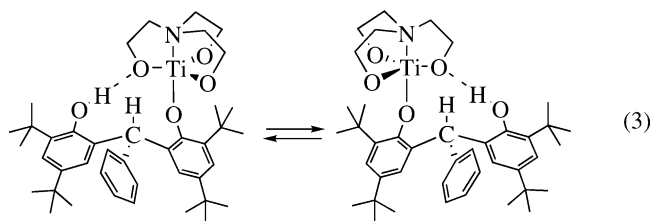
**Table 2.** Selected Bond Lengths (Å) and Angles (deg) for  $[N(CH_2CH_2O)_3]TiOL^1$  (**1**) and  $L^2(OH)(OTi[N(CH_2CH_2O)_3])$  (**2**)

	$[N(CH_2CH_2O)_3]TiOL^1$ ( <b>1</b> )	$L^2(OH)(OTi[N(CH_2CH_2O)_3])$ ( <b>2</b> )
Ti–O1	1.8406(15)	1.823(2)
Ti–O2	1.8308(15)	1.8754(15)
Ti–O3	1.837(2)	1.818(2)
Ti–O4	1.8231(14)	1.8183(14)
Ti–N	2.263(2)	2.280(2)
O1–Ti–O2	118.10(7)	112.90(7)
O1–Ti–O3	115.79(7)	115.86(8)
O2–Ti–O3	113.08(7)	118.46(7)
O1–Ti–O4	100.96(7)	101.32(7)
O2–Ti–O4	102.95(7)	103.47(6)
O3–Ti–O4	102.72(7)	101.42(7)
O1–Ti–N	77.73(6)	78.00(7)
O2–Ti–N	77.69(7)	78.01(6)
O3–Ti–N	78.00(7)	77.78(7)
O4–Ti–N	178.68(7)	178.52(6)
Ti–O4–C10	165.36(14)	166.47(13)



**Figure 3.** Eyring plot of the rate constant for degenerate phenoxide–phenol interchange in **2** (toluene- $d_8$ ).

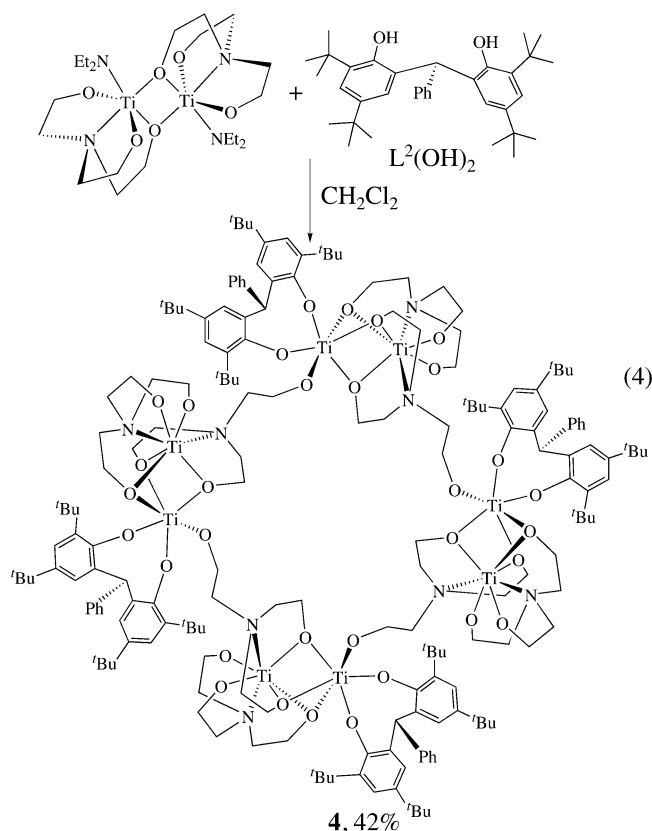
The  $^1H$  NMR spectrum of **2** indicates that the hydrogen bond is probably maintained in solution, as judged by the downfield shift of the OH resonance ( $\delta$  6.77 vs 4.55 for free  $L^1OH$ ), but that it is rapidly breaking and reforming, since the three ethylene arms of the nitrilotriethoxide ligand are equivalent on the NMR time scale. At room temperature, the bound and free phenoxide groups of **2** are distinct, but the resonances due to the aryl groups are slightly broadened. As the temperature is raised, the resonances reversibly broaden and eventually coalesce, indicating that the titanium must be hopping from the bound to the free phenol at a reasonable rate (eq 3). The rate of this reaction was measured



quantitatively by line shape simulation of the exchanging *o*-*tert*-butyl resonances in toluene- $d_8$  ( $T_c = 343$  K) and Eyring analysis of the rate data (Figure 3) gives activation parameters for the exchange ( $\Delta H^\ddagger = 7.12 \pm 0.16$  kcal/mol,  $\Delta S^\ddagger = -28.8 \pm 0.5$  cal/mol·K). Observed exchange rates are

unaffected by increasing the concentration of **2** by a factor of 10 in toluene-*d*<sub>8</sub> and are similar in CD<sub>2</sub>Cl<sub>2</sub>. Complex **3** undergoes analogous exchange of the two free phenol groups with the bound phenoxide, and activation parameters for that reaction are the same, within experimental error, as in the reaction of **2** ( $\Delta H^\ddagger = 7.03 \pm 0.13$  kcal/mol,  $\Delta S^\ddagger = -30.9 \pm 1.6$  cal/mol·K).

**Preparation and Characterization of a Polymetalated Hydroxylated Triphenylmethane.** While one phenol group per molecule in L<sup>1</sup>OH, L<sup>2</sup>(OH)<sub>2</sub>, or L<sup>3</sup>(OH)<sub>3</sub> can be readily metalated, the presence of the first titanium center substantially disfavors metalation of the remaining phenols. Treatment of the polyphenols L<sup>2</sup>(OH)<sub>2</sub> or L<sup>3</sup>(OH)<sub>3</sub> with an excess of the *tert*-butoxide complex [N(CH<sub>2</sub>CH<sub>2</sub>O)<sub>3</sub>]<sub>2</sub>Ti(O<sup>*t*</sup>Bu) results in clean formation of **2** and **3**, respectively, but further metalation does not take place. To achieve polymetalation, the more reactive titanium amide complex {[N(CH<sub>2</sub>CH<sub>2</sub>O)<sub>3</sub>]-Ti(NEt<sub>2</sub>)<sub>2</sub>}<sub>2</sub> must be used. For example, treatment of the bisphenol ligand L<sup>2</sup>(OH)<sub>2</sub> with a stoichiometric quantity of the diethylamidotitanatranne dimer results in the formation of orange solutions. NMR spectra of these solutions indicate that all of the phenol groups have been consumed, with liberation of diethylamine, but resonances due to the phenolic ligands are very broad, possibly indicating the formation of a variety of different oligomers. This mixture can be crystallized to give complex **4** in 42% yield as orange crystals, which lose solvent rapidly when removed from the mother liquor (eq 4). Reactions of L<sup>3</sup>(OH)<sub>3</sub> with {[N(CH<sub>2</sub>-

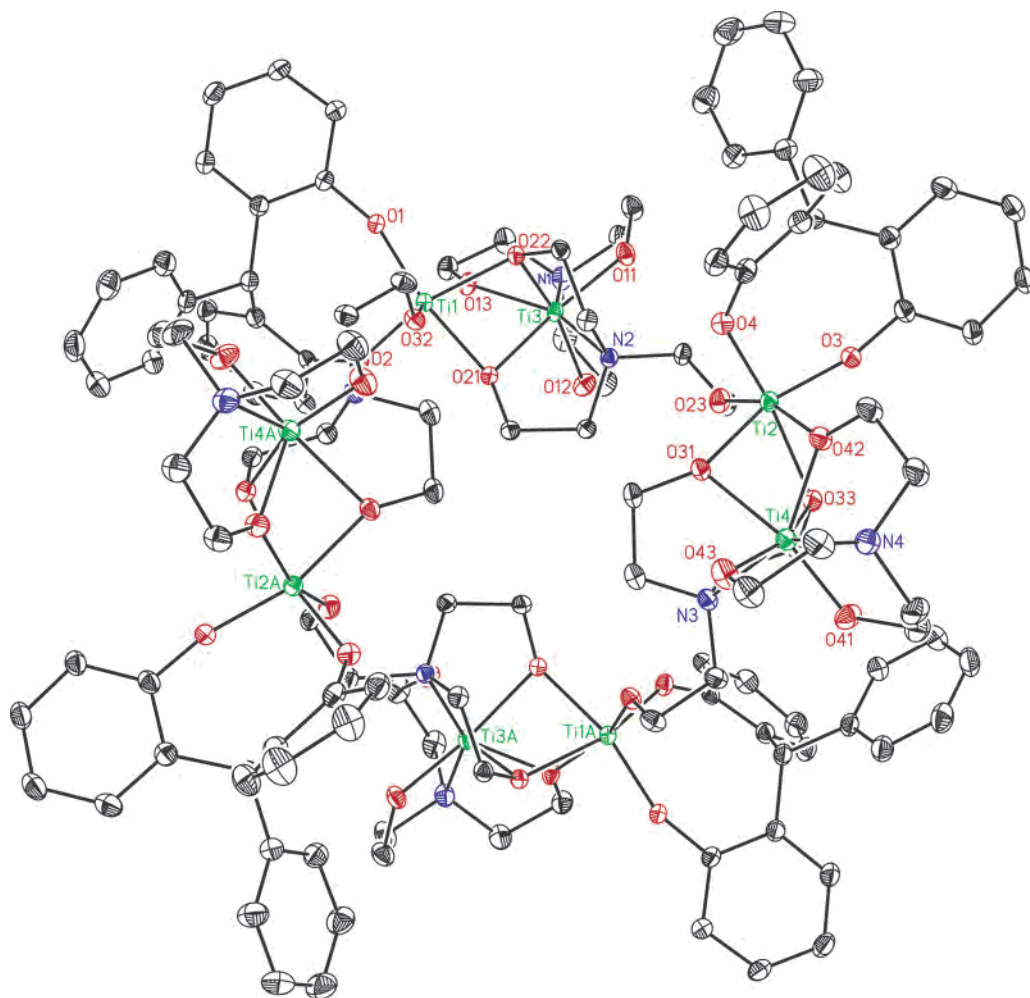


(CH<sub>2</sub>O)<sub>3</sub>]<sub>2</sub>Ti(NEt<sub>2</sub>)<sub>2</sub> gave similar broad NMR spectra in situ, but no crystalline material was obtained.

The structure of **4** as determined by X-ray crystallography is illustrated in Figure 4. The complex consists of a cyclic tetramer of fully metalated L<sup>2</sup>(O)<sub>2</sub>Ti<sub>2</sub>[(OCH<sub>2</sub>CH<sub>2</sub>)<sub>3</sub>N]<sub>2</sub> units, creating a metallamacrocycle with a minimum ring size of 28 members. Each dititanium unit is connected to the succeeding one by a dangling CH<sub>2</sub>CH<sub>2</sub>O arm from one of the nitrilotriethoxide units. This architecture is thus quite different from previously characterized high-nuclearity hexatitanium<sup>8</sup> and octatitanium<sup>9a,b</sup> clusters containing N(CH<sub>2</sub>CH<sub>2</sub>O)<sub>3</sub><sup>3-</sup> ligands, where adjoining metal centers are linked by bridging alkoxides. Complex **4** has crystallographic C<sub>2</sub> symmetry, but in fact the overall symmetry is very close to S<sub>4</sub>, with the Ti1/Ti3 unit showing extremely similar bond distances and angles to its crystallographically inequivalent but chemically equivalent Ti2/Ti4 counterpart (Table 3).

While this repeating dititanium unit has the formula L<sup>2</sup>(O)<sub>2</sub>-Ti<sub>2</sub>[(OCH<sub>2</sub>CH<sub>2</sub>)<sub>3</sub>N]<sub>2</sub>, the two titanium atoms experience very different coordination environments (Figure 5). Most surprisingly, one of the titanium atoms in the repeating unit (Ti3 or Ti4) coordinates *both* of the triethanolamine nitrogens. Such an aminetriethoxide shift has never been observed before in polynuclear metallatranes. The nitrogen-coordinated titanium atoms are seven-coordinate, with one triethanolamine unit supplying two terminal alkoxides and one bridging alkoxide and the other triethanolamine supplying two bridging alkoxides. The other titanium atom in the repeating unit (Ti1 or Ti2) is six-coordinate and is chelated by the bisphenoxide ligand L<sup>2</sup>(O)<sub>2</sub><sup>2-</sup>, with both aryloxides terminal. The average O–Ti–O bite angle of 99.8° is typical of titanium chelates of methylenebis(aryloxides), with the average Ti–OAr distance of 1.87 Å on the long end of the range of observed values.<sup>20</sup> The coordination geometry of Ti1 and Ti2 is roughly octahedral, but with a severe trigonal distortion, such that the octahedral face occupied by the terminal alkoxides shows much shorter distances (1.85(3) Å avg) and wider angles (99.1(8)° avg) than does the bridging alkoxide face (2.06(3) Å, 73(3)° respectively). The seven-coordinate geometry of Ti3 and Ti4 can be described most simply as a capped octahedron, with O13 for example capping the N1–O21–O22 face on Ti3 (Figure 5). Because this bridging alkoxide has, effectively, no trans ligand on the seven-coordinate titanium, it has a much shorter bond distance than any of the other bridging alkoxides (1.965(2) Å vs 2.07(3) Å). The overall coordination spheres of the two titaniums in each repeating unit share a (very approximate) mirror plane which contains both nitrogens and

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**Figure 4.** SHELXTL plot (30% thermal ellipsoids) of  $\{L^2[OTi[N(CH_2CH_2O)_3]_2]_4$  (**4**). *Tert*-butyl groups are omitted for clarity.

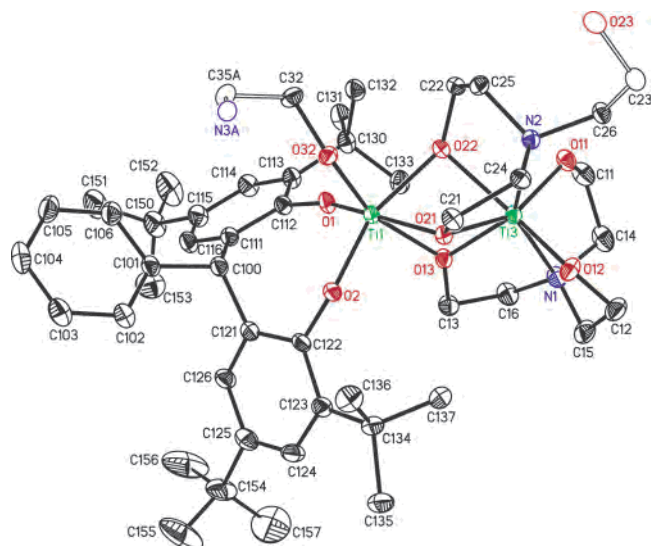
**Table 3.** Selected Bond Lengths (Å) and Angles (deg) for  $\{L^2[OTi[N(CH_2CH_2O)_3]_2]_4 \cdot 2C_5H_{12} \cdot 8.5CH_2Cl_2$  (**4**· $2C_5H_{12} \cdot 8.5CH_2Cl_2$ )

Ti1—O1	1.842(2)	Ti2—O3	1.850(2)	Ti3—O11	1.864(3)	Ti4—O41	1.852(3)
Ti1—O2	1.884(2)	Ti2—O4	1.895(3)	Ti3—O12	1.865(3)	Ti4—O43	1.869(3)
Ti1—O32	1.825(2)	Ti2—O23	1.806(3)	Ti3—O13	1.963(2)	Ti4—O42	1.967(2)
Ti1—O13	2.099(2)	Ti2—O42	2.085(3)	Ti3—O21	2.093(2)	Ti4—O31	2.106(3)
Ti1—O21	2.007(2)	Ti2—O31	2.032(2)	Ti3—O22	2.086(2)	Ti4—O33	2.070(3)
Ti1—O22	2.078(2)	Ti2—O33	2.076(2)	Ti3—N1	2.323(3)	Ti4—N4	2.329(3)
				Ti3—N2	2.322(3)	Ti4—N3	2.334(3)
O1—Ti1—O2	99.38(11)	O3—Ti2—O4	100.31(11)				
O1—Ti1—O32	98.09(12)	O3—Ti2—O23	99.77(12)				
O2—Ti1—O32	99.25(11)	O4—Ti2—O23	97.96(12)				
O13—Ti1—O21	72.56(10)	O31—Ti2—O42	71.39(10)				
O13—Ti1—O22	69.90(9)	O33—Ti2—O42	71.14(10)				
O21—Ti1—O22	77.15(9)	O31—Ti2—O33	76.86(10)				
N1—Ti3—N2	147.89(11)	N3—Ti4—N4	149.13(11)				
Ti1—O1—C112	161.3(2)	Ti2—O3—C212	163.0(3)				
Ti1—O2—C122	140.0(2)	Ti2—O4—C222	132.6(2)				
Ti1—O32—C32	139.0(2)	Ti2—O23—C23	142.7(2)				
Ti1—O13—Ti3	93.95(10)	Ti2—O42—Ti4	94.44(10)				
Ti1—O21—Ti3	92.86(9)	Ti2—O31—Ti4	91.92(10)				
Ti1—O22—Ti3	91.04(9)	Ti2—O33—Ti4	91.68(10)				

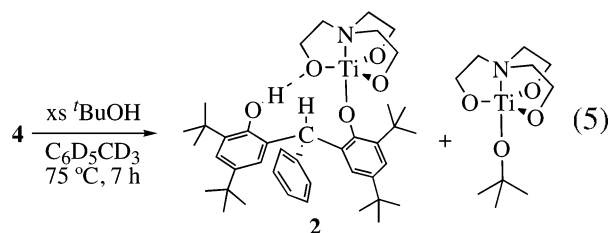
both titaniums, and which bisects the bis(aryloxy) ligand. However, this mirror plane is violated by the dangling alkoxide arms that link the dititanium units. The orientations of these links are enantiomorphous in the Ti1/Ti3 and Ti2/Ti4 subunits.

The isolated octatitanium complex **4** is insoluble in all organic solvents, which precludes its characterization by NMR spectroscopy, and we were unable to obtain satisfac-

tory elemental analysis of the complex, possibly because of variable entrapment of solvent. However, in the presence of excess *tert*-butyl alcohol in toluene- $d_8$ , solid **4** dissolves on heating to form equimolar amounts of  $[N(CH_2CH_2O)_3]Ti[OL^2(OH)]$  (**2**) and  $[N(CH_2CH_2O)_3]TiO^tBu$  (eq 5). This confirms the bulk composition of **4**, as well as the thermodynamic instability of the fully metalated aryloxy with respect to alcoholysis.



**Figure 5.** Repeating unit in the structure of  $\{L^2(OTi[N(CH_2CH_2O)_3])_2\}_4$  (4). The Ti2–Ti4 unit (linked to the Ti1–Ti3 unit by O23) is chemically equivalent to the Ti1–Ti3 unit but is crystallographically inequivalent.

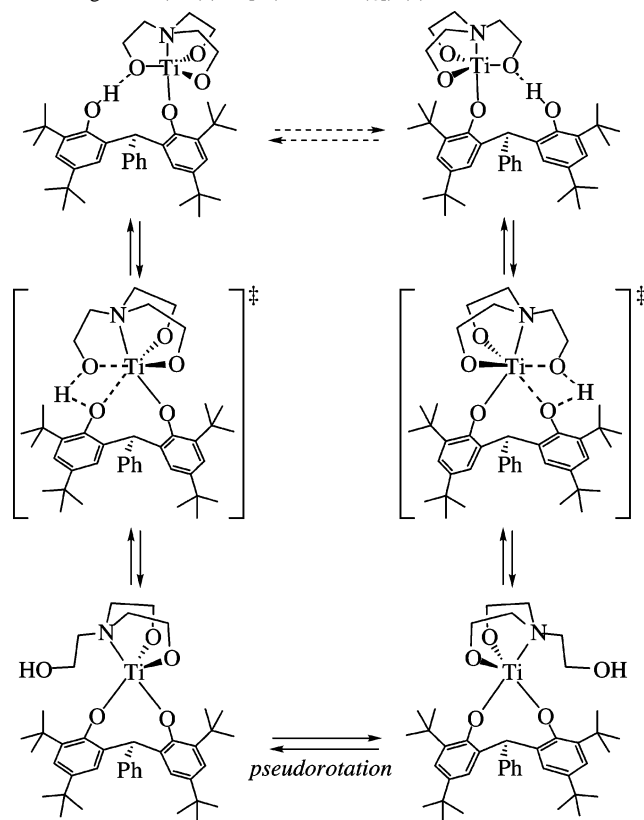


## Discussion

The hydroxylated triphenylmethanes  $Ph_{3-n}CH(C_6H_2-3,5-tBu_2-2-OH)_n$  ( $n = 1, L^1OH$ ;  $n = 2, L^2(OH)_2$ ;  $n = 3, L^3(OH)_3$ ) react readily with *tert*-butoxytitanatranes  $[N(CH_2CH_2O)_3]Ti(O^tBu)$ , undergoing metathesis of the phenol with the *tert*-butoxide to give the aryloxytitanatranes **1**, **2**, and **3**, respectively, and free *tert*-butyl alcohol. Regardless of the stoichiometry used, only one phenol group per triphenylmethane is metalated by *tert*-butoxytitanatranes. In all cases, the complexes form monomeric, trigonal bipyramidal complexes with fully chelated and deprotonated triethanolamine ligands and monodentate phenoxides, as confirmed by X-ray crystallography for **1** and **2**. Complex **2** thus contains one free OH group and compound **3** two free OH groups.

NMR spectra of **2** and **3** confirm that free and bound aryloxy groups are distinct on the NMR time scale near room temperature, but begin to exchange as the temperature is raised. Thus, the titanium can “hop” from one oxygen of  $L^2(OH)_2$  or  $L^3(OH)_3$  to another, with the proton of the newly metalated oxygen taking the place vacated by the titanium. The reactions are first-order in titanium, but have surprisingly negative entropies of activation ( $\Delta S^\ddagger = -28.8 \pm 0.5$  cal/mol·K for **2**,  $-30.9 \pm 1.6$  cal/mol·K for **3**). This degenerate phenol metathesis is analogous to the *tert*-butoxide/phenol interchange used in the synthesis of compounds **1–3**, and metathesis of alcohols or phenols with metal alkoxides is ubiquitous in the synthetic chemistry of titanium. Surprisingly, few mechanistic studies of this reaction have been reported for titanium or indeed for any transition metal, with

**Scheme 1.** Proposed Mechanism of Degenerate Phenol/Phenoxide Interchange in  $L^2(OH)(OTi[N(CH_2CH_2O)_3])$  (**2**)



the only thorough study one of exchange of rhenium alkoxides  $L_2Re(CO)_3(OR)$  with alcohols or phenols reported by Simpson and Bergman.<sup>21</sup> The principal mechanism inferred in this system, involving protonation of the alkoxide and dissociation to a  $[L_2Re(CO)_3]^+[RO^-H^-OR]^-$  ion pair, seems unlikely to be relevant to the highly oxophilic and electronically unsaturated titanium complexes studied here. The lack of a significant solvent effect (between toluene and methylene chloride) also argues against the formation of ionic intermediates in the reaction.

Instead, we propose that exchange involves coordination of the free phenolic oxygen to titanium, with proton transfer to one arm of the aminetriethoxide ligand taking place concurrently or in a subsequent step (Scheme 1). Dissociation of the protonated arm of the triethanolamine and pseudorotation of the five-coordinate, “arm-off” species would position the protonated arm appropriately to exchange with the originally apical phenoxide group, completing the interchange. Direct exchange between phenoxide and phenol by an analogous pathway would also effect an interchange between the groups. However, the constraints imposed by the chelate ring would require extremely acute C–O–H angles during the proton transfer, if both phenoxide oxygens are coordinated to titanium. In contrast, the crystal structure of **2** demonstrates the feasibility of forming a hydrogen bond between a phenol and the deprotonated triethanolamine, though this is only indirectly relevant to proton transfer in a

(21) Simpson, R. D.; Bergman, R. G. *Organometallics* **1993**, *12*, 781–796.



species with both groups coordinated to titanium. Initial exchange with a triethanolamine arm, rather than with the phenoxide, is also favored by the greater basicity of the alkoxide. In general, metal alkoxides react favorably with phenols,<sup>22</sup> though there are rare exceptions.<sup>23</sup> Finally, the strongly negative entropies of activation and low enthalpies of activation suggest that phenol binding to titanium is taking place and are consistent with a highly ordered four-center transition state.

The facility with which partial dechelation of the triethanolamine ligand takes place in the phenol interchange reactions of **2** or **3** is surprising, given the well-known stability of the metallatrane structure. Nevertheless, this dynamic dechelation is pushed even farther in fully metalated complex **4**, where triethanolamine slippage is observed even in the static structure. Although metalation of the free phenols in **2** or **3** is relatively difficult, requiring titanium amides rather than alkoxides, once the second titanium does bind in **4**, there is a net ligand shift. The bisphenoxide chelates with terminal aryloxides to one titanium, which effectively loses its aminetriethoxide group to a neighboring titanium, which binds the two nitrogens and five of the six oxygens of two aminetriethoxide ligands. The sixth CH<sub>2</sub>CH<sub>2</sub>O group extends to ligate the phenoxide-bound titanium of a neighboring dititanium unit in the cyclic complex **4**. It thus appears that the relative proclivities of the bisphenoxide and the aminetriethoxide to chelate are closely balanced, with aminetriethoxide chelation preferred (although only modestly) in **2** and **3**, and the bis(phenoxide) ligand chelating preferentially in the fully metalated **4**.

Metallatranes where two nitrilotriethanol ligands are bound to a single metal center are known.<sup>8,24</sup> In these cases, though, the second triethanolamine is bound as a simple terminal alkoxide, with the amine uncoordinated. There is no precedent for a "double atrane" structure similar to **4**. Conversely, methylenebis(phenoxide) ligands<sup>20d,25</sup> and methylidynetris(phenoxide)<sup>11</sup> ligands are well-known to be able to bridge metal centers. Even if the phenoxides adopt a terminal bonding mode, an alternative structure for L<sup>2</sup>(OTi[(OCH<sub>2</sub>-CH<sub>2</sub>)<sub>3</sub>N])<sub>2</sub> where each aryloxy is bonded to a different titanium appears reasonable. A simple bis(complex) similar to **1** or **2** might be possible, and if this brought the two titanium centers too close to each other, the nitrilotriethoxide oxygens could presumably bridge the titaniums. For example,

a structure analogous to dimeric {[N(CH<sub>2</sub>CH<sub>2</sub>O)<sub>3</sub>Ti(O'Pr)]<sub>2</sub>}, except with the axial groups syn rather than anti, seems reasonable.

In light of these other, apparently less exotic, possibilities, why does complex **4** adopt its observed "slipped" structure? One possible factor that may be important is a preference for forming a chelated eight-membered ring with terminal aryloxides. Normally, one thinks of five- and six-membered chelate rings as being most favorable.<sup>26</sup> However, d<sup>0</sup> metal alkoxides generally have rather obtuse M–O–C angles, presumably to maximize  $\pi$  donation from the oxygen lone pairs to the electron-poor metal center.<sup>27</sup> Such large angles are incompatible with five- or six-membered rings, yet the eight-membered rings here allow relatively large angles of 149° on average, only modestly more acute than the 165° angles seen in the unconstrained phenoxides **1** and **2**. Indeed, even larger chelate rings containing alkoxides are known for titanium and show little evidence of strain.<sup>28</sup> Complex **4** provides a dramatic example of how this preference for chelation can even outweigh the well-known predilection of the nitrilotriethoxide ligand to adopt a tetradentate binding mode.

## Conclusions

Mono-, di-, and trihydroxylated triphenylmethanes L<sup>1</sup>OH, L<sup>2</sup>(OH)<sub>2</sub>, and L<sup>3</sup>(OH)<sub>3</sub> are readily monometalated by [N(CH<sub>2</sub>-CH<sub>2</sub>O)<sub>3</sub>]TiO'Bu to give complexes **1–3**. In these monomeric complexes, the nitrilotriethoxide is fully chelated, and the aryloxy is monodentate. However, complexes **2** and **3**, which contain free phenols, readily undergo intramolecular migration of titanium between the phenol units, apparently via an intermediate which contains a chelated bis(phenoxide) and a monoprotonated nitrilotriethoxide. Further metalation of the free phenols in **2** and **3** is difficult, requiring metathesis with titanium amides, and mixtures of products are formed. In the crystallographically characterized fully metalated complex **4**, the bisphenoxide ligand L<sup>2</sup>(O)<sub>2</sub><sup>2-</sup> is chelated, even though this requires an unprecedented displacement of the nitrilotriethoxide ligand from the chelated titanium onto a neighboring titanium in the cyclic octatitanium complex. Thus, the proclivity of methylenebis(phenoxides) to chelate to titanium appears to rival or even exceed the propensity of nitrilotriethoxide to form the usual chelated atrane structure.

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**Supporting Information Available:** Crystallographic data for **1**, **2**, and **4**·2C<sub>5</sub>H<sub>12</sub>·8.5CH<sub>2</sub>Cl<sub>2</sub> in CIF format. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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