

Ortho-Linked Polyaryloxiide Ligands and Their Titanium Complexes

Ajay Kayal, Andrew F. Ducruet, and Sonny C. Lee*

Department of Chemistry, Princeton University, Princeton, New Jersey 08544

Received March 10, 2000

Ortho-linked polyphenols, quaterphenol $L(OH)_4$, and moderately hindered terphenol $PhL(OH)_3$ are developed as new multidentate polyaryloxiide ligands for transition-metal chemistry. The polyphenols are synthesized using ortho-metalation and metal-catalyzed cross-coupling methodologies; the synthetic routes allow for facile electronic and steric modification of the basic ligand design. The Ti(IV) coordination chemistry of these ligands reveals a diverse collection of bridged structures: dimeric $[Ti(\mu-PhLO_3)(O^iPr)]_2$ ($P2_1/n$, $a = 12.2699(5)$ Å, $b = 11.7957(5)$ Å, $c = 21.238(1)$ Å, $\beta = 94.551(1)^\circ$, $Z = 2$, $T = 170(2)$ K), dimeric $[Ti_2(\mu-PhLO_3)_2(\mu-Cl)(Cl)(THF)]$ ($P1$, $a = 11.212(1)$ Å, $b = 14.165(1)$ Å, $c = 22.447(2)$ Å, $\alpha = 90.440(4)^\circ$, $\beta = 93.345(4)^\circ$, $\gamma = 111.164(4)^\circ$, $Z = 2$, $T = 170(2)$ K), and trimeric $[Ti_3(\mu,\mu'-LO_4)(\mu-O^iPr)_2(O^iPr)_6]$ ($P2_1/n$, $a = 11.1022(5)$ Å, $b = 18.7015(9)$ Å, $c = 24.409(1)$ Å, $\beta = 95.369(2)^\circ$, $Z = 4$, $T = 170(2)$ K). The reaction of $TiCl_3(THF)_3$ with $[PhLO_3]^{3-}$ results in oxidation of Ti(III) to Ti(IV) and formation of the oxo dimer $[Ti(PhLO_3)(THF)]_2(\mu-O)$ ($P1$, $a = 10.8649(6)$ Å, $b = 12.1882(7)$ Å, $c = 14.3349(9)$ Å, $\alpha = 65.602(3)^\circ$, $\beta = 84.390(3)^\circ$, $\gamma = 86.582(3)^\circ$, $Z = 1$, $T = 200(2)$ K); the oxo group presumably originates from the THF solvent. The titanium centers in these environments are either 5- or 6-coordinate, with distorted square pyramidal/trigonal bipyramidal and distorted octahedral geometries, respectively; the polyphenoxide chelate ligands are capable of bridging multiple oxophilic titanium sites.

Introduction

Alkoxide and aryloxiide donors (RO^-) constitute a broad and important ligand class in transition-metal chemistry.¹ The versatility of RO^- ligation stems from the tunable electronic and steric properties of the organic (R) substituents and the easy availability of the corresponding parent alcohols; these characteristics have prompted the application of RO^- ligands to diverse areas ranging from materials synthesis^{1a,2,3} to catalysis.⁴ Sterically demanding monodentate RO^- spectator ligands have proven particularly effective in the study of reactive metal centers,^{4c,d,5,6} and their use illustrates a recurring theme in ligand design: the enhancement of reactivity, selectivity, or stability through ligand-directed control of the metal-coordination sphere.

The power of this approach has been reaffirmed by the recent advances in catalysis⁷ and bioinorganic model chemistry⁸ that have depended on geometry-constraining chelates, multidentate ancillary ligands specifically engineered to force highly structured coordination environments. The success of these latest iterations in ligand design and the established utility of RO^- ligation suggest that the development of synthetically adaptable, geometry-constraining RO^- chelates has potential in expanding the scope of transition-metal reactivity.

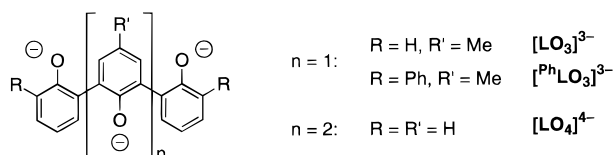
RO^- groups are ubiquitous in multidentate ligands, occurring frequently and with variation as components of mixed donor sets.⁹ Multidentate ligands with pure RO^- donor environments are more restricted in construction and can be organized broadly into three basic categories of parent alcohols:¹⁰ (i) aliphatic polyols — predominantly diols, but also tripodal and cyclic triols;^{1a,11} (ii) polyphenols prepared through condensation reactions of aldehydes and phenols, and distinguished by phenol

- (1) (a) Mehrotra, R. C.; Singh, A. *Prog. Inorg. Chem.* **1997**, *46*, 239. (b) Rothwell, I. P.; Chisholm, M. H. Alkoxides and Aryloxides. In *Comprehensive Coordination Chemistry*; Wilkinson, G., Gillard, R. D., McCleverty, J. A., Eds.; Pergamon Press: New York, 1987; Vol. 2, pp 335–364.
- (2) Bradley, D. C. *Chem. Rev.* **1989**, *89*, 1317.
- (3) (a) Vaid, T. P.; Tanski, J. M.; Pette, J. M.; Lobkovsky, E. B.; Wolczanski, P. T. *Inorg. Chem.* **1999**, *38*, 3394. (b) Vaid, T. P.; Lobkovsky, E. B.; Wolczanski, P. T. *J. Am. Chem. Soc.* **1997**, *119*, 8742.
- (4) See the following for examples. (a) Asymmetric ring-closing metathesis: Zhu, S. S.; Cefalo, D. R.; La, D. S.; Jamieson, J. Y.; Davis, W. M.; Hoveyda, A. H.; Schrock, R. R. *J. Am. Chem. Soc.* **1999**, *121*, 8251. (b) Alkane oxidation: Fujiwara, M.; Qiang, X.; Souma, Y.; Kobayashi, T. *J. Mol. Catal. A: Chem.* **1999**, *142*, 77. (c) Claisen rearrangement: Saito, S.; Yamamoto, H. *Chem. Commun.* **1997**, 1585, and references therein. (d) Arene hydrogenation: Rothwell, I. P. *Chem. Commun.* **1997**, 1331. (e) Alkene metathesis: Schrock, R. R. *Polyhedron* **1995**, *14*, 3177. (f) Olefin polymerization: Linden, A. V. R.; Schaverian, C. J.; Meijboom, N.; Ganter, C.; Orpen, A. G. *J. Am. Chem. Soc.* **1995**, *117*, 3008. (g) Diels–Alder reaction: Boyle, T. J.; Eilerts, N. W.; Heppert, J. A.; Takusagawa, F. *Organometallics* **1994**, *13*, 2218, and references therein. (h) Asymmetric epoxidation: Finn, M. G.; Sharpless, K. B. *J. Am. Chem. Soc.* **1991**, *113*, 113.
- (5) (a) Wolczanski, P. T. *Polyhedron* **1995**, *14*, 3335, and references therein. (b) Lubben, T. V.; Wolczanski, P. T. *J. Am. Chem. Soc.* **1987**, *109*, 424.

- (6) (a) Rothwell, I. P. *Acc. Chem. Res.* **1988**, *21*, 153, and references therein. (b) Waratuke, S. A.; Thorn, M. G.; Fanwick, P. E.; Rothwell, A. P.; Rothwell, I. P. *J. Am. Chem. Soc.* **1999**, *121*, 9111. (c) Vilaro, J. S.; Lockwood, M. A.; Hanson, L. G.; Clark, J. R.; Parkin, B. C.; Fanwick, P. E.; Rothwell, I. P. *J. Chem. Soc., Dalton Trans.* **1997**, 3553.
- (7) For some recent examples, see: (a) Britovsek, G. J. P.; Gibson, V. C.; Wass, D. F. *Angew. Chem., Int. Ed.* **1999**, *38*, 428. (b) Younkin, T. R.; Connor, E. F.; Henderson, J. I.; Friedrich, S. K.; Grubbs, R. H.; Bansleben, D. A. *Science* **2000**, *287*, 460, and references therein.
- (8) See for example: (a) Holland, P. L.; Tolman, W. B. *J. Am. Chem. Soc.* **1999**, *121*, 7270. (b) Wang, Y. D.; DuBois, J. L.; Hedman, B.; Hodgson, K. O.; Stack, T. D. P. *Science* **1998**, *279*, 5350. (c) Zhou, Z.; Munck, E.; Holm, R. H. *J. Am. Chem. Soc.* **1996**, *118*, 1966. (d) Kitajima, N.; Tolman, W. B. *Prog. Inorg. Chem.* **1995**, *43*, 419.
- (9) See the following for examples. (a) Schiff bases: Calligaris, M.; Randaccio, L. Schiff Bases as Acyclic Polydentate Ligands. In *Comprehensive Coordination Chemistry*; Wilkinson, G., Gillard, R. D., McCleverty, J. A., Eds.; Pergamon Press: New York, 1987; Vol. 2, pp 715–738. (b) Atranis: Verkade, J. G. *Acc. Chem. Res.* **1993**, *26*, 483.

units connected at *ortho* positions through single carbon (usually methylene) linkers;^{12–15} and (iii) 2,2'-biphenol/binaphthol derivatives with direct *ortho* aryl–aryl bonds.¹⁶ Although pure RO[−] chelates have been employed with some success in mediating metal-centered reactivity,^{4a,f,g,14e,h–j} the systematic modification of these ligand designs has only recently attracted attention.^{4a,14c,d,15}

We are investigating direct *ortho*-linked polyphenoxides, higher-denticity homologues of type (iii) 2,2'-biphenoxide chelates, as new multidentate RO[−] ligands that can be readily modified to create tailored metal-coordination environments. This report describes flexible synthetic routes to simple tridentate ([^PhLO₃]^{3−}) and tetradentate ([LO₄]^{4−}) ligands, and initial structural studies of the coordination chemistry of these chelates at Ti(IV) centers.



- (10) Only simple RO[−] donors are considered here; catechol- and silasesquioxane-derived ligands are excluded from this classification. (a) For a recent review on the coordination chemistry of catecholate ligands, see: Pierpont, C. G.; Lange, C. W. *Prog. Inorg. Chem.* **1994**, *41*, 331. (b) For a recent review on silasesquioxane ligands, see: Feher, F. J.; Budzichowski, T. A. *Polyhedron* **1995**, *14*, 3239.
- (11) Some examples include: (a) Boyle, T. J.; Schwartz, R. W.; Doedens, R. J.; Ziller, J. W. *Inorg. Chem.* **1995**, *34*, 1110, and references therein. (b) Clark, D. L.; Click, D. R.; Grumbine, S. K.; Scott, B. L.; Watkin, J. G. *Inorg. Chem.* **1998**, *37*, 6237. (c) Chen, Q.; Chang, Y. D.; Zubieta, J. *Inorg. Chim. Acta* **1997**, *258*, 257. (d) Bebedorf, J.; Burgi, H. B.; Gamp, E.; Hitchman, M. A.; Murphy, A.; Reinen, D.; Riley, M. J.; Stratemeier, H. *Inorg. Chem.* **1996**, *35*, 7419. (e) Gainsford, G. J.; Kemmitt, T.; Lensink, C.; Milestone, N. B. *Inorg. Chem.* **1995**, *34*, 746–748. (f) Lehtonen, A.; Sillanpaa, R. *Polyhedron* **1994**, *13*, 2519. (g) Bachand, B.; Belanger-Gariepy, F.; Wuest, J. D. *Organometallics* **1990**, *9*, 2860. (h) Galeffi, B.; Simad, M.; Wuest, J. D. *Inorg. Chem.* **1990**, *29*, 955.
- (12) Type (ii) polyphenols encompass a range of structure types, including bidentate diphenols,¹³ cyclic calixarenes of four, six, and eight phenols,¹⁴ and, more recently, tripodal and linear tridentate triphenols.¹⁵
- (13) (a) Fokken, S.; Spaniol, T. P.; Okuda, J. *Organometallics* **1997**, *16*, 4240. (b) Chisholm, M. H.; Huang, J. H.; Huffmann, J. C.; Streib, W. E.; Tiedtke, D. *Polyhedron* **1997**, *16*, 2941. (c) Okuda, J.; Fokken, S.; Kang, H.-C.; Massa, W. *Chem. Ber.* **1995**, *128*, 221. (d) Corazza, F.; Floriani, C.; Chiesi-Villa, A.; Guastini, C. *Inorg. Chem.* **1991**, *30*, 445. (e) Floriani, C.; Corazza, F.; Lesueur, W.; Chiesi-Villa, A.; Guastini, C. *Angew. Chem., Intl. Ed. Engl.* **1989**, *93*, 101.
- (14) (a) Roundhill, D. M. *Prog. Inorg. Chem.* **1995**, *43*, 533. (b) Weiser, C.; Dieleman, C. B.; Matt, D. *Coord. Chem. Rev.* **1997**, *165*, 93. (c) Dienst, E. V.; Bakker, W. I. I.; Engbersen, J. F. J.; Verboom, W.; Reinhoudt, D. N. *Pure Appl. Chem.* **1993**, *65*, 387. (d) Bohmer, V.; Vogt, W. *Pure Appl. Chem.* **1993**, *65*, 403. (e) Floriani, C. *Chem. – Eur. J.* **1999**, *5*, 19. (f) Caselli, A.; Solari, E.; Scopelliti, R.; Floriani, C. *J. Am. Chem. Soc.* **1999**, *121*, 8296. (g) Giannini, L.; Dovesi, S.; Solari, E.; Floriani, C.; Chiesi-Villa, A.; Rizzoli, C. *Angew. Chem., Intl. Ed.* **1999**, *38*, 807. (h) Castellano, B.; Solari, E.; Floriani, C.; Re, N.; Chiesi-Villa, A.; Rizzoli, C. *Organometallics* **1998**, *17*, 2328. (i) Giannini, L.; Solari, E.; Floriani, C.; Chiesi-Villa, A.; Rizzoli, C. *J. Am. Chem. Soc.* **1998**, *120*, 823. (j) Zanotti-Gerosa, A.; Solari, E.; Giannini, L.; Floriani, C.; Chiesi-Villa, A.; Rizzoli, C. *J. Am. Chem. Soc.* **1998**, *120*, 437. (k) Chisholm, M. H.; Foltling, K.; Streib, W. E.; Wu, D.-D. *Chem. Commun.* **1998**, 379. (l) Zanotti-Gerosa, A.; Solari, E.; Giannini, L.; Floriani, C.; Re, N.; Chiesi-Villa, A.; Rizzoli, C. *Inorg. Chim. Acta* **1998**, *270*, 298. (m) Gibson, V. C.; Redshaw, C.; Clegg, W.; Elsegood, M. R. *J. Chem. Commun.* **1997**, 1605, and references therein. (n) Corazza, F.; Floriani, C.; Chiesi-Villa, A.; Guastini, C. *J. Chem. Soc., Chem. Commun.* **1990**, 640.
- (15) (a) Gordon, B. W. F.; Scott, M. J. *Inorg. Chim. Acta* **2000**, *297*, 206. (b) Dinger, M. B.; Scott, M. J. *Inorg. Chem.* **2000**, *39*, 1238. (c) Dinger, M. B.; Scott, M. J. *Chem. Commun.* **1999**, 2525. (d) Gordon, B. W. F.; Scott, M. J. *Abstr. Pap. – Am. Chem. Soc. (Inorg. – Part 1)* **1999**, 218, 636.

Results and Discussion

Ligand Design and Synthesis. The ability of the 2,2'-biaryl framework to direct stereochemistry is well-known and has been exploited extensively in 2,2'-binaphthyl derivatives for asymmetric induction.^{4a,16} *Ortho* steric interactions between adjacent rings drive torsional rotation at the aryl–aryl bond; for biaryl ligands that coordinate through 2,2'-donor substituents, this nonplanar dihedral preference is reinforced by the formation of a seven-membered metallacycle upon chelation. These stereochemical properties have led us to investigate ligand designs based on an extended *ortho*-linked polyphenoxide skeleton: the polyaryl backbone is expected to twist, creating distinctly nonplanar chelates with potentially useful metal-coordination geometries. A range of substituents can be incorporated onto the polyaryl framework to further modify electronic and steric properties at the metal center.

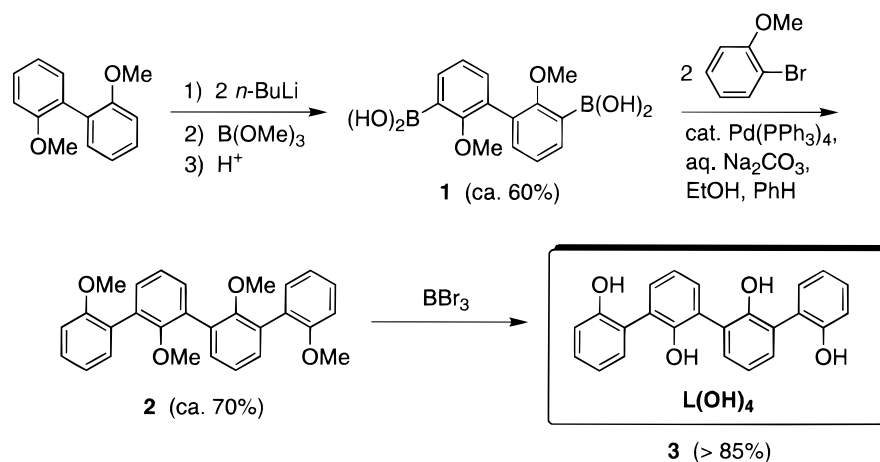
Ortho-linked polyphenols can be synthesized directly through radical-based oxidative phenolic coupling reactions.¹⁷ Although these syntheses are simple, direct, and inexpensive, they entail separation of limited quantities of product from a syrup of mixed oligomers and are not well-suited for selective functionalization. The extensive and powerful synthetic repertoire of aromatic chemistry, however, allows for more specific, yet flexible, routes to this chelate design, thereby enhancing the versatility of polyaryloxy ligands. The obligatory phenoxide groups in the target molecules, when protected as aryl ethers, confer particular utility to the complementary tactics of *ortho*-metalation¹⁸ and metal-catalyzed cross-coupling;¹⁹ the sequential application of these two methodologies permits the elaboration of the ligand framework at the important *ortho* positions.

The combination of *ortho*-metalation and cross-coupling chemistry is demonstrated in the facile preparation of quaterphenol **3**, L(OH)₄ (Scheme 1). 2,2'-Dimethoxybiphenyl is *ortho*-dilithiated,²⁰ and then quenched with excess B(OMe)₃ to give the bis(boronic acid) **1** upon acidification.²¹ Palladium-catalyzed cross-coupling of **1** with 2 equiv of 2-bromoanisole under Suzuki conditions²² affords quateranisole **2**, which is isolated and then deprotected with BBr₃ to give the desired quaterphenol **3** in 36% overall yield from commercial 2,2'-dimethoxybiphenyl.

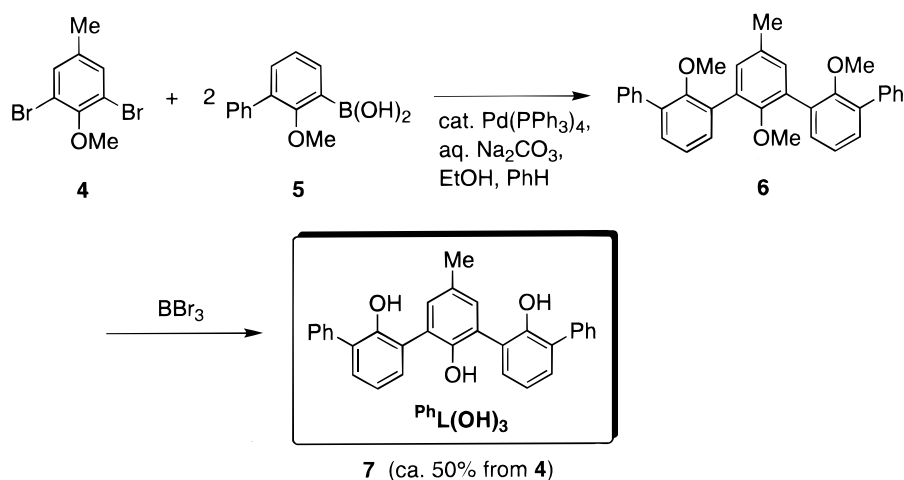
Terphenol **7**, ^PhL(OH)₃, is prepared in a similar fashion (Scheme 2). Suzuki coupling of 2,6-dibromo-4-methylanisole (**4**)²³ with 2 equiv of 2-methoxy-3-phenylphenylboronic acid

- (16) (a) Pu, L. *Chem. Rev.* **1998**, *98*, 2405, and references therein. (b) Eilerts, N. W.; Heppert, J. A. *Polyhedron* **1995**, *14*, 3255.
- (17) (a) Sartori, G.; Maggi, R.; Bigi, F.; Grandi, M. *J. Org. Chem.* **1994**, *59*, 3701. (b) Sartori, G.; Maggi, R.; Bigi, F.; Grandi, M. *J. Org. Chem.* **1993**, *58*, 7271. (c) Sartori, G.; Maggi, R.; Bigi, F.; Arienti, A.; Casnati, G.; Bocelli, G.; Mori, G. *Tetrahedron Lett.* **1992**, *48*, 9483. (d) Majumder, P. L.; Kundu, A. *J. Indian Chem. Soc.* **1984**, *61*, 142. (e) Lee, R. J.; Kurasiewicz, A. S.; Richardson, E. E. Poly-hindered phenolphosphites and process for preparation. U.S. Patent 4,416,829, Nov 12, 1983. (f) Koening, K. E.; Lein, G. M.; Stuckler, P.; Kaneda, T.; Cram, D. J. *J. Am. Chem. Soc.* **1979**, *101*, 3553.
- (18) (a) Gschwend, H. W.; Rodriguez, H. R. *Org. React. (N. Y.)* **1979**, *26*, 1. (b) Beak, P.; Snieckus, V. *Acc. Chem. Res.* **1982**, *15*, 306. (c) Snieckus, V. *Chem. Rev.* **1990**, *90*, 879.
- (19) *Comprehensive Organic Synthesis: Carbon–Carbon σ-Bond Formation*; Trost, B. M., Fleming, I., Pattenden, G., Eds.; Pergamon Press: Oxford, U.K, 1991; Vol. 3.
- (20) Cram, D. J.; deGrandpre, M.; Knobler, C. B.; Trueblood, K. N. *J. Am. Chem. Soc.* **1984**, *106*, 3286.
- (21) The 1,1'-binaphthyl homologue has been reported: Simonsen, K. B.; Gothelf, K. V.; Jorgensen, K. A. *J. Org. Chem.* **1998**, *63*, 7536.
- (22) (a) Miyaura, N.; Suzuki, A. *Chem. Rev.* **1995**, *95*, 2457. (b) Schwartz, E. A.; Knobler, C. B.; Cram, D. J. *J. Am. Chem. Soc.* **1992**, *114*, 10775.
- (23) (a) Koln, M.; Segel, A. *Monatsh. Chem.* **1925**, *46*, 661. (b) Wang, X.; Snieckus, V. *Tetrahedron Lett.* **1991**, *37*, 4879. (c) Lehmann, P. A. *F. Org. Magn. Reson.* **1973**, *5*, 67.

Scheme 1



Scheme 2



(5, prepared by literature procedure,²⁴) gives teranisole 6, which is then deprotected to yield terphenol 7. The unsubstituted terphenol **L(OH)₃** has also been synthesized by the analogous coupling of 4 with 2 equiv of 2-methoxyphenylboronic acid (prepared²⁵ from 2-bromoanisole); titanium complexes of this ligand, however, have proven resistant to crystallization, prompting the use of the moderately hindered and more crystalline phenyl-substituted derivative 7 reported here.

The syntheses of the polyphenols are straightforward, with reaction products isolable in pure form by bulk recrystallization or by a single uncomplicated chromatographic separation at the final synthetic step. The palladium-catalyzed Suzuki cross-coupling protocol²² is especially convenient: the boronic acid precursors are readily prepared and isolated by crystallization, and the boron-containing coproducts from the coupling reactions are easily removed by aqueous extraction.

Titanium Complexes. To our knowledge, there are no structurally characterized complexes of *ortho*-linked polyaryloxides with denticity greater than 2,²⁶ and molecular models²⁷ indicate a number of accessible metal stereochemistries for these ligands. The initial metal-binding studies described here focus, therefore, on the structural chemistry of the polyaryloxide

complexes. The coordination chemistry of polyphenols **L(OH)₄** (3) and **PhL(OH)₃** (7) was explored using Ti(IV), a high-valent, oxophilic, early-transition metal center expected to interact well with the polyaryloxide chelates to give neutral complexes; the use of a *d*⁰ metal center also allows for the examination of ligand coordination preferences in the absence of *d*-orbital occupancy effects on structure. Complexes are accessed from simple precursors by protonolysis (via the parent polyphenols) or anion metathesis (via the deprotonated polyphenoxides). Because of the emphasis on structural characterization synthetic yields are not optimized, and other species may be formed in the syntheses that are not isolated under our crystallization conditions. All complexes have been characterized by single-crystal X-ray diffraction (Table 1) with the homogeneity of the bulk crystalline sample assessed by ¹H NMR spectroscopy, elemental analysis (C, H, N, Ti), and unit cell determinations on multiple, randomly chosen single crystals. The titanium complexes are very sensitive to hydrolysis, as expected for titanium alkoxides/aryloxides.

(i) **[Ti(μ-PhLO₃)(OⁱPr)]₂** (8). The reaction of Ti(OⁱPr)₄ with **PhL(OH)₃** (7) in CH₂Cl₂ results in an immediate solution color change to yellow-orange; vapor diffusion crystallization from CH₂Cl₂/*n*-pentane allows isolation of pure yellow-orange 8. The ¹H NMR spectrum of the crystalline sample dissolved in CD₂Cl₂

(24) Direct *ortho*-lithiation of 2-phenylanisole gives a complex product mixture, presumably because of competing metalation of the pendant phenyl ring; a more involved, three-step synthesis was necessary to obtain 5 (33% overall yield from commercial 2-phenylphenol): Yuang, H.; Hay, A. S. *J. Polym. Sci., Part A: Polym. Chem.* **1993**, *31*, 1261.
 (25) Thompson, W. J.; Gaudino, J. *J. Org. Chem.* **1984**, *49*, 5237.

(26) (a) *Cambridge Structural Database*, Version 5.18; Cambridge University: Cambridge, U.K., Oct. 1999. (b) Allen, F. H.; Kennard, O. *Chem. Des. Autom. News* **1993**, *8*, 31.
 (27) *Spartan 5.0.3*; Wavefunction, Inc., 18401 Van Karman Ave., # 370: Irvine, CA 92612.

Table 1. Crystallographic Data^a for [Ti(μ -^{Ph}LO₃)(OⁱPr)]₂·2CH₂Cl₂ (**8**·2CH₂Cl₂), [Ti₂(μ -^{Ph}LO₃)₂(μ -Cl)(Cl)(THF)]·4CH₂Cl₂ (**9**·4CH₂Cl₂), [Ti(^{Ph}LO₃)(THF)]₂(μ -O)·4CH₂Cl₂ (**10**·4CH₂Cl₂), and [Ti₃(μ , μ' -LO₄)(μ -OⁱPr)₂(OⁱPr)₆] (**11**)

	8 ·2CH ₂ Cl ₂	9 ·4CH ₂ Cl ₂	10 ·4CH ₂ Cl ₂ ^b	11
formula	C ₇₀ H ₆₀ O ₈ Ti ₂ Cl ₄	C ₇₀ H ₅₈ O ₇ Ti ₂ Cl ₁₀	C ₇₄ H ₆₆ O ₉ Ti ₂ Cl ₈	C ₄₈ H ₇₀ O ₁₂ Ti ₃
fw	1266.78	1461.46	1478.67	982.74
cryst syst	monoclinic	triclinic	triclinic	monoclinic
space group	<i>P</i> 2 ₁ / <i>n</i> (No. 14)	<i>P</i> $\bar{1}$ (No. 2)	<i>P</i> $\bar{1}$ (No. 2)	<i>P</i> 2 ₁ / <i>c</i> (No. 14)
<i>Z</i>	2	2	1	4
<i>a</i> , Å	12.2699(5)	11.212(1)	10.8649(6)	11.1022(5)
<i>b</i> , Å	11.7957(5)	14.165(1)	12.1882(7)	18.7015(9)
<i>c</i> , Å	21.238(1)	22.447(2)	14.3349(9)	24.409(1)
α , deg		90.440(4)	65.602(3)	
β , deg	94.551(1)	93.345(4)	84.390(3)	95.369(2)
γ , deg		111.164(4)	86.582(3)	
<i>V</i> , Å ³	3064.1(2)	3317.0(6)	1720.1(2)	5045.8(4)
temp, K	170(2)	170(2)	200(2)	170(2)
θ_{\max} , deg	27.51	27.29	25.07	27.49
completeness of data, %	99.4	93.1	97.6	99.6
ρ_{calc} , g cm ⁻³	1.373	1.463	1.427	1.294
μ , mm ⁻¹	0.492	0.698	0.600	0.520
<i>R</i> (<i>wR</i> 2), ^c %	5.30 (13.62)	5.84 (12.46)	5.55 (13.12)	6.45 (14.83)
goodness of fit ^d	1.027	1.017	1.043	1.031

^a Data collected with graphite-monochromatized Mo K α radiation ($\lambda = 0.71073$ Å) using ω scans. ^b Complex **10** also crystallizes as a CH₂Cl₂ disolvate.⁴² ^c Calculated for $I > 2\sigma(I)$: $R = \sum ||F_o| - |F_c|| / \sum |F_o|$, $wR2 = \{ \sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2] \}^{1/2}$. ^d Goodness of fit = $[\sum w(F_o^2 - F_c^2)^2 / (n - p)]^{1/2}$, where *n* is the number of reflections and *p* is the number of parameters refined.

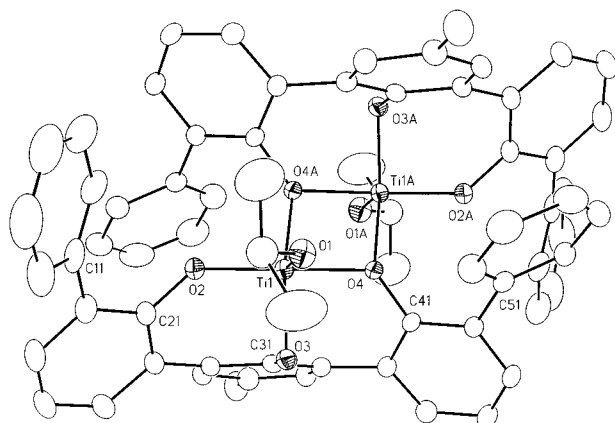


Figure 1. Structure of [Ti(μ -^{Ph}LO₃)(OⁱPr)]₂·2CH₂Cl₂ (**8**·2CH₂Cl₂) with thermal ellipsoids (35% probability level) and selected atom labels; hydrogen atoms are not shown. Atoms with labels ending in "A" are generated by a crystallographic inversion center. The isopropoxide in the asymmetric unit is disordered; only one of the two components is shown.

reveals one coordinated ligand **1** with no internal symmetry and one bound isopropoxide with diastereotopic methyl resonances.

Single-crystal X-ray diffraction analysis revealed complex **8** to be a centrosymmetric dimer (Figure 1); selected metrical parameters are given in Table 2. The dimer is composed of two inversion-related, distorted square pyramidal Ti(IV) centers,²⁸ edge-fused at cis equatorial sites with trans axial ligand orientations; the solid-state structure is consistent with the solution NMR data. The equatorial positions of each square pyramid are occupied exclusively by terphenoxide donors [O(2,3,4,4A)] whereas the axial position is taken up by a terminal isopropoxide ligand [O(1)]; one phenoxide arm [O(4)] of the tridentate ligand serves as an equatorial bridge to the

(28) The coordination polyhedron is intermediate between a square pyramid and trigonal bipyramid. In the distorted trigonal bipyramidal assignment, the central oxygen donor [O(3)] of a terphenoxide ligand occupies an equatorial site on the metal center, whereas the outer chelate arms [O(2, 4)] sit at axial positions; one chelate arm [O(4)] bridges to an equatorial position on the other metal center. The remaining equatorial positions are completed by a chelate arm from the other metal [O(4A)] and a terminal isopropoxide.

Table 2. Selected Interatomic Distances (Å) and Angles (deg) in [Ti(μ -^{Ph}LO₃)(OⁱPr)]₂·2CH₂Cl₂ (**8**·2CH₂Cl₂)

Distances			
Ti(1)–O(1)	1.748(2)	Ti(1)···Ti(1A)	3.312(1)
Ti(1)–O(2)	1.826(2)	Ti(1)···C(21)	2.964(2)
Ti(1)–O(3)	1.859(2)	Ti(1)···C(41)	3.115(2)
Ti(1)–O(4)	2.072(2)	Ti(1)–C(31)	2.548(2)
Ti(1)–O(4A)	2.023(2)		
Angles			
O(1)–Ti(1)–O(2)	102.02(8)	O(3)–Ti(1)–O(4A)	138.24(7)
O(1)–Ti(1)–O(3)	106.27(8)	O(3)–Ti(1)–O(4)	85.12(7)
O(1)–Ti(1)–O(4)	102.86(8)	O(4A)–Ti(1)–O(4)	72.09(7)
O(1)–Ti(1)–O(4A)	112.57(8)	C(21)–O(2)–Ti(1)	137.1(2)
O(2)–Ti(1)–O(3)	91.94(7)	C(31)–O(3)–Ti(1)	102.8(1)
O(2)–Ti(1)–O(4A)	94.43(7)	C(41)–O(4)–Ti(1)	127.5(1)
O(2)–Ti(1)–O(4)	154.76(7)		

other metal, resulting in a [μ : η^3 , η^1] chelate coordination mode. The metal center is raised 0.695(1) Å above the plane defined by the four equatorial ligands. The structure resembles those of known dinuclear 5-coordinate Ti(IV)-binaphthoxide complexes.^{4g,29}

(ii) [Ti₂(μ -^{Ph}LO₃)₂(μ -Cl)(Cl)(THF)] (**9**). Treatment of TiCl₄ with triply deprotonated **7** [^{Ph}LO₃]³⁻, generated in situ as the trilitium salt in THF results in an instant color change to dark red; orange-red crystals of complex **9** can be obtained from CH₂Cl₂/*n*-pentane vapor diffusion. The ¹H NMR spectrum of this product is complex: two equal-intensity methyl signals and numerous well-dispersed aromatic resonances are evident, suggesting two inequivalent chelates with no internal symmetry. Broadened resonances integrating to one bound THF are also present.

Complex **9** exists as an asymmetric (*C*₁) dimer in the solid state (Figures 2 and 3) with two distorted octahedral Ti(IV) centers connected through facial bridging; this low symmetry structure is in agreement with the observed solution NMR data. The two inequivalent chelate ligands each span both metals in a [μ : η^2 , η^2] manner, with the central phenoxides [O(3,30)] of the two chelates serving as the bridges; a chloride ligand [Cl(2)] is the final bridging atom. The metal coordination spheres are

(29) Boyle, T. J.; Barnes, D. L.; Heppert, J. A.; Morales, L.; Takusagawa, F. *Organometallics* **1992**, *11*, 1112.

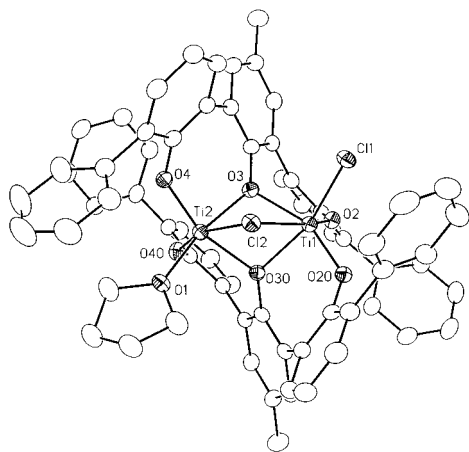


Figure 2. Structure of $[\text{Ti}_2(\mu\text{-PbLO}_3)_2(\mu\text{-Cl})(\text{Cl})(\text{THF})] \cdot 9 \cdot 4\text{CH}_2\text{Cl}_2$ with thermal ellipsoids (35% probability level) and selected atom labels; hydrogen atoms are not shown. The aryl rings of the chelate ligands are labeled as follows: [C(11–16)]–[O(2)C(21–26)]–[O(3)C(31–36)]–[O(4)C(41–46)]–[C(51–56)]; [C(101–106)]–[O(20)C(201–206)]–[O(30)C(301–306)]–[O(40)C(401–406)]–[C(501–506)].

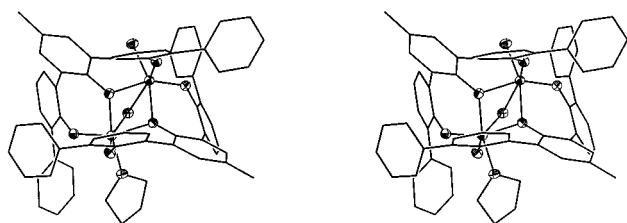


Figure 3. Stereoview of $[\text{Ti}_2(\mu\text{-PbLO}_3)_2(\mu\text{-Cl})(\text{Cl})(\text{THF})] \cdot 9 \cdot 4\text{CH}_2\text{Cl}_2$.

Table 3. Selected Interatomic Distances (Å) and Angles (deg) in $[\text{Ti}_2(\mu\text{-PbLO}_3)_2(\mu\text{-Cl})(\text{Cl})(\text{THF})] \cdot 4\text{CH}_2\text{Cl}_2$ (**9**·**4CH₂Cl₂**)

Distances			
Ti(1)–O(2)	1.787(2)	Ti(2)–O(40)	1.779(2)
Ti(1)–O(3)	2.052(2)	Ti(2)–O(1)	2.037(3)
Ti(1)–O(20)	1.823(2)	Ti(1)–Cl(1)	2.273(1)
Ti(1)–O(30)	2.049(2)	Ti(1)–Cl(2)	2.624(1)
Ti(2)–O(3)	1.998(3)	Ti(2)–Cl(2)	2.476(1)
Ti(2)–O(4)	1.821(2)	Ti(1)–Ti(2)	3.062(1)
Ti(2)–O(30)	2.018(2)		
Angles			
Ti(1)–O(3)–Ti(2)	98.2(1)	O(30)–Ti(1)–O(3)	71.52(9)
Ti(1)–O(30)–Ti(2)	97.71(9)	O(30)–Ti(1)–Cl(2)	73.52(7)
Ti(1)–Cl(2)–Ti(2)	73.74(3)	O(40)–Ti(2)–O(4)	102.8(1)
O(2)–Ti(1)–O(20)	102.5(1)	O(40)–Ti(2)–O(3)	99.2(1)
O(2)–Ti(1)–Cl(1)	99.85(9)	O(40)–Ti(2)–O(30)	87.3(1)
O(2)–Ti(1)–Cl(2)	164.65(9)	O(40)–Ti(2)–O(1)	90.7(1)
O(20)–Ti(1)–O(3)	102.34(8)	O(4)–Ti(2)–O(3)	88.8(1)
O(20)–Ti(1)–O(3)	155.9(1)	O(4)–Ti(2)–O(1)	99.3(1)
O(30)–Ti(1)–Cl(1)	157.40(7)	O(30)–Ti(2)–O(1)	96.9(1)
O(3)–Ti(2)–O(30)	73.3(1)	C(401)–O(40)–Ti(2)	131.5(2)
O(3)–Ti(2)–O(1)	165.6(1)	C(401)–O(40)–Ti(2)	139.6(2)
O(4)–Ti(2)–O(30)	160.7(1)	C(31)–O(3)–Ti(2)	135.5(2)
O(40)–Ti(2)–Cl(2)	164.2(1)	C(31)–O(3)–Ti(1)	124.8(2)
O(4)–Ti(2)–Cl(2)	80.84(7)	C(21)–O(2)–Ti(1)	145.1(2)
O(30)–Ti(2)–Cl(2)	77.46(7)	C(301)–O(30)–Ti(2)	133.6(2)

completed by terminal chloride [Cl(1)] on Ti(1) and a neutral THF donor for Ti(2). Selected structural metrics are presented in Table 3. The two Ti(1)–O(Ar)–Ti(2) bridges are approximately symmetric and equivalent. The Ti(1)–Cl(2)–Ti(2) bridge, however, is asymmetric, with a significantly stronger association with Ti(2); this structural preference is attributed to the terminal anionic Cl(1) donor on Ti(1), relative to the weak THF donor at the equivalent position on Ti(2). Several structurally characterized examples of facially bridged Ti-dimers are

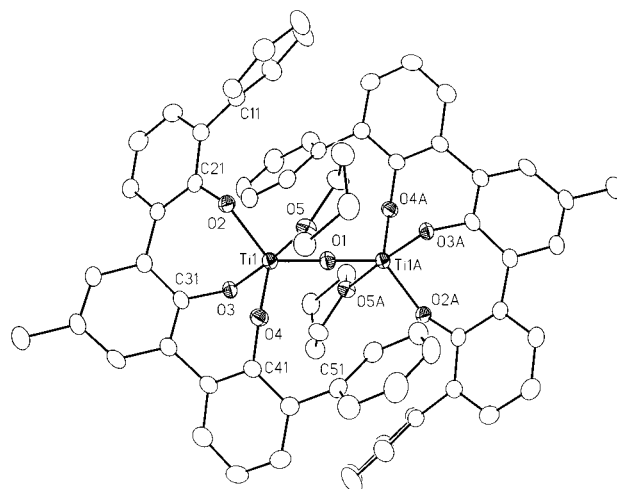


Figure 4. Structure of $[\text{Ti}(\text{PbLO}_3)(\text{THF})]_2(\mu\text{-O}) \cdot 10 \cdot 4\text{CH}_2\text{Cl}_2$ with thermal ellipsoids (35% probability level) and selected atom labels; hydrogen atoms are not shown. Atoms with labels ending in “A” are generated by a crystallographic inversion center; O(1) lies on the inversion center. The THF bound to the unique titanium center is disordered; only one of the two components is shown.

known. Most derive from the $[\text{Ti}_2(\mu\text{-X})_3]^{5+}$ core (X = halide)³⁰ although dimers with mixed bridges^{31,32} have also been observed; in general, the bridging ligands are symmetrically shared between the two metals.³²

(iii) $[\text{Ti}(\text{PbLO}_3)(\text{THF})]_2(\mu\text{-O})$ (**10**). The reaction of $\text{TiCl}_3(\text{THF})_3$ ³³ with triply deprotonated **7** ($[\text{PbLO}_3]^{3-}$) gives an immediate color change from light blue to dark orange-red; vapor-diffusion crystallization from $\text{CH}_2\text{Cl}_2/n$ -pentane yields orange crystals of **12**. The ¹H NMR spectrum of crystalline **12** shows signals with diamagnetic chemical shifts corresponding to one bound chelate and one coordinated THF.

Crystallographic characterization shows complex **12** to be a centrosymmetric dimer of trigonal bipyramidal titanium centers sharing an equatorial vertex (Figure 4); the idealized C_{2h} symmetry of the dimer fits the observed solution NMR spectrum. Unlike the situations in complexes **8** and **9**, the terphenoxide chelate ligand in dimer **10** coordinates solely to one metal center without bridging. The central phenoxide [O(3)] of the chelate ligand occupies an axial position, whereas the outer phenoxide arms [O(2,4)] bind to equatorial sites; the remaining axial ligand is supplied by a THF donor. The Ti atom is situated 0.094(1) Å above the plane defined by the equatorial donors, and is oriented toward the axial phenoxide ligand. Selected metrical parameters are provided in Table 4.

The single atom equatorial bridging ligand, located on a crystallographic inversion center, was identified as an oxo group by the metal–ligand distance (1.819(1) Å) and by structural refinement; this allows assignment of the metal oxidation state as Ti(IV). The appearance of the oxo ligand is consistently

(30) Ti(IV) facial bi-octahedra: (a) Feng, Q.; Luo, S.; Olmstead, M.; Rauchfuss, T. B.; Stafford, P. R. *Chem. Mater.* **1997**, *9*, 641, and references therein. (b) Kistenmacher, T. J.; Stucky, G. D. *Inorg. Chem.* **1971**, *10*, 122. Ti(III) facial bi-octahedra: (c) Chen, L.; Cotton, F. A.; Dunbar, K. R.; Feng, X.; Heintz, R. A.; Uzelmeir, C. *Inorg. Chem.* **1996**, *35*, 7358.

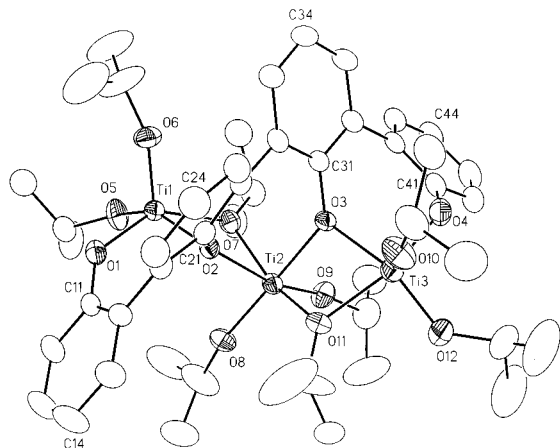
(31) $[\text{Ti}(\mu\text{-O})(\mu\text{-X})_2]^{4+}$: Friedrich, S.; Gade, L. H.; Li, W.-S.; McPartlin, M. *Chem. Ber.* **1996**, *129*, 1287.

(32) Two facially bridged Ti-dimers have been reported with asymmetric bridges. (a) Valence-trapped Ti(IV)=O···Ti(III): Castro, S. L.; Sreib, W. J. C.; Christou, G. *Chem. Commun.* **1996**, 2177. (b) THF-bridge: Herzog, A.; Liu, F.-Q.; Roesky, H. W.; Demsar, A.; Kellar, K.; Noltemeyer, M.; Pauer, F. *Organometallics* **1994**, *13*, 1251.

(33) Manzer, L. E. *Inorg. Synth.* **1982**, *21*, 135.

Table 4. Selected Interatomic Distances (Å) and Angles (deg) in $[\text{Ti}(\text{PbLO}_3)(\text{THF})_2(\mu\text{-O})\cdot 4\text{CH}_2\text{Cl}_2$ (**10**·**4CH}_2\text{Cl}_2)**

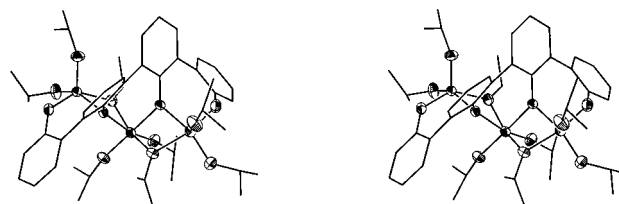
Distances			
Ti(1)–O(1)	1.819(1)	Ti(1)–O(5)	2.121(4)
Ti(1)–O(2)	1.870(2)	Ti(1)···C(21)	2.980(3)
Ti(1)–O(3)	1.846(2)	Ti(1)···C(31)	2.711(3)
Ti(1)–O(4)	1.847(2)	Ti(1)···C(41)	2.922(3)
Angles			
O(1)–Ti(1)–O(2)	121.99(8)	O(4)–Ti(1)–O(5)	82.2(6)
O(1)–Ti(1)–O(4)	116.78(7)	O(3)–Ti(1)–O(2)	90.7(1)
O(4)–Ti(1)–O(2)	120.5(1)	O(3)–Ti(1)–O(4)	90.9(1)
O(3)–Ti(1)–O(5)	168.7(7)	O(1)–Ti(1)–O(3)	97.25(7)
Ti(1)–O(1)–Ti(1A)	180.0	C(21)–O(2)–Ti(1)	134.0(2)
O(2)–Ti(1)–O(5)	85.3(9)	C(31)–O(3)–Ti(1)	113.8(2)
O(1)–Ti(1)–O(5)	93.9(8)	C(41)–O(4)–Ti(1)	130.6(2)

**Figure 5.** Structure of $[\text{Ti}_3(\mu, \mu'\text{-LO}_4)(\mu\text{-O}^i\text{Pr})_2(\text{O}^i\text{Pr})_6]$ (**11**) with thermal ellipsoids (35% probability level) and selected atom labels; hydrogen atoms are not shown.

reproducible, even in an anaerobic glovebox environment using rigorously purified solvents. The oxygen atom presumably originates by abstraction from the THF solvent in a reaction known for Ti(III),³⁴ although the possibility of adventitious dioxygen or water contamination cannot be completely excluded. The Ti–O–Ti motif is relatively common and several examples in 5-coordinate Ti(IV) environments are known.³⁵

(iv) $[\text{Ti}_3(\mu, \mu'\text{-LO}_4)(\mu\text{-O}^i\text{Pr})_2(\text{O}^i\text{Pr})_6]$ (**11**). The reaction of $\text{L}(\text{OH})_4$ (**3**) with 3 equiv of $\text{Ti}(\text{O}^i\text{Pr})_4$ gives rise to a golden-yellow solution; pale yellow (nearly colorless) crystals of **11** grow from vapor diffusion using $\text{CH}_2\text{Cl}_2/n$ -pentane. The ^1H NMR spectrum displays very complex, highly dispersed signal envelopes that integrate to a 1:8 ratio of quaterphenoxide to isopropoxide ligation. From molecular modeling,²⁷ chelate ligand **2** is not expected to bind with all donors on a single Ti center, and this proved to be the case in the solid-state structure (vide infra). Even at 1:1 ligand/metal reaction ratios, trimeric complex **11** proved to be the only crystalline material isolated.

Crystallographic analysis establishes complex **11** as a bent trinuclear Ti(IV) cluster, with all three metal centers spanned by a single quaterphenoxide ligand in a $[\mu, \mu': \eta^2, \eta^2, \eta^2]$ coordination mode (Figures 5 and 6); selected metrical parameters are listed in Table 5. The trimer has approximate C_2 symmetry, with two outer 5-coordinate metal sites [Ti(1,3)] bracketing a 6-coordinate metal center [Ti(2)]. The coordination sphere of the central distorted octahedral Ti(2) atom consists of two

**Figure 6.** Stereoview of $[\text{Ti}_3(\mu, \mu'\text{-LO}_4)(\mu\text{-O}^i\text{Pr})_2(\text{O}^i\text{Pr})_6]$ (**11**).**Table 5.** Selected Interatomic Distances (Å) and Angles (deg) in $[\text{Ti}_3(\mu, \mu'\text{-LO}_4)(\mu\text{-O}^i\text{Pr})_2(\text{O}^i\text{Pr})_6]$ (**11**)

Distances			
Ti(1)–O(1)	1.863(3)	Ti(2)–O(9)	1.764(3)
Ti(1)–O(2)	2.030(2)	Ti(2)–O(11)	2.005(3)
Ti(1)–O(5)	1.804(3)	Ti(3)–O(3)	2.016(3)
Ti(1)–O(6)	1.751(3)	Ti(3)–O(4)	1.863(3)
Ti(1)–O(7)	1.989(3)	Ti(3)–O(10)	1.734(3)
Ti(2)–O(2)	2.071(2)	Ti(3)–O(11)	2.019(3)
Ti(2)–O(3)	2.077(3)	Ti(3)–O(12)	1.795(3)
Ti(2)–O(7)	2.025(3)	Ti(1)···Ti(2)	3.211(1)
Ti(2)–O(8)	1.781(3)	Ti(2)···Ti(3)	3.218(1)
Angles			
Ti(1)···Ti(2)···Ti(3)	130.15(3)	O(9)–Ti(2)–O(3)	92.1(1)
O(5)–Ti(1)–O(2)	150.7(1)	O(7)–Ti(2)–O(3)	90.9(1)
O(1)–Ti(1)–O(7)	140.7(1)	O(8)–Ti(2)–O(2)	88.4(1)
O(6)–Ti(1)–O(1)	105.3(1)	O(8)–Ti(2)–O(7)	96.4(1)
O(6)–Ti(1)–O(7)	109.5(1)	O(9)–Ti(2)–O(8)	100.7(1)
O(1)–Ti(1)–O(2)	82.6(1)	O(8)–Ti(2)–O(11)	99.3(1)
O(5)–Ti(1)–O(1)	93.8(1)	O(9)–Ti(2)–O(11)	96.3(1)
O(6)–Ti(1)–O(2)	103.2(1)	O(9)–Ti(2)–O(7)	96.6(1)
O(6)–Ti(1)–O(5)	105.8(2)	O(7)–Ti(2)–O(2)	70.8(1)
O(7)–Ti(1)–O(2)	72.3(1)	O(4)–Ti(3)–O(11)	145.3(1)
O(5)–Ti(1)–O(7)	93.8(1)	O(10)–Ti(3)–O(12)	108.6(2)
O(9)–Ti(2)–O(2)	165.4(1)	O(10)–Ti(3)–O(3)	108.9(1)
O(8)–Ti(2)–O(3)	164.5(1)	O(12)–Ti(3)–O(3)	141.5(1)
O(11)–Ti(2)–O(7)	157.4(1)	O(4)–Ti(3)–O(3)	83.4(1)
O(2)–Ti(2)–O(3)	81.0(1)	O(10)–Ti(3)–O(4)	103.9(1)
O(11)–Ti(2)–O(3)	70.2(1)	O(12)–Ti(3)–O(4)	95.3(1)
O(10)–Ti(3)–O(11)	106.5(1)	C(21)–O(2)–Ti(2)	135.4(2)
O(12)–Ti(3)–O(11)	90.6(1)	C(11)–O(1)–Ti(1)	137.9(2)
O(3)–Ti(3)–O(11)	71.2(1)	C(31)–O(3)–Ti(2)	134.2(2)
C(21)–O(2)–Ti(1)	119.6(2)	C(31)–O(3)–Ti(3)	120.4(2)
C(41)–O(4)–Ti(3)	133.6(3)		

aryloxy donors [O(2,3)] cis to each other and bridged to separate metals, two isopropoxide ligands [O(7,11)] arranged trans to each other and also bridged to different metals, and two terminal isopropoxide ligands [O(8,9)] oriented cis. The outer Ti(1,3) positions are distorted square pyramidal in geometry,³⁶ with the Ti centers raised ca. 0.53–0.56 Å above the equatorial planes; the tetradentate chelate coordinates via an outer phenoxide [O(1/4)] and a bridging inner phenoxide [O(2/3)], both located at equatorial positions cis to each other, while isopropoxides occupy the remaining sites [O(5,6,7/9,10,11)], with one bridging at an equatorial position [O(7/11)]. The tetradentate chelate ligand imparts a helical twist to the trinuclear cluster and forces a bent structure (Ti(1)···Ti(2)···Ti(3) = 130.15(3)°) with significant puckering of the 1,3-dioxatitanacycle (Ti₂O₂: magnitude of the dihedral angle defined by Ti(1/2)–O(2/3)–Ti(2/3)–O(7/11) = 20.6(1)/22.1(1)°). A similar bent trinuclear structure, with a central 6-coordinate and flanking 5-coordinate Ti(IV) centers, has been reported

(34) Strel'tsova, N. R.; Ivakina, L. V.; Bel'skii, V. K.; Storozhenko, P. A.; Bulychev, B. M. *Sov. J. Coord. Chem.* **1988**, *14*, 237.

(35) (a) Olmstead, M. M.; Power, P. P.; Viggiano, M. *J. Am. Chem. Soc.* **1983**, *105*, 2927. (b) Kuhn, N.; Kratz, T.; Blaser, D.; Boese, R. *Inorg. Chim. Acta* **1995**, *238*, 179.

(36) The 5-coordinate metal geometries are intermediate between square pyramidal and trigonal bipyramidal. The outer Ti positions can be described alternatively as distorted trigonal bipyramids, with an outer chelate phenoxide [O(1/4)] at an equatorial site, and a bridging chelate inner phenoxide [O(2/3)] at an axial site; the remaining positions are completed by isopropoxides, with one bridging at an equatorial position.

Table 6. Dihedral Angles (deg) between Adjacent Aryl Ring Planes

ring planes	8·2CH ₂ Cl ₂	9·4CH ₂ Cl ₂	10·4CH ₂ Cl ₂	11
C(11–16)/C(21–26)	43.9(1)	60.2(1)	56.8(1)	44.4(2)
C(21–26)/C(31–36)	45.4(1)	43.7(1)	45.8(1)	48.6(1)
C(31–36)/C(41–46)	46.1(1)	43.1(1)	42.8(1)	47.9(2)
C(41–46)/C(51–56)	48.6(1)	68.1(1)	60.2(1)	
C(101–106)/C(201–206)		50.1(1)		
C(201–206)/C(301–306)		48.7(2)		
C(301–306)/C(401–406)		38.4(1)		
C(401–406)/C(501–506)		72.3(1)		

recently³⁷ although the chelate type (*cis,cis*-cyclohexane-1,3,5-trialkoxide), coordination mode ($[\mu,\mu':\eta^1,\eta^3,\eta^1]$), and stoichiometry (two chelates and six isopropoxides per trimer) differ considerably from those found for complex **11**.

Although the combined NMR integral ratios agree with the solid-state structure, the signal patterns are substantially more complex than that of an idealized C_2 -symmetric complex. The bulk sample appears to be homogeneous, on the basis of visual inspection and unit cell measurements of multiple, randomly chosen single crystals. Possible explanations for the solution NMR spectrum include hindered rotation of the isopropyl groups leading to multiple conformers (the disordered isopropyl groups in the crystal structure indicate that this situation occurs in the solid state) or disproportionation equilibria giving rise to multiple species upon dissolution.

General Features of *Ortho*-Linked Polyphenoxide Chelates. The $[\text{PhLO}_3]^{3-}$ and $[\text{LO}_4]^{4-}$ ligands bind Ti(IV) centers in 5- or 6-coordinate geometries with a range of structural distortions; metal–ligand bond lengths³⁸ and ligand structure metrics, however, show no significant deviations from typical values. The dihedral angles between adjacent chelate phenoxides range consistently from 38 to 49° (Table 6) which is somewhat less than the equivalent angles for the more sterically demanding 2,2'-binaphthoxide ligands (60–70°).²⁹ Terminal (noncoordinating) *ortho*-phenyl substituents on bound $[\text{PhLO}_3]^{3-}$ span a larger torsional range, reflecting their greater rotational freedom within the confines of the metal coordination sphere. $[\text{PhLO}_3]^{3-}$ serves as a tridentate ligand to a single metal for complexes **8** and **10**. To attain these tridentate geometries, compression of the central oxygen donor angle appears to be necessary (Ti–O–C_{ipso} = 102.8(1)/113.8(2)° for the central phenoxide of **8/10**, respectively, vs >130° for the outer phenoxides) resulting in very close contact between the *ipso*-carbon and the metal center (2.548(2)/2.711(3) Å for **8/10**). For the 9119 titanium aryloxy fragments found in the Cambridge Crystallographic Database,^{26a} Ti···C_{ipso} distances range from 2.557 to 3.924 Å, with a mean of 2.991(2) Å; the Ti(1)···C(31)_{ipso} distance in complex **8** is shorter than any distance previously reported.

The $[\text{PhLO}_3]^{3-}$ and $[\text{LO}_4]^{4-}$ ligands can (and probably do, in general) bridge between oxophilic Ti(IV) centers, with spanning sites provided by oxygen donors of either inner or outer chelate phenoxides. Although the structural framework of the quaterphenoxide ligand cannot support tetradentate mononuclear coordination to a single Ti(IV) site (on the basis of molecular models), terphenoxide $[\text{PhLO}_3]^{3-}$ is capable of tridentate mononuclear coordination, as demonstrated in complex **10**. The *ortho*-phenyl substituents on the phenoxide arms of $[\text{PhLO}_3]^{3-}$, however, are not sterically sufficient to preclude bridging at the outer donor positions, and this consideration must be factored into future modifications of the ligand design.

Summary

Ortho-linked polyphenoxides are a promising multidentate expansion of the well-known 2,2'-biphenoxide/naphthoxide ligand design. In this first study, we have developed facile ligand syntheses to tri- and tetradentate members of the ligand class and have encountered a complex structural chemistry associated with Ti(IV) that originates (not surprisingly) from bridging interactions between the oxophilic metal centers. We anticipate that, with this particular ligand set, these uncontrolled bridging interactions will be less of an issue for the coordination chemistry of softer, less oxophilic, later-transition elements. The flexibility of the ligand syntheses should also enable simple modifications that will support not only mononuclear complexes of early-transition elements, but also well-defined, highly structured coordination environments for the study of metal-centered reactivity.

Experimental Section

Preparation of Compounds. Air-sensitive reactions (lithiation, Pd-catalyzed cross-coupling, BBr₃ deprotection, and titanium coordination chemistry) were performed in oven-dried glassware under a pure dinitrogen atmosphere using standard techniques;³⁹ manipulations involving Ti(IV) in particular were conducted under rigorous anaerobic conditions to minimize hydrolytic decomposition. Where appropriate, solvents were freshly distilled from scavenging agents (hydrocarbons, ethers, and benzene from sodium benzophenone ketyl, toluene from Na, and CH₂Cl₂ from CaH₂) and degassed prior to use. Chemical reagents were used as purchased (Aldrich and Acros) except for TMEDA, which was distilled from CaH₂ and stored over 4 Å molecular sieves under a nitrogen atmosphere. 2-Methoxy-3-phenylphenylboronic acid **5**²⁴ and TiCl₃(THF)₃³³ were prepared according to literature procedures. Deuterated NMR solvents were purchased from Cambridge Isotope Laboratories and dried over 4 Å molecular sieves under nitrogen atmosphere before use.

2,2'-Dimethoxy-1,1'-biphenyl-3,3'-bisboronic Acid (1**).** To a rapidly stirred solution of 2,2'-dimethoxy-1,1'-biphenyl (5.00 g, 23.4 mmol) and TMEDA (7.2 mL, 47.7 mmol) in 60 mL of ether at –78 °C was added dropwise 5.59 mL of a 10 M solution of *n*-butyllithium in hexanes (55.9 mmol). The resulting mixture was allowed to warm to room temperature and stirred for an additional 5 h. After the mixture was recooled to –78 °C, B(OMe)₃ (30 mL, 264 mmol) was rapidly added to the reaction mixture. The reaction mixture was warmed to room temperature, stirred for 9 h, and treated with 100 mL of 6 N NaOH to give a resultant solution with pH 11. After being stirred for 1 h, the red-brown aqueous layer was separated and acidified to pH 1 with concentrated HCl to give a sticky yellow-brown precipitate that was filtered and dissolved in acetone. The resulting orange solution was dried over MgSO₄ and concentrated in vacuo to yield pink crystalline flakes which were isolated, rinsed with *n*-pentane, and air-dried to give 4.42 g (63%) of bisboronic acid **1**. The product was stored at –20 °C to inhibit the formation of anhydride. ¹H NMR (500 MHz, acetone-*d*₆): δ 3.47 (s, CH₃, 6H), 7.23 (t, *J* = 7.5 Hz, ArH, 2H), 7.24 (br, B(OH)₂, 4H), 7.48 (dd, *J* = 7.5, 2 Hz, ArH, 2H), 7.84 (dd, *J* = 7.5, 2 Hz, ArH, 2H). ¹³C NMR (125 MHz, acetone-*d*₆): δ 61.7, 124.6, 131.8, 135.4, 136.8, 164.0. MS (EI): *m/z* 302 [M⁺, 29], 258 [(M – B(O₂H))⁺, 18], 214 [(M – 2B(O₂H))⁺, 100]. HRMS (EI): *m/z* 302.11572, [calcd M⁺ for C₁₄H₁₆B₂O₆, 302.11329].

2,2',2'',2'''-Tetramethoxy-1,1':3',1':3'',1'''-quaterphenyl, [L(OMe)₄ (2**).** A mixture of bis(boronic acid) **3** (1.00 g, 3.32 mmol), 2-bromoanisole (1.24 g, 6.64 mmol), and Pd(PPh₃)₄ (0.230 g, 0.199 mmol, 3 mol % per boronic acid group) in 30 mL of benzene, 25 mL of ethanol, and 15 mL of 2 M aqueous Na₂CO₃ was heated to reflux (ca. 80 °C) for 23 h. After the mixture was cooled to room temperature, 50 mL of H₂O was added, and the mixture was filtered through diatomaceous earth (Celite). The turbid yellow organic layer was separated and the

(37) Corden, J. P.; Errington, W.; Moore, P.; Partridge, M. G.; Wallbridge, M. G. *H. J. Chem. Soc., Dalton Trans.* **1999**, 2647.

(38) Orpen, A. G.; Brammer, L.; Allen, F. H.; Kennard, O.; Watson, D. G. *J. Chem. Soc., Dalton Trans.* **1989**, S1.

(39) Shriver, D. F.; Drezdon, M. A. *The Manipulation of Air-Sensitive Compounds*, 2nd ed.; Wiley-Interscience: New York, 1986.

aqueous layer was extracted with benzene (3 × 30 mL); the organic fractions were combined, washed with 50 mL of brine, and dried over MgSO₄. The solvent was removed in vacuo to leave a pale yellow oil that was stored at -20 °C overnight. Microcrystals appeared in the oil by the following day, and the product was crystallized from toluene/methanol to yield 0.98 g (69%) of quateranisole **2** as white microcrystalline solid, mp 125–27 °C. ¹H NMR (500 MHz, CDCl₃): δ 3.29 (s, OCH₃, 6H), 3.80 (s, OCH₃, 6H), 6.98–7.04 (m, ArH, 4H), 7.18 (t, *J* = 7.5 Hz, ArH, 2H), 7.27–7.30 (m, ArH, 2H), 7.33–7.36 (m, ArH, 4H), 7.37–7.39 (m, ArH, 2H). ¹³C NMR (125 MHz, CDCl₃): δ 55.8, 60.7, 111.1, 120.6, 123.0, 128.4, 128.8, 131.2, 131.3, 131.7, 132.2, 132.4, 156.1, 157.1. MS (EI): *m/z* 426 [M⁺, 15], 320 [(M - C₆H₃-OMe)⁺, 33], 262 [(M - C₆H₃OMe - 2Me - CO)⁺, 72], 184 [(M - 2C₆H₃OMe - CH₂O)⁺, 100]. HRMS (EI): *m/z* 426.18288 [calcd M⁺ for C₂₈H₂₆O₄, 426.18311].

2,2',2'',2'''-Tetrahydroxy-1,1':3',1'':3'',1''':3''',1''''-quaterphenyl, [L(OH)₄] (**3**). BBr₃ (0.887 mL, 9.38 mmol) was added dropwise via gastight syringe to a pale yellow solution of quateranisole **5** (1.00 g, 2.35 mmol) in 20 mL of CH₂Cl₂ at -78 °C, yielding a yellow precipitate. The reaction mixture was allowed to warm to room temperature and stirred for 4 h, during which time the precipitate redissolved. The mixture was then slowly treated with 30 mL of H₂O, resulting in vigorous gas evolution and the appearance of a fluffy white precipitate. After the mixture was acidified with concentrated HCl, additional CH₂Cl₂ (60 mL) was added, and the yellow organic layer and creamy white aqueous suspension were partitioned. The aqueous layer was extracted with CH₂Cl₂ (3 × 30 mL); all organic fractions were then combined, washed with 50 mL of brine, dried over MgSO₄, and evaporated in vacuo to yield an orange glass. This residue was dissolved in toluene (30 mL) and concentrated until the appearance of crystalline material; an equal volume of hexanes was then added slowly with swirling, and the mixture was stored at -20 °C. The pale orange crystalline solid was filtered, washed with hexanes, and dried in vacuo to yield 0.72 g (83%) of **3** as a white microcrystalline solid, mp 157–58 °C (dec). ¹H NMR (500 MHz, acetone-*d*₆): δ 6.95–7.01 (m, ArH, 4H), 7.08–7.12 (t, *J* = 7.5 Hz, ArH, 2H), 7.23–7.27 (m, ArH, 2H), 7.29–7.36 (m, ArH, 6H), 7.92 (s, 1H, OH), 8.30 (s, 1H, OH). ¹³C NMR (125 MHz, acetone-*d*₆): δ 117.2, 121.2, 121.8, 127.0, 128.0, 128.1, 129.8, 132.19, 132.23, 132.8, 152.1, 155.0. MS (EI): *m/z* 370 [M⁺, 100]. HRMS (EI): *m/z* 370.12003 [calcd M⁺ for C₂₄H₁₈O₄, 370.12051].

2,6-Dibromo-4-methylanisole (4).²³ In our experience, the following procedure gives a cleaner product than previously reported preparation methods. A mixture of 2,6-dibromo-4-methylphenol (19.90 g, 75 mmol), dimethyl sulfate (14.16 g, 112 mmol), and benzyltri-*n*-butylammonium chloride (1.0 g) was stirred in a biphasic solvent system (200 mL of CH₂Cl₂/200 mL of H₂O/5.2 g of NaOH) for 24 h at room temperature. After excess dimethyl sulfate was disposed by treatment with 300 mL of 28–30% aqueous NH₄OH, the organic layer was separated, washed with water (2 × 200 mL), and dried over anhydrous Na₂SO₄. The solvent was removed in vacuo to afford 20.67 g (98.5%) of **4** as a yellow oil. The ¹H NMR spectrum (500 MHz, CDCl₃) is identical to that reported in the literature:^{23c} δ 2.28 (s, 3H, ArMe), 3.86 (s, 3H, OMe), 7.31 (s, 2H, ArH). EI MS: (*m/z*) 280 [M⁺, 100].

5''-Methyl-2',2'',2'''-trimethoxy-1,1':3',1'':3'',1''':3''',1''''-quinquephenyl, [P^hL(OMe)₃] (**6**). The biphasic coupling protocol described for the preparation of **4** was used to couple dibromoanisole **4** (5 g, 17.9 mmol) and boronic acid **5** (9 g, 39.3 mmol). The reaction mixture was refluxed for 48 h, and then quenched with water and partitioned; the organic layer was filtered twice through diatomaceous earth (Celite) and then evaporated in vacuo to a brown oil. The oil was treated with CH₂Cl₂, filtered through a silica gel plug, and dried in vacuo to yield 8.2 g of crude teranisole **6** as a solidified yellow foam that was used in the next step without further purification. The crude material was contaminated by minor amounts (<10%) of monocoupled product, PPh₃, and Pd-derived material. ¹H NMR (500 MHz, acetone-*d*₆): δ 2.39 (s, ArMe, 3H), 3.25 (s, 6H, OMe), 3.30 (s, 3H, OMe), 7.24–7.27 (m, 2H, ArH), 7.35–7.38 (m, 8H, ArH), 7.45 (t, 4H, ArH), 7.61–7.63 (m, 4H, ArH). MS (EI): *m/z* 486 [M⁺, 100].

5''-Methyl-2',2'',2'''-trihiydroxy-1,1':3',1'':3'',1''':3''',1''''-quinquephenyl, [P^hL(OH)₃] (**7**). Crude teranisole **6** (3.873 g, 7.97 mmol) was deprotected using 3 equiv of BBr₃ (2.26 mL, 23.9 mmol) by the

procedure described for quaterphenol **3**. The resulting orange glass was purified by column chromatography (silica gel, 2:1 CH₂Cl₂/hexanes) to afford 1.85 g (52% yield in two steps based on **4**) of terphenol **7** as a pure white powder, mp 143–45 °C (dec). ¹H NMR (500 MHz, acetone-*d*₆): δ 2.37 (s, CH₃, 3H), 7.05 (t, *J* = 7.5 Hz, ArH, 2H), 7.14 (d, *J* = 1.5 Hz, ArH, 2H), 7.25–7.33 (m, ArH, 6H), 7.38–7.44 (m, ArH, 4H), 7.60–7.63 (m, ArH, 4H). ¹³C NMR (125 MHz, acetone-*d*₆): δ 20.6, 121.2, 121.8, 127.4, 127.6, 127.9, 128.9, 129.1, 130.5, 130.7, 131.1, 131.3, 131.7, 132.1, 133.2, 140.1, 152.5. MS (EI): *m/z* 444 [M⁺, 100]. HRMS (EI): *m/z* 444.1727 [calcd M⁺ for C₃₁H₂₄O₃, 444.17255].

[Ti₂(μ-P^hLO₃)₂(OⁱPr)₂] (**8**). Ti(OⁱPr)₄ (0.067 mL, 0.227 mmol) was added to a solution of **7** (0.100 g, 0.225 mmol) in 15 mL of CH₂Cl₂, giving a yellow-orange solution color. The reaction mixture was stirred for 12 h, filtered, and dried in vacuo to afford yellow-orange solid. The residue was washed with cold (-30 °C) *n*-pentane to remove residual Ti(OⁱPr)₄ and then redissolved in a minimum volume of CH₂-Cl₂. Vapor diffusion of several vol equiv of *n*-pentane into the solution at -30 °C over 7 d gave yellow-orange diamond-shaped crystals of **8** which were collected, washed with cold (-30 °C) *n*-pentane, and dried in vacuo (0.050 g, 36%). ¹H NMR (500 MHz, CD₂Cl₂): δ 0.54 (d, *J* = 6 Hz, 6H, OCH(*Me*)₂), 0.64 (d, *J* = 6 Hz, 6H, OCH(*Me*)₂), 2.33 (s, 6H, ArMe), 3.55 (tt, *J* = 6, 6 Hz, 2H, OCH(*Me*)₂), 6.73 (d, *J* = 7.5 Hz, 4H, ArH), 6.76 (br, 2H, ArH), 7.01 (t, *J* = 7.5 Hz, 2H, ArH), 7.12 (br, 2H, ArH), 7.15–7.22 (m, 6H, ArH), 7.23–7.26 (m, 2H, ArH), 7.29–7.38 (m, 14H, ArH), 7.45 (d, *J* = 7 Hz, ArH, 4H). Anal. Calcd for C₆₈H₅₆O₈Ti₂·1.5CH₂Cl₂:⁴⁰ C, 68.18; H, 4.86; Ti, 7.82. Found: C, 67.99; H, 4.89; Ti, 8.12.

[Ti₂(μ-P^hLO₃)₂(μ-Cl)(Cl)(THF)] (**9**). Triply deprotonated ligand trianion was generated in situ by the dropwise addition of *n*-BuLi in hexanes (0.135 mL of 2.5 M solution, 0.337 mmol) to a rapidly stirred solution of **7** (0.050 g, 0.112 mmol) in 10 mL of THF at -78 °C. The reaction mixture was allowed to warm to room temperature and stirred for an additional 1 h, after which TiCl₄ (0.012 mL, 0.112 mmol) was added, giving an instantaneous solution color change to dark red. The reaction was stirred at room temperature for 24 h; the solvent was then removed in vacuo to afford a red glass that was dissolved in a minimum volume of CH₂Cl₂ and filtered to remove LiCl. Vapor diffusion of several vol equiv of *n*-pentane into the filtrate at -30 °C over 3 weeks resulted in the formation of orange-red crystalline blocks of complex **9** which were collected by filtration, washed with *n*-pentane, and dried in vacuo to give 0.027 g (21%) of product. ¹H NMR (500 MHz, CD₂-Cl₂): δ 1.26 (br, 4H, coordinated THF), 2.38 (s, 3H, Me), 2.33 (s, 3H, Me), 2.98 (br, 4H, coordinated THF), 6.40–7.68 (m, 36H, ArH). Anal. Calcd for C₆₆H₅₀O₇Cl₂Ti₂·0.25CH₂Cl₂:⁴⁰ C, 69.61; H, 4.45; Ti, 8.38. Found: C, 69.45; H, 4.36; Ti, 8.07.

[Ti₂(μ-O)(P^hLO₃)₂(THF)₂] (**10**). Triply deprotonated ligand trianion was prepared in situ by the dropwise addition of *n*-BuLi in hexane (0.675 mL of 2.5 M solution, 1.69 mmol) to a rapidly stirred solution of **7** (0.250 g, 0.562 mmol) in 25 mL of THF at -78 °C. The reaction mixture was allowed to warm to room temperature and stirred for an additional 1 h. The ligand trianion solution was then rapidly added to TiCl₃(THF)₃ (0.208 g, 0.562 mmol) in 5 mL of THF, resulting in an instantaneous color change from blue to dark orange-red. After the mixture was stirred at room temperature for 24 h, the solvent was removed in vacuo to afford a red glass that was extracted with ca. 5 mL of CH₂Cl₂ and filtered to remove LiCl. Vapor diffusion of several vol equiv of *n*-pentane into the filtrate at -30 °C over 5 d yielded orange crystalline blocks which were collected, washed with cold (-30 °C) *n*-pentane, and dried in vacuo to give 0.057 g (17%) of complex **10**. ¹H NMR (500 MHz, CD₂Cl₂): δ 1.26 (br, 8H, bound THF), 2.41 (s, 6H, Me), 3.18 (br, 8H, bound THF), 6.94–7.08 (m, 32H, ArH), 7.46 (dd, *J* = 7.5, 2 Hz, 4H, ArH). Anal. Calcd for C₇₀H₅₈O₉Ti₂·0.5CH₂-Cl₂:⁴⁰ C, 71.67; H, 5.03; Ti, 8.11. Found: C, 71.94; H, 5.09; Ti, 8.40.

[Ti₃(μ,μ'-LO₄)(μ-OⁱPr)₂(OⁱPr)₆] (**11**). Ti(OⁱPr)₄ (0.598 mL, 2.03 mmol) was added by gastight syringe to a solution of **3** (0.250 g, 0.674

(40) The crystalline samples were dried rigorously under vacuum prior to elemental analysis; the resultant analytical data are consistent with partial desolvation of the lattice-bound CH₂Cl₂ molecules characterized in single-crystal X-ray diffraction experiments.

mmol) in 15 mL of CH_2Cl_2 and 5 mL of Et_2O , resulting in an instantaneous color change to yellow-orange; the color evolved to light yellow as the reaction progressed. After the mixture was stirred for 24 h, the solvent was removed in vacuo to afford a solidified yellow foam. The residue was washed with a small amount of cold ($-30\text{ }^\circ\text{C}$) *n*-pentane to remove unreacted $\text{Ti}(\text{O}^i\text{Pr})_4$ and dissolved in a minimum volume of CH_2Cl_2 ; several vol equiv of *n*-pentane were vapor diffused into the solution at $-30\text{ }^\circ\text{C}$ over the course of 5 d. The crystalline solid was collected, washed with cold ($-30\text{ }^\circ\text{C}$) *n*-pentane, and dried in vacuo to give 0.100 g (15%) of complex **11** as faint yellow (almost colorless) prisms. ^1H NMR (500 MHz, CD_2Cl_2): δ 0.84–1.58 (m, 48H, $\text{OCH}(\text{Me})_2$), 4.0–5.20 (m, br, 8H, $\text{OCH}(\text{Me})_2$), 6.74–7.47 (m, 14H, ArH). Anal. Calcd for $\text{C}_{48}\text{H}_{70}\text{O}_{12}\text{Ti}_3$:⁴¹ C, 58.66; H, 7.18; Ti, 14.62. Found: C, 57.86; H, 6.99; Ti, 16.37.

Collection and Reduction of X-ray Data. Diffraction-quality crystals of the titanium complexes (**8** as yellow-orange diamonds of the CH_2Cl_2 disolvate, **9** as red blocks of the CH_2Cl_2 tetrasolvate, **10** as orange blocks of the CH_2Cl_2 tetrasolvate,⁴² and **11** as colorless prisms) were obtained by vapor diffusion of *n*-pentane into saturated CH_2Cl_2 solutions at $-30\text{ }^\circ\text{C}$. Single crystals were mounted onto the tips of thin glass fibers with Apiezon-N grease and immediately transferred into the cold dinitrogen gas stream of the diffractometer cryostat. Data were collected⁴³ using Mo $K\alpha$ radiation on a Nonius KappaCCD diffractometer equipped with an MSC X-stream cryosystem operating at ca. 170 or 200 K. Data sets were indexed, integrated, and corrected for Lorentz and polarization effects using DENZO-SMN and SCALE-PAK software.⁴⁴ Systematic absences uniquely defined the space groups of **8**· $2\text{CH}_2\text{Cl}_2$ and **11**; simple *E* statistics suggested the centrosymmetric space group choice for **9**· $4\text{CH}_2\text{Cl}_2$ and **10**· $4\text{CH}_2\text{Cl}_2$. The proper choice of space group was confirmed by successful structure solution and refinement to convergence. Relevant crystallographic data are provided in Table 1.

Solution and Refinement of Structures. The structures were solved using direct methods and refined by full-matrix least squares on F^2 using SHELXTL 5.04.⁴⁵ Scattering factors were taken from the *International Tables for Crystallography*, Volume C.⁴⁶ All non-hydrogen atoms, including disordered atoms, were refined with anisotropic displacement coefficients. In the final stages of refinement, hydrogen atoms were introduced through a fixed idealized "riding model" with isotropic thermal parameters 1.2 times (or 1.5 times in the case of methyl hydrogens) those of their parent carbon atoms. For all structures, all parameters shifted by <1% of their esds in the final cycles of refinement. Final difference Fourier maps of **9**· $4\text{CH}_2\text{Cl}_2$ and

10· $4\text{CH}_2\text{Cl}_2$ showed no significant electron density (0.510 and 0.505 electrons/ \AA^3 , respectively). The highest peaks in the final difference Fourier maps of **8**· $2\text{CH}_2\text{Cl}_2$ and **11** were observed in the vicinity of disordered isopropoxide (0.829, 0.904 electrons/ \AA^3 , respectively); the final maps showed no other significant features. Final *R* values are provided in Table 1.

All four titanium crystal structures exhibited some degree of disorder; for resolvable cases, the total occupancy of the disordered components was fixed at unity.

(1) Complex 8·2CH₂Cl₂. The methine carbon [C(1)] of the bound isopropoxide was disordered over two positions. The two components were resolved and refined to give occupancy factors of 0.78 and 0.22, and the following restraints⁴⁵ were applied: (a) DFIX (distance) restraints for methine–methyl [1.52(1) \AA], methyl–methyl [2.53(2) \AA], O–methine [1.43(1) \AA], and O–methyl [2.40(2) \AA] contacts and (b) DELU (equalized anisotropic displacement parameters along the bond axis direction) restraints (esd = 0.01) for the carbon atoms on the disordered isopropoxide fragment. The CH_2Cl_2 solvate molecule was disordered over three orientations; these were resolved and refined to occupancy factors of 0.21, 0.38, and 0.41, with the following restraints: ⁴⁵ (a) DFIX restraints for C–Cl [1.77(1) \AA] and Cl–Cl [2.89(2) \AA] contacts and (b) DELU restraints (esd = 0.01) for all of the disordered atoms.

(2) Complex 9·4CH₂Cl₂. One of the four CH_2Cl_2 solvate molecules was disordered over two orientations; these were resolved and refined to occupancy factors of 0.51 and 0.49, with the following restraints:⁴⁵ (a) DFIX restraints for C–Cl [1.75(1) \AA] and Cl–Cl [2.89(1) \AA] contacts, (b) DELU restraints (esd = 0.01) for all disordered atoms, and (c) SIMU (equalized U_{ij} anisotropic displacement parameters) restraints (esd = 0.04) for all spatially adjacent disordered atoms.

(3) Complex 10·4CH₂Cl₂. The bound THF ligand was disordered over two orientations; these were resolved and refined to occupancy factors of 0.56 and 0.44, with the following restraints:⁴⁵ (a) SADI (equalized distances) restraints (esd = 0.005) for Ti–O(THF) bonds, (b) DFIX restraints for O–C [1.44(1) \AA] and C–C [1.54(1) \AA], (c) DELU restraints (esd = 0.01) for all disordered atoms, and (d) SIMU restraints (esd = 0.04) for all spatially adjacent disordered atoms.

(4) Complex 11. Four of the eight isopropoxide groups [methines C(52, 60, 72, 74)] were disordered; a satisfactory model could not be achieved, so the disordered groups were each refined simply as single isopropoxide fragments with distorted anisotropic displacement parameters.

Other Physical Measurements. All measurements on the metal complexes were performed under a pure dinitrogen atmosphere. ^1H and ^{13}C NMR spectra were recorded on a Varian Unity/INOVA spectrometer with chemical shifts referenced to solvent. Mass spectra were recorded on a KRATOS MS50TC spectrometer. Elemental analyses were performed by the Microanalysis Laboratory at the School of Chemical Sciences, University of Illinois, Urbana, IL 61801.

Acknowledgment. The support of the Arnold and Mabel Beckman Foundation (Beckman Young Investigator Award) is gratefully acknowledged. We thank Dr. Douglas M. Ho for crystallographic assistance.

Supporting Information Available: Crystallographic data for **8**· $2\text{CH}_2\text{Cl}_2$, **9**· $4\text{CH}_2\text{Cl}_2$, **10**· $4\text{CH}_2\text{Cl}_2$, **11**, and **10**· $2\text{CH}_2\text{Cl}_2$ (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

IC000275F

(41) Elemental analyses for crystalline complex **11** were consistently off, despite several attempts with different samples. Multiple unit cell measurements all gave the same lattice parameters, with no indication of sample heterogeneity.

(42) Complex **10** also crystallizes as a CH_2Cl_2 disolvate (**10**· $2\text{CH}_2\text{Cl}_2$) under similar conditions. Crystal parameters for $\text{C}_{70}\text{H}_{58}\text{O}_9\text{Ti}_2\cdot 2\text{CH}_2\text{Cl}_2$ (data collected at $T = 170(2)\text{ K}$): triclinic, *P*1 (No. 2), $Z = 1$; $a = 10.109(2)\text{ \AA}$, $b = 13.178(4)\text{ \AA}$, $c = 13.394(4)\text{ \AA}$, $\alpha = 63.460(8)^\circ$, $\beta = 76.96(1)^\circ$, $\gamma = 79.16(1)^\circ$, $V = 1547.3(7)\text{ \AA}^3$. Complete crystallographic data are available as Supporting Information.

(43) COLLECT *Data Collection Software*; Nonius B. V. Rontgenweg: Delft, The Netherlands, 1998.

(44) Otwinowski, Z.; Minor, W. *Methods Enzymol.* **1997**, *276*, 307.

(45) Sheldrick, G. M. *SHELXTL*, Version 5.04; Siemens Analytical X-ray Instruments: Madison, WI, 1996.

(46) Creagh, D. C.; McAnley, W. J. *International Tables for Crystallography: Mathematical, Physical and Chemical Tables*, Vol. C.; Kluwer: Dordrecht, The Netherlands, 1992; p 206.