

# Coordination Chemistry of *N,N,N',N'*-Tetrakis(3,5-substituted benzyl-2-oxide)-2,2'-(ethylenedioxy)diethanamine Modified Group 4 Metal Alkoxides

Timothy J. Boyle,\* Daniel T. Yonemoto, and Leigh Anna Steele

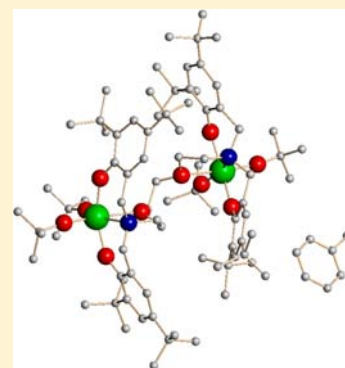
Sandia National Laboratories, Advanced Materials Laboratory, 1001 University Boulevard, SE, Albuquerque, New Mexico 87106, United States

Joshua Farrell, Peter Renehan, and Taylor Huhta

Department of Chemistry, College of the Holy Cross, Box C, 1 College Street, Worcester, Massachusetts 01610, United States

## S Supporting Information

**ABSTRACT:** The coordination behavior of a set of (ethylenedioxy)diethanamine-based tetraphenol ligands with a series of Group 4 metal alkoxides ( $[M(OR)_4]$ ) was determined. The ligands were synthesized from a modified Mannich reaction and fully characterized as *N,N,N',N'*-tetrakis(3,5-*tert*-butyl-benzyl-2-hydroxy)-2,2'-(ethylenedioxy)diethanamine, termed  $H_4$ -OEA-DBP<sub>4</sub> (1), and *N,N,N',N'*-tetrakis(3,5-chloro-benzyl-2-hydroxy)-2,2'-(ethylenedioxy)diethanamine, termed  $H_4$ -OEA-DCP<sub>4</sub> (2). The reaction of 1 with a set of  $[M(OR)_4]$  [ $M = Ti, Zr, \text{ or } Hf$ ;  $OR = \textit{iso}$ -propoxide ( $OPr^i$ ), *neo*-pentoxide ( $ONep$ ), or *tert*-butoxide ( $OBu^t$ )] precursors led to the isolation of  $[(OPr^i)_2Ti]_2(\mu\text{-OEA-DBP}_4)$  (3),  $[(ONep)_2Ti]_2(\mu\text{-OEA-DBP}_4)$  (4), and  $[(OBu^t)_2M]_2(\mu\text{-OEA-DBP}_4)$  where  $M = Ti$  (5),  $Zr$  (6), or  $Hf$  (7). In addition, the  $[(ONep)_2Ti]_2(\mu\text{-OEA-DCP}_4)$  (4a) derivative was isolated from the reaction of 2 and  $[Ti(ONep)_4]$ , demonstrating the similarity of coordination behavior between the two OEA- $R_4$  ligands. For 3–7, the metal center adopts a slightly distorted octahedral geometry by binding the two O atoms of the phenoxide moiety, as well as one N and one O atom from the OEA moieties, while retaining two of the original OR ligands. Solution NMR demonstrates inequivalent protons for the majority of the bound OEA ligands, which argues for retention of structure in solution. The synthesis and characterization of these compounds are presented in detail.



## INTRODUCTION

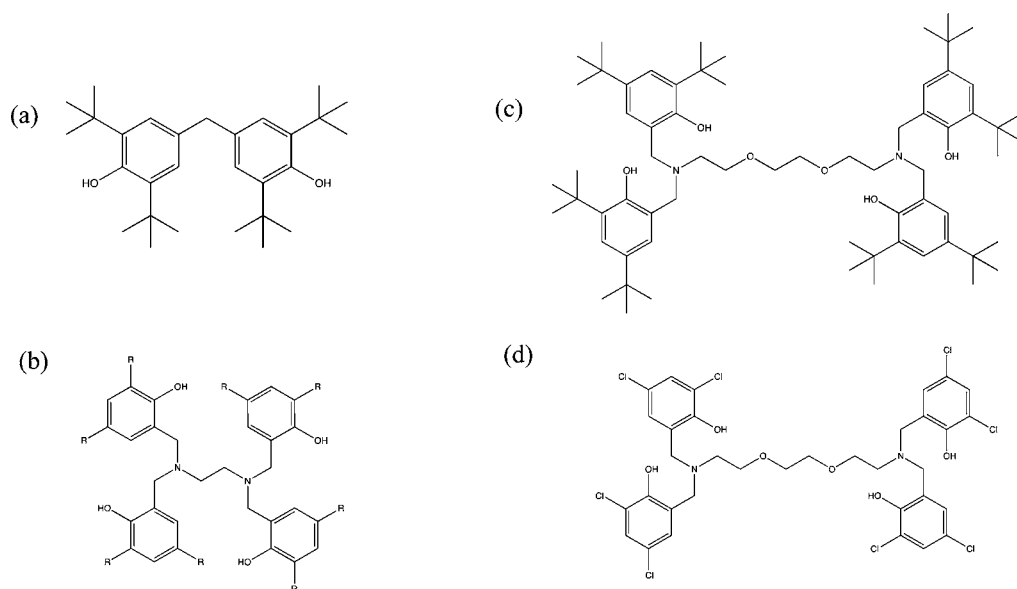
Metal alkoxides ( $[M(OR)_x]$ ) have found increased utility in production of ceramic materials due to their commercial availability, ease with which they can be modified, and low, clean decomposition temperatures. A close connection between the structural properties of the starting  $[M(OR)_x]$  precursor and final ceramic properties (i.e., density, morphology, processing temperature, etc.) has been demonstrated.<sup>1–17</sup> Therefore, the rational development of tailored ceramic materials requires some control over the structure of the  $[M(OR)_x]$  compounds, and developing these precursors with predetermined structure types becomes an important endeavor. The *a priori* determination of  $[M(OR)_x]$  structures is often difficult due to oligomerization based on the large cation size to ligand charge ratio, unanticipated ligand coordination (i.e., solvents), and inclusion of unexpected anions and/or cations.<sup>18–22</sup>

We have been exploring the impact that a number of polydentate alcohols have on the final  $[M(OR)_x]$  structure. In particular the pyridine carbinol ( $H\text{-OPy}$ )<sup>23,24</sup> ligand demonstrated the kind of systematic modification necessary to generate controlled structured precursors. As this effort has

expanded, a series of linked phenol ligands such as 4,4'-methylene bis(2,6-di-*tert*-butylphenol) ( $H_2$ -4DBP, Figure 1a)<sup>25</sup> and the tetrakis(3,5-substituted benzyl-2-oxide)-*N,N'*-ethylene diamine ligated compounds ( $H_4$ -ED- $R_4$ , Figure 1b)<sup>26</sup> were considered promising on the basis of their arrangement of the multihydroxide functional groups, rigid backbone, and high solubility in organic solvents. The 4DBP ligand was successful in generating disubstituted species such as  $[(OR)_3M]_2(\mu\text{-4DBP})$ ,<sup>25</sup> whereas the ED- $R_4$  species yielded only encapsulated complexes such as  $[M(ED-R_4)]$ .<sup>26</sup> From these studies, it became evident that the orientation of the "chain linkage" plays a large role in how the final substituted  $[M(OR)_x]$  is constructed. Therefore, we sought to change the chain linkage while maintaining the tetra-phenol component of the ED- $R_4$  ligands; however, these are not commercially available and new ligands had to be synthesized. As we designed the desired ligands, the inclusion of an O atom in the chain was opted for, based on the ease of synthesis and increased potential for binding to the early transition metal centers. These novel

Received: September 4, 2012

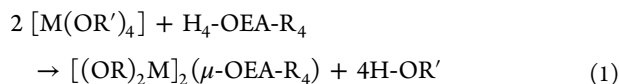
Published: October 22, 2012



**Figure 1.** Schematic representation of polydentate ligands investigated: (a)  $H_2$ -4DBP, (b)  $H_4$ -ED- $R_4$ , (c)  $H_4$ -OEA-DBP $_4$ , (d)  $H_4$ -OEA-DCP $_4$ .

ligands were synthesized from a modified Mannich reaction and fully characterized as the  $N,N,N',N'$ -tetrakis(3,5-*tert*-butylbenzyl-2-hydroxy)-2,2'-(ethylenedioxy)diethanamine, termed  $H_4$ -OEA-DBP $_4$  (**1**, Figure 1c), and  $N,N,N',N'$ -tetrakis(3,5-chloro-benzyl-2-hydroxy)-2,2'-(ethylenedioxy)diethanamine, termed  $H_4$ -OEA-DCP $_4$  (**2**, Figure 1d). Collectively, these ligands are referred to as  $H_4$ -OEA- $R_4$ .

Our initial reactions with  $H_4$ -OEA- $R_4$  focused on Group 4  $[M(OR)_4]$  ( $M = Ti, Zr, Hf$ ) precursors since the resulting ceramic oxide materials are critical components for a wide variety of electronic applications including solar cells, capacitors, and gate insulators. The reaction of **1** with the  $[M(OR)_4]$  ( $OR = iso$ -propoxide ( $OPr^i$ ), *neo*-pentoxide ( $ONep$ ), or *tert*-butoxide ( $OBu^t$ )) precursors (eq 1) led to the isolation of  $[(OPr^i)_2M]_2(\mu$ -OEA-DBP $_4)$  (**3**),  $[(ONep)_2Ti]_2(\mu$ -OEA-DBP $_4)$  (**4**), and  $[(OBu^t)_2M]_2(\mu$ -OEA-DBP $_4)$  where  $M = Ti$  (**5**),  $Zr$  (**6**),  $Hf$  (**7**). In addition, the  $[(ONep)_2Ti]_2(\mu$ -OEA-DCP $_4)$  (**4a**) derivative was isolated from the reaction of **2** and  $[Ti(ONep)_4]$  and demonstrates the similarity of coordination for the Cl versus the DBP derivative of the OEA- $R_4$  ligands. Full details of the synthesis and characterization of these unusual ligands and their controlled  $[M(OR)_4]$  coordination compounds are presented.



## EXPERIMENTAL SECTION

**Organic Synthesis.** All reactions were undertaken in a high flow hood behind a blast shield for additional safety. NMR spectra were recorded on an Oxford AS400 spectrometer and referenced to residual peak in deuterated chloroform ( $CDCl_3$ ). MS data were collected on either a Bruker Daltonics-LC Ion trap mass spectrometer (ESI) or a JEOL MStation JMS 700 (FAB) both located at the UMass Amherst Mass Spectrometry Center. Melting point determinations were made using a Stuart SMP10 melting point apparatus. The following chemicals were purchased from Aldrich and used without further purification: toluene, formaldehyde (37 wt %), 2,2'-(ethylenedioxy)-bis(ethylamine), 2,4-di-*tert*-butyl phenol, and 2,4-dichlorophenol. House distilled water was used for all reactions.

$H_4$ -OEA-DBP $_4$  (**1**). To a 70 mL pressure flask equipped with a magnetic stir bar were added  $H_2O$  (40 mL), formaldehyde (4.5 mL, 61 mmol), 2,4-di-*tert*-butyl phenol (8.3 g, 40 mmol), and 2,2'-(ethylenedioxy)bis(ethylamine) (1.5 mL, 10 mmol). The reaction was heated in the pressure flask for 48 h at 105 °C, after which the  $H_2O$  was decanted and ~20 mL of MeOH was added. The resulting yellow gel was sonicated until a white precipitate formed. The solid was isolated by vacuum filtration. Recrystallization of this product from 30 mL of heated MeOH resulted in isolation of **1**. Yield = 33% (3.4 g).  $^1H$  NMR ( $CDCl_3$ )  $\delta$  7.20 (4H, d,  $\{[OC_6H_2(C(CH_3)_3)-2,6]_2CH_2NCH_2CH_2OCH_2\}_2$ ,  $J_{H-H} = 2.8$  Hz), 6.86 (4H, d,  $\{[OC_6H_2(C(CH_3)_3)-2,6]_2CH_2NCH_2CH_2OCH_2\}_2$ ,  $J_{H-H} = 2.8$  Hz), 3.86 (4H, s,  $\{[OC_6H_2(C(CH_3)_3)-2,6]_2CH_2NCH_2CH_2OCH_2\}_2$ ), 3.71 (8H, s,  $\{[OC_6H_2(C(CH_3)_3)-2,6]_2CH_2NCH_2CH_2OCH_2\}_2$ ), 3.69 (4H, t,  $\{[OC_6H_2(C(CH_3)_3)-2,6]_2CH_2NCH_2CH_2OCH_2\}_2$ ,  $J_{H-H} = 5.1$  Hz), 2.73 (4H, t,  $\{[OC_6H_2(C(CH_3)_3)-2,6]_2CH_2NCH_2CH_2OCH_2\}_2$ ,  $J_{H-H} = 5.1$  Hz), 1.38 (18H, s,  $\{[OC_6H_2(C(CH_3)_3)-2,6]_2CH_2NCH_2CH_2OCH_2\}_2$ ), 1.26 (18H, s,  $\{[OC_6H_2(C(CH_3)_3)-2,6]_2CH_2NCH_2CH_2OCH_2\}_2$ ).  $^{13}C$  NMR ( $CDCl_3$ )  $\delta$  152.8, 140.8, 135.9, 124.9, 123.4, 121.5 ( $CH_2$ - $C_6H_2(C(CH_3)_3)_2$ ), 70.3 ( $O-CH_2$ ), 69.9 ( $O-CH_2$ ), 57.9 ( $N-CH_2$ ), 51.3 ( $N-CH_2$ ), 34.9 ( $C-(CH_3)_3$ ), 34.1 ( $C-(CH_3)_3$ ), 31.7 ( $C-(CH_3)_3$ ), 29.6 ( $C-(CH_3)_3$ ). Mp 134–136 °C. HRMS (ESI $^+$ ): calcd for  $[C_{66}H_{104}N_2O_6 + H^+]^+$  = 1021.7972; found = 1021.7952.

$H_4$ -OEA-DCP $_4$  (**2**). To a 70 mL pressure flask equipped with a magnetic stir bar were added toluene (20 mL), 2,4-dichlorophenol (9.8 g, 60 mmol), formaldehyde (2.9 mL, 39 mmol), and 2,2'-(ethylenedioxy)bis(ethylamine) (15 mL, 10 mmol). The reaction was heated in the pressure flask for 96 h at 120 °C, yielding a clear orange solution. The solvent was removed by rotary evaporation yielding a brown gel. Recrystallization from hot MeOH (20 mL) followed by vacuum filtration yielded **2**. Yield 60% (5.1 g).  $^1H$  NMR ( $CDCl_3$ )  $\delta$  7.24 (4H, d,  $\{[OC_6H_2(Cl)-2,6]_2CH_2NCH_2CH_2OCH_2\}_2$ ,  $J_{H-H} = 2.9$  Hz), 6.94 (4H, d,  $\{[OC_6H_2(Cl)-2,6]_2CH_2NCH_2CH_2OCH_2\}_2$ ,  $J_{H-H} = 2.9$  Hz), 3.75 (8H, s,  $\{[OC_6H_2(Cl)-2,6]_2CH_2NCH_2CH_2OCH_2\}_2$ ), 3.71 (4H, t,  $\{[OC_6H_2(Cl)-2,6]_2CH_2NCH_2CH_2OCH_2\}_2$ ,  $J_{H-H} = 5.1$  Hz), 3.68 (4H, s,  $\{[OC_6H_2(Cl)-2,6]_2CH_2NCH_2CH_2OCH_2\}_2$ ), 2.70 (4H, t,  $\{[OC_6H_2(Cl)-2,6]_2CH_2NCH_2CH_2OCH_2\}_2$ ,  $J_{H-H} = 5.1$  Hz).  $^{13}C$  NMR ( $CDCl_3$ )  $\delta$  151.6, 129.5, 129.1, 125.2, 124.8, 122.1 ( $CH_2$ - $C_6H_2(C(CH_3)_3)_2$ ), 70.8 ( $O-CH_2$ ), 68.7 ( $O-CH_2$ ), 56.0 ( $N-CH_2$ ), 52.4 ( $N-CH_2$ ). Mp 158–160 °C.

**Inorganic Characterization.** All compounds and reactions described below were handled with rigorous exclusion of air and water using standard Schlenk line and argon-filled glovebox techniques. All solvents were stored under argon and used as received

(Aldrich) in Sure/Seal bottles, including toluene (tol). The following chemicals were used as received (Aldrich and Alfa Aesar):  $\text{Ti}(\text{OCH}(\text{CH}_3)_2)_4$  ( $[\text{Ti}(\text{OPr}^i)_4]$ ),  $\text{Hf}(\text{OC}(\text{CH}_3)_3)_4$  ( $[\text{Hf}(\text{O}i\text{Bu})_4]$ ), and  $\text{H}-\text{OCH}_2\text{C}(\text{CH}_3)_3$  (H-ONep).  $[\text{Ti}(\mu\text{-ONep})(\text{ONep})_3]_2$  ( $[\text{Ti}(\text{ONep})_4]$ ) was prepared according to literature procedures.<sup>27</sup> FTIR data were obtained for KBr pressed pellets using a Bruker Vector 22 Instrument under an atmosphere of flowing nitrogen. Elemental analyses were performed on a Perkin-Elmer 2400 CHN-S/O Elemental Analyzer. All NMR samples were prepared from dried crystalline materials that were handled and stored under an argon atmosphere and redissolved in  $\text{CDCl}_3$ . Spectra were collected on a Bruker Avance 500 NMR spectrometer, using a 5 mm inverse probe, under standard experimental conditions:  $^1\text{H}$  analysis was performed with a 4-s recycle delay at 16 scans; spectra were referenced to the residual proton peak of  $\text{CDCl}_3$  at 7.24 ppm.

**General  $\text{M}(\text{OR})_4$  Synthesis.** Due to the similarity of synthesis of 3–7, a general description is presented here with specific details listed for the respective compounds. The desired  $\text{H}_4\text{-OEA-R}_4$  was slowly added to a stirring solution of the appropriate  $\text{M}(\text{OR})_4$  dissolved in toluene. Upon addition of the  $\text{H}_4\text{-OEA-R}_4$  ligand, the initially clear, colorless solutions turned a yellow to an orange color (*vide infra*). After 12 h, if a precipitate was present, the reaction was warmed slightly until it dissolved and then set aside to slowly cool. The unheated reactions were set aside to allow crystals to grow by slow evaporation. Yields were not optimized.

**$[(\text{OPr}^i)_2\text{Ti}]_2(\mu\text{-OEA-DBP}_4)$  (3).** Used  $\text{Ti}(\text{OPr}^i)_4$  (0.500 g, 1.76 mmol) and  $\text{H}_4\text{-OEA-DBP}_4$  (0.898 g, 0.879 mmol) in tol (~10 mL). Turned orange-yellow upon mixing. Yield 56.5% (0.718 g). FTIR (KBR,  $\text{cm}^{-1}$ ) 2961(s), 2904(s), 2866(s), 1603(m), 1478(s), 1458(m), 1446(m), 1414(m), 1388(w), 1374(w), 1360(m), 1322(m), 1291(s), 1278(s), 1240(m), 1203(m), 1168(m), 1163(m), 1130(s), 1113(s, sh), 1080(m), 1068(m), 1005(s, br), 982(s, sh), 935(w), 915(m), 876(m), 848(s), 808(m), 755(m), 614(m), 595(m), 564(m), 473(s, br).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  7.59 (2H, d,  $\{[\text{OC}_6\text{H}_2(\text{C}(\text{CH}_3)_3)-2,6]_2\text{CH}_2\text{NCH}_2\text{CH}_2\text{OCH}_2\}_2$ ,  $J_{\text{H-H}} = 1.1$  Hz), 7.24 (2H, d,  $\{[\text{OC}_6\text{H}_2(\text{C}(\text{CH}_3)_3)-2,6]_2\text{CH}_2\text{NCH}_2\text{CH}_2\text{OCH}_2\}_2$ ,  $J_{\text{H-H}} = 1.1$  Hz), 5.40 (1H, sept,  $\text{OCH}(\text{CH}_3)_2$ ,  $J_{\text{H-H}} = 6.1$  Hz), 5.27 (1H, sept,  $\text{OCH}(\text{CH}_3)_2$ ,  $J_{\text{H-H}} = 6.1$  Hz), 4.72 (2H, d,  $\{[\text{OC}_6\text{H}_2(\text{C}(\text{CH}_3)_3)-2,6]_2\text{CH}_2\text{NCH}_2\text{CH}_2\text{OCH}_2\}_2$ ,  $J_{\text{H-H}} = 6.4$  Hz), 4.11 (2H, s,  $\{[\text{OC}_6\text{H}_2(\text{C}(\text{CH}_3)_3)-2,6]_2\text{CH}_2\text{NCH}_2\text{CH}_2\text{OCH}_2\}_2$ ,  $J_{\text{H-H}} = 6.4$  Hz), 3.57 (2H, d,  $\{[\text{OC}_6\text{H}_2(\text{C}(\text{CH}_3)_3)-2,6]_2\text{CH}_2\text{NCH}_2\text{CH}_2\text{OCH}_2\}_2$ ,  $J_{\text{H-H}} = 6.4$  Hz), 3.21 (2H, t,  $\{[\text{OC}_6\text{H}_2(\text{C}(\text{CH}_3)_3)-2,6]_2\text{CH}_2\text{NCH}_2\text{CH}_2\text{OCH}_2\}_2$ ,  $J_{\text{H-H}} = 5.2$  Hz), 2.69 (2H, t,  $\{[\text{OC}_6\text{H}_2(\text{C}(\text{CH}_3)_3)-2,6]_2\text{CH}_2\text{NCH}_2\text{CH}_2\text{OCH}_2\}_2$ ,  $J_{\text{H-H}} = 5.2$  Hz), 1.76 (18H, s,  $\{[\text{OC}_6\text{H}_2(\text{C}(\text{CH}_3)_3)-2,6]_2\text{CH}_2\text{NCH}_2\text{CH}_2\text{OCH}_2\}_2$ ), 1.69 (20H, s,  $\{[\text{OC}_6\text{H}_2(\text{C}(\text{CH}_3)_3)-2,6]_2\text{CH}_2\text{NCH}_2\text{CH}_2\text{OCH}_2\}_2$ ), 1.63 (7H, d,  $\text{OCH}(\text{CH}_3)_2$ ,  $J_{\text{H-H}} = 3.7$  Hz), 1.48 (7H, d,  $\text{OCH}(\text{CH}_3)_2$ ,  $J_{\text{H-H}} = 3.7$  Hz). Anal. Calcd for  $\text{C}_{78}\text{H}_{128}\text{N}_2\text{O}_{10}\text{Ti}_2$  (3 + 1 tol; MW = 1349.85) 70.81, C; 9.56, H; 2.08, N; Found 70.73, C; 9.24, H; 1.93, N.

**$(\text{ONep})_2\text{Ti}_2(\mu\text{-OEA-DBP}_4)$  (4).** Used  $\text{Ti}(\text{ONep})_4$  (0.500 g, 1.26 mmol) and  $\text{H}_4\text{-OEA-DBP}_4$  (0.644 g, 0.631 mmol) in tol (~10 mL). Turned orange-yellow upon mixing. Yield 47.7% (0.465 g). FTIR (KBR,  $\text{cm}^{-1}$ ) 2952(s), 2903(s), 2866(s), 1603(m), 1478(s), 1458(s,sh), 1444(s,sh), 1413(m), 1391(m), 1360(m), 1324(m), 1304(m,sh), 1291(s), 1275(s), 1239(s), 1204(m), 1170(m), 1131(m), 1090(s, br), 1064(s,br), 1022(s), 968(w), 934(w), 915(m), 876(m), 846(s), 808(m), 754(s), 683(s,br), 647(w), 621(w), 593(w), 563(s), 557(s), 501(w), 472(s, br).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  7.22 (2H, d,  $\{[\text{OC}_6\text{H}_2(\text{C}(\text{CH}_3)_3)-2,6]_2\text{CH}_2\text{NCH}_2\text{CH}_2\text{OCH}_2\}_2$ ,  $J_{\text{H-H}} = 1.2$  Hz), 6.87 (2H, d,  $\{[\text{OC}_6\text{H}_2(\text{C}(\text{CH}_3)_3)-2,6]_2\text{CH}_2\text{NCH}_2\text{CH}_2\text{OCH}_2\}_2$ ,  $J_{\text{H-H}} = 1.2$  Hz), 4.38 (2H, s,  $\text{OCHC}(\text{CH}_3)_3$ ), 4.35 (2H, d,  $\{[\text{OC}_6\text{H}_2(\text{C}(\text{CH}_3)_3)-2,6]_2\text{CH}_2\text{NCH}_2\text{CH}_2\text{OCH}_2\}_2$ ,  $J_{\text{H-H}} = 6.4$  Hz), 4.22 (2H, s,  $\text{OCHC}(\text{CH}_3)_3$ ), 3.72 (2H, s,  $\{[\text{OC}_6\text{H}_2(\text{C}(\text{CH}_3)_3)-2,6]_2\text{CH}_2\text{NCH}_2\text{CH}_2\text{OCH}_2\}_2$ ), 3.15 (2H, d,  $\{[\text{OC}_6\text{H}_2(\text{C}(\text{CH}_3)_3)-2,6]_2\text{CH}_2\text{NCH}_2\text{CH}_2\text{OCH}_2\}_2$ ,  $J_{\text{H-H}} = 6.4$  Hz), 2.69 (2H, t,  $\{[\text{OC}_6\text{H}_2(\text{C}(\text{CH}_3)_3)-2,6]_2\text{CH}_2\text{NCH}_2\text{CH}_2\text{OCH}_2\}_2$ ,  $J_{\text{H-H}} = 5.5$  Hz), 2.21 (2H, t,  $\{[\text{OC}_6\text{H}_2(\text{C}(\text{CH}_3)_3)-2,6]_2\text{CH}_2\text{NCH}_2\text{CH}_2\text{OCH}_2\}_2$ ,  $J_{\text{H-H}} = 5.5$  Hz), 1.43 (18H, s,  $\{[\text{OC}_6\text{H}_2(\text{C}(\text{CH}_3)_3)-2,6]_2\text{CH}_2\text{NCH}_2\text{CH}_2\text{OCH}_2\}_2$ ), 1.37 (21H, s,  $\{[\text{OC}_6\text{H}_2(\text{C}(\text{CH}_3)_3)-$

$2,6]_2\text{CH}_2\text{NCH}_2\text{CH}_2\text{OCH}_2\}_2$ ), 0.90 (9H, s,  $\text{OCHC}(\text{CH}_3)_3$ ), 0.76 (9H, s,  $\text{OCHC}(\text{CH}_3)_3$ ). Anal. Calcd for  $\text{C}_{86}\text{H}_{144}\text{N}_2\text{O}_{10}\text{Ti}_2$  (MW = 1461.83) 70.66, C; 9.93, H; 1.92, N; Found 71.72, C; 9.23, H; 2.58, N.

**$(\text{O}i\text{Bu})_2\text{Ti}_2(\mu\text{-OEA-DBP}_4)$  (5)-2tol.** Used  $\text{Ti}(\text{O}i\text{Bu})_4$  (0.500 g, 1.47 mmol) and  $\text{H}_4\text{-OEA-DBP}_4$  (0.750 g, 0.734 mmol) in tol (~10 mL). Turned orange-yellow upon mixing. Yield 84.1% (0.925 g). FTIR (KBR,  $\text{cm}^{-1}$ ) 2962(s), 2928(s,sh), 2905(s,sh), 2867(s), 1604(m), 1477(s), 1458(m), 1439(m), 1414(m), 1388(m), 1359(s), 1325(m), 1289(m), 1278(s), 1263(s), 1240(m), 1230(m), 1188(s), 1170(s), 1132(m), 1107(m), 1085(m), 1069(m), 1017(s), 985(s), 936(m), 915(m), 876(m), 807(m), 788(m), 753(m), 729(w), 694(w), 6868(w), 646(w), 624(w), 594(w), 574(w), 552(s,br), 498(m), 474(s,br).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  7.21 (2H, d,  $\{[\text{OC}_6\text{H}_2(\text{C}(\text{CH}_3)_3)-2,6]_2\text{CH}_2\text{NCH}_2\text{CH}_2\text{OCH}_2\}_2$ ,  $J_{\text{H-H}} = 1.2$  Hz), 6.84 (2H, d,  $\{[\text{OC}_6\text{H}_2(\text{C}(\text{CH}_3)_3)-2,6]_2\text{CH}_2\text{NCH}_2\text{CH}_2\text{OCH}_2\}_2$ ,  $J_{\text{H-H}} = 1.2$  Hz), 4.42 (2H, d,  $\{[\text{OC}_6\text{H}_2(\text{C}(\text{CH}_3)_3)-2,6]_2\text{CH}_2\text{NCH}_2\text{CH}_2\text{OCH}_2\}_2$ ,  $J_{\text{H-H}} = 6.3$  Hz), 3.65 (2H, s,  $\{[\text{OC}_6\text{H}_2(\text{C}(\text{CH}_3)_3)-2,6]_2\text{CH}_2\text{NCH}_2\text{CH}_2\text{OCH}_2\}_2$ ), 3.25 (2H, d,  $\{[\text{OC}_6\text{H}_2(\text{C}(\text{CH}_3)_3)-2,6]_2\text{CH}_2\text{NCH}_2\text{CH}_2\text{OCH}_2\}_2$ ,  $J_{\text{H-H}} = 6.4$  Hz), 2.95 (2H, t,  $\{[\text{OC}_6\text{H}_2(\text{C}(\text{CH}_3)_3)-2,6]_2\text{CH}_2\text{NCH}_2\text{CH}_2\text{OCH}_2\}_2$ ,  $J_{\text{H-H}} = 5.5$  Hz), 2.44 (2H, t,  $\{[\text{OC}_6\text{H}_2(\text{C}(\text{CH}_3)_3)-2,6]_2\text{CH}_2\text{NCH}_2\text{CH}_2\text{OCH}_2\}_2$ ,  $J_{\text{H-H}} = 5.5$  Hz), 1.46 (29H, s (br),  $\{[\text{OC}_6\text{H}_2(\text{C}(\text{CH}_3)_3)-2,6]_2\text{CH}_2\text{NCH}_2\text{CH}_2\text{OCH}_2\}_2$  and  $\text{OC}(\text{CH}_3)_3$ ), 1.38 (7H, s,  $\text{OC}(\text{CH}_3)_3$ ), 1.34 (17H, s,  $\{[\text{OC}_6\text{H}_2(\text{C}(\text{CH}_3)_3)-2,6]_2\text{CH}_2\text{NCH}_2\text{CH}_2\text{OCH}_2\}_2$ ). Anal. Calcd for  $\text{C}_{82}\text{H}_{136}\text{N}_2\text{O}_{10}\text{Ti}_2$  (MW = 1405.73) 70.06, C; 9.75, H; 1.99, N; Found 71.55, C; 9.58, H; 2.11, N.

**$(\text{O}i\text{Bu})_2\text{Zr}_2(\mu\text{-OEA-DBP}_4)$  (6)-2tol.** Used  $\text{Zr}(\text{O}i\text{Bu})_4$  (0.500 g, 1.30 mmol) and  $\text{H}_4\text{-OEA-DBP}_4$  (0.665 g, 0.652 mmol) in tol (~10 mL). Remained colorless upon mixing. Yield 74.8% (0.763 g). FTIR (KBR,  $\text{cm}^{-1}$ ) 2964(s), 2925(s,sh), 2904(s), 2867(s), 1604(m), 1480(s), 1457(m,sh), 1449(m,sh), 1439(m,sh), 141(m), 1386(m), 1358(s), 1329(m), 1298(s), 1281(s), 1258(w), 1239(m), 1230(m), 1200(s), 1175(m,sh), 1169(m), 1132(m), 1106(m), 1075(m), 1056(m), 1032(s), 1020(s,sh), 1000(s), 966(m), 934(m), 913(m) 877(s), 844(s,br), 807(m), 783(m), 767(w), 752(s), 728(m), 694(m), 668(w), 646(w), 623(w), 596(w), 579(w), 541(s), 505(w), 474(s,br).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  7.59 (2H, d,  $\{[\text{OC}_6\text{H}_2(\text{C}(\text{CH}_3)_3)-2,6]_2\text{CH}_2\text{NCH}_2\text{CH}_2\text{OCH}_2\}_2$ ,  $J_{\text{H-H}} = 1.2$  Hz), 7.23 (2H, d,  $\{[\text{OC}_6\text{H}_2(\text{C}(\text{CH}_3)_3)-2,6]_2\text{CH}_2\text{NCH}_2\text{CH}_2\text{OCH}_2\}_2$ ,  $J_{\text{H-H}} = 1.2$  Hz), 4.90 (2H, d,  $\{[\text{OC}_6\text{H}_2(\text{C}(\text{CH}_3)_3)-2,6]_2\text{CH}_2\text{NCH}_2\text{CH}_2\text{OCH}_2\}_2$ ,  $J_{\text{H-H}} = 6.3$  Hz), 4.34 (2H, s,  $\{[\text{OC}_6\text{H}_2(\text{C}(\text{CH}_3)_3)-2,6]_2\text{CH}_2\text{NCH}_2\text{CH}_2\text{OCH}_2\}_2$ ), 3.45 (2H, d,  $\{[\text{OC}_6\text{H}_2(\text{C}(\text{CH}_3)_3)-2,6]_2\text{CH}_2\text{NCH}_2\text{CH}_2\text{OCH}_2\}_2$ ,  $J_{\text{H-H}} = 6.3$  Hz), 3.09 (2H, t,  $\{[\text{OC}_6\text{H}_2(\text{C}(\text{CH}_3)_3)-2,6]_2\text{CH}_2\text{NCH}_2\text{CH}_2\text{OCH}_2\}_2$ ,  $J_{\text{H-H}} = 5.5$  Hz), 2.41 (2H, t,  $\{[\text{OC}_6\text{H}_2(\text{C}(\text{CH}_3)_3)-2,6]_2\text{CH}_2\text{NCH}_2\text{CH}_2\text{OCH}_2\}_2$ ,  $J_{\text{H-H}} = 5.5$  Hz), 1.80 (19H, s,  $\{[\text{OC}_6\text{H}_2(\text{C}(\text{CH}_3)_3)-2,6]_2\text{CH}_2\text{NCH}_2\text{CH}_2\text{OCH}_2\}_2$ ), 1.77 (16H, s,  $\{[\text{OC}_6\text{H}_2(\text{C}(\text{CH}_3)_3)-2,6]_2\text{CH}_2\text{NCH}_2\text{CH}_2\text{OCH}_2\}_2$ ), 1.72 (10H, s,  $\text{OC}(\text{CH}_3)_3$ ), 1.62 (9H, s,  $\text{OC}(\text{CH}_3)_3$ ). Anal. Calcd for  $\text{C}_{96}\text{H}_{152}\text{N}_2\text{O}_{10}\text{Zr}_2$  (MW = 1676.64) 68.77, C; 9.14, H; 1.67, N; Found 67.07, C; 8.44, H; 2.05, N.

**$(\text{O}i\text{Bu})_2\text{Hf}_2(\mu\text{-OEA-DBP}_4)$  (7)-2tol.** Used  $\text{Hf}(\text{O}i\text{Bu})_4$  (0.500 g, 1.06 mmol) and  $\text{H}_4\text{-OEA-DBP}_4$  (0.542 g, 0.530 mmol) in tol (~10 mL). Turned pale yellow upon mixing. Yield 76.4% (0.732 g). FTIR (KBR,  $\text{cm}^{-1}$ ) 2963(s), 2927(s,sh), 2905(s,sh), 2867(m), 1604(m), 1480(s), 1457(m), 1439(m), 1415(m), 1386(m), 1359(m), 1330(m), 1298(s), 1282(s), 1261(m), 1239(m), 1231(m), 1203(s), 1195(sh, m), 1169(m), 1132(m), 1105(m), 1074(m), 1074(m), 1053(sh, m), 1038(m), 1008(s), 983(m), 966(w), 933(w), 913(m), 877(m), 852(s,sh), 845(s), 807(m), 793(m), 785(w), 767(w), 752(m), 730(w), 694(w), 668(w), 646(w), 596(w), 539(s), 507(w), 462(s, br).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  7.21 (2H, d,  $\{[\text{OC}_6\text{H}_2(\text{C}(\text{CH}_3)_3)-2,6]_2\text{CH}_2\text{NCH}_2\text{CH}_2\text{OCH}_2\}_2$ ,  $J_{\text{H-H}} = 1.2$  Hz), 6.82 (2H, d,  $\{[\text{OC}_6\text{H}_2(\text{C}(\text{CH}_3)_3)-2,6]_2\text{CH}_2\text{NCH}_2\text{CH}_2\text{OCH}_2\}_2$ ,  $J_{\text{H-H}} = 1.2$  Hz), 4.54 (2H, d,  $\{[\text{OC}_6\text{H}_2(\text{C}(\text{CH}_3)_3)-2,6]_2\text{CH}_2\text{NCH}_2\text{CH}_2\text{OCH}_2\}_2$ ,  $J_{\text{H-H}} = 6.3$  Hz), 3.99 (2H, s,  $\{[\text{OC}_6\text{H}_2(\text{C}(\text{CH}_3)_3)-$

Table 1. Data Collection Parameters for 3–7

	compound		
	3	4	4a
chemical formula	C <sub>78</sub> H <sub>127</sub> N <sub>2</sub> O <sub>10</sub> Ti <sub>2</sub>	C <sub>86</sub> H <sub>144</sub> N <sub>2</sub> O <sub>10</sub> Ti <sub>2</sub>	C <sub>54</sub> H <sub>72</sub> Cl <sub>8</sub> N <sub>2</sub> O <sub>10</sub> Ti <sub>2</sub>
formula weight	1348.62	1461.83	1288.54
temp (K)	173(2)	173(2)	188(2)
space group	triclinic, <i>P</i> $\bar{1}$	triclinic, <i>P</i> $\bar{1}$	triclinic, <i>P</i> $\bar{1}$
<i>a</i> (Å)	14.3506(9)	14.6280(7)	11.1671(14)
<i>b</i> (Å)	14.3701(9)	18.2723(9)	14.0685(17)
<i>c</i> (Å)	24.9092(16)	19.0406(10)	21.670(3)
$\alpha$ (deg)	78.638(3)	85.188(3)	72.970(2)
$\beta$ (deg)	79.518(3)	75.049(3)	82.350(2)
$\gamma$ (deg)	66.563(3)	79.783(3)	70.906(2)
<i>V</i> (Å <sup>3</sup> )	4589.9(5)	4835.2(4)	3073.5(6)
<i>Z</i>	2	2	2
<i>D</i> <sub>calcd</sub> (Mg/m <sup>3</sup> )	0.976	1.004	1.392
$\mu$ (Mo <i>K</i> $\alpha$ ) (mm <sup>-1</sup> )	0.221	0.214	0.662
<i>R</i> <sub>int</sub>	0.0373	0.0409	0.0767
<i>R</i> 1 <sup>a</sup> (%) (all data)	9.46(11.10)	6.60(9.10)	6.19(12.38)
w <i>R</i> 2 <sup>b</sup> (%) (all data)	25.44 (26.34)	21.90(24.46)	14.73 (18.68)

	compound		
	5·2tol	6·2tol	7·2tol
chemical formula	C <sub>82</sub> H <sub>136</sub> N <sub>2</sub> O <sub>10</sub> Ti <sub>2</sub>	C <sub>96</sub> H <sub>152</sub> N <sub>2</sub> O <sub>10</sub> Zr <sub>2</sub>	C <sub>96</sub> H <sub>152</sub> Hf <sub>2</sub> N <sub>2</sub> O <sub>10</sub>
formula weight	1405.73	1676.64	1851.18
temp (K)	173(2)	173(2)	193(2)
space group	monoclinic, <i>C</i> 2/ <i>c</i>	monoclinic, <i>C</i> 2/ <i>c</i>	monoclinic, <i>C</i> 2/ <i>c</i>
<i>a</i> (Å)	15.9322(6)	16.0838(13)	16.0892(14)
<i>b</i> (Å)	23.3733(6)	23.7108(13)	23.729(2)
<i>c</i> (Å)	26.3238(6)	26.2422(15)	26.233(3)
$\beta$ (deg)	101.795(2)	101.242(5)	101.3630(10)
<i>V</i> (Å <sup>3</sup> )	9595.7(5)	9815.7(11)	9819.0(16)
<i>Z</i>	4	4	4
<i>D</i> <sub>calcd</sub> (Mg/m <sup>3</sup> )	0.973	1.135	1.252
$\mu$ (Mo <i>K</i> $\alpha$ ) (mm <sup>-1</sup> )	0.213	0.265	2.166
<i>R</i> <sub>int</sub>	0.0839	0.0530	0.0216
<i>R</i> 1 <sup>a</sup> (%) (all data)	8.13(12.29)	4.08(6.80)	2.25(2.71)
w <i>R</i> 2 <sup>b</sup> (%) (all data)	20.78(23.07)	11.71(14.98)	8.38(9.47)

$$^a R1 = \frac{\sum |F_o| - |F_c|}{\sum |F_o|} \times 100. \quad ^b wR2 = \left[ \frac{\sum w(F_o^2 - F_c^2)^2}{\sum (wF_o^2)^2} \right]^{1/2} \times 100.$$

2,6]CH<sub>2</sub>NCH<sub>2</sub>CH<sub>2</sub>OCH<sub>2</sub>}, 3.04 (2H, d, {[OC<sub>6</sub>H<sub>2</sub>(C(CH<sub>3</sub>)<sub>3</sub>)-2,6]CH<sub>2</sub>NCH<sub>2</sub>CH<sub>2</sub>OCH<sub>2</sub>}, *J*<sub>H-H</sub> = 6.3 Hz), 2.73 (2H, t, {[OC<sub>6</sub>H<sub>2</sub>(C(CH<sub>3</sub>)<sub>3</sub>)-2,6]CH<sub>2</sub>NCH<sub>2</sub>CH<sub>2</sub>OCH<sub>2</sub>}, *J*<sub>H-H</sub> = 5.6 Hz), 2.01 (2H, t, {[OC<sub>6</sub>H<sub>2</sub>(C(CH<sub>3</sub>)<sub>3</sub>)-2,6]CH<sub>2</sub>NCH<sub>2</sub>CH<sub>2</sub>OCH<sub>2</sub>}, *J*<sub>H-H</sub> = 5.6 Hz), 1.39 (18H, s, {[OC<sub>6</sub>H<sub>2</sub>(C(CH<sub>3</sub>)<sub>3</sub>)-2,6]CH<sub>2</sub>NCH<sub>2</sub>CH<sub>2</sub>OCH<sub>2</sub>}, 1.37 (17H, s, {[OC<sub>6</sub>H<sub>2</sub>(C(CH<sub>3</sub>)<sub>3</sub>)-2,6]CH<sub>2</sub>NCH<sub>2</sub>CH<sub>2</sub>OCH<sub>2</sub>}, 1.33 (10H, s, OC(CH<sub>3</sub>)<sub>3</sub>), 1.23 (9H, s, OC(CH<sub>3</sub>)<sub>3</sub>). Anal. Calcd for C<sub>96</sub>H<sub>152</sub>Hf<sub>2</sub>N<sub>2</sub>O<sub>10</sub> (MW = 1851.18) 62.29, C; 8.28, H; 1.51, N. C<sub>188</sub>H<sub>296</sub>Hf<sub>4</sub>N<sub>4</sub>O<sub>20</sub> (2\*7 - 1 tol); MW = 3610.36) 61.55, C; 8.26, H; 1.55, N. Found 61.21, C; 8.23, H; 1.53, N.

**General X-ray Crystal Structure Information.**<sup>28</sup> Crystals were mounted from a pool of Fluorolube and immediately placed in a cold N<sub>2</sub> vapor stream, on a Bruker AXS diffractometer equipped with a SMART 1000 CCD detector using graphite monochromatized Mo *K* $\alpha$  radiation ( $\lambda$  = 0.7107 Å) or a Bruker AXS diffractometer equipped with a APEX II detector. Lattice determination, data collection, and data reduction were performed using the appropriate software suite, either SMART or APEX II.

Structures were solved by direct methods that yielded the heavy atoms, along with a number of the lighter atoms or by using the PATTERSON method, which yielded the heavy atoms. Subsequent Fourier syntheses yielded the remaining light-atom positions. The hydrogen atoms were fixed in positions of ideal geometry and refined using Shelxl-97 software. The final refinement of each compound included anisotropic thermal parameters for all non-hydrogen atoms.

All final CIF files were checked at <http://www.iucr.org/>. Additional information concerning the data collection and final structural solutions can be found in the Supporting Information or by accessing CIF files through the Cambridge Crystallographic Data Base. Data collection parameters for 3–7 are given in Table 1. Specific issues associated with individual structures are discussed below.

Compounds 3 and 7 possessed significant ligand disorder for one of the OR groups, which necessitated modeling of the ligand. For 3, the disorder led to removal of a H and thus the discrepancy between the final observed MW in Table 1 and the chemically reasonable structure presented. For the following compounds, the stated volume was squeezed out of the unit cell, representing various disordered toluene molecule(s) listed: 3 (1007.6 Å<sup>3</sup> = ~1 tol), 4 (771.1 Å<sup>3</sup> = ~1 tol), and 5 (1946.3 Å<sup>3</sup> = ~2 tol, included in MW in Table 1). Compound 4a had significant disorder in a number of the OR ligands, which prevented solving for the hydrogen atoms. A sin( $\theta$ <sub>max</sub>)/wavelength error occurred in the final check; however, the original collection parameters predetermined by the APEXII software and the recorded values were found to yield the best structural solution.

**Thermogravimetric Analysis (TGA).** Thermogravimetric analyses were performed on a Mettler Toledo TGA/DSC 1, STAR<sup>c</sup> System under a flowing atmosphere of argon at a ramp rate of 5 °C/min up to 650 °C. The dried crystalline powder was transferred from a glass vial to a TGA ceramic weigh boat and analyzed.

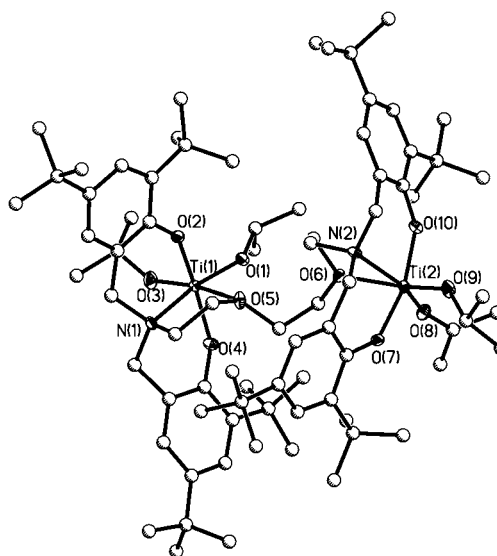
**Powder X-ray Diffraction (PXRD).** Powder X-ray diffraction (PXRD) was performed by a PANalytical X'Pert Pro XRD in the  $2\theta$  range of  $10\text{--}100^\circ$  at a scan rate of  $0.15^\circ/\text{s}$  on nanomaterials using a zero background holder. The dried crystalline powder was transferred from a glass vial to a pre-fired ceramic boat (at  $850^\circ\text{C}$ ) and placed into a box furnace and heated to  $650^\circ\text{C}$  under circumjacent atmosphere and held for 1 h. After this time it was transferred to a zero background holder, and the PXRD pattern obtained.

## RESULTS AND DISCUSSION

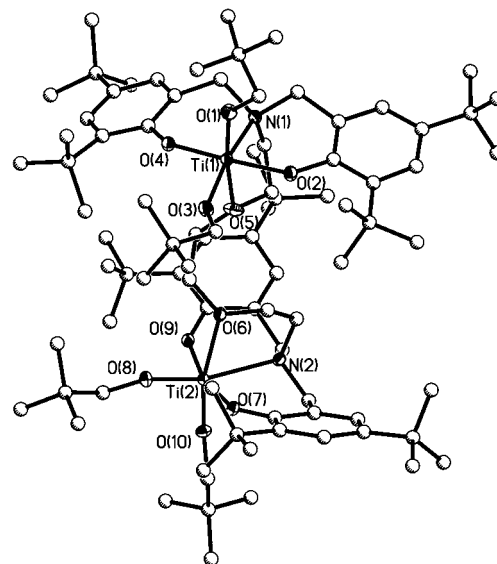
This study focused on developing new ligands that were analogous to the previously reported  $\text{H}_4\text{-ED-R}_4$  tetra-phenols but were capable of satisfying the coordination demands of larger metal ions without fully encapsulating them. The initial design included a longer chain between the benzyl phenol moieties, thereby isolating the reactive OH sites. Further, the addition of potentially binding heteroatoms in the chain was of interest in order to assist in filling the open coordination sites on the metals. These characteristics were realized using 2,2'-(ethylenedioxy)diethanamine ( $\text{H}_4\text{-OEA}$ ) as the starting diamine, increasing the “linker” to eight atoms, with two oxygen atoms from the ether moieties. The  $\text{H}_4\text{-OEA-DBP}_4$  (**1**) and  $\text{H}_4\text{-OEA-DCP}_4$  (**2**) were prepared in a similar fashion as the previously reported  $\text{H}_2\text{-ED-R}_4$  ligands.<sup>26</sup> The DCP versus DBP derivatives were of interest based on the variations in electron-withdrawing effect of the Cl versus the *tert*-butyl substituents. For the OEA derivatives, the number of purification steps was significantly reduced, which has led to an increased yield. All analytical data on the bulk powders were found to be in agreement with the proposed formulation of  $\text{H}_4\text{-OEA-DBP}_4$  and  $\text{H}_4\text{-OEA-DCP}_4$ , which was further verified by the structures described below.

With these novel  $\text{H}_4\text{-OEA-R}_4$  ligands in hand, their coordination behavior with  $[\text{M}(\text{OR})_4]$  was explored following eq 1. Upon addition of the  $\text{H}_4\text{-OEA-DBP}_4$  to a stirring solution of the desired  $[\text{M}(\text{OR})_4]$  in toluene, the initially clear, colorless reaction instantly turned to a yellow-orange color. After stirring for 12 h, the reactions were set aside with their respective caps loose until crystals grew. The mother liquor was then decanted, followed by a wash with cold hexanes, and some of the crystals were set aside for single crystal studies (*vide infra*). The remaining crystalline material was dried *in vacuo*, and the resulting free-flowing powders were analyzed by FTIR spectroscopy. Disappearance of the broad phenol O–H stretches centered at  $3364\text{ cm}^{-1}$  for the  $\text{H}_4\text{-OEA-R}_4$  ligands proved to be a useful handle in gauging the progress of the metalation reactions. The loss of this stretch in the spectra of **3–7** indicated the reactions had gone to completion. In addition, the presence of the parent OR and the OEA- $\text{R}_4$  stretches and bends indicated the reaction had proceeded as detailed in eq 1.

To ascertain the coordination behavior of the OEA-DBP<sub>4</sub> ligand, single crystal X-ray structure studies were undertaken. Similar disubstituted arrangements were solved for **3–7**, which are shown in Figures 2–7, respectively. For **3** (Figure 2), the two -OH groups of adjacent DBP moieties were found to have reacted and bound a single Ti metal center, which results in a disubstituted, bridging OEA-DBP<sub>4</sub> ligand. Each of the metals was found to adopt a distorted 6-coordinated octahedral (OC-6) geometry through the additional coordination of a N and an O atom of the OEA chain, as well as retaining two of the original OPr<sup>f</sup> ligands. This places both of the OEA-DBP moieties *trans* to each other in the axial position, while the OR



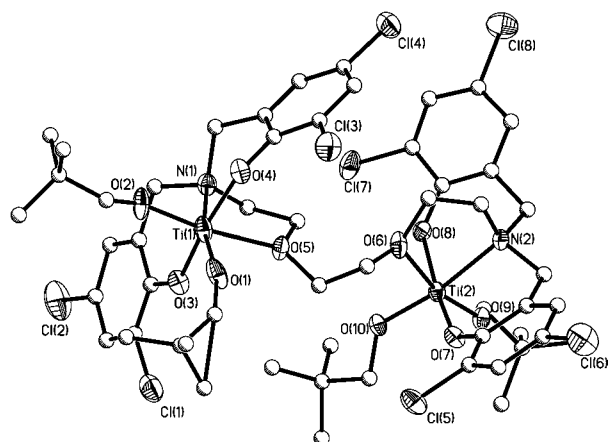
**Figure 2.** Structure plot of **3**. Thermal ellipsoids of heavy atoms drawn at the 30% level with carbon atoms drawn as ball and stick and H-atoms omitted for clarity.



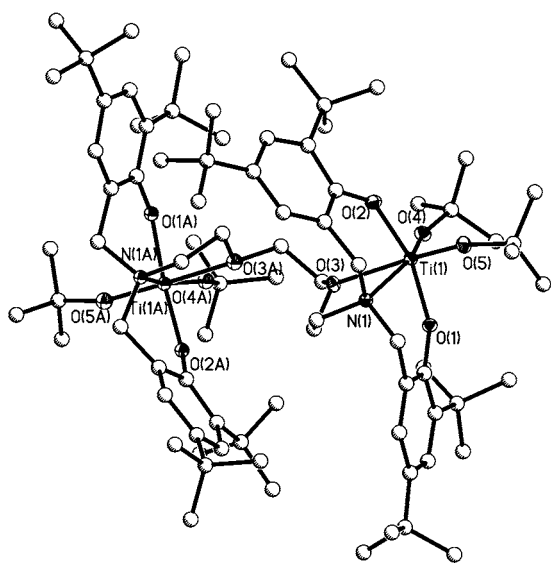
**Figure 3.** Structure plot of **4**. Thermal ellipsoids of heavy atoms drawn at the 30% level with carbon atoms drawn as ball and stick and H-atoms omitted for clarity.

ligands were solved in equatorial sites, in a *cis* arrangement. As a result, three rings around the Ti are formed: a five-membered ring from the -NCH<sub>2</sub>CH<sub>2</sub>O- moiety and two six-membered rings with each of the DBP oxygen atoms. Since compounds **4** (ONep, Figure 3) and **5** (OBU<sup>f</sup>, Figure 5) adopt identical arrangements, increasing the steric bulk of the terminal alkoxy was found to have had no impact on the overall structure. Investigation of the congener metals were undertaken to determine if the larger cation would impart structural variations. The reaction with the OBU<sup>f</sup> derivatives of Zr (**6**) and Hf (**7**) yielded X-ray quality crystals, and the structures are shown in Figures 6 and 7, respectively. Again, the overall coordination behavior of the OEA-DBP<sub>4</sub> ligands for **6** and **7** was found to be similar to that observed previously.

Investigation of the dichlorophenoxide derivatives, termed  $\text{H}_4\text{-OEA-DCP}_4$ , was undertaken to determine the impact the



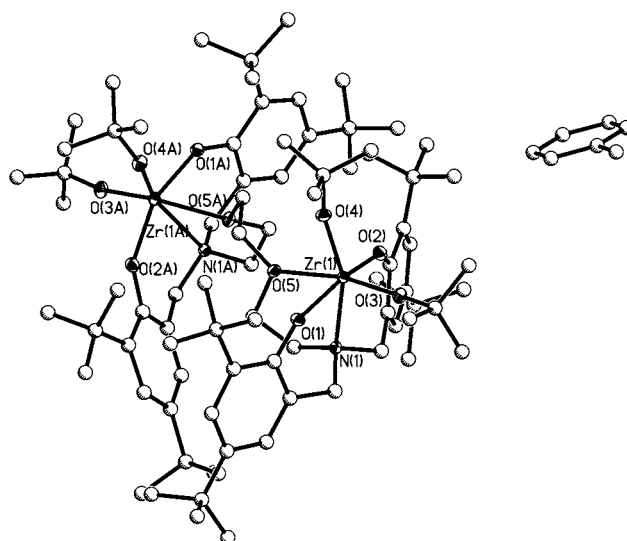
**Figure 4.** Structure plot of **4a**. Thermal ellipsoids of heavy atoms drawn at the 30% level with carbon atoms drawn as ball and stick and H-atoms omitted for clarity.



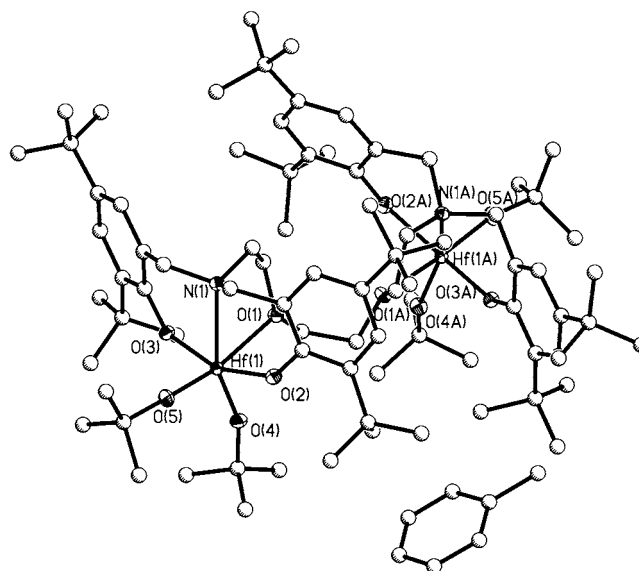
**Figure 5.** Structure plot of **5**. Thermal ellipsoids of heavy atoms drawn at the 30% level with carbon atoms drawn as ball and stick and H-atoms omitted for clarity.

electron-withdrawing Cl would have on the final products. The reaction of  $\text{Ti}(\text{ONep})_4$  with **2** led to crystals of **4a** (Figure 4). The basic structure of **4a** is identical to that noted for the OEA-DBP<sub>4</sub> ligated compounds with the OC-6 geometry formed from a comparable ligand set. Due to the similarity in the structures observed for the OEA-R<sub>4</sub>, further characterization into the coordination of the DCP derivatives was not pursued.

The successful isolation of the homometallic complexes (**3–7**) led us to explore the synthesis of heterometallic species. Under analogous conditions as used to generate **3–7**, with the exception of using mixtures of metals (i.e., Ti/Zr, Ti/Hf, and Zr/Hf) or stepwise addition), only the homoleptic derivatives were isolated. It has been reported that the use of chelating ligands may lend some stability to metal alkoxides in the solid state, but in solution these ligands will favor a charge distribution, making them more reactive due to easily realized equilibria.<sup>29,30</sup> Due to an increased acidity of the remaining unreacted hydroxyl protons, the higher reactive  $\text{M}(\text{OR})_4$  would therefore preferentially react with one ligand leading to the homoleptic compounds. Additional efforts are therefore



**Figure 6.** Structure plot of **6**. Thermal ellipsoids of heavy atoms drawn at the 30% level with carbon atoms drawn as ball and stick and H-atoms omitted for clarity. Lattice toluene shown.



**Figure 7.** Structure plot of **7**. Thermal ellipsoids of heavy atoms drawn at the 30% level with carbon atoms drawn as ball and stick and H-atoms omitted for clarity. Lattice toluene shown.

underway to utilize/synthesize mixed functional groups on these tetra-phenol ligands that will lead to selective reactivity.

The metrical data of **3–7** show the variations induced by the OEA-R<sub>4</sub> ligand (see Table 2) within this family of compounds. The interactions of the Ti derivatives with the O and N atoms of the OEA chain all appear to be consistent. The Ti–OR distances were found to be on average 1.80 Å and are in agreement with the literature values.<sup>31</sup> The Ti...Ti distances (ranging from 7.14 to 7.42 Å) demonstrate the flexibility of the OEA backbone to minimize any steric interaction; however, there does appear to be a crystallization effect that may be influencing the final distance (i.e., the triclinic **3** and **4** were shorter than observed for the monoclinic **5**). The angles around the Ti metal centers argue for a distorted OC-6 geometry. The interaction of the Ti metal centers with O of the OEA chain are in line with expected Ti–O values of the “(OAr)<sub>2</sub>Ti(OR)<sub>2</sub>(N)”

Table 2. Metrical Data Summary for 1–7<sup>a</sup>

	3	4	5	6	7
	Distances (Å)				
M–OR	1.80	1.81	1.79	1.93	1.93
M–O <sub>DBP</sub>	1.89	1.89	1.91	2.04	2.03
M–O <sub>OEA</sub>	2.34	2.29	2.3617(16)	2.4146(15)	2.389(2)
M–N <sub>OEA</sub>	2.34	2.33	2.3354(19)	2.4535(18)	2.427(2)
M···M	7.19	7.14	7.42	7.42	7.38
	Angles (deg)				
OR–M–OR	107.1	104.8	107.29(8)	106.35(7)	106.79(8)
OR–M–O <sub>DBP</sub>	95.2	94.6	95.2	95.0	96.2
O <sub>DBP</sub> –M–O <sub>DBP</sub>	163.7	164.4	162.28(7)	157.75(6)	158.73(7)
OR–M–N <sub>OEA</sub>	159.2 and 93.6	160.6 and 94.6	156.48(7) and 96.23(7)	154.12(6) 99.53(6)	154.49(7) 98.71(8)
O <sub>OEA</sub> –M–N <sub>OEA</sub>	85.7	72.2	70.94(6)	68.68(5)	69.33(7)

<sup>a</sup>All values are averaged unless a unique value was used (indicated by an error bar).

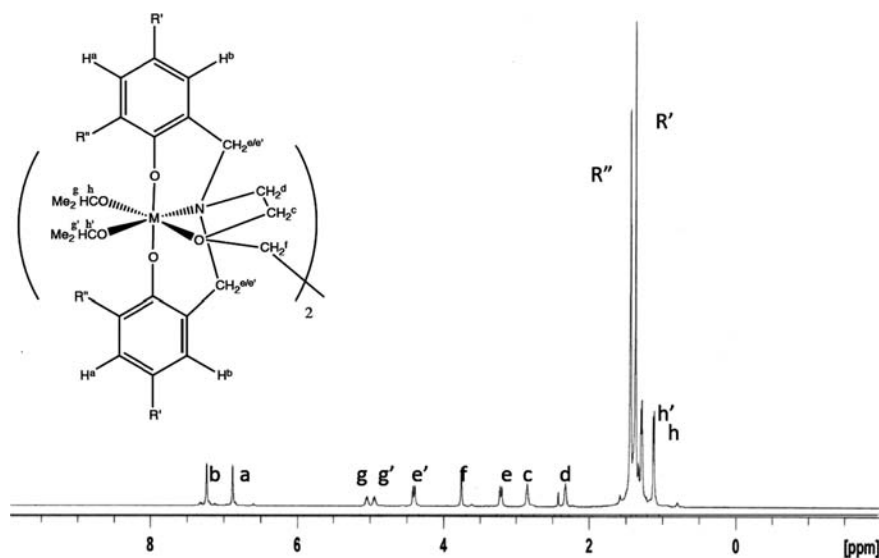


Figure 8. <sup>1</sup>H NMR (CDCl<sub>3</sub>) spectrum of 3. Inset indicates proposed assignments.

moiety; however, they are on the long end of the range observed, approaching distances associated with calixarene compounds for the Ti–O.<sup>32–34</sup> Similar, long Ti–N interactions are noted for similar aromatic benzyl–N compounds.<sup>31</sup> The variations noted in the distances and angles for 6 and 7 versus 3–5 are more a reflection of the change in cation size from Zr or Hf to Ti, respectively. While the Zr–OR and Hf–OR distances are in line with existing distances noted in the literature,<sup>31</sup> the Zr–O and Zr–N interaction with the OEA ligand are long and approach a calixarene-type interaction.<sup>28,35,36</sup> In fact, the Zr–O distance is the longest reported to date for any ZrO<sub>5</sub>N moiety but well within the reported values for all Zr–O distances. The Hf–O distances are more in the middle of reported values for the same moiety, but this may be more of a reflection of the limited number of Hf compounds available.

Obviously, the novelty of 3–7 means there are only a limited number of reasonable models useful for metrical comparisons. The ED-R<sub>4</sub> (Figure 1c) modified compounds were selected as the model system based on the similarity of the linked OAr moieties. The metrical data of these M(ED-R<sub>4</sub>) compounds have average M–O and average M–N distances of (i) Ti, 1.85 and 2.26 Å; (ii) Zr, 2.03 and 2.42 Å; (iii) Hf, 2.03 and 2.39 Å, respectively. In comparison, the M–(OEA-DBP<sub>4</sub>) distances of 3–7 are slightly longer, which may be a reflection of the MO<sub>5</sub>N

core for OEA versus a MO<sub>4</sub>N<sub>2</sub> core reported for the ED-R<sub>4</sub><sup>26</sup> or the presence of the two terminal OR.

Analyses of the bulk powders were undertaken to determine if they were consistent with the observed crystal structures. Elemental analyses of the dried powders were found to be in agreement when selected values of toluene solvent molecules were added or subtracted (see Experimental Section). The inclusion/loss of unit cell solvent molecules is not uncommon for elemental analyses of [M(OR)<sub>x</sub>].<sup>26</sup> These “adjusted” molecular weight values were used to determine the yield of the materials.

Attempts were made to understand the decomposition behavior of these compounds using thermal analyses. Surprisingly, each of the Ti–OEA-DBP<sub>4</sub> precursors was found to melt (3, 193 °C; 4, 220 °C; 5, 210 °C) prior to decomposition. In addition, the larger congeners also melted but at significantly higher temperatures (6, 323 °C; 7, 323 °C). Further analyses of the combustion behavior of 3–7 were undertaken using TGA under a flowing atmosphere of argon. For the Ti-bearing compounds (3–5), the endotherm associated with the previously observed melt was noted in the spectrum followed by a major weight loss, associated with the organic fraction decomposition initiating at 300 °C that was complete by 500 °C. Only one small endotherm was observed

around 350 °C for 3–5. For 6 and 7, no endotherm was noted until 380 °C, which coincides with the loss of the organic species. The weight losses occur in one step with a few slope changes observed; however, it was not possible to determine when the OR, the OEA, or the DBP moieties decomposed. The weight losses calculated for these samples were not consistent with the complete conversion to the metal oxide. Several reasonable explanations could account for this, such as the degree of toluene solvation, incomplete combustion, or molecular volatility due to the low melting point. However, for these compounds it was assumed they retained toluene (*vide* elemental analyses) or retention of C upon combustion under an Ar atmosphere, which is consistent with the black powders obtained; however, there was not enough powder remaining to analyze properly. Therefore, additional powders of each of the precursors were independently placed in a ceramic boat and fired up to 650 °C (as determined by the TGA spectrum to ensure crystallization) under atmospheric conditions. The resulting white powders were collected and analyzed by PXRD. The patterns obtained indicated the compounds had cleanly converted to their respective metal oxide [compound, phase (JCPDS-ID)]: 3, rutile (00-021-1276); 4, rutile (00-021-1276); 5, anatase/rutile (98-00-0081/00-021-1276); 6, zirconium oxide (00-017-0923); 7, hafnium oxide (00-034-0104). The mixed phases observed for 5 is an interesting result since the thermal decomposition appears identical based on the TGA spectrum. While further exploration is necessary to understand this behavior, the variation in phases generated can only be associated with the OBU<sup>t</sup> versus the OPr<sup>i</sup> or ONep ligand decomposition properties.

Studies using solution <sup>1</sup>H NMR spectroscopy were undertaken to explore the purity of the compounds and attempt to determine the solution behavior of 3–7. Dissolution of crystalline material led to complicated spectra. It was expected with the chelation noted in the crystal structure that there would be a mirror plane down the dioxoethylene (i.e., OCH<sub>2</sub>CH<sub>2</sub>O) chain that would equate the two halves of the molecule. The remainder of the molecule would then be asymmetric, and 5 types of protons from the OEA chain should be noted (along with the two aryl and two Bu<sup>t</sup> groups of the DBP<sub>4</sub> moiety and the OR). For 3 (see Figure 8) the two aryl protons of the DBP fraction were noted around 7.0 ppm, but instead of being the expected singlets, these were doublets with small *J*<sub>H–H</sub> splittings. This is most likely due to “cross-talk” between the aryl protons and was previously noted for the ED-R<sub>4</sub> system.<sup>26</sup> In addition, two Bu<sup>t</sup> groups were noted for the DBP ligand around 1.5 ppm. The two disparate OR groups were also present as two septuplets for the methane and doublets for the methyls around 5 and 1 ppm, respectively. The remainder of the spectrum consists of two doublets, two triplets, and singlets that have integration consistent with ~2 H each. The singlet was assigned as the methylene protons on the dioxoethane chain, equated by the mirror plane and free rotation around the C–C bond. The triplets were assigned as part of the two types of protons located on the dioxodiamine chain, i.e., those protons on the C next to the N and those next to the oxygen. This leaves the doublets arising from the protons on the benzyl carbon. It was assumed these would be equivalent, but the hindered rotation converts them to diastereomers. The <sup>1</sup>H NMR spectra of the remaining compounds (4–7) were found to present a similar pattern with the appropriate OR resonances replacing the OPr<sup>i</sup> of 3. For 5, one of the OBU<sup>t</sup> and one of the Bu<sup>t</sup> from the OEA ligand

appear to overlap, which is verified by the integration of the broad singlet present in the spectrum. The observed resonances argue for retention of the structures of 4–7 in solution and further establishes the purity of these compounds. On the basis of the unique signatures of the <sup>1</sup>H NMR spectra for 3–7, which fully establish the identity and purity (along with the elemental analyses) of these compounds, the corresponding <sup>13</sup>C NMR data were not collected.

## SUMMARY AND CONCLUSIONS

A set of *N,N,N',N'*-tetrakis(3,5-substituted benzyl-2-oxide)-2,2'-(ethylenedioxy)diethanamine ligands were synthesized, and the coordination chemistry investigated using the Group 4 [M(OR)<sub>4</sub>]. These novel ligands were synthesized from a modified Mannich and found to be easily isolated in high yield by filtration. The reaction of the H<sub>4</sub>-OEA-DBP<sub>4</sub> derivative with [M(OR)<sub>4</sub>] was found to generate dinuclear species (independent of the metal or ligand) employing the two O atoms of the DBP, one N and one O atom of the OEA chain. The metals retain some reactivity with the parent OR ligands readily available. Thermal conversion studies indicate the organic fractions of the [(OR)<sub>4</sub>M<sub>2</sub>(OEA-DBP<sub>4</sub>)] precursors are decomposed by 350 °C and cleanly converted to their fully crystallized metal oxides [rutile (3, 4), zirconium oxide (6), and hafnium oxide (7)] by 650 °C. The one exception is 5, which generates a mixed phase of anatase and rutile. Solution state <sup>1</sup>H NMR studies confirms that the molecules are retained in solution. While the OEA-R<sub>4</sub> moieties allow for controlled metal placement, alternative chains with removal of the heteroatoms are being investigated to reduce the chelation behavior, leaving open coordination sites on the metal centers. Further, since the tetra-ol process successfully generated the homometallic but precluded the production of the heterometallic species, additional similar polydentate ligands that are polyfunctional, are being pursued.

## ASSOCIATED CONTENT

### Supporting Information

Crystallographic files in CIF format. This material is available free of charge via the Internet at <http://pubs.acs.org>. CCDC 897416–897420 contains the supplementary crystallographic data for 3–7, respectively. These data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/conts/retrieving.html> or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail.

## AUTHOR INFORMATION

### Corresponding Author

\* Phone: (505)272-7625. Fax: (505)272-7336. E-mail: [tjboyle@sandia.gov](mailto:tjboyle@sandia.gov).

### Notes

The authors declare no competing financial interest.

## ACKNOWLEDGMENTS

The authors would like to thank the following personnel: C. Lockhart (SNL) for technical assistance and Prof R. A. Kemp (UNM) for the use of the Bruker X-ray diffractometer purchased via the National Science Foundation CRIF:MU award to the University of New Mexico (CHE04-43580). This work was supported by the National Institute for Nano-Engineering (NINE) and the Laboratory Directed Research



and Development (LDRD) programs at Sandia National Laboratories. Sandia National Laboratories is a multiprogram laboratory managed and operated by Sandia Corporation, a wholly owned subsidiary of Lockheed Martin Corporation, for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-AC04-94AL85000.

## REFERENCES

- (1) Boyle, T. J.; Tribby, L. J.; Ottley, L. A. M.; San, S. M. *Eur. J. Inorg. Chem.* **2009**, 36, 5550.
- (2) Boyle, T. J.; Hernandez-Sanchez, B. A.; Baros, C. M.; Brewer, L. N.; Rodriguez, M. A. *Chem. Mater.* **2007**, 19, 2016.
- (3) Boyle, T. J.; Bunge, S. D.; Andrews, N. L.; Matzen, L. E.; Sieg, K.; Rodriguez, M. A.; Headley, T. J. *Chem. Mater.* **2004**, 16, 3279.
- (4) Caulton, K. G.; Hubert-Pfalzgraf, L. G. *Chem. Rev.* **1990**, 90, 969.
- (5) Chandler, C. D.; Roger, C.; Hampden-Smith, M. J. *Chem. Rev.* **1993**, 93, 1205.
- (6) Hubert-Pfalzgraf, L. G. *New J. Chem.* **1987**, 11, 663.
- (7) Turova, M. Y.; Turevskaya, E. P.; Kessler, V. G.; Yanovskaya, M. I. *The Chemistry of Metal Alkoxides*; Kluwer Academic Publishers: Boston, 2002.
- (8) Gerung, H.; Boyle, T. J.; Tribby, L. J.; Bunge, S. D.; Brinker, C. J.; Han, S. M. *J. Am. Chem. Soc.* **2006**, 128, 5244.
- (9) Boyle, T. J.; Bunge, S. D.; Alam, T. M.; Holland, G. P.; Headley, T. J.; Avilucea, G. *Inorg. Chem.* **2005**, 44, 1309.
- (10) Bradley, D. C.; Mehrotra, R. C.; Rothwell, I. P.; Singh, A. *Alkoxo and Aryloxo Derivatives of Metals*; Academic Press: San Diego, 2001.
- (11) Carta, G.; Habra, N. E.; Rossetto, G.; Crociani, L.; Torzo, G.; Zanella, P.; Casarin, M.; Cavinato, G.; Pace, G.; Kaciulis, S.; Mezzi, A. *Thin Solid Films* **2008**, 516, 7354.
- (12) Mehring, M. *Coord. Chem. Rev.* **2007**, 251, 974.
- (13) Thomas, R.; Rije, E.; Ehrhart, P.; Milanov, A.; Bhakta, R.; Bauneman, A.; Devi, A.; Fischer, R.; Waser, R. *J. Electrochem. Soc.* **2007**, 154, G77.
- (14) Roh, H. S.; CKang, Y. C.; Lee, C. H.; Park, H. D.; Park, S. B. *Jpn. J. Appl. Phys., Part 1* **2003**, 42, 3429.
- (15) Athar, T. *Int. J. Nano Biomater.* **2009**, 2, 172.
- (16) Hakim, S. H.; Shanks, B. H. *Microporous Mesoporous Mater.* **2010**, 135, 105.
- (17) Kessler, V. G.; Spijksma, G. I.; Seisenbaeva, G. A.; Hakansson, S.; Blank, D. H. A.; Bouwmeester, H. J. M. *J. Sol-Gel Sci. Technol.* **2006**, 163.
- (18) Bradley, D. C. *Chem. Rev.* **1989**, 89, 1317.
- (19) Bradley, D. C.; Mehrotra, R. C.; Gaur, D. P. *Metal Alkoxides*; Academic Press: London, 1978.
- (20) Caulton, K. G.; Hubert-Pfalzgraf, L. G. *Chem. Rev.* **1990**, 90, 969.
- (21) Chandler, C. D.; Roger, C.; Hampden-Smith, M. J. *Chem. Rev.* **1993**, 93, 1205.
- (22) Hubert-Pfalzgraf, L. G. *New J. Chem.* **1987**, 11, 663.
- (23) Boyle, T. J.; Ottley, L. A. M.; Rodriguez, M. A.; Sewell, R. M.; Alam, T. M.; McIntyre, S. K. *Inorg. Chem.* **2008**, 47, 10708.
- (24) Boyle, T. J.; Sewell, R. M.; Ottley, L. A. M.; Pratt, H. D.; Quintana, C. J.; Bunge, S. D. *Inorg. Chem.* **2007**, 46, 1825.
- (25) Boyle, T. J.; Steele, L. A. M.; Yonemoto, D. T. *J. Coord. Chem.* **2012**, 65, 487.
- (26) Higham, C. S.; Dowling, D. P.; Shaw, J. L.; Cetin, A.; Ziegler, C. J.; Farrell, J. R. *Tetrahedron Lett.* **2006**, 47, 4419.
- (27) Boyle, T. J.; Alam, T. M.; Mechenbier, E. R.; Scott, B. L.; Ziller, J. W. *Inorg. Chem.* **1997**, 36, 3293.
- (28) Caselli, A.; Giannini, L.; Solari, E.; Floriani, C.; Re, N.; Chiesi-Villa, A.; Rizzoli, C. *Organometallics* **1997**, 16, 5457.
- (29) Kessler, V. G. *J. Sol-Gel Sci. Technol.* **2009**, 51, 264.
- (30) Seisenbaeva, G. A.; Gohil, S.; Kessler, V. G. *J. Sol-Gel Sci. Technol.* **2004**, 32, 11.
- (31) *Conquest Version 1.13*, Cambridge Crystallographic Data Centre: support@ccdc.cam.ac.uk or <http://www.ccdc.cam.ac.uk> [CSD version 5.33 (November 2011)].
- (32) Friedrich, A.; Radius, U. *Eur. J. Inorg. Chem.* **2004**, 4300.
- (33) Clulow, A. J.; Selby, J. D.; Cushion, M. G.; Scharz, A. D.; Mountford, P. *Inorg. Chem.* **2008**, 47, 12049.
- (34) Johnson, A. L.; Davidson, M. G.; Mahon, M. F. *Dalton Trans.* **2007**, 5405.
- (35) Giannini, L.; Caselli, A.; Solari, E.; Floriani, C.; Chiesi-Villa, A.; Rizzoli, C.; Re, N.; Sgamellotti, A. *J. Am. Chem. Soc.* **1997**, 119, 9198.
- (36) Cohen, A.; Kopilov, J.; Goldberg, I.; Kol, M. *Organometallics* **2009**, 28, 1391.