Inorg. Chem. **2007**, *46*, 1825–1835

Inorganic Chemistry
Article

Controlled Synthesis of a Structurally Characterized Family of Sterically Constrained Heterocyclic Alkoxy-Modified Titanium Alkoxides

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Received September 29, 2006

The reaction of $[Ti(\mu\text{-ONep})(ONep)_3]_2$ (ONep = $OCH_2C(CH_3)_3$) with a series of heterocyclic methanol derivatives [tetrahydrofurfuryl alcohol (H–OTHF), thiophene methanol (H–OTPM), or 2-pyridylcarbinol (H–OPy)—collectively termed H–OR*], led to the isolation of a novel family of OR*-substituted titanium alkoxide precursors. Independent of the initial stoichiometry for the H–OTHF reaction, a monosubstituted, dinuclear species was isolated as $[(ONep)_3Ti(\mu_c\text{-OTHF})]_2$ (**1**). For **1**, each Ti was octahedrally (Oh) bound by three terminal ONep ligands, one bidentate bridging OTHF ligand (μ_c-OTHF), and an oxygen from the other μ_c-OTHF ligand. For the OTPM derivatives, the product was identified as $[(ONep)_3Ti(\mu\text{-OTPM})]_2$ (**2**). For this ligand, the soft S atom does not bind to the Ti but the O atom does act as a bridge between the two trigonal bipyramidal bound Ti metal centers. The OPy system yielded $(OPy)_2Ti(OR)_2$ independent of the OR and the stoichiometry used [OR = ONep (**3**), $OCHMe_2$ (**4**), $OCMe_3$ (**5**)]. For **3**–**5**, the two OPy ligands chelate to the Oh-bound Ti metal center with two terminal OR ligands. Compounds **1**–**5** were fully characterized using a variety of analytical techniques. An initial investigation of the proposed chemical stability of the '$(OPy)_2Ti$' moiety of **3**–**5** to alcoholysis exchange pathways involving (i) alkyl alcohols, (ii) aryl alcohols, (iii) substituted phenols, (iv) H–OR* derivatives, and (v) silanols proved successful through the isolation of a novel family of structurally characterized $(OPy)_2Ti(OR')_2$ (**7**–**24**) compounds.

Introduction

Metal alkoxides ($M(OR)_x$) are excellent precursors for the preparation of ceramic oxide materials.[1−6] In numerous instances it has been clearly demonstrated that the structural arrangement of the precursor plays a significant role in determining the properties of the final materials.[7−12] However, $M(OR)_x$ display a great deal of variability in their nuclearity[1−6] which is attributed to the small charge-to-large cation radius ratio that requires the metal to bind additional ligands (i.e., bridging) to complete their coordination sphere.[4−6] Further complicating things is the fact that the alkoxide ligands often decompose or react with modifiers to form oxides, yielding unexpected structural rearrangements even for supposed 'simple' modifications.[1−12] This variability in nuclearity makes tailoring material properties difficult since a priori prediction of $M(OR)_x$ structures is not exact. Therefore, it is of interest to develop $M(OR)_x$ compounds that can be modified in a controlled manner.

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(1) Bradley, D. C.; Mehrotra, R. C.; Gaur, D. P. *Metal Alkoxides*; Academic Press: New York, 1978.

(2) Bradley, D. C.; Mehrotra, R. C.; Rothwell, I. P.; Singh, A. *Alkoxo and Aryloxo Derivatives of Metals*; Academic Press: New York, 2001; p 704.

(3) Turova, N. Y.; Turevskaya, E. P.; Kessler, V. G.; Yanovskaya, M. I. *The Chemistry of Metal Alkoxide*; Kluwer Academic Publishers: Boston, 2002; p 568.

(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) Boyle, T. J.; Bunge, S. D.; Alam, T. M.; Holland, G. P.; Headley, T. J.; Avilucea, G. *Inorg. Chem.* **2005**, *44*, 1309.

(8) Boyle, T. J.; Bunge, S. D.; Andrews, N. L.; Matzen, L. E.; Sieg, K.; Rodriguez, M. A.; Headley, T. J. *Chem. Mater.* **2004**, *24*, 3279.

(9) Boyle, T. J.; Bunge, S. D.; Clem, P. G.; Richardson, J.; Dawley, J. T.; Ottley, L. A. M.; Rodriguez, M. A.; Tuttle, B. A.; Avilucea, G.; Tissot, R. G. *Inorg. Chem.* **2005**, *44*, 1588.

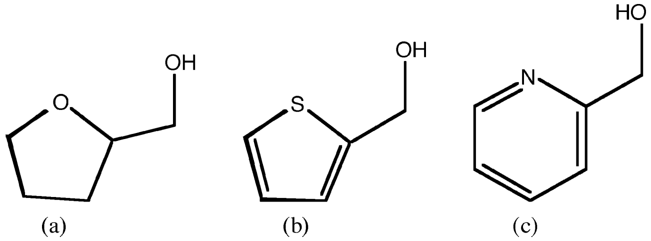
(10) Boyle, T. J.; A., R. M.; Ingersoll, D.; Headley, T. J.; Bunge, S. D.; Pedrotty, D. M.; De'Angeli, S. M.; Vick, S. C.; Fan, H. *Chem. Mater.* **2003**, *15*, 3903.

(11) Boyle, T. J.; Schwartz, R. W. *Comments Inorg. Chem.* **1994**, *16*, 243.

(12) Boyle, T. J.; Tyner, R. P.; Alam, T. M.; Scott, B. L.; Ziller, J. W.; Potter, B. G. *J. Am. Chem. Soc.* **1999**, *121*, 12104.

(13) Conquest Version 1.8, Cambridge Crystallographic Data Centre; support@ccdc.cam.ac.uk or www.ccdc.cam.ac.uk (2004-Aug 2006 update).

10.1021/ic0618798 CCC: $37.00



(a) (b) (c)

Figure 1. Schematic representation of the H−OR* family of ligands (a) H−OTHF, (b) H−OTPM, and (c) H−OPy.

One method to limit structural rearrangements or uncontrolled cluster formation is to introduce bidentate ligands,[1−6,13] such as tetrahydrofurfuryl alcohol (H−OTHF, shown in Figure 1a). The OTHF ligand along with thiophene methanol (H−OTPM), and pyridine methanol or 2-pyridylcarbinol (H−OPy) analogues have been collectively referred to as H−OR*.[14−16] These OR* ligands are of interest due to their pendent alcohol chain, high solubility, and the varied rigid heterocycles which resemble solvents widely used in $M(OR)_4$ syntheses.[14−16] The OTHF ligand has been successfully used to minimize cluster formation in metal alkyl systems[17−26] and was of interest to determine the utility of this, and the other OR* ligand in controlling the structural characteristics of $M(OR)_x$.

A survey of the literature showed that no systematic investigation of the OR* ligands with Group 4 cations was available.[13] This study sought to fill this void and explore the controlled construction of $Ti(OR)_4$. The H−OR* ligands were reacted with the previously isolated $[Ti(\mu\text{-ONep})(ONep)_3]_2$[27] (ONep = OCH_2CMe_3) to form $[(\mu_c\text{-OTHF})Ti(ONep)_3]_2$ (**1**; μ_c = chelating bridging), $[(\mu\text{-OTPM})Ti(ONep)_3]_2$ (**2**), and $(OPy)_2Ti(ONep)_2$ (**3**). Additional reactions between H-OPy and other $Ti(OR)_4$ led to the isolation of $(OPy)_2Ti(OR)_2$ where OR = $OCHMe_2$ (O^{i}Pr, **4**[28]) and $OCMe_3$ (O^{t}Bu, **5**). The synthesis and characterization of these OR* derivatives are discussed in detail.

Further, determining the reactivity of the ‘$(OPy)_2Ti$’ moiety to alcohol substitution was undertaken using a series of sterically varied: (**i**) alkyl alcohols, (**ii**) aryl alcohols, (**iii**) substituted arylalcohols, (**iv**) H−OR*, and (**v**) silanols, including (**i**) 2-methyl propanol (H−OPr^{Me}), 2,2′-diphenyl ethanol (H−DPE), 1-adamantanol (H−OAdam); (**ii**) 4-adamantane phenol (H−OPh−Adam), *ortho*-methylphenol (H−oMP), *ortho*-propylphenol (H−oPP), *ortho*-butylphenol (H−oBP), 2,6-dimethylphenol (H−DMP), 2,6-diisopropylphenol (H−DIP), 2,6-di-*tert*-butylphenol (H−DBP), 2,6-diphenylphenol (H−DPP); (**iii**) 2-bromophenol (H−2BP) 2,4,6-trichlorophenol (H−TCP), 4-mercaptophenol (H−4MP), 4-aminophenol (H−4AP), 2,3-diaminophenol (H−DAP); (**iv**) H−OTPM, (**v**) dimethyl-*tert*-butylsilanol (H−DMBS), triphenylsilanol (H−TPS), tri-*tert*-butoxysilanol (H−TOBS). The products isolated and crystallographically characterized were found to be the isostructural species $(OPy)_2Ti(OR')_2$ where OR′ = DPE (**7**), OPh-Adam **(8)**, oPP (**10**), oBP (**11**), DMP (**12**), DIP (**13**), DPP (**15**), 2BP (**16**), TCP (**17**), 4MP (**18**), 4AP (**19**), DAP (**20**), OTPM (**21**), DMBS (**22**), TPS (**23**), and TOBS (**24**). Crystal structures of the disubstituted species for OPr^{Me} (**6**), oMP (**9**), and DBP (**14**) were not obtained. Full details are presented on the synthesis and structures of **1**−**24**.

Experimental Section

All compounds described below were handled with rigorous exclusion of air and water using standard Schlenk line and glove box techniques. All solvents were used as received (Aldrich) in sure-seal bottles and only handled under an inert atmosphere of argon. The following compounds were stored under argon upon receipt (Aldrich) and used without further purification: $Ti(OR)_4$ (OR = O^{i}Pr, O^{t}Bu), H−ONep, H−OTHF, H−OTPM, H−OPy, H−OPr^{Me}, H−OAdam, H−DPE, H−OPh−Adam, H−oMP, H−oPP, H−oBP, H−DMP, H−DIP, H−DBP, H−DPP, H−2BP, H−TCP, H−4MP, H−4AP, H−DAP, H−DMBS, H−TPS, and H−TOBS. $[Ti(\mu\text{-ONep})(ONep)_3]_2$ was synthesized according to the literature report.[27]

Analytical data were collected on dried crystalline samples. FT−IR data were obtained on a Bruker Vector 22 MIR spectrometer using KBr pellets under an atmosphere of flowing nitrogen. Elemental analyses were performed on a Perkin-Elmer 2400 CHN-S/O elemental analyzer. NMR spectra were collected on a Bruker DRX400 spectrometer at 400.1 MHz for ^1H experiments using concentrated crystalline samples dissolved in toluene-d_8.

General Synthesis. Due to the similarity of the syntheses of these compounds, a general preparatory route is presented. To a stirring clear solution of $Ti(OR)_4$ in toluene, the appropriate H−OR* was added via pipet and left to stir. After 12 h, the reactions were set aside to slowly evaporate the volatile component of the reaction until X-ray quality crystals formed.

$[(\mu_c$-OTHF)Ti(ONep)$_3]_2$ (1). Used $Ti(ONep)_4$ (2.00 g, 5.05 mmol), H−OTHF (0.516 g, 5.05 mmol), ∼10 mL of toluene. Yield

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(14) Andrews, N. L.; Boyle, T. J. In *Synthesis and characterization of novel early, late, and lanthanide metals modified with bidentate alkoxide ligands*; 225th National Meeting of the American Chemical Society, New Orleans, LA, March 23−27, 2003; pp U71−U71.

(15) Boyle, T. J.; Rodriguez, M. A.; Alam, T. M.; Bunge, S. D. In *Controlled construction of metal alkoxides using polydentate alcohols*; 227th National Meeting of the American Chemical Society, Anaheim, CA, March 28−April 01, 2004; p U1562.

(16) Hernandez-Sanchez, B. A.; Boyle, T. J.; Rodriguez, M. A.; Alam, T. M. In *Rational construction of group IV metal alkoxide structures using sterically rigid bridging ligands;* 229th National Meeting of the American-Chemical-Society, San Diego, CA, March 13−17, 2005; pp U1019−U1019.

(17) John, L.; Utko, J.; Jerzykiewicz, L. B.; Sobato, P. *Inorg. Chem.* **2005**, *44*, 9131.

(18) Jerzykiewicz, L. B.; Utko, J.; Sobota, P. *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.* **1997**, *53*, 1393.

(19) Janas, Z.; Sobota, P.; Kimowicz, M.; Szafert, S.; Szczegot, K.; Jerzykiewicz, L. B. *J. Chem. Soc. Dalton Trans.* **1997**, 3897.

(20) Janas, Z.; Sobota, P.; Kasprzak, M.; Glowiak, T. *Chem. Commun.* **1996**, 2727.

(21) Sobota, P.; Utko, J.; Ejfler, J.; Jerzykiewicz, L. B. *Organometallics* **2000**, *19*, 4929.

(22) Sobota, P.; Utko, J.; Janas, Z.; Szafert, S. *Chem. Commun.* **1996**, 1923.

(23) Sobota, P.; Utko, J.; Sztajnowska, K.; Ejfler, J.; Jerzykiewicz, L. B. *Inorg. Chem.* **2000**, *39*, 235.

(24) Janas, Z.; Jerzykiewicz, L. B.; Sobota, P.; Utko, J. *New J. Chem.* **1999**, *23*, 185.

(25) Utko, J.; Przybylak, S.; Jerzykiewicz, L. B.; Szafert, S.; Sobota, P. *Chem.-Eur. J.* **2003**, *9*, 181.

(26) Boyle, T. J.; Alam, T. M.; Bunge, S. D.; Segall, J. M.; Avilucea, G. R.; Tissot, R. G.; Rodriguez, M. A. *Organometallics 24*, 731.

(27) Boyle, T. J.; Alam, T. M.; Mechenbier, E. R.; Scott, B. L.; Ziller, J. W. *Inorg. Chem.* **1997**, *36*, 6479.

(28) Aragon, P. J.; Carrillo-Hermosilla, F.; Villasenor, E.; Otero, A.; Antinolo, A.; Rodriguez, A. M. *Eur. J. Inorg. chem.* **2006**, 965.

1.82 g (87.9%). FTIR (KBr pellet, cm^{-1}) 3365 (w), 2952 (s), 2904 (s), 2866 (s), 2940 (sh), 2691 (m), 2634 (w), 2569 (w), 2506 (vw), 2403 (w), 2367 (w), 2293 (w), 2206 (w), 2140 (w), 1484 (s), 1463 (sh), 1393 (s), 1361 (s), 1331 (sh), 1292 (m), 1257 (m), 1216 (sh), 1067 (s), 1022 (sh), 953 (sh), 933 (m), 902 (m), 850 (sh), 814 (m), 750 (m), 678 (s), 554 (m), 482 (s). ^{1}H NMR (400.1 MHz, toluene-d_8) δ 4.37 (2H, bs, $OCH_2(OC_4H_7)$), 4.25 (6H, s, $OCH_2C(CH_3)_3$), 4.04 (1H, bs, $OCH_2(OC_4H_7)$), 3.69 (2H, bs, $OCH_2(OC_4H_7)$), 1.71 (2H, bs, $OCH_2(OC_4H_7)$), 1.56 (2H, bs, $OCH_2(OC_4H_7)$), 1.04 (28H, s, $OCH_2C(CH_3)_3$). Anal. Calcd for $C_{20}H_{42}O_5Ti$: 58.53 %C, 10.31 %H. Found: 57.84 %C, 10.32 %H.

[(μ-OTPM)Ti(ONep)$_3$]$_2$ (2). Used Ti(ONep)$_4$ (2.00 g, 5.05 mmol), H−OTPM (0.577 g, 5.05 mmol), ~10 mL of toluene. Yield 2.01 g (94.4%). FTIR (KBr pellet, cm^{-1}) 2903(s), 2681(m), 1606(m), 1570(sh), 1478(m), 1274(m), 1089(s), 843(sh), 762(s). ^{1}H NMR (400.1 MHz, toluene-d_8) δ 6.90 (1H, bs, $OCH_2(SC_4H_3)$), 6.87 (1H, dd, $OCH_2(SC_4H_3)$), J_{H-H} = 2.8 Hz), 6.74 (1H, mult, $OCH_2(SC_4H_3)$), J_{H-H} = 3.6 Hz), 5.53 (2H, s, $OCH_2(SC_4H_3)$), 4.00 (6H, s, $OCH_2C(CH_3)_3$), 0.94 (41H, s, $OCH_2C(CH_3)_3$). Anal. Calcd for $C_{20}H_{38}O_4STi$: 56.86 %C, 9.07 %H. Found: 56.86 %C, 9.15 %H.

(OPy)$_2$Ti(ONep)$_2$ (3). Used Ti(ONep)$_4$ (2.00 g, 5.05 mmol), H−OPy (1.10 g, 10.1 mmol), ~10 mL of toluene. Yield 2.02 g (91.4%). FTIR (KBr pellet, cm^{-1}) 2950.36(s), 2902.77(s), 2857.89(s), 2795(s), 1605(s), 1478(s), 1435(s), 1391(m), 1356(s), 1271(m), 1147(s), 1083(s), 1043(s), 1020(s), 761(s), 724(s), 658(s), 538(s), 481(s), 451(m). ^{1}H NMR (400.1 MHz, toluene-d_8) δ 8.62 (1H, dd, $OCH_2(NC_5H_4)$, J_{H-H} = 2.60 Hz), 6.73 (1H, dt, $OCH_2(NC_5H_4)$, J_{H-H} = 7.2 Hz) 6.45 (1H, dt, $OCH_2(NC_5H_4)$, J_{H-H} = 4.0 Hz) 6.35 (1H, dd, $OCH_2(NC_5H_4)$, J_{H-H} = 4.0 Hz), 5.52 (0.2H, s, $OCH_2(NC_5H_4)$), 5.51 (2H, s, $OCH_2(NC_5H_4)$) 4.32 (2H, s, $OCH_2C(CH_3)_3$)), 1.10 (11H, s, $OCH_2C(CH_3)_3$)). Anal. Calcd for $C_{22}H_{34}N_2O_4Ti$: 60.27 %C, 7.82 %H, 6.39 %N. Found: 59.77 %C, 7.00 %H, 6.08 %N.

(OPy)$_2$Ti(O^{i}Pr)$_2$ (4). Used Ti(O^{i}Pr)$_4$ (2.00 g, 7.04 mmol), H−OPy (1.54 g, 14.1 mmol), ~10 mL of toluene. Yield 2.56 g (95.2%). FTIR (KBr pellet, cm^{-1}) 3095 (sh), 3075 (m), 3060(sh), 3030 (m), 2961 (s), 2923 (s), 2855 (sh), 2838 (sh), 2817 (s), 2781 (sh), 2689 (s), 2656 (sh), 2609 (m), 2301 (m), 2344 (m), 2332 (m), 1604 (s), 1570 (s), 1523 (w), 1474 (s), 1549 (sh), 1438 (s), 1371 (s), 1356 (s), 1320 (s), 1277 (s), 1222 (s), 1159 (s), 1125 (s), 1095 (s), 1047 9s), 994 (s), 843 (s), 823 (sh), 775 (s), 722 (s), 643 (s), 601 (s), 636 (s). ^{1}H NMR (400.1 MHz, toluene-d_8) δ 8.62 (1H, dd, $OCH_2(NC_5H_4)$, J_{H-H} = 5.2 Hz) 6.19 (1H, dt, $OCH_2(NC_5H_4)$, J_{H-H} = 7.2 Hz), 6.50 (1H, dt, $OCH_2(NC_5H_4)$, J_{H-H} = 7.2 Hz), 6.40 (1H, dd, $OCH_2(NC_5H_4)$, J_{H-H} = 7.6 Hz), 5.74, (0.2H, s, $OCH_2(NC_5H_4)$), 5.52 (2H, s, $OCH_2(NC_5H_4)$), 5.02 (1H, s, $OCH(CH_3)_2$), J_{H-H} = 6.0 Hz), 1.30 (6H, d, $OCH(CH_3)_2$), J_{H-H} = 6.0 Hz). Anal. Calcd for $C_{18}H_{26}N_2O_4Ti$: 56.55 %C, 6.86 %H, 7.33 %N. Found: 56.55 %C, 6.85 %H, 7.32 %N

(OPy)$_2$Ti(O^{t}Bu)$_2$ (5). Used Ti(O^{t}Bu)$_4$ (2.00 g, 5.88 mmol), H−OPy (1.28 g, 11.8 mmol), ~10 mL of toluene. Yield 1.65 g (68.5%). FTIR (KBr pellet, cm^{-1}) 3173 (w), 3139 (w), 3095 (sh), 3074 (m), 3058 (sh), 3024 (m), 2966 (s), 2923 (s), 2854 (s), 2836 (s), 2814 (s), 2780 (sh), 2960 (m), 2656 (w), 2610 (w), 2570 (w), 1608 (s), 1574 (m), 1481 (m), 1462 (sh), 1441 (s), 1369 (sh), 1357 (s), 1323 (s), 1280 (m), 1262 (sh), 1224 (m), 1160 (s), 1122 (s), 1091 (s), 1063 (sh), 1048 (s), 995 (s), 847 (s), 825 (sh), 847 (s), 775 (s), 720 (s), 646 (s), 639 (s), 599 (s), 538 (s), 485 (m), 457 (m), 448(sh). ^{1}H NMR (400.1 MHz, toluene-d_8) δ 8.69 (1H, dd, $OCH_2(NC_5H_4)$, J_{H-H} = 2.4 Hz), 6.79 (1H, dt, $OCH_2(NC_5H_4)$, J_{H-H} = 7.6 Hz), 6.47 (1H, dt, $OCH_2(NC_5H_4)$ J_{H-H} = 6.0 Hz), 6.41 (1H, dd, $OCH_2(NC_5H_4)$ J_{H-H} = 3.2 Hz), 5.52 (2H, s, $OCH_2(NC_5H_4)$), 5.54 (0.3H, s, $OCH_2(NC_5H_4)$), 1.35 (26H, s, $OC(CH_3)_3$)). Anal. Calcd for $C_{20}H_{30}N_2O_4Ti$: 58.54 %C, 7.37 %H, 6.83 %N. Found: 58.18 %C, 6.95 %H, 6.83 %N.

General Alkoxide Substitution Synthesis. Due to the similarity of the syntheses of these compounds, a general preparatory route is presented. To a stirring clear solution of **4** in toluene, the appropriate H−OR′ was added and left to stir. For any of the compounds that did not instantly form a clear solution, the reaction mixture was heated until clear. For the amide-substituted species, it was necessary to add pyridine and heat to solubilize the reaction mixture. After 12 h, the reactions were set aside to slowly evaporate the volatile component of the reaction until X-ray quality crystals formed. Yields are based on the first batch of crystals isolated and were not optimized.

(OPy)$_2$Ti(O^{i}Pr)(OPr^{Me}) (6a). Used **4** (1.00 g, 2.62 mmol), H−OPr^{Me} (0.640 g, 5.23 mmol), ~5 mL of toluene. Anal. Calcd for $C_{19}H_{28}N_2O_4Ti$: 57.58 %C, 7.12 %H, 7.07 %N. Found: 55.61 %C, 7.05 %H, 6.71 %N.

(OPy)$_2$Ti(OAdam)$_2$ (6b). Used **4** (1.00 g, 2.62 mmol), H−OAdam (0.796 g, 5.23 mmol), ~5 mL of toluene. Anal. Calcd for $C_{32}H_{42}N_2O_4Ti$: 67.84 %C, 7.47 %H, 4.94 %N. Found: 67.34 %C, 7.38 %H, 5.15 %N.

(OPy)$_2$Ti(DPE)$_2$ (7). Used **4** (1.00 g, 2.62 mmol), H−DPE (1.04 g, 5.23 mmol), ~5 mL of toluene. Yield 1.09 g (63.4%). Anal. Calcd for $C_{47}H_{46}N_2O_4Ti$(**7**•tol): 75.19 %C, 6.18 %H, 3.73 %N. Found: 75.11 %C, 6.15 %H, 3.19 %N.

(OPy)$_2$Ti(OPh−Adam)$_2$ (8). Used **4** (1.00 g, 2.62 mmol), H−OPh−Adam (1.19 g, 5.23 mmol), ~5 mL of toluene. Yield 0.906 g (48.0%). Anal. Calcd for $C_{51}H_{58}N_2O_4Ti$ (**8**•tol): 75.53 %C, 7.21 %H, 3.46 %N. Found: 75.00 %C, 7.10 %H, 3.68 %N.

(OPy)$_2$Ti(oMP)$_2$ (9). Used **4** (1.00 g, 2.62 mmol), H−oMP (0.57 g, 5.23 mmol), ~5 mL of toluene. Yield 0.512 g (40.8%). Anal. Calcd for $C_{26}H_{26}N_2O_4Ti$: 65.28 %C, 5.48 %H, 5.86 %N. Found: 64.99 %C, 5.28 %H, 5.96 %N.

(OPy)$_2$Ti(oPP)$_2$ (10). Used **4** (1.00 g, 2.62 mmol), H−oPP (0.713 g, 5.23 mmol), ~5 mL of toluene. Yield 0.440 g (31.5%). Anal. Calcd for $C_{30}H_{34}N_2O_4Ti$: 67.42 %C, 6.41 %H, 5.24 %N. Found: 66.91 %C, 6.78 %H, 5.15 %N.

(OPy)$_2$Ti(oBP)$_2$ (11). Used **4** (1.00 g, 2.62 mmol), H−oBP (0.786 g, 5.23 mmol), ~5 mL of toluene. Yield 1.28 g (87.1%). Anal. Calcd for $C_{32}H_{38}N_2O_4Ti$: 68.32 %C, 6.80 %H, 4.97 %N; for $C_{35.5}H_{42}N_2O_4Ti$ (**11**•1/2tol): 70.06 %C, 6.95 %H, 4.60 %N;. Found: 69.48 %C, 6.65 %H, 4.28 %N.

(OPy)$_2$Ti(DMP)$_2$ (12). Used **4** (1.00 g, 2.62 mmol), H−DMP (0.638 g, 5.23 mmol), ~5 mL of toluene. Yield 0.822 g (62.0%). Anal. Calcd for $C_{28}H_{30}N_2O_4Ti$: 66.41 %C, 5.97 %H, 5.53 %N. Found: 66.07 %C, 6.17 %H, 5.78 %N.

(OPy)$_2$Ti(DIP)$_2$ (13). Used **4** (1.00 g, 2.62 mmol), H−DIP (0.933 g, 5.23 mmol), ~5 mL of toluene. Yield 0.457 g (28.2%). Anal. Calcd for $C_{36}H_{46}N_2O_4Ti$: 69.89 %C, 7.49 %H, 4.53 %N. Found: 69.68 %C, 7.77 %H, 4.31 %N.

(OPy)$_2$Ti(DPP)$_2$ (15). Used **4** (1.00 g, 2.62 mmol), H−DPP (1.29 g, 5.23 mmol), ~5 mL of toluene. Yield 1.74 g (88.3%). Anal. Calcd for $C_{55}H_{46}N_2O_4Ti$ (**15**• tol): 78.31 %C, 5.40 %H, 3.26 %N. Found: 78.03 %C, 5.51%H, 3.17 %N.

(OPy)$_2$Ti(2BP)$_2$ (16). Used **4** (1.00 g, 2.62 mmol), H−2BP (0.905 g, 5.23 mmol), ~5 mL of toluene. Yield 1.74 g (81.7%). Anal. Calcd for $C_{24}H_{20}Br_2N_2O_4Ti$: 47.40 %C, 3.32 %H, 4.61 %N. Found: 46.57 %C, 3.21 %H, 4.14 %N.

(OPy)$_2$Ti(TCP)$_2$ (17). Used **4** (10.0 g, 26.2 mmol) H−TCP (10.4 g, 52.4 mmol), ~50 mL of toluene. Yield 16.4 g (83.6%). Anal. Calcd for $C_{24}H_{16}Cl_6N_2O_4Ti$: 43.88 %C, 2.45 %H, 4.26 %N. Found: 43.73 %C, 2.31 %H, 4.29 %N.

Table 1. Data Collection Parameters for **1**−**5**

compound	**1**	**2**
chemical formula	$C_{40}H_{84}O_{10}Ti_2$	$C_{20}H_{38}O_4STi$
fw	820.86	422.12
temp (K)	203(2)	173(2)
space group	orthorhombic *Pbcn*	monoclinic, *P*2(1)/*n*
a (Å)	24.107(4)	9.894(2)
b (Å)	10.4854(16)	24.600(6)
c (Å)	19.624(3)	39.224(9)
β (deg)		90.016(5)
V ($Å^3$)	4960.6(13)	9546(4)

compound	**3**	**4**	**5**
chemical formula	$C_{22}H_{34}N_2O_4Ti$	$C_{18}H_{26}N_2O_4Ti$	$C_{20}H_{30}N_2O_4Ti$
fw	438.20	382.30	410.35
temp (K)	168(2)	168(2)	168(2)
space group	monoclinic *Cc*	monoclinic *P*21/*n*	monoclinic *P*21/*c*
a (Å)	10.185(2)	11.268(2)	15.122(4)
b (Å)	22.944(6)	14.820(3)	17.851(5)
c (Å)	10.047(2)	12.104(2)	16.628(4)
β (deg)	91.516(18)	92.635(4)	101.728(5)
V ($Å^3$)	2346.9(9)	2019.1(7)	4395(2)
Z	4	4	8
D_{calcd}(Mg/m^3)	1.241	1.258	1.240
μ,(Mo, Kα) (mm^{-1})	0.393	0.446	0.415
R1 (%) (all data)	4.78 (9.01)	5.92 (7.89)	8.88 (20.42)
wR2 (%) (all data)	9.90 (11.66)	13.27 (14.11)	16.05 (24.65)

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

$(OPy)_2Ti(4MP)_2$ (18). Used **4** (10.0 g, 26.2 mmol), H−4MP (6.60 g, 52.3 mmol), ~50 mL of pyridine, heated to dissolution. Yield 11.3 g (84.5%). Anal. Calcd for $C_{24}H_{22}N_2O_4S_2Ti$: 56.03 %C, 4.31 %H, 5.45 %N. Found: 55.97 %C, 4.16 %H, 5.40 %N.

$(OPy)_2Ti(4AP)_2$ (19). Used **4** (6.27 g, 16.4 mmol), H−4AP (3.58 g, 32.8 mmol), ~50 mL of pyridine, heated to dissolution. Yield 8.97 g (97.1% for **19**•py). Anal. Calcd for $C_{24}H_{24}N_4O_4Ti$: 60.01 %C, 5.04 %H, 11.66 %N. Found: 60.65 %C, 5.08 %H, 11.74%N.

$(OPy)_2Ti(DAP)_2$ (20). Used **4** (10.0 g, 26.2 mmol), H−DAP (6.50 g, 52.3 mmol), ~50 mL of pyridine, heated to dissolution. Yield 13.0 g (84.4% for **19**•py). Anal. Calcd for $C_{24}H_{26}N_6O_4Ti$: 56.93 %C, 4.38 %H, 16.59 %N. $C_{29}H_{31}N_7O_4Ti$ (**19**•py): 59.09 %C, 5.30 %H, 16.63 %N. Found: 58.57 %C, 4.96 %H, 15.84 %N.

$(OPy)_2Ti(OTPM)_2$ (21). Used **4** (1.00 g, 2.62 mmol), H−OTPM (0.597 g, 5.23 mmol), ~5 mL of toluene. Yield 1.03 g (80.1%). Anal. Calcd for $C_{22}H_{22}N_2O_4S_2Ti$: 53.88 %C, 4.52 %H, 5.71 %N. Found: 54.16 %C, 4.70 %H, 5.93 %N.

$(OPy)_2Ti(DMBS)_2$ (22). Used **4** (1.00 g, 2.62 mmol), H−DMBS (0.693 g, 5.23 mmol), ~5 mL of toluene. Yield 0.450 g (32.8%). Anal. Calcd for $C_{24}H_{42}N_2O_4Si_2Ti$: 54.73 %C, 8.04 %H, 5.32 %N. Found: 54.54 %C, 8.03 %H, 5.28 %N.

$(OPy)_2Ti(TPS)_2$ (23). Used **4** (1.00 g, 2.62 mmol), H−TPS (1.45 g, 5.23 mmol), ~5 mL of toluene. Yield 1.06 g (50.2%). Anal. Calcd for $C_{48}H_{42}N_2O_4Si_2Ti$: 70.75 %C, 5.19 %H, 3.44 %N. Found: 70.30 %C, 5.06 %H, 3.68 %N.

$(OPy)_2Ti(TOBS)_2$ (24). Used **4** (1.00 g, 2.62 mmol), H−TOBS (1.38 g, 5.23 mmol), ~5 mL of toluene. Yield 0.938 g (46.0%). Anal. Calcd for $C_{36}H_{66}N_2O_{10}Si_2Ti$: 54.67 %C, 8.41 %H, 3.54 %N. Found: 54.74 %C, 8.22 %H, 3.36 %N.

General X-ray Crystal Structure Information.[29] Crystals were mounted onto a glass fiber from a pool of Fluorolube and immediately placed in a cold N_2 vapor stream, on a Bruker AXS diffractometer equipped with a SMART 1000 CCD detector using graphite-monochromatized Mo Kα radiation ($\lambda = 0.7107$ Å). Lattice determination and data collection were carried out using SMART Version 5.054 software. Data reduction was performed using SAINTPLUS Version 6.01 software and corrected for absorption using the SADABS program within the SAINT software package.

Structures were solved using 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 SHELXS software. The final refinement of each compound included anisotropic thermal parameters for all non-hydrogen atoms. It is of note that crystal structures of $M(OR)_x$ often contain disorder within the atoms of the ligand chain causing higher than normal final correlations.[1−6] 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. Data collection parameters for **1**−**5** are given in Table 1 and that for **6a**−**24** are found in Table 2. Metrical data for the high-quality structures are listed in Table 3. Specific issues associated with individual structures are discussed below.

The metrical data of **1** and **2** were not of sufficient quality to be useful for analysis but do establish the connectivity of the final compounds. The final solutions were not included in the CIF file, and only limited crystal data parameters were presented in Table 2 for identification purposes. For structures **8**, **11**, and **17**, it was necessary to squeeze disorder electron density of 494.9, 446.6, and 677.4 $Å^3$, respectively, which is in agreement with ~1 toluene molecule. The structure of **8** solved in the space groups ($P\bar{1}$, *P*1, and *Cc*) but not in the *C*2/*c* as suggested by the ADDSYM program with $P\bar{1}$ yielding the best solution. The structure of **3** was solved in the monoclinic non-centrosymmetric space group *Cc* with well-behaved thermal ellipsoids and a clear break in symmetry that could be observed due to the *t*-butyl groups. Compound **18** was solved in the triclinic *P*1 space group, rather than $P\bar{1}$ as suggested by ADDSYM, with well-behaved thermal ellipsoids and a clear break in symmetry due to the 4MP groups.

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(29) Caulton, K. G.; Chisholm, M. H.; Drake, S. R.; Folting, K. *Chem. Commun.* **1990**, 1349.

Table 2. Data Collection Parameters for **6a**−**8**, **10**−**13**, and **15**−**24**

compound	**6a**	**7**·tol	**8**	**10**	**11**	**12**
chemical formula	$C_{19}H_{28}N_2O_4Ti$	$C_{40}H_{38}N_2O_4Ti\cdot C_7H_8$	$C_{44}H_{50}N_2O_4Ti$	$C_{30}H_{34}N_2O_4Ti$	$C_{32}H_{38}N_2O_4Ti$	$C_{28}H_{30}\ N_2O_4Ti$
fw	396.32	750.77	718.76	534.49	562.54	506.44
temp (K)	152(2)	203(2)	203(2)	173(2)	173(2)	173(2)
space group	monoclinic *P*21/*c*	monoclinic *P*2(1)/*n*	triclinic $P\bar{1}$	Monoclinic *P*2(1)/*c*	triclinic $P\bar{1}$	monoclinic *C*2/*c*
a (Å)	9.0231(16)	14.9826(10)	12.663(8)	12.1440(17)	10.3667(16)	26.126(4)
b (Å)	12.405(2)	17.7669(12)	13.221(8)	14.409(2)	13.955(2)	11.7662(16)
c (Å)	18.676(3)	15.9923(11)	14.489(12)	16.027(2)	14.328(2)	19.326(3)
α (deg)			63.106(11)		69.324(3)	
β (deg)	99.375(3)	111.4920(10)	82.596(19)	97.499(2)	85.345(3)	121.224
γ (deg)			89.942(13)		68.971(3)	
V (Å^3)	2062.5(6)	3961.1(5)	2141(3)	2780.6(7)	9546(4)	5080.3(12)
Z	4	4	2	4	2	8
D_{calcd}(Mg/m^3)	1.276	1.259	1.115	1.277	1.034	1.324
μ(Mo Kα) (mm^{-1})	0.439	0.262	0.240	0.345	0.268	0.373
R1^a (%) (all data)	8.50 (20.33)	4.34 (10.86)	8.85(17.70)	6.60 (9.89)	4.39(5.71)	3.48 (3.94) 8.97 (9.31)
wR2^b (%) (all data)	11.51 (22.42)	5.59 (11.69)	20.14(21.42)	14.16 (15.68)	10.42(11.02)	

compound	**13**	**15**·tol	**16**	**17**	**18**	**19**·py
chemical formula	$C_{36}H_{46}N_2O_4Ti$	$C_{48}H_{38}N_2O_4Ti\cdot C_7H_8$	$C_{24}H_{20}Br_2N_2O_4Ti$	$C_{24}H_{16}Cl_6\ N_2O_4Ti$	$C_{24}H_{22}N_2O_4S_2Ti$	$C_{24}H_{24}N_4O_4Ti\cdot C_5H_5N$
fw	618.65	846.84	608.12	656.96	514.45	559.47
temp (K)	157(2)	160(2)	297(2)	203(2)	203(2)	273(2)
space group	monoclinic *P*2(1)/*n*	monoclinic *P*2(1)/*n*	triclinic $P\bar{1}$	monoclinic *C*2/*c*	triclinic *P*1	orthorhombic *Pccn*
a (Å)	13.142(4)	17.035(4)	8.995(18)	14.5686(11)	8.4060(13)	12.5716(18)
b (Å)	15.747(4)	12.937(3)	11.89(2)	8.4738(6)	10.4494(16)	12.8307(19)
c (Å)	17.206(5)	19.793(4)	12.11(2)	26.0177(19)	14.278(2)	16.406(2)
α (deg)			95.62(3)		104.405(3)	
β (deg)	110.007(4)	98.875(4)	90.64(3)	95.6800(10)	90.340(3)	
γ (deg)			102.69(3)		99.668(3)	
V (Å^3)	3345.7(16)	4309.7(16)	1257(4)	3196.2(4)	1195.9(3)	2646.3(7)
Z	4	4	2	4	2	4
D_{calcd}(Mg/m^3)	1.228	1.305	1.607	1.365	1.429	1.404
μ(Mo Kα) (mm^{-1})	0.296	0.251	3.551	0.799	0.566	0.369
R1^a (%) (all data)	3.46 (3.84))	4.76 (10.04)	7.87 (17.28)	4.24 (9.94)	7.66 (14.42)	7.50 (12.07)
wR2^b (%) (all data)	8.95 (9.26	7.10 (11.04)	19.66 (26.03)	4.95 (10.29)	8.21 (14.92)	12.44 (13.74)

compound	**20**·py	**21**	**22**	**23**	**24**
chemical formula	$C_{24}H_{26}N_6O_4Ti\cdot\ C_5H_5N$	$C_{22}H_{22}N_2O_4S_2Ti$	$C_{24}H_{42}N_2O_4Si_2Ti$	$C_{48}H_{42}N_2O_4Si_2Ti$	$C_{36}H_{66}N_2O_{10}Si_2Ti$
fw	589.49	490.43	526.66	814.92	790.98
temp (K)	173(2)	168(2)	203(2)	203(2)	203(2)
space group	monoclinic *P*2(1)/*n*	monoclinic *C*2/*c*	triclinic $P\bar{1}$	monoclinic *P*2(1)/*n*	monoclinic $P\bar{1}$
a (Å)	13.045(3)	23.995(5)	9.9310(15)	13.5219(15)	9.198(6)
b (Å)	12.353(2)	14.479(3)	14.414(2)	15.4673(17)	14.460(9)
c (Å)	18.017(4)	16.710(3)	21.413(3)	20.153(2)	18.529(12)
α (deg)			92.430(3)		108.046(9)
β (deg)	94.391(4)	129.346(4)	100.152(2)	100.152(2)	97.543(9)
γ (deg)			101.664(3)		103.088(10)
V (Å^3)	2894.7(10)	4492(3)	2998.4(8)	4149.1(8)	2228(2)
Z	4	8	2	4	2
D_{calcd}(Mg/m^3)	1.353	1.386	1.167	1.305	1.179
μ(Mo Kα) (mm^{-1})	0.343	0.596	0.394	0.311	0.296
R1^a (%) (all data)	7.28 (13.71)	15.98 (38.14)	8.63 (19.58)	4.91 (10.74)	9.65 (26.33)
wR2^b (%) (all data)	13.71(15.98)	25.24 (43.16)	15.19 (23.70)	6.94 (11.73)	10.23 (26.55)

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

Results and Discussion

As mentioned previously, there are several alkyl OTHF species known and numerous examples of metal halide derivatives of the OTHF species; however, there are no OTHF-substituted transition M(OR)$_x$ reported in the literature.[13] Further, there are no examples of OTPM-substituted transition metal species reported. In contrast, there are numerous examples of OPy-substituted species available bound to a wide variety of transition metals but surprisingly none with any of the Group 4 cations.[13] While preparing this report, $(OPy)_2Ti(O^iPr)_2$ was published which is discussed below.[28] We undertook the reaction of [Ti(μ-ONep)(ONep)$_3$]$_2$[27] with H−OR* ligands (eq 1). The synthesis, characterization, and structure of these compounds are discussed below.

Synthesis. A stoichiometric (1:1 and 1:2) investigation of the reactivity between [Ti(μ-ONep)(ONep)$_3$]$_2$[27] and the HOR* was undertaken according to eq 1. After being stirred for 12 h, each clear reaction mixture was dried by rotary evaporation, yielding off-white powders. For the majority of these reactions, crystals were isolated through slow evaporation of the volatile component of the reaction mixture. Upon analysis, it was found that the OTHF system consistently generated the monosubstituted species and the OPy system consistently generated the disubstituted species. All attempts to change the stoichiometry through substoichio-

Table 3. Metrical Data for (OPy)$_2$Ti(OR)$_2$ Derivatives

compd	OR abbrev	av Ti−N$_{OPy}$ (Å) av Ti−O$_{OPy}$ (Å) av Ti−OR (Å)	selected angles (deg)	color	UV−vis λ_{max} (tol, nm)
H−OPy	H-OPy	−	−	pale brown	281
3	ONep	2.25 1.92 1.86	O(3)−Ti(1)−O(4) 101.34(18) O(3)−Ti(1)−N(1) 89.9(7) O(1)−Ti(1)−O(2) 153.65(18) O(3)−Ti(1)−N(2) 165.8(6)	white	283
4	O^{i}Pr	2.25 1.91 1.82	O(3)−Ti(1)−O(4) 102.13(12) O(3)−Ti(1)−N(2) 89.42(11) O(2)−Ti(1)−O(1) 154.51(10) O(4)−Ti(1)−N(2) 165.19(10)	white	282
5	O^{t}Bu	2.26 1.91 1.81	O(2)−Ti(1)−O(1) 103.2(2) O(2)−Ti(1)−N(1) 90.3(2) O(4)−Ti(1)−O(3) 154.14(19) O(1)−Ti(1)−N(1) 163.7(2)	white	282
7	DPE	2.27 1.90 1.82	O(4)−Ti(1)−O(3) 103.28(6) O(3)−Ti(1)−N(2) 87.55(6) O(1)−Ti(1)−O(2) 154.28(6) O(4)−Ti(1)−N(2) 165.36(6)	white	282
8	OPh−Adam	2.24 1.87 1.88	O(1)−Ti(1)−O(2) 100.86(18) N(2)−Ti(1)−O(3) 84.8(3) O(3)−Ti(1)−O(4) 153.64(18) O(1)−Ti(1)−N(2) 162.2(4)	yellow	281, 336(b)
10	oPP	2.24 1.87 1.85	O(1)−Ti(1)−O(2) 98.72(10) O(1)−Ti(1)−N(2) 88.73(10) O(3)−Ti(1)−O(4) 155.26(10) N(1)−Ti(1)−O(1) 167.44(10)	yellow	281, 338(b)
11	oBP	2.21 1.88 1.86	O(1)−Ti(1)−O(3) 97.8(3) O(2)−Ti(1)−N(1) 85.8(3) O(2)−Ti(1)−O(4) 154.3(2) N(1)−Ti(1)−O(3) 170.2(3)	orange	281, 347(b)
12	DMP	2.23 1.89 1.87	O(1)−Ti(1)−O(2) 98.89(6) O(3)−Ti(1)−N(1) 83.04(6) O(3)−Ti(1)−O(4) 151.90(6) O(1)−Ti(1)−N(2) 166.99(6)	orange	282, 356(b)
13	DIP	2.24 1.89 1.86	O(1)−Ti(1)−O(2) 98.62(6) O(3)−Ti(1)−N(2) 83.30(6) O(3)−Ti(1)−O(4) 152.09(6) O(2)−Ti(1)−N(3) 165.63(6)	orange	281, 358(b)
15	DPP	2.22 1.89 1.87	O(4)−Ti(1)−O(3) 98.79(8) O(2)−Ti(1)−N(1) 83.41(8) O(1)−Ti(1)−O(2) 150.44(8) O(3)−Ti(1)−N(1) 167.95(8)	yellow	281, 373(b)
16	2BP	2.25 1.90 1.90	O(3)−Ti(1)−O(4) 99.8(4) O(2)−Ti(1)−N(2) 85.9(3) O(1)−Ti(1)−O(2) 153.6(3) O(3)−Ti(1)−N(2) 168.1(3)	yellow	281, 327(b)
17	TCP	2.21 1.87 1.89	O(3)−Ti(1)−O(4) 99.27(13) O(3)−Ti(1)−N(2) 87.9(3) O(1)−Ti(1)−O(2) 152.20(13) O(4)−Ti(1)−N(2) 169.4(3)	yellow	281, 296(b)
18	4MP	2.22 1.89 1.87	O(3)−Ti(1)−O(4) 100.1(2) O(1)−Ti(1)−N(2) 86.5(2) O(2)−Ti(1)−O(1) 156.1(2) O(4)−Ti(1)−N(1) 164.2(2)	red-orange	281, 306, 350(b)
19	4AP	2.24 1.87 1.86	O(1)−Ti(1)−O(1)#1 101.79(18) O(1)−Ti(1)−N(3) 88.67(12) O(2)#1−Ti(1)−O(2) 153.06(18) O(1)−Ti(1)−N(3)#1 167.01(12)	red-orange	281, 313(b), 384(b)
20	DAP	2.21 1.87 1.85	O(4)−Ti(1)−O(3) 101.79(14) O(3)−Ti(1)−N(2) 88.74(14) O(1)−Ti(1)−O(2) 156.33(14) O(3)−Ti(1)−N(1) 166.93(14)	red-brown	281, 354(vb)
22	DMBS	2.28 1.89 1.82	O(2)−Ti(1)−O(3) 101.78(18) O(4)−Ti(1)−N(1) 85.13(16) O(4)−Ti(1)−O(1) 153.30(16) O(2)−Ti(1)−N(2) 166.14(18)	white	281
23	TPS	2.25 1.88 1.85	O(1)−Ti(1)−O(2) 101.42(8) O(3)−Ti(1)−N(1) 84.63(8) O(4)−Ti(1)−O(3) 152.70(8) O(2)−Ti(1)−N(1) 165.85(8)	white	281
24	TOBS	2.28 1.90 1.84	O(3)−Ti(1)−O(7) 104.4(2) O(2)−Ti(1)−N(1) 86.3(2) O(2)−Ti(1)−O(1) 155.4(2) O(7)−Ti(1)−N(2) 164.6(2)	white	281

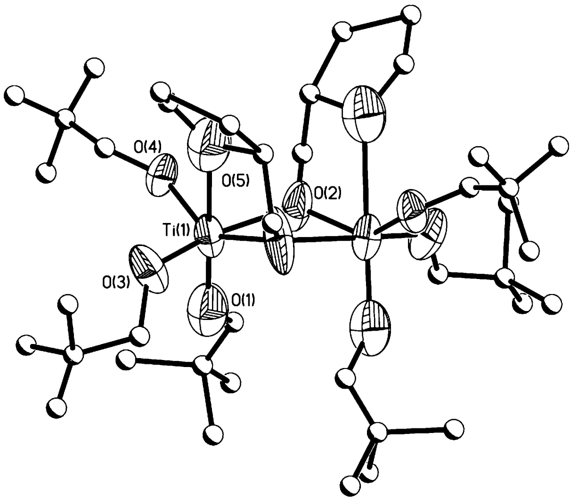

Figure 2. Structure plot of **1**. Thermal ellipsoids of heavy atoms drawn at the 30% level, and carbon atoms represented by ball-and-stick diagrams for clarity.

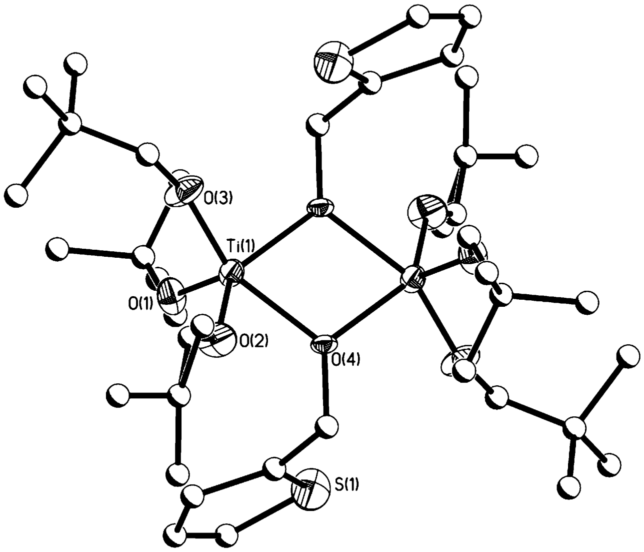

Figure 3. Structure plot of **2**. Thermal ellipsoids of heavy atoms drawn at the 30% level, and carbon atoms represented by ball-and-stick diagrams for clarity.

metric additions or heating at reflux temperatures for extended times did not change the products isolated. Crystals were easily isolated by slow evaporation and the compounds identified as **1**−**3**, and while not well behaved crystallographically, the connectivity was unequivocally established (see Figures 2−4, respectively). Compounds of **1**−**3** were then rationally synthesized on the basis of the degree of substitution noted above for the specific OR* ligands.[14−16]

$$[\mathrm{Ti}(\mu\text{-ONep})(\mathrm{ONep})_3]_2 + 2n\mathrm{H{-}OR^*} \rightarrow 2\ \text{“}(\mathrm{OR^*})_n\mathrm{Ti}(\mathrm{ONep})_{4-n}\text{”} + 2n\mathrm{H{-}ONep} \quad (1)$$

$$n = 1, 2;\ \mathrm{OR^*} = \mathrm{OTHF, OTPM, OPy}$$

X-ray Structures. Single-crystal X-ray diffraction studies were undertaken for **1**−**3** to initially establish the identity of these products. Table 1 lists the data collection parameters of **1**−**3**. Additional structural information can be found in the Supporting Information.

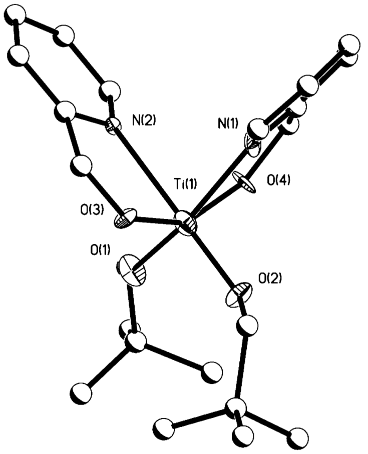

Figure 4. Structure plot of **3**. Thermal ellipsoids of heavy atoms drawn at the 30% level, and carbon atoms represented by ball-and-stick diagrams for clarity.

For compound **1** (Figure 2), a standard edge-shared bioctahedral (Oh) dinuclear species was isolated. Each metal center uses three terminal ONep’s and one chelating bridging (μ_c-OTHF) ligand to fill its coordination sphere. The μ_c-OTHF binding mode of the OTHF is consistent with what was observed for several other transition metal complexes; however, these species all contain halide ligands.[18,19,25] The metrical data of **1** are not of sufficient quality to be useful for further discussion but do establish the connectivity of the final compound. Structural comparisons are made to the starting $[\mathrm{Ti}(\mu\text{-ONep})(\mathrm{ONep})_3]_2$,[27] the oxygen of the THF− moiety fills an open coordination site and may display enhanced reactivity in comparison to $[\mathrm{Ti}(\mu\text{-ONep})(\mathrm{ONep})_3]_2$.

The metrical data for dinuclear **2** are also not of high enough quality to draw any conclusions, but the general connectivity is firmly established, see Figure 3. This is the first OTPM transition metal species reported. Each Ti metal center is five-coordinated forming what appears to be a trigonal bipyramidal (TBP) geometry. The OTPM acts only as a bridging ligand with the soft S atom not binding to the hard Ti metal center.

Using the OPy ligand led to the isolation of a monomeric species. The strong Lewis basic pyridine moiety of each of the two OPy ligands binds to the Ti metal centers in a chelating mode without bridging. The remainder of the coordination sites in the Oh-bound Ti metal centers were filled by the two ORs of the starting $\mathrm{Ti(OR)_4}$. For transition metals, numerous species have been crystallized that possess two OPy’s; however, these ligands are often protonated (H−OPy),[30−41] have bridging OPy ligands,[33,42−4545] isolated as salt derivatives,[31,33,35,37,40,43−49] or possess halides.[49−52] The one species of this family that most closely resembles **3** is

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(30) Yilmaz, V. T.; Guney, S.; Andac, O.; Harrison, W. T. A. *Polyhedron* **2002**, *21*, 2393.

(31) Hamamci, S.; Yilmaz, V. T.; Thone, C. *Acta Crystallogr., Sect. E: Struct. Rep. Online* **2004**, *60*, m6.

(32) Hoang, N. N.; Valach, F.; Dunaj-Jurco, M.; Melnik, M. *Acta Crystallogr. Sect. C: Cryst. Struct. Commun.* **1992**, *48*, 443.

(33) Tesmer, M.; Muller, B.; Vahrenkamp, H. *Chem. Commun.* **1997**, 721.

(34) Yilmaz, V. T.; Guney, S.; Andac, O.; Harrison, W. T. A. *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.* **2002**, *58*, m427.

$Mo(O)_2(OPy)_2$.[53] The isostructural O^{i}Pr derivative was recently reported using CH_2Cl_2 instead of toluene.[28]

In order to verify that the bulk material was consistent with the single-crystal structures noted above for **1**−**3**, the dried powder was also analyzed by FTIR spectroscopy and elemental analysis. The FTIR spectrum of each sample revealed the respective ligand stretches minus the OH stretch. Further, representative stretches for the neo-pentoxides are present for **1**−**3**. The strong stretches at 678, 762, and 724 cm^{-1} for **1**−**3**, respectively, are in the range of the literature values for Ti−O stretches.[1] Combined, these data imply that the bulk material has OR* ligands that have reacted fully and are bound to the Ti metal center. Elemental analyses of the bulk powders of **1**−**3** were undertaken using crystalline material and handled under inert atmospheres, and for all samples, the analyses were consistent with the single-crystal X-ray structure.

Due to the interest that the disubstituted OPy structure of **3**, it was of interest to determine what structures alternative alkoxides, such as $Ti(O^iPr)_4$ or $Ti(O^tBu)_4$ ($O^iPr = OCH(CH_3)_2$ and $O^tBu = OC(CH_3)_3$), would yield. The products isolated from toluene proved to be $(OPy)_2Ti(OR)_2$ (OR = O^{i}Pr (**4**), O^{t}Bu (**5**)).[14−16] This substitution clearly demonstrates the control that the '$(OPy)_2Ti$' moiety can impart to rational metal alkoxide construction, much like metallocenes allowed for organometallic species to be synthesized.[13] The structural similarity of these derivatives is surprising with such varied pendent alkoxides which often lead to different structures.[1−6,13] The metrical data of **3**−**5** are self-consistent. Again, IR data reveal the representative alkyl stretches along with Ti−O stretches at 724, 722, and 720 cm^{-1} for **3**−**5**, respectively. Elemental analysis data of the bulk powders for **3**−**5** were also found to be in agreement with the single-crystal data.

Solution Behavior. Dried crystalline materials of **1**−**5** were re-dissolved in toluene-d_8 under an inert atmosphere at saturated concentrations to explore the solution behavior of these compounds. Not unexpectedly, the asymmetric nature of the ligand set did not allow for a ^{47,49}Ti NMR spectra to be obtained. ^{1}H NMR data were therefore used for further investigation of the solution behavior of **1**−**5**.

The ^{1}H NMR spectrum of **1** was found to possess a set of resonances that were consistent with bound OTHF and ONep ligands in the 1:3 ratio noted for the solid-state structure. The peaks are slightly broad, indicating rapid exchange of the ligands; however, variable-temperature (VT) NMR data did not show any substantial changes in the spectrum over a temperature range of −50 to +50 °C. From these data, it is not possible to determine the nuclearity of **1** in solution; however, since the crystals formed at room temperature and there was no significant change in the spectra over a 100 °C temperature range, it is reasoned that the dinuclear arrangement is favored and most likely retained in solution. $[Ti(\mu\text{-}ONep)(ONep)_3]_2$ was determined to be monomeric in solution; however, there were no μ_c-OR ligands present in this compound to assist retaining the dinuclear solution noted for **1**.

For **2**, the OTPM and ONep resonances are sharp, defined, and clearly observed in the 1:3 ratio except for the methylene resonances that were slightly broad. This implies there is little dynamic behavior occurring. VT NMR data (+50 to −50 °C) revealed no change in the spectrum. The same reasoning used above for the retention of structure **1** would apply for **2** and the dinuclear species are believed to be retained in solution.

The ^{1}H NMR spectra of **3**−**5** presented a spectrum wherein a 1:1 ratio was observed for the OPy/OR (OR = ONep, O^{i}Pr, O^{t}Bu) ligand sets of compounds **3**−**5**, respectively; however, two types of methylene and OPy resonances were observed for these samples. In particular, two methylene resonances were clearly observed for each of these compounds in an ∼1:10 ratio. The diastereotopic methylene protons of the OPy should be observable but would be expected to give equal intensities, which these clearly do not. VT NMR data showed the extra set of OPy resonances quickly disappeared by 0 °C. Further lowering the temperature did not show any evidence of additional changes except for selected precipitation of **3**−**5**. The literature NMR data for **4** in $CDCl_3$[28] indicated that the OPy ligand was fluctuating between chelating and terminal; therefore, only one set of OPy resonances was reported. The diastereotopic methylenes were reportedly observed at low temperature prior to precipitation. Therefore, it is not unreasonable to expect in the less-polar toluene a slightly different solution behavior, wherein the bound OPy ligand is preferentially present with

(35) Christmas, C. A.; Tsai, H.-L.; Pardi, L.; Kesselman, J. M.; Gantzel, P. K.; Chadha, R. K.; Gatteschi, D.; Harvey, D. F.; Hendrickson, D. N. *J. Am. Chem. Soc.* **1993**, *115*, 12483.
(36) Moncol, J.; Mudra, M.; Lonnecke, P.; Koman, M.; Melnik, M. *J. Coord. Chem.* **2004**, *57*, 1065.
(37) Yilmaz, V. T.; Hamamci, S.; Thone, C. *Polyhedron* **2004**, *23*, 841.
(38) Bacsa, J.; Zhao, H.; Dunbar, K. R. *Acta Crystallogr. Sect. E: Struct. Rep. Online* **2004**, *60*, m1040.
(39) Moncol, J.; Kalinakova, B.; Svorec, J.; Keleinova, M.; Koman, M.; Hudecova, D.; Melnik, M.; Mazur, M.; Valko, M. *Inorg. Chim. Acta* **2004**, *357*, 3211.
(40) Ito, M.; Onaka, S. *Inorg. Chim. Acta* **2004**, *357*, 1039.
(41) He, F.; Liu, D. *Acta Crystallogr., Sect. E: Struct. Rep. Online* **2005**, *61*, m1350.
(42) Clemente-Juan, J. M.; Mackiewicz, C.; Verelst, M.; Dahan, F. *Inorg. Chem.* **2002**, *41*, 1478.
(43) Bolcar, M. A.; Aubin, S. M. J.; Folting, K.; Hendrickson, D. N.; Christou, G. *Chem. Commun.* **1997**, 1485.
(44) Yang, E.-C.; Harden, N.; Wensdorfer, W.; Zakharov, L. N.; Brechin, E. K.; Rheingold, A. L.; Christou, G.; Hendrickson, D. N. *Polyhedron* **2003**, *22*, 1857.
(45) Yoo, J.; Yamaguchi, A.; Nakano, M.; Krzystek, J.; Streib, W. E.; Brunel, L.-C.; Ishimoto, H.; Christou, G.; Hendrickson, D. N. *Inorg. Chem.* **2001**, *40*, 4604.
(46) Sanudo, E. C.; Brechin, E. K.; Boskovic, C.; Wernsdorfer, W.; Yoo, J.; Yamaguchi, A.; Concolino, T. R.; Abboud, K. A.; Rheingold, A. L.; Ishimoto, H.; Hendrickson, D. N.; Christou, G. *Polyhedron* **2003**, *22*, 2267.
(47) Harden, N.; Bolcar, M. A.; Wernsdorfer, W.; Abboud, K. A.; Streib, W. E.; Christou, G. *Inorg. Chem.* **2003**, *42*, 7067.
(48) Sanudo, E. C.; Wernsdorfer, W.; Abboud, K. A.; Christou, G. *Inorg. Chem.* **2004**, *43*, 4137.
(49) Martos-Calvente, R.; O'Shea, V. A. P.; Campos-Martin, J. M.; Fierro, J. L. G.; Gutierrez-Puebla, E. *J. Mol. Catal. A: Chem.* **2004**, *214*, 269.
(50) Suzuki, Y.; Tomizawa, H.; Miki, E. *Inorg. Chim. Acta* **1991**, *290*, 36.
(51) Rochon, F. D.; Melanson, R.; Kong, P.-C. *Inorg. Chim. Acta* **1997**, *254*, 303.
(52) Gerber, T. I. A.; Luzipo, D. G.; Mayer, P. *J. Chem. Cryst.* **2005**, *35*, 39.
(53) Li, G.; Li, R.-J.; Song, Y.-L.; Xie, L.-X.; Wei, Y.-L.; Fan, Y.-T.; Hou, H.-W. *Huaxue Xuebao (Chin.) (Acta Chim. Sinica)* **2002**, *60*, 1258.

some degree of fluctionality. This behavior prevents observation of the diastereotopic methylene protons. The reduced solubility prevents the identification of these protons at even slightly reduced temperatures. Combined, these data favor the retention of the monomeric nature of **3**−**5** in toluene solutions and offers an opportunity to rationally construct a series of $(OPy)_2Ti(OR)_2$.

Alcoholysis of $(OPy)_2Ti(OR)_2$. In order to verify the stability of the '$(OPy)_2Ti$' moiety to alcoholysis exchange, we initiated a series of reactions following eq 2. The alcohol ligands investigated included alkyl alcohols, aryl alcohols, substituted aryl alcohols, H−OR*, and silanols. The synthesis and characterization of these OR* derivatives are discussed in detail.

$$(OPy)_2Ti(O^iPr)_2 + 2H{-}OR' \rightarrow \text{“}(OPy)_2Ti(OR')_2\text{”} + 2H{-}O^iPr \quad (2)$$

$OR' = OPr^{Me}$, OAdam, DPE, OPh−Adam,
oMP, oPP, oBP, DMP, DIP, DBP, DPP, 2BP,
TCP, 4MP, 4AP, DAP, OTPM, DMBS, TPS, TOBS

Synthesis. While all the precursors have demonstrated the ability to exchange their alkoxide ligands, **4** was selected as the main starting material for several reasons. $Ti(O^iPr)_4$ is commercially available and less expensive than $Ti(O^tBu)_4$ and further, it is the least sterically demanding ligand and thus more susceptible to exchange. To a stirring solution of compound **4** in toluene, 2 equiv of the appropriate H−OR′ were added and allowed to stir for 12 h. In case of lower soluble alcohols, typically the aryloxides, heat was applied forming highly colored and completely soluble products. For the polyfunctional aryloxide derivatives, pyridine at elevated temperatures was required to solubilize these compounds. FTIR data showed for each sample that the OR′ ligand had successfully replaced the OR moiety of the starting materials, based on the lack of an −OH stretch and the presence of the respective bends and stretches associated with the particular ligand. In addition, the OPy stretches were also present in each sample's spectrum. Preliminarily, this data suggested that the exchange had been successful.

Elemental analysis was found to be in agreement with the "$(OPy)_2Ti(OR')_2$" species (**7**−**24**). For **7**, **15**, and **20**, the inclusion of solvent molecules, as noted in their respective structural solutions (see Table 2), was required for agreement; however, **17** (lattice solvent removed by the squeeze program of the PLATON software package) and **19** did not require the structurally characterized lattice solvent molecule for agreement. For **8** and **11**, a molecule of toluene needed to be added to the molecular formula that is consistent with the toluene solvent molecule that was removed by the squeeze program in the final refinement of the structure. Compounds **6** and **14** did not agree completely with expected disubstituted compounds and were not self-consistent during analysis. Attempts to synthesize the disubstituted species $(OPy)_2Ti(OPr^{Me})_2$ (**6**), under room-temperature conditions, led to a heteroligated species instead, forming the $(OPy)_2Ti(O^iPr)(OPr^{Me})$ (**6a**) derivative. The elemental analysis of the bulk material was not consistent with the single-crystal structure wherein the carbon content was consistently lower than expected. Due to this ambiguity and the lack of symmetric exchange, we are only reporting the crystal structure of **6a** while we explore the availability of asymmetric substitution afforded by the isolation of this compound. For the **6b** (OAdam) and **9** (oMP) derivatives, crystals that had elemental analyses consistent with the disubstituted species were isolated but X-ray quality crystals were not obtained. For **14**, at room temperature, substitution of the O^iPr ligands by the sterically hindering DBP moieties was not realized even for monosubstitution. Additional studies are underway to explore and understand the observed behavior for these compounds.

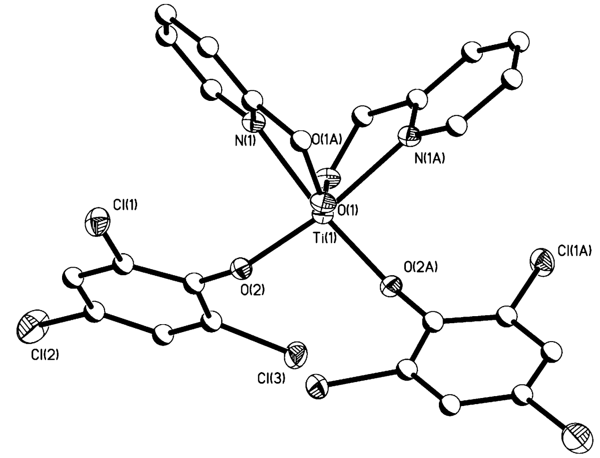

Figure 5. Structure plot of **17**. Thermal ellipsoids of heavy atoms drawn at the 30% level, and carbon atoms represented by ball-and-stick diagrams for clarity.

The ^{1}H NMR data of **7**−**24** (**14** was omitted from the study) demonstrated similar behavior as noted above for **3**−**5**. Combined, these data indicate that the '$(OPy)_2Ti$' moiety has been retained. In order to verify this claim, the structure of each compound was determined.

Crystal Structures. The following species were investigated structurally as $(OPy)_2Ti(OR')_2$: OR′ = DPE (**7**), OPh−Adam (**8**), oPP (**10**), oBP (**11**), DMP (**12**), DIP (**13**), DPP (**15**), 2BP (**16**), TCP (**17**), 4MP (**18**), 4AP (**19**), DAP (**20**), OTPM (**21**), DMBS (**22**), TPS (**23**), and TOBS (**24**). Table 2 lists the collection data for each of these compounds. Table 3 lists the compounds and their respective alcohols. Figures 5−7 are representative species (**17**, **21**, **24**) of the resultant chemistry (**8** is shown in the Table of Contents figure).

Since the initial OPr^{Me} reaction formed **6a** and not the desired disubstituted species, it was of interest to determine what factors would control the exchange, and therefore, additional sterically varied alcohols were investigated. For the OAdam (**6b**) and DPE (**7**) ligand sets, analytical data (FTIR and elemental analysis) were consistent with the disubstitution product. For each, NMR data were also consistent with the monomeric disubstituted species. While **7** was easily isolated in crystalline form and structurally characterized as the disubstituted species, all attempts to get

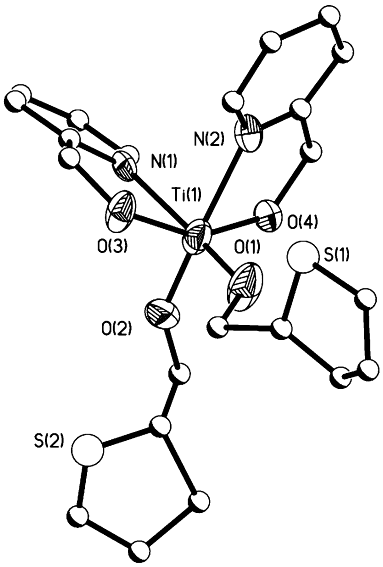

Figure 6. Structure plot of **21**. Thermal ellipsoids of heavy atoms drawn at the 30% level, and carbon atoms represented by ball-and-stick diagrams for clarity.

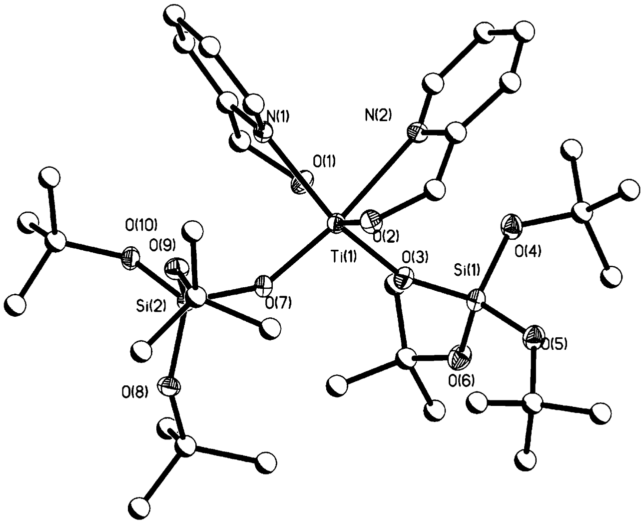

Figure 7. Structure plot of **24**. Thermal ellipsoids of heavy atoms drawn at the 30% level, and carbon atoms represented by ball-and-stick diagrams for clarity.

crystallographic data on **6b** were unsuccessful. This led us to explore the more rigid and sterically varied aryloxides.

In most of the M(OR)$_x$ systems that we have explored, aryloxides offer significant variation in structural complexity in comparison to alkyl alkoxides;[9,54−56] therefore, we were interested in the effect these large ligands would have on this system. For all of the aromatic species, the color of the resultant crystals were a bright orange to yellow, based on the specific ligand. The color variations were presumed to be from ligand to metal charge transfer as determined by the UV−vis spectra collected (vide infra). The '(OPy)$_2$Ti' moiety remained intact for all the alcohols investigated including a derivative that contained the adamantane moiety (OAdam−Ph, **8**, see Table of Contents figure), mono- and dialkyl ortho-substituted phenoxide derivatives (**9**−**13**), and phenyl-substituted species (**15**). Even more complex aryloxides (**16**−**21**) did not yield any variations in the '(OPy)$_2$Ti' moiety upon exchange. This was surprising since the amine-substituted compounds (**19** and **20**) could only be dissolved in boiling pyridine but there was no evidence of coordinating solvent. This is most likely a reflection of the stable nature of the bidentate OPy ligands preventing additional Lewis base coordination. Substitution by the other OR* ligand only produced a terminal OTPM set of ligands (**21**) similar to what was noted for **2** in terms of the binding mode. Full substitution by the OPy ligand or modification by the OTHF derivatives did not yield crystalline material. Switching to silanols presented a slightly different electronic and steric ligand set, but again the '(OPy)$_2$Ti' moiety was unaffected by any silanol substitution **22**−**23**. A slight variation with an alkoxy siloxide ligand, TOBS that would provide a more electron-withdrawing effect, also retained the basic structural motif (**24**). As can be observed from this unusually stable family of compounds, exchange was readily realized without destruction of the stabilizing moiety; therefore, we have developed a scaffold from which controlled metal alkoxides can be systematically built. The metrical data for **3**−**24** are comparable with surprisingly little variation noted by the presence of the substituted alkoxide ligand (see Table 3).

UV−vis spectra were obtained for **3**−**24** in toluene (see Table 3) in an attempt to understand the color variations noted for these compounds. The light brown H−OPy was found to have one large absorption at λ_{max} 281 nm attributed to the py ring of the OPy compound. A stretch consistent with the OPy ligand was observed in every sample ranging from λ_{max} 281 to 283 nm. For the colored species (**8**−**20**), several additional broad peaks at higher energies were noted ranging from λ_{max} 296 to 384 nm. The color variations from yellow to orange are paralleled by shifts in the second absorption peaks. The mixed-color species either have two peaks in addition to the OPy ligand absorptions (**18**−**19**) or a very broad peak (**20**) that covers the same regions. It is obvious from this study that the aromatic ligands, not the OPy ligands, are imparting a ligand-to-metal charge transfer to produce the observed colors for these compounds. Further, the emission color can be fine-tuned on the basis of the substitution of the ring or the number and types of ligands present on the '(OPy)$_2$Ti' moiety.

Summary and Conclusion

Using the OR* ligands (OTHF, OTPM, and OPy), a new family of heterocyclic alkoxides have been isolated as **1**−**5**. For the OTHF- and OTPM-ligated species, monosubstituted dinuclear compounds were isolated with the ligand acting either as a μ_c-OR or as a μ-OR ligand, respectively; for the OPy, disubstituted chelating ligation was observed. It appears from solution NMR data that these structures are retained in solution. Due to the steric constraints imparted by the disubstituted OPy ligated species with a variety of sterically

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(54) Boyle, T. J.; Andrews, N. L.; Rodriguez, M. A.; Campana, C.; Yiu, T. *Inorg. Chem.* **2003**, *42*, 5357.

(55) 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.

(56) Boyle, T. J.; Pedrotty, D. M.; Alam, T. M.; Vick, S. C.; Rodriguez, M. A. *Inorg. Chem.* **2000**, *39*, 5133−5146.

hindering OR groups, the opportunity to pursue controlled chemistry of metal alkoxides is readily available. The ‘$(OPy)_2Ti$’ moiety is reminiscent of metallocene derivatives ‘$(Cp)_2Ti$’ moieties wherein the Cp ligands protect one side of the metal center and allow for controlled chemistries to be carried out on the opposite side. We have for the first time clearly demonstrated the utility of the ‘$(OPy)_2Ti$’ moiety as a useful stable building block for a number of complex structures (**6**−**24**), each of which surprisingly do not disrupt this moiety. This allows for the first time controlled modifications of $Ti(OR)_4$ leading to predictable structures. Currently, several metal systems and carboxylate systems are under investigation to determine the extent of this reactivity and to control the properties of the ‘$(OPy)_2Ti$’ scaffold.

Acknowledgment. The authors thank Prof. A. L. Rheingold (UCSD) for helpful discussions and for support of this research, the Office of Basic Energy Sciences, and the U.S. Department of Energy under Contract No. DE-AC04-94AL85000. Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy.

Supporting Information Available: Crystallographic data in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

IC0618798