# Synthesis and Structure of Chiral Titanium(IV) Complexes Containing N-Substituted Amino Alcohols

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Several Ti(IV)−amino alcohol complexes of the type $TiX_2$[OCHPhCHPhN(R)] (X = $NMe_2$, $NEt_2$, $O^iPr$; R = $SO_2CF_3$ (Tf), $SO_2Ar$, $CH_2Ar$) have been synthesized by protonolysis of Ti($NMe_2$)$_4$, Ti($NEt_2$)$_4$, or Ti($O^iPr$)$_4$ with various N-substituted amino alcohol ligands derived from (1*S*,2*R*)-(+)-2-amino-1,2-diphenylethanol. X-ray crystal structures of [Ti[OCHPhCHPhN(Tf)]($NMe_2$)$_2$]$_2$ (**2a**), [Ti[OCHPhCHPhN($CH_2$[2,4,6-($CH_3$)$_3C_6H_2$])]($NMe_2$)$_2$]$_2$ (**2d**), and [Ti[OCHPhCHPhN(Tf)]($O^iPr$)$_2$]$_2$ (**4**) show these compounds to be dimeric in the solid state, bridging through the amino alcohol oxygens; vapor pressure osmometry (VPO) molecular weight measurements on **2**−**4** confirm a dimeric solution structure. The dimers [Ti[OCHPhCHPhN(Tf)]($NEt_2$)$_2$]$_2$ (**3**) and **4** form 4-(dimethylamino)pyridine (DMAP) adducts which exhibit a concentration-dependent monomer−dimer equilibrium by VPO. An X-ray crystal structure of Ti[OCHPhCHPhN(Tf)]($O^iPr$)$_2$[DMAP] (**6**), however, indicates that it is monomeric in the solid state.

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## Introduction

The use of chiral amino alcohol- and amino acid-derived ligands is widespread in the area of Lewis acid-promoted or -catalyzed asymmetric organic transformations.[1] There are a plethora of examples of boron-based catalysts using these types of ligands[2] as well as several examples in which aluminum,[3] zinc,[4] and titanium[5] are used as the metal core. In situ-generated titanium(IV)−amino alcohol catalysts, for example, are known to stereospecifically catalyze the Diels−Alder reaction,[5a] the kinetic resolution of epoxy alcohols,[5b] and the alkylation of aldehydes.[5c]

To our knowledge, no solution and/or solid-state structural information exists for in situ-generated Ti(IV)−amino alcohol catalysts. However, solid-state structural information on related titanium(IV) pyridine−alkoxide polymerization catalysts,[6] Ti(IV) quinolinolato compounds,[7] a [$Cp_2$Ti(α-amino acid)$_2$]$^{2+}$[$Cl^-$]$_2$ compound,[8] and related Ti(IV)−diamine[9] and −diol[10] complexes are known. These compounds, although helpful in predicting the structure(s) of Ti(IV)−amino alcohol catalysts, do not substitute for direct structural data. To address this deficiency, we report herein the synthesis and structural characterization (solution and solid-state) of Ti(IV)−amino alcohol complexes with the empirical formula $TiX_2$[OCHPhCHPhN(R)] (where X = $NMe_2$, $NEt_2$, or $O^iPr$; R= Tf, $SO_2Ar$, or $CH_2Ar$) in addition to documenting their reactivity with neutral Lewis base ligands.

## Results and Discussion

**Synthesis.** The amino alcohol bisamido compounds **2a**−**d** were directly generated via the aminolysis of Ti-

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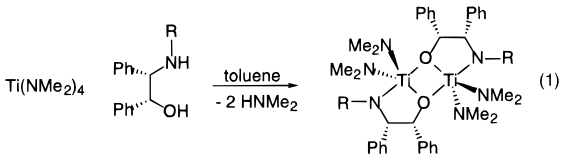
**Table 1. Vapor Pressure Osmometry Molecular Weight Measurements for 2a−d, 3, and 4**

| | 2a | 2b | 2c | 2d | 3 | 4 |
|---|---|---|---|---|---|---|
| *T* (°C) | 33.9 | 35.3 | 32.2 | 34.7 | 33.9 | 34.7 |
| solvent | THF | toluene | toluene | toluene | THF | toluene |
| monomer conc (mM) | 43.1 | 49.5 | 50.1 | 29.5 | 38.6 | 36.4 |
| observed conc (mM) | 22.0(5) | 24.5(15) | 25.8(14) | 13.8(7) | 19.3(4) | 18.9(9) |
| aggregation state | 1.96(5) | 2.0(1) | 1.9(1) | 2.1(1) | 2.01(4) | 1.94(9) |

$(NMe_2)_4$ with chiral N-substituted amino alcohols derived from (1*S*,2*R*)-(+)-2-amino-1,2-diphenylethanol (eq 1). Similar aminolysis synthetic strategies have previously been reported with chiral bissulfonamide[9a,b] and bidentate pyridine-alkoxide[6] ligands. The sulfonylated amino alcohol compounds **2a**−**c** were readily prepared at 23 °C over a 20 h period, while the 2,4,6-trimethylbenzyl-substituted amino alcohol compound (**2d**) required elevated temperatures (∼90 °C, 18 h). Although unknown byproducts accompanied the syntheses of **2a** and **2d**, analytically pure material was obtained by selective precipitation of the desired product, albeit in slightly lowered yields. As indicated in eq 1, **2a**−**d** are formulated as dimers based on solution vapor phase osmometry (VPO) and X-ray crystallography (vide infra).

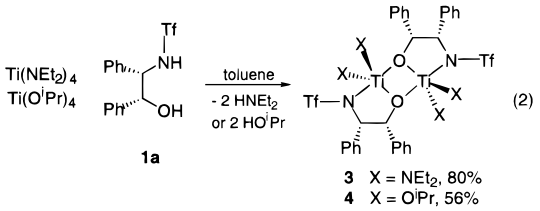



**1a** R = $SO_2CF_3$ (Tf) **2a** 55%
**1b** R = $SO_2$[p-$C_6H_4CH_3$] **2b** 78%
**1c** R = $SO_2$[p-$C_6H_4C(CH_3)_3$] **2c** 62%
**1d** R = $CH_2$[2,4,6-$(CH_3)_3C_6H_2$] **2d** 52%
**1e** R = Si-$^i$Pr$_3$ **NR**

The $^1$H NMR spectra of **2a**−**d** each point to a structure with a single backbone and two unique $NMe_2$ sites. If Ti−N bond rotation is rapid, as is usual in these types of complexes,[9a−b,11] these data are consistent with a tetrahedral monomeric or alkoxide-bridged $C_2$-symmetric dimeric structure (shown in eq 1). VPO experiments in THF and toluene indicate that **2a**−**d** are dimeric in solution (14−26 mM), suggesting that dimers are the principle solution species, at least at these concentrations (Table 1).

Unexpectedly, the N-silylated amino alcohol **1e** showed no evidence for aminolysis with $Ti(NMe_2)_4$ at elevated temperatures (>100 °C). Since silylamines are more acidic than alkylamines, this observation points to dominating steric effects for the bulky TIPS-protected ligand.[12]

In analogy to **2a**−**d**, **3** and **4** could be synthesized via ligand exchange/metathesis of $Ti(NEt_2)_4$ or $Ti(O^iPr)_4$ with **1a** (eq 2). Compound **3** readily forms at 23 °C over a 20 h time period, while **4** requires elevated temperatures (60 °C). Both could be isolated in analytically pure form by selective precipitation from toluene/hexane at −78 °C (**3**) or $CH_2Cl_2$ at 0 °C (**4**). $^1$H NMR analysis of **3** revealed four sets of diastereotopic methylene hydrogens, again consistent with fast Ti−N bond rotation at two chemically inequivalent $NR_2$ sites and a chiral metal assembly. Also diagnostic of such an arrangement in **4** are the four sets of diastereotopic isopropyl methyl groups observed in the $^{13}$C NMR spectrum.




**1a**

**3** X = $NEt_2$, 80%
**4** X = O$^i$Pr, 56%

**Dimer Fragmentation Studies.** Simple NMR experiments to test for ligand-induced fragmentation[13] of these dimers in solution were performed by treating compounds **2a**/**3**, **2c**, **2d**, and **4** with an excess of THF, $PEt_3$, or DMAP.[14,15] Based on the lack of observable shifts in the $^1$H or $^{31}$P NMR, neither THF nor $PEt_3$ displayed any evidence of coordinating to the dimers. Although the *N*-mesityl-substituted complex **2d** does not appear to form a DMAP adduct (<5%), the sulfonamide **2c** reacts with DMAP to establish an equilibrium with a new compound, the concentration of which is [DMAP] dependent and predominates (>50%) only with >5 equiv of DMAP. The $^1$H NMR of this species is consistent with, but not necessarily conclusive for, a DMAP adduct. That both species are independently observable indicates that coordination/decoordination rates are slow relative to the NMR time scale.

In contrast, the reaction of DMAP with **3** and **4** cleanly forms new complexes (**5** and **6**, eq 3), as evidenced by shifts in the ligand and DMAP resonances.[16] Both species were independently synthesized, and spectroscopic studies on isolated materials confirmed that a single DMAP was associated with each titanium center. Despite DMAP coordination, the overall geometry of the products does not change substantially as the products retain two inequivalent $NR_2$ and O$^i$Pr sites, each of which is in a chiral environment, as judged by the four sets of diastereotopic methylenes ($^1$H NMR) and four diastereotopic methyls ($^1$H NMR) for **5** and **6**, respectively. These results are consistent with coordination of DMAP to the dimer to form an edge-shared octahedron (**5a**/**6a**) or deaggregation to a monomeric 5-coordinate species **5b**/**6b** (eq 3).

Despite the fact that X-ray crystallography on **6** indicates that it is monomeric in the solid state (vide infra), VPO molecular weight measurements on **5** and **6** show a concentration-dependent aggregation state

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(12) Relevant p$K_a$'s in DMSO are triflamide (9.7); benzene sulfonamide (16.1); bistrimethylsilylamine (30); ethanol (28); and dialkylamine ($^i$Pr$_2$NH, 36); see: Bordwell, F. G. *Acc. Chem. Res.* **1988**, *21*, 456−463.

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(14) For similar studies using aldehydes, ethers, and esters, see: Gau, H.-M.; Lee, C.-S.; Lin, C.-C.; Jiang, M.-K.; Ho, Y.-C.; Kuo, C.-N. *J. Am. Chem. Soc.* **1996**, *118*, 2936−2941.

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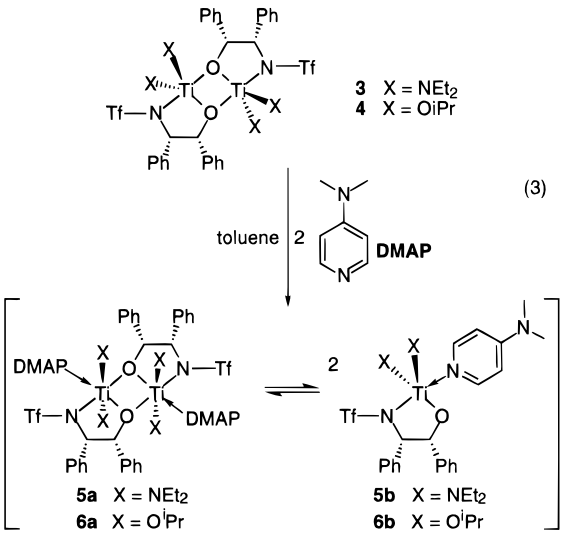


ranging from 2.1(1) to 1.15(15) (Table 2). This observation is most easily interpreted in terms of the equilibrium in eq 3; curiously, it is the monomeric form that crystallizes. This equilibrium, if rapid on the NMR time scale, is consistent with the $^1$H NMR spectra of **5** and **6**, as the overall symmetry of the monomers and dimers are similar. $^1$H NMR spectra of concentrated (30−50 mM; dimers predominate) and dilute (3−7 mM; monomers predominate) samples of each compound in $C_6D_6$ are qualitatively similar but show slight upfield shifts (0.05−0.1 ppm) in the DMAP aromatic and N−Me resonances. We therefore conclude that the products resulting from DMAP addition to **3** and **4** are **5** and **6** and that in solution they rapidly equilibrate between monomers and dimers, with the monomer of **6** dominating in the solid state.

The trend in Lewis acidity of the dimers (**2a**, **3**, **4** > **2c** > **2d**) is most reasonably interpreted as reflecting the donating ability of ligands **1a**−**d**. Triflamide ligands, being the most electron withdrawing, induce the largest degree of electronic unsaturation and thereby favor binding of Lewis bases. In comparison, *N*-alkyl-substituted amine ligands are good $\pi$-donors,[11] effectively reducing the Lewis acidity of the Ti-center and making it a poorer binder. N-Substituted arylsulfonamide ligands, being intermediate in their donating character, lead to the equilibrium-binding scenario described above.

The VPO results on **5** and **6** have additional implications in titanium Lewis acid catalysis, as stereochemically relevant monomer/dimer equilibria have been implicated in Ti(IV)−BINOL-catalyzed enantioselective ene and Diels−Alder reactions.[17] The catalyst species in these reactions are proposed to equilibrate between inactive dimeric and catalytically active monomeric forms resulting in high positive nonlinear/asymmetric amplification effects.[18] The results obtained herein suggest that analogous monomer/dimer equilibria may be important in Ti(IV)−amino alcohol catalysts.[5]

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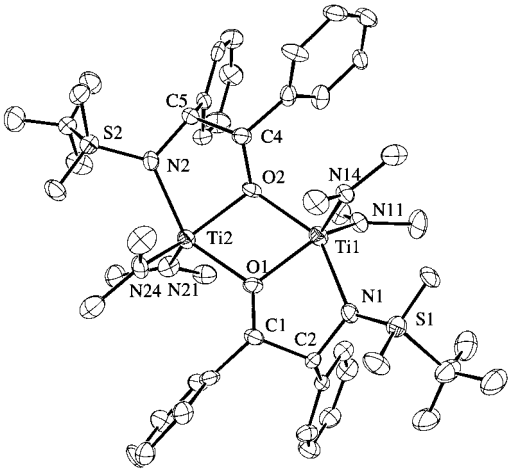


**Figure 1.** ORTEP drawing of **2a**. Selected bond distances (Å) and angles (deg): Ti1−O1 = 2.029(6), Ti1−O2 = 2.055(6), Ti2−O1 = 2.044(6), Ti2−O2 = 2.040(5), Ti1−N1 = 2.132(8), Ti1−N11 = 1.855(8), Ti1−N14 = 1.850(8), Ti2−N2 = 2.144(7), Ti2−N21 = 1.872(8), Ti2−N24 = 1.844(8), O1−Ti1−O2 = 71.97(22), O1−Ti2−O2 = 71.98(22), N11−Ti1−N14 = 109.3(3), N21−Ti2−N24 = 110.7(4).

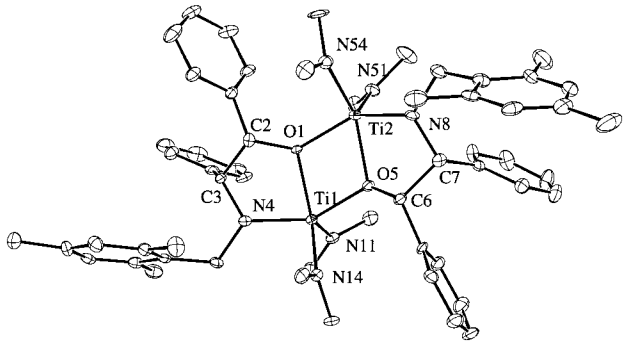


**Figure 2.** ORTEP drawing of **2d**. Selected bond distances (Å) and angles (deg): Ti1−O1 = 2.095(4), Ti1−O5 = 2.032(4), Ti2−O1 = 2.035(4), Ti2−O5 = 2.081(4), Ti1−N4 = 1.938(4), Ti1−N11 = 1.907(5), Ti1−N14 = 1.900(5), Ti2−N8 = 1.959(4), Ti2−N51 = 1.918(5), Ti2−N54 = 1.923(5), O1−Ti1−O5 = 71.76(14), O1−Ti2−O5 = 71.96(14), N11−Ti1−N14 = 107.18(19), N51−Ti2−N54 = 102.77(22).

**Table 2. Vapor Pressure Osmometry Molecular Weight Measurements for 5 and 6 in Toluene**

| compd | *T* (°C) | monomer conc (mM) | observed conc (mM) | aggregation state |
|---|---|---|---|---|
| **5** | 33.6 | 19.8 | 10.2(7) | 1.9(1) |
| | 34.7 | 8.9 | 5.6(4) | 1.6(1) |
| | 35.5 | 4.9 | 3.6(2) | 1.3(1) |
| **6** | 34.1 | 19.9 | 9.7(4) | 2.1(1) |
| | 35.3 | 9.9 | 6.5(3) | 1.5(1) |
| | 35.3 | 4.6 | 4.1(5) | 1.15(15) |

**Crystallography.** To more fully characterize the above products and address issues of molecularity raised by VPO measurements, X-ray crystal structures of **2a**, **2d**, **4**,[19] and **6** were obtained. ORTEP diagrams of these structures are shown in Figures 1−4, and crystallographic data/collection parameters assembled in Table 3. The three base-free compounds are dinuclear with

(19) Three disordered isopropyl groups were identified on the basis of planar methine carbons and large thermal ellipsoids (C1, C4, and C10). These atoms were replaced by two carbon atoms with 50% occupancy and refined isotropically. Associated H positions were then calculated, including those on the neighboring methyl groups, and modeled with six 50% H positions.

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**Table 3. Crystallographic Data and Collection Parameters for 2a, 2d, 5, and 7**

| | 2a | 2d | 5·2$CD_2Cl_2$ | 7 |
|---|---|---|---|---|
| formula | $Ti_2S_2F_6C_{45}H_{56}N_6O_6$ | $Ti_2C_{56}H_{62}N_6O_2$ | $Ti_2C_{44}H_{56}F_6N_2O_{10}S_2Cl_4$ | $TiSF_3C_{28}H_{36}N_3O_5$ |
| fw | 1050.87 | 946.93 | 1188.65 | 631.56 |
| color, habit | yellow, crystal | yellow, crystal | white, crystal | white, crystal |
| cryst size, mm | 0.22 × 0.20 × 0.10 | 0.10 × 0.12 × 0.24 | 0.35 × 0.20 × 0.15 | 0.25 × 0.15 × 0.40 |
| cryst syst | monoclinic | monoclinic | orthorhombic | monoclinic |
| space group | $P2_1$ | $P2_1$ | $P22_12_1$ | $P2_1$ |
| $a$, Å | 11.6407(6) | 12.3128(6) | 13.8319(6) | 8.53389(7) |
| $b$, Å | 12.3320(7) | 16.8019(8) | 19.1638(9) | 11.7152(9) |
| $c$, Å | 17.9723(10) | 13.5273(6) | 20.4139(9) | 15.8283(13) |
| $\beta$, deg | 105.5990(10) | 107.1310(10) | | 98.039(1) |
| $V$, Å$^3$ | 2484.95(24) | 2674.35(22) | 5411.1(4) | 1567.82(22) |
| $Z$ | 2 | 2 | 4 | 2 |
| $T$, °C | −100 | −100 | −100 | −100 |
| $D_c$, g/cm$^3$ | 1.404 | 1.176 | 1.459 | 1.338 |
| $F$(000) | 1094.33 | 1001.61 | 2455.11 | 661.24 |
| radiation | Mo Kα (0.71073) | Mo Kα (0.71073) | Mo Kα (0.71073) | Mo Kα (0.71073) |
| $\mu$, mm$^{-1}$ | 0.48 | 0.34 | 0.64 | 0.40 |
| scan mode | $\omega$ | $\omega$ | $\omega$ | $\omega$ |
| data collected | $\pm h, \pm k, \pm l$ | $\pm h, \pm k, \pm l$ | $\pm h, \pm k, \pm l$ | $\pm h, \pm k, \pm l$ |
| $2\theta_{max}$, deg | 47.5 | 50.0 | 50.0 | 50.0 |
| total no. of rflns | 12 044 | 16 625 | 28 920 | 14 919 |
| no. of unique rflns | 6785 | 8757 | 9536 | 5557 |
| $R_{merge}$ | 0.029 | 0.038 | 0.031 | 0.021 |
| no. of rflns with $I > 2.5\alpha(I)$ | 4539 | 7022 | 8654 | 4564 |
| no. of variables | 604 | 595 | 632 | 369 |
| $R_f$[a] | 0.069 | 0.059 | 0.044 | 0.045 |
| $R_w$[b] | 0.070 | 0.066 | 0.048 | 0.049 |
| GoF[c] | 2.20 | 1.96 | 2.65 | 2.19 |
| max $\Delta/\sigma$ | 0.004 | 0.007 | 0.002 | 0.015 |
| residual density, e/Å$^3$ | −0.50, 0.48 | −0.64, 0.52 | −0.38, 0.57 | −0.30, 0.49 |

[a] $R_f = \sum(F_o - F_c)/\sum F_o$. [b] $R_w = [\sum w(F_o - F_c)^2/\sum wF_o^2]^{1/2}$. [c] GoF = $[\sum w(F_o - F_c)^2/(n - p)]^{1/2}$, where $n$ = number of reflections and $p$ = number of parameters.

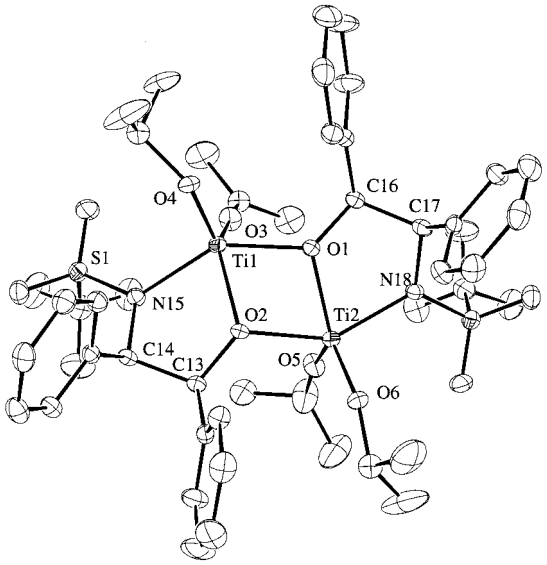


**Figure 3.** ORTEP drawing of **4**. Selected bond distances (Å) and angles (deg): Ti1−O1 = 2.0389(20), Ti1−O2 = 2.0257(20), Ti1−O3 = 1.7370(25), Ti−O4 = 1.7452(23), Ti2−O1 = 2.0331(20), Ti2−O2 = 2.0183(21), Ti2−O5 = 1.741(3), Ti2−O6 = 1.7391(23), Ti1−N15 = 2.0920(25), Ti2−N18 = 2.0872(25), O1−Ti1−O2 = 69.63(8), O1−Ti2−O2 = 69.89(8), O3−Ti1−O4 = 111.32(12), O5−Ti2−O6 = 111.44(12), O2−Ti1−N15 = 75.30(9), O1−Ti2−N18 = 75.40(9).

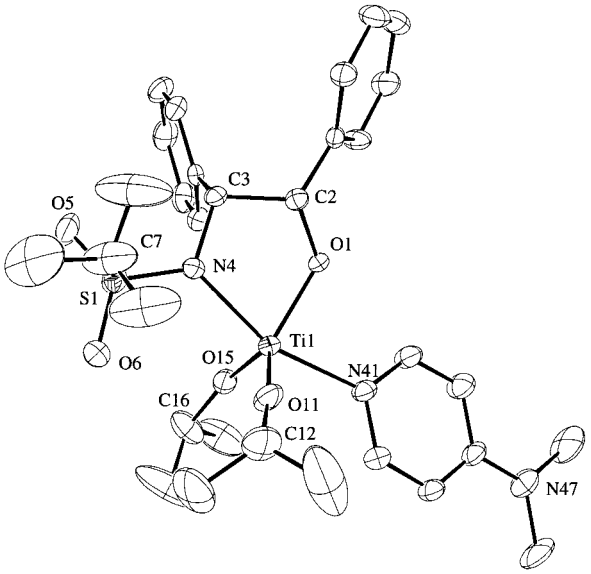


**Figure 4.** ORTEP drawing of **6**. Selected bond distances (Å) and angles (deg): Ti1−O1 = 1.0881(2), Ti1−O11 = 1.747(3), Ti1−O15 = 1.750(3), Ti1−N4 = 2.127(3), Ti1−N41 = 2.169(3), O11−Ti1−O15 = 114.29(15), O1−Ti1−N4 = 76.97(11), O1−Ti1−N41 = 83.34(11).

bridging oxygens and are best described as having highly distorted trigonal bipyramidal titanium centers, with identifiable $C_2$-axes perpendicular to each Ti−O−Ti−O plane. The role of bridging oxygens in creating polynuclear species is common in titanium(IV) chemistry[10b,c,e] and was not unexpected. Like the bisamido compounds **2a** and **2d**, **4** prefers to bridge through the amino alcohol oxygens rather than the O$^i$Pr ligands.[20] Clear in each of these structures are the different isopropoxide and amido sites present on each Ti-center, one *syn* and the second *anti* to the *cis*-phenyl substit-

(20) For an example of bridging diol ligands predominating over bridging −O$^i$Pr ligands, see: Boyle, T. J.; Barnes, D. L.; Heppert, J. A.; Morales, L.; Takusagawa, F. *Organometallics* **1992**, *11*, 1112−1126. For examples of bridging −O$^i$Pr groups in Ti(IV) compounds, see refs 10b and 10e.

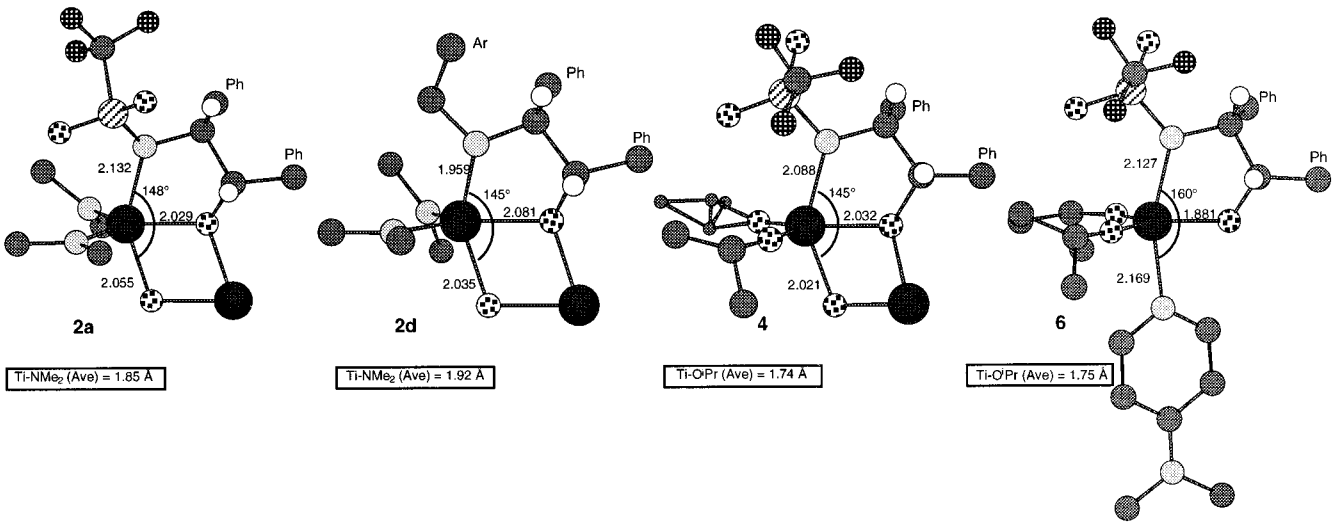


**Figure 5.** Selected bond distances and angles for **2a**, **2d**, **4**, and **6**. The Ti dimers (**2a**, **2d**, and **4**) are depicted with the ligands stripped from the bottom Ti. The phenyl groups have been removed from the backbone of each compound for clarity.

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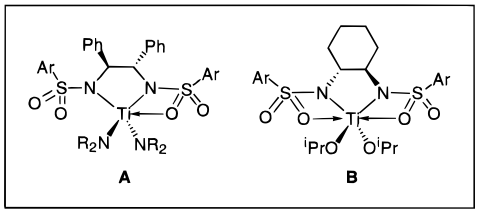
uents on the backbone, consistent with solution spectroscopic studies.

Analysis of these structures indicates that the metrical parameters are unexceptional compared to known Ti(IV) complexes.[9,21] Trends in bond lengths across the family of structures are instructive however (Figure 5). For example, although the Ti−$NMe_2$ bond lengths in **2a** and **2d** fall into the normal range for dialkyl amido ligands (1.85 and 1.92 Å, respectively), the shorter bond lengths in **2a** probably reflect the enhanced $p_\pi$-donation of the $\pi$-basic $NMe_2$ ligand to the more electron-deficient metal. Similarly reflecting the better donation (both $\sigma$ and $\pi$) of the N($CH_2$Ar) vs N(Tf) moiety, the Ti−NR-($CH_2$Ar) bond length in **2d** (1.96 Å) is significantly shorter than the Ti−NR(Tf) bond lengths in **2a**, **4**, and **6** (2.13, 2.09, and 2.13 Å, respectively), the latter distances also being consistent with known Ti−sulfonamide bond lengths.[9a,b] The alkoxide bridges that create the Ti−O−Ti−O rings in **2a**, **2d**, and **4** are expectedly longer (2.02−2.10 Å) than typical terminal Ti−OR linkages (1.76−1.92 Å), but are otherwise similar to known Ti−O(R)−Ti bridges.[6,10b−e] Interestingly enough, there is little difference between the two types of bridging Ti−O bond lengths, except in **2d**, which has a lengthened Ti−O (internal) bond length relative to the second bridging alkoxide.[22] This lengthening may be a structural response to the shortened Ti−NR($CH_2$Ar) bond length. The terminal Ti−O$^i$Pr bond lengths in both **4** and **6** are consistent with literature values.[20]

Notable changes in bond lengths upon coordination of DMAP to **4** are an elongation of the Ti−N(sulfonamide) bond (from 2.088 to 2.127 Å) and a shortening of the Ti−O(amino alkoxide) bond (from 2.032 to 1.881 Å). These observations are consistent with an increase in the electron-donating character of the ligand *trans* to the NR(Tf) ligand (i.e., $\mu$-O to DMAP) relaxing this bond length and/or reflecting the response of the N,O ligand as it shifts from a bridging to a terminal alkoxide mode. Recall that a reverse of this effect was observed in **2d** as the shortened Ti−NR($CH_2$Ar) ligand caused a sympathetic lengthening of the Ti−O bond. The Ti−N(DMAP) bond length at 2.169 Å is unsurprisingly longer than the $NR_2$ ligands, but is similar to the triflamide bond lengths and literature values.[16] A second consequence of the new axial ligand no longer bridging is the larger diaxial bond angle (160°), which now more closely resembles an ideal trigonal bipyramid.

An additional point of interest in structures **2a**, **4**, and **6** is the absence of a secondary bonding interaction by the sulfonamide oxygens as seen in monomeric titanium (IV)−bissulfonamide compounds (**A** and **B**).[9a−c] Presumably the bridging oxygens and DMAP provide an electronically more satisfying ligand to the electrophilic metal centers.




## Summary

In summary, we have synthesized and characterized several chiral Ti(IV)−amino alcohol complexes based on N-substituted derivatives of (1*S*,2*R*)-(+)-2-amino-1,2-diphenylethanol. X-ray crystal structures of compounds **2a**, **2d**, and **4** and VPO molecular weight measurements on **2**−**4** show these compounds to be dimeric in the solid state and in solution, each bridging through the amino alcohol oxygen. By VPO, the DMAP adducts **5** and **6** show a concentration-dependent monomer−dimer equilibrium, despite the fact that an X-ray structure of **6** shows it to be monomeric in the solid state. The latter observation is especially relevant in the context of nonlinear effects in asymmetric catalysis, as it shows

(21) (a) Johnson, A. R.; Davis, W. M.; Cummins, C. C. *Organometallics* **1996**, *15*, 3825−3835. (b) Clark, H. C. S.; Cloke, F. G. N.; Hitchcock, P. B.; Love, J. B.; Wainwright, A. P. *J. Organomet. Chem.* **1995**, *501*, 333−340. (c) Lappert, M. F.; Power, P. P.; Sanger, A. R.; Srivastava, R. C. *Metal and Metalloid Amides*; Ellis Horwood Limited: Chichester, 1980; Chapter 8.

(22) The internal alkoxide refers to the oxygen that is part of the N,O ligand coordinated to one Ti-center. The second alkoxide oxygen refers to the ligand primarily coordinated to the other Ti-center.

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that it is possible for dimers to coordinate and ultimately activate (i.e., like **5a**/**6a**) carbonyl substrates for catalysis. It is therefore conceivable that the nonlinear effects reported for Ti−Lewis acid catalysts might actually reflect the different reactivities of homo- and heterosubstituted dimers, rather than the normally invoked equilibrating reactive-monomer/inactive-dimer scenario.[17,18]

## Experimental Section

**General Details.** All reactions were carried out under an atmosphere of dry argon or dinitrogen using standard Schlenk techniques or in an MBraun Lab-Master 100 glovebox. All solvents used were dried either by passing through a column of activated alumina (toluene, hexanes, pentane, $CH_2Cl_2$) or by distillation from Na/benzophenone−ketyl (THF). Most deuterated solvents ($C_6D_6$, $CD_2Cl_2$, and THF-$d_8$) were vacuum-transferred from either Na/benzophenone−ketyl (nonchlorinated solvents) or $CaH_2$ ($CD_2Cl_2$) and stored under an argon or dinitrogen atmosphere. All solvents (protiated and deuterated) were also freeze−pump−thaw degassed before use. $Ti(NR_2)_4$[23] and the sulfonylated amino alcohols[24] were prepared according to literature procedures or via the modifications described herein. Diethylamine was distilled from $CaH_2$, triethylphosphine was freeze−pump−thaw degassed, and all other reagents were used as obtained from commercial sources.

$^1H$ and $^{13}C$ NMR spectra were obtained at ambient temperatures on a Bruker AC200 spectrometer. All $^{19}F$ and $^{31}P$ NMR spectra were recorded on a Varian Gemini 2000 spectrometer (300 MHz, $^1H$) with $CFCl_3$, $PEt_3$, and $PCl_3$ as external references. Optical rotation measurements were obtained on a Jasco DIP-1000 digital polarimeter and VPO measurements on a Knauer vapor pressure osmometer. Elemental analyses were performed by E + R Microanalytical Laboratory, Inc., Parsippany, NJ.

**HOCHPhCHPh(H)N(Tf) (1a).** (1*S*,2*R*)-(+)-2-Amino-1,2-diphenylethanol (2.84 g, 13.3 mmol), $NEt_3$ (3.80 mL, 27.3 mmol), and a small amount of DMAP were combined in $CH_2Cl_2$ (150 mL) and cooled to −78 °C. Over the course of 20 min, $Tf_2O$ (2.50 mL, 14.9 mmol) in $CH_2Cl_2$ (10 mL) was added dropwise to the cooled, magnetically stirred reaction solution. After the addition was complete, the reaction solution was allowed to stir at 23 °C for 2 h and was then poured into 5% $NaHCO_3$ (150 mL). The organic phase was washed three times with 1 M HCl and one time with brine, dried over anhydrous $MgSO_4$, and filtered, and the solvent was removed in vacuo to yield a yellow solid. This material was dissolved in 15% EtOAc/85% hexane and run through a pad of silica gel using 15% EtOAc/85% hexane as eluent. The filtrate was concentrated in vacuo to dryness and the resultant solid recrystallized from $CH_2Cl_2$/hexane to yield a white solid, which was collected by filtration and dried under vacuum (3.37 g, 9.77 mmol, 74%). $^1H$ NMR (200 MHz, $C_6D_6$): $\delta$ 6.92 (m, 6 H, Ar), 6.62 (m, 4 H, Ar), 5.71 (d, $J$ = 8.8 Hz, 1 H, −C*H*), 4.71 (dd, $J$ = 8.6, 3.2 Hz, 1 H, −C*H*), 4.57 (m, 1 H, −N*H*), 1.21 (d, $J$ = 4.2 Hz, 1 H, −O*H*). $^{13}C\{^1H\}$ NMR (50.28 MHz, $CDCl_3$): $\delta$ 138.3, 134.9, 128.4, 128.3, 128.1, 127.6, 126.1 (Ph), 76.9, 63.8 (−*C*H).[25] $^{19}F$ NMR (282.33 MHz, $C_6D_6$): $\delta$ −77.9 (s, −C$F_3$). $[\alpha]_D^{22.4}$ = +60.9° (*c* 0.57, $CHCl_3$). Anal. Calcd for $C_{15}H_{14}F_3NO_3S$: C, 52.17; H, 4.09; N, 4.06. Found: C, 52.15; H, 4.03; N, 4.00.

**HOCHPhCHPh(H)N[SO$_2$(4-C$_6$H$_4$−Me)] (1b).** (1*S*,2*R*)-(+)-2-Amino-1,2-diphenylethanol (956 mg, 4.48 mmol), $NEt_3$ (1.40 mL, 10.0 mmol), and a small amount of DMAP were combined in $CH_2Cl_2$ (40 mL) and cooled to −78 °C. Over the course of 20 min, *p*-$(CH_3)C_6H_4SO_2Cl$ (883 mg, 4.63 mmol) in $CH_2Cl_2$ (10 mL) was added dropwise to the cooled, magnetically stirred reaction solution. After the addition was complete, the solution was allowed to warm to 23 °C and stir for 2 h and was then treated with 5% $NaHCO_3$ (10 mL) and 1 M HCl (20 mL). The resultant biphasic mixture was stirred for 10 min and then filtered to isolate the insoluble white product. The crude solid was washed with $CH_2Cl_2$ and hexane and dried under vacuum (1.47 g, 4.00 mmol, 89%). $^1H$ NMR (200 MHz, acetone-$d_6$): $\delta$ 7.49 (d, $J$ = 8.2 Hz, 2 H, Ar), 7.15, 7.02 (m, 12 H total, Ar), 4.95 (d, $J$ = 5 Hz, 1 H, −C*H*), 4.51 (d, $J$ = 4.8 Hz, 1 H, −C*H*), 2.32 (s, 3 H, −C$H_3$). $^{13}C\{^1H\}$ NMR (50.28 MHz, acetone-$d_6$): $\delta$ 142.7, 130.0, 129.6, 128.5, 128.1, 127.8, 127.6, 127.6 (Ar), 77.0, 64.6 (−*C*H), 21.4 (−*C*$H_3$).[25] $[\alpha]_D^{26.1}$ = +25.8° (*c* 0.50, acetone). See ref 24 for another synthetic route to and further characterization of **1b**.

**HOCHPhCHPh(H)N[SO$_2$(4-C$_6$H$_4$−CMe$_3$)] (1c).** (1*S*,2*R*)-(+)-2-Amino-1,2-diphenylethanol (1.13 g, 5.30 mmol), $NEt_3$ (1.70 mL, 12.2 mmol), and a small amount of DMAP were combined in $CH_2Cl_2$ (40 mL) and cooled to −78 °C. Over the course of 20 min, *p*-$[(CH_3)_3C]C_6H_4SO_2Cl$ (1.31 g, 5.63 mmol) in $CH_2Cl_2$ (10 mL) was added dropwise to the cooled, magnetically stirred reaction solution. After the addition was complete, the solution was allowed to warm to 23 °C and stir for 2 h and was then poured into 5% $NaHCO_3$ (50 mL). The organic phase was washed three times with 1 M HCl (50 mL) and one time with brine (50 mL), dried over anhydrous $MgSO_4$, and evaporated to dryness. The resultant white solid was then washed with hexane and dried under vacuum (2.0 g, 4.9 mmol, 93%). $^1H$ NMR (200 MHz, $CDCl_3$): $\delta$ 7.25, 6.98, 6.77, 6.55 (m, 14 H total, Ar), 5.22 (d, $J$ = 8.2 Hz, 1 H, −C*H*), 4.79 (m, 1 H, −N*H*), 4.34 (dd, $J$ = 8.4, 4.5 Hz, 1 H, −C*H*), 2.18 (d, $J$ = 4.6 Hz, 1 H, −O*H*), 1.03 (s, 9 H, −C(C$H_3$)$_3$). $^{13}C\{^1H\}$ NMR (50.28 MHz, $CDCl_3$): $\delta$ 157.0, 139.1, 136.9, 135.6, 128.1, 128.0, 127.8, 127.6, 126.8, 126.5, 125.6, 102.5 (Ar), 76.9, 63.2 (−*C*H), 34.9 (−*C*(CH$_3$)$_3$), 31.0 (−C(*C*H$_3$)$_3$). $[\alpha]_D^{26.3}$ = +21.6° (*c* 0.50, $CH_2Cl_2$).

**HOCHPhCHPh(H)N(CH$_2$[2,4,6-C$_6$H$_2$−Me$_3$]) (1d).** (1*S*,2*R*)-(+)-2-Amino-1,2-diphenylethanol (2.70 g, 12.7 mmol) and mesitaldehyde (2.20 mL, 14.9 mmol) were combined in toluene (50 mL) and refluxed for 1.5 h to azeotropically remove the water produced by the reaction. Once cooled to room temperature, the reaction solution was diluted with MeOH (50 mL) and $NaBH_4$ (0.580 g, 15.3 mmol) was slowly added. The resultant reaction solution was allowed to stir at 23 °C for 16 h and then acidified with 1 M HCl until a white precipitate formed. The resulting suspension was washed with EtOAc and then basified (pH ≥ 10) with 1 M NaOH, followed by the addition of EtOAc. The resultant two phases were separated, and the aqueous layer was extracted two times with EtOAc. The combined organic extracts were washed with brine, dried over anhydrous $MgSO_4$, filtered, and evaporated to dryness. The crude white solid was recrystallized from 6:1 hexane/$CH_2Cl_2$, and pure compound was isolated by filtration and dried under vacuum (3.3 g, 9.6 mmol, 73%). $^1H$ NMR (200 MHz, $C_6D_6$): $\delta$ 7.25, 7.12, 7.03 (m, 10 H total, Ar), 6.70 (s, 2 H, Ar), 4.65 (d, $J$ = 6.2 Hz, 1 H, −C*H*), 3.86 (d, $J$ = 6.2 Hz, 1 H, −C*H*), 3.57, 3.44 (d, $J$ = 11.8 Hz, 2 H total, −C$H_2$), 2.10, 2.09 (s, 9 H total, −C$H_3$). $^{13}C\{^1H\}$ NMR (50.28 MHz, $CDCl_3$): $\delta$ 140.5, 139.7, 137.0, 136.6, 133.1, 128.9, 128.3, 128.1, 127.7, 126.9 (Ar), 76.7, 69.8 (−*C*H), 45.9 (−*C*$H_2$), 20.8, 19.2 (−C$H_3$).[25] $[\alpha]_D^{26.0}$ = −5.1° (*c* 0.50, $CH_2Cl_2$). Anal. Calcd for $C_{24}H_{27}NO$: C, 83.44; H, 7.88; N, 4.05. Found: C, 83.48; H, 8.01; N, 4.13.

**HOCHPhCHPh(H)N(Si[CHMe$_2$]$_3$) (1e).** (1*S*,2*R*)-(+)-2-Amino-1,2-diphenylethanol (1.2 g, 5.6 mmol) was dissolved in $CH_2Cl_2$ (50 mL) and cooled to −78 °C. To this magnetically stirring solution was added neat $^iPr_3SiOSO_2CF_3$ (1.6 mL, 6.0 mmol), precipitating a white solid. Triethylamine (1.0 mL, 7.2 mmol) was added to the suspension, generating a homogeneous solution that was warmed to 23 °C and stirred for 1 h. The

(23) For the synthesis of $Ti(NR_2)_4$ see: Bradley, D. C.; Thomas, I. M. *J. Chem. Soc.* **1960**, 3857−3861.

(24) For the synthesis of (**1b**) see: Li, G.; Chang, H.; Sharpless, K. B. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 5, 451−454.

(25) Not all aromatic carbon atoms were observed in the $^{13}C$ NMR spectra.

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solution was evaporated to dryness and the residual crude oil dissolved in hexane (10 mL) and cooled to 0 °C. The solution was filtered via cannula from the white precipitate and evaporated to dryness under vacuum to yield a pale yellow oil (1.7 g, 4.6 mmol, 82%). $^1$H NMR (200 MHz, $C_6D_6$): $\delta$ 7.04 (m, 10 H, Ph), 4.82 (dd, $J$ = 6.0, 4.6 Hz, 1 H, −C*H*), 4.24 (dd, $J$ = 12.2, 4.4 Hz, 1 H, −C*H*), 2.19 (d, $J$ = 6.4 Hz, 1 H, −O*H*), 1.34 (d, $J$ = 12.4 Hz, 1H, −N*H*), 1.00 (m, 21 H, −Si[C*H*(C$H_3$)$_2$]$_3$). $^{13}$C{$^1$H} NMR (50.28 MHz, $CD_2Cl_2$): $\delta$ 143.8, 141.6, 128.3, 128.2, 127.8, 127.3 (Ar), 79.6, 62.8 (−*C*H), 18.7, 18.6 (−Si[CH-(*C*H$_3$)$_2$]$_3$), 12.6 (−Si[*C*H(CH$_3$)$_2$]$_3$).[25] $[\alpha]_D^{26.2} = -29.3°$ (*c* 0.51, $CH_2Cl_2$). Anal. Calcd for $C_{23}H_{35}NOSi$: C, 74.74; H, 9.54; N, 3.79. Found: C, 72.72; H, 9.82; N, 4.13.

**[Ti[OCHPhCHPhN(Tf)](NMe$_2$)$_2$]$_2$ (2a).** Ti(NMe$_2$)$_4$ (430 mg, 1.92 mmol) and **1a** (657 mg, 1.90 mmol) were combined in toluene (15 mL) at 23 °C, resulting in an orange homogeneous solution. The reaction solution was magnetically stirred for 20 h and then concentrated in vacuo to several milliliters. Hexane was added via syringe (5 mL), precipitating a yellow solid from the orange solution. The slurry was cooled to −78 °C for 1 h and then filtered via cannula to yield a yellow solid. The crude solid was redissolved in toluene (3 mL), cooled to 0 °C, and filtered to yield a purified yellow solid (502 mg, 1.05 mmol, 55%). Crystals suitable for X-ray crystallography were grown at 0 °C from a $C_6D_6$ solution layered with hexane. $^1$H NMR (200 MHz, $C_6D_6$): $\delta$ 6.90, 6.82, 6.58, 6.32 (m, 20 H, Ph), 5.66 (d, $J$ = 4.0 Hz, 2 H, −C*H*), 5.03 (d, $J$ = 4.4 Hz, 2 H, −C*H*), 3.22 (s, 12 H, −C$H_3$), 2.75 (s, 12 H, −C$H_3$). $^{13}$C{$^1$H} NMR (50.28 MHz, $CD_2Cl_2$): $\delta$ 139.0, 138.0, 128.9, 128.6, 128.1, 127.9, 127.8, 127.5 (Ar), 120.7 (q, $^1J_{CF}$ = 327 Hz, −*C*F$_3$), 95.4, 71.2 (−*C*H), 46.1, 44.3 (−*C*H$_3$). $^{19}$F NMR (282.33 MHz, $C_6D_6$): $\delta$ −74.8 (s, −C*F*$_3$). Anal. Calcd for $C_{42.6}H_{53.3}F_6N_6O_6S_2Ti_2$ (**2a** with 0.66 equiv toluene by $^1$H NMR):[26] C, 50.21; H, 5.27; N, 8.24. Found: C, 50.37; H, 5.45; N, 8.00.

**[Ti[OCHPhCHPhN(SO$_2$(4-C$_6$H$_4$−Me))](NMe$_2$)$_2$]$_2$ (2b).** Ti(NMe$_2$)$_4$ (219 mg, 0.978 mmol) and **1b** (359 mg, 0.977 mmol) were combined in toluene (20 mL) at 23 °C, resulting in an orange homogeneous solution. The reaction solution was magnetically stirred for 20 h and then concentrated in vacuo to several milliliters. Pentane was added via syringe (5 mL), precipitating a yellow solid from the orange solution. The slurry was cooled to −78 °C for 1 h and filtered via cannula. The yellow solid was washed with pentane to yield the purified product (381 mg, 0.758 mmol, 78%). $^1$H NMR (200 MHz, $C_6D_6$): $\delta$ 7.66 (d, $J$ = 7.8 Hz, 4 H, Ar), 6.87, 6.71, 6.51 (m, 20 H total, Ar), 6.38 (d, $J$ = 7.4 Hz, 4 H, Ar), 5.95 (d, $J$ = 4.6 Hz, 2 H, −C*H*), 4.67 (d, $J$ = 4.8 Hz, 2 H, −C*H*), 3.49, 3.10 (s, 12 H each, −N(C$H_3$)$_2$), 1.75 (s, 6 H, −C$H_3$). $^{13}$C{$^1$H} NMR (50.28 MHz, $CD_2Cl_2$): $\delta$ 141.6, 140.6, 140.0, 139.5, 129.1, 128.8, 128.3, 128.0, 127.8, 127.7, 127.0, 126.5 (Ar), 95.2, 72.2 (−*C*H), 46.3, 44.6 (−N(C$H_3$)$_2$), 21.4 (−C$H_3$; 2 are expected). Anal. Calcd for $C_{51.4}H_{63.6}N_6O_6S_2Ti_2$ (**2b** with 0.2 equiv toluene by $^1$H NMR):[26] C, 60.44; H, 6.28; N, 8.23. Found: C, 60.24; H, 6.09; N, 8.02.

**[Ti[OCHPhCHPhN(SO$_2$[4-C$_6$H$_4$−CMe$_3$])](NMe$_2$)$_2$]$_2$ (2c).** Ti(NMe$_2$)$_4$ (200 mg, 0.893 mmol) and **1c** (365 mg, 0.891 mmol) were combined in toluene (20 mL) at 23 °C, resulting in an orange homogeneous solution. The reaction solution was magnetically stirred for 20 h and then concentrated in vacuo to several milliliters. Hexane was added via syringe (5 mL), precipitating a yellow solid from the orange solution. The slurry was cooled to −78 °C for 1 h and filtered via cannula. The yellow solid was washed with hexane to yield the purified product (301 mg, 0.554 mmol, 62%). $^1$H NMR (200 MHz, $C_6D_6$): $\delta$ 7.66, 6.91, 6.71, 6.57 (m, 24 H total, Ar), 6.33 (d, $J$ = 7.4 Hz, 4 H, Ar), 5.96 (d, $J$ = 4.8 Hz, 2H, −C*H*), 4.64 (d, $J$ = 4.6 Hz, 2H, −C*H*), 3.52, 3.12 (s, 12 H each, −N(C$H_3$)$_2$), 0.97 (s, 18 H, −C(C$H_3$)$_3$). $^{13}$C{$^1$H} NMR (50.28 MHz, $CD_2Cl_2$): $\delta$ 154.3, 140.4, 139.3, 139.2, 128.8, 127.9, 127.8, 127.5, 127.5, 126.9, 126.3, 124.9 (Ar), 95.1, 72.0 (−*C*H), 46.1, 44.4 (−N(C$H_3$)$_2$), 34.8 (−*C*(CH$_3$)$_3$), 31.1 (−C(*C*H$_3$)$_3$). Anal. Calcd for $C_{61.6}H_{80.4}N_6O_6S_2Ti_2$ (**2c** with 0.9 equiv toluene by $^1$H NMR):[26] C, 64.00; H, 6.99; N, 7.18. Found: C, 63.52; H, 6.92; N, 6.73.

**[Ti[OCHPhCHPhN(CH$_2$[2,4,6-C$_6$H$_2$−Me$_3$])](NMe$_2$)$_2$]$_2$ (2d).** Ti(NMe$_2$)$_4$ (389 mg, 1.74 mmol) and **1d** (599 mg, 1.73 mmol) were combined in toluene (20 mL) at 23 °C, resulting in an orange homogeneous solution. The reaction solution was magnetically stirred at 90 °C for 18 h, cooled to room temperature, and then concentrated in vacuo to several milliliters. Hexane was added via syringe (5 mL), precipitating a yellow solid from the solution. The solution was cooled to −78 °C for 1 h and filtered via cannula to yield the yellow solid (430 mg, 0.896 mmol, 52%). Crystals suitable for X-ray crystallography were also grown from a saturated toluene solution upon slow diffusion of hexane. $^1$H NMR (200 MHz, $C_6D_6$): $\delta$ 6.96, 6.89, 6.73 (m, 24 H total, Ar), 6.10 (d, $J$ = 5.0 Hz, 2 H, −C*H*), 5.03 (d, $J$ = 11.2 Hz, 2 H, −C*H*HAr), 4.81 (d, $J$ = 11.4 Hz, 2 H, −CH*H*Ar), 4.25 (d, $J$ = 4.6 Hz, 2 H, −C*H*), 3.26, 2.98 (s, 12 H each, −N(C$H_3$)$_2$), 2.15 (s, 6 H, −C$H_3$), 2.12 (s, 12 H, −C$H_3$). $^{13}$C{$^1$H} NMR (50.28 MHz, THF-$d_8$): $\delta$ 143.8, 143.4, 138.8, 135.9, 134.6, 130.2, 129.1, 128.1, 127.5, 127.4, 126.6, 126.5 (Ar), 91.4, 78.4 (−*C*H), 54.9 (−*C*H$_2$), 45.9, 45.8 (−N(*C*H$_3$)$_2$), 20.9, 20.5 (−*C*H$_3$). Anal. Calcd for $C_{56}H_{74}N_6O_2Ti_2$: C, 70.13; H, 7.78; N, 8.76. Found: C, 69.98; H, 8.00; N, 8.54.

**[Ti[OCHPhCHPhN(Tf)](NEt$_2$)$_2$]$_2$ (3).** Ti(NEt$_2$)$_4$ (614 mg, 1.82 mmol) and **1a** (630 mg, 1.83 mmol) were combined in toluene (20 mL) at 23 °C, resulting in a red homogeneous solution, which became heterogeneous over the course of the reaction. The reaction solution/slurry was magnetically stirred for 20 h and then concentrated in vacuo to several milliliters. Hexane was added via syringe (5 mL), precipitating an orange solid from the red solution. The solution was cooled to −78 °C for 1 h and filtered via cannula. The orange solid was washed with hexane to yield the purified product (777 mg, 1.45 mmol, 80%). $^1$H NMR (200 MHz, $C_6D_6$): $\delta$ 6.96, 6.92, 6.70 (m, 20 H, Ph), 5.93 (d, $J$ = 4.4 Hz, 2 H, −C*H*), 5.10 (d, $J$ = 4.2 Hz, 2 H, −C*H*), 4.75, 3.94, 3.70, 3.24 (m, 4 H each, −C$H_2$CH$_3$), 0.91 (m, 24 H, −CH$_2$C$H_3$). $^{13}$C{$^1$H} NMR (50.28 MHz, $CD_2Cl_2$): $\delta$ 138.9, 137.2, 129.4, 128.9, 128.3, 127.8, 127.4, 126.5 (Ar), 95.4, 71.3 (−*C*H), 45.7, 44.4 (−*C*H$_2$CH$_3$), 12.6, 11.7 (−CH$_2$*C*H$_3$).[27] $^{19}$F NMR (282.33 MHz, $C_6D_6$): $\delta$ −74.1 (s, −C*F*$_3$). Anal. Calcd for $C_{46}H_{64}F_6N_6O_6S_2Ti_2$: C, 51.59; H, 6.02; N, 7.85. Found: C, 52.09; H, 6.13; N, 7.42.

**[Ti[OCHPhCHPhN(Tf)](O$^i$Pr)$_2$]$_2$ (4).** Ti(O$^i$Pr)$_4$ (435 mg, 1.53 mmol) and **1a** (520 mg, 1.51 mmol) were combined in toluene (25 mL) at 23 °C, resulting in a clear homogeneous solution. The reaction solution was magnetically stirred for 20 h at 60 °C and then concentrated in vacuo to dryness. $CH_2Cl_2$ was added via syringe (15 mL), and the solution was cooled to −78 °C for 1 h. The resultant white precipitate was then isolated by filtering off (via cannula) the pale yellow solution. The product was then dried under vacuum (439 mg, 0.431 mmol, 57%). Crystals suitable for X-ray crystallography were also grown from a $CD_2Cl_2$ solution at 0 °C. $^1$H NMR (200 MHz, $C_6D_6$): $\delta$ 6.95, 6.87 (m, 20 H total, Ph), 6.23 (d, $J$ = 5.4 Hz, 2 H, −C*H*), 5.20 (m, 2 H, −C*H*(CH$_3$)$_2$), 5.18 (d, $J$ = 6.0 Hz, 2 H, −C*H*), 3.96 (m 2 H, −C*H*(CH$_3$)$_2$), 1.35 (m, 12 H, CH(C$H_3$)$_2$), 0.85 (d, 12 H, CH(C$H_3$)$_2$). $^{13}$C{$^1$H} NMR (50.28 MHz, $CD_2Cl_2$): $\delta$ 139.3, 137.8, 129.0, 128.5, 128.2, 128.1, 127.8, 127.8 (Ar), 93.6, 87.4, 86.9, 72.2 (−*C*H), 26.2, 25.9, 25.1, 24.5 (−*C*H$_3$). $^{19}$F NMR (282.33 MHz, $C_6D_6$): $\delta$ −74.6 (s, −C*F*$_3$). Anal. Calcd for $C_{44}H_{54}F_6Cl_6N_2O_{10}S_2Ti_2$: C, 46.79; H, 4.93; N, 2.54. Found: C, 46.80; H, 4.99; N, 2.56.

**Ti[OCHPhCHPhN(Tf)](NEt$_2$)$_2$[DMAP] (5).** **3** (374 mg, 0.349 mmol) and DMAP (85.7 mg, 0.701 mmol) were combined

(26) Several Ti(IV) compounds consistently and tenaciously retained fractional amounts of solvent, particularly toluene. Efforts to remove the residual solvent before analysis (by drying under reduced pressure for an extended amount of time or by sequential washings with a lower boiling solvent) were unsuccessful or resulted in decomposition.

(27) The $CF_3$ resonance was not observed in the $^{13}$C NMR spectra.

in toluene (10 mL) at 23 °C, resulting in an orange homogeneous solution. The reaction solution was magnetically stirred for 3 h at 23 °C and then concentrated in vacuo to dryness. The resultant orange solid was washed with pentane (5 mL) and dried under vacuum (320 mg, 0.487 mmol, 70%). $^1$H NMR (200 MHz, $C_6D_6$): $\delta$ 8.52 (d, $J$ = 7.0 Hz, 2 H, DMAP Ar), 7.24, 7.06 (m, 10 H total, Ph), 6.80 (d, $J$ = 5.2 Hz, 1 H, −C*H*), 5.71 (d, $J$ = 4.8 Hz, 1 H, −C*H*), 5.65 (d, $J$ = 7.0 Hz, 2 H, DMAP Ar), 4.18, 3.99 (m, 8 H total, −C$H_2$CH$_3$), 1.98 (s, 6 H, −N(C$H_3$)$_2$), 1.11, 0.99 (m, 12 H total, −CH$_2$C$H_3$). $^{13}$C{$^1$H} NMR (50.28 MHz, $CD_2Cl_2$): $\delta$ 149.8 (DMAP Ar), 143.3, 140.8, 129.0, 127.8, 127.7, 126.7, 126.3 (Ph), 106.2 (DMAP Ar), 90.0, 73.3 (−*C*H), 45.7, 45.0 (−N(*C*H$_2$CH$_3$)$_2$), 39.4 (−N(*C*H$_3$)$_2$), 13.4, 13.2 (−N(CH$_2$*C*H$_3$)$_2$).[25,27] $^{19}$F NMR (282.33 MHz, $C_6D_6$): $\delta$ −74.9 (s, −C$F_3$).

**Ti[OCHPhCHPhN(Tf)](O$^i$Pr)$_2$[DMAP] (6).** **4** (439 mg, 0.431 mmol) and DMAP (106 mg, 0.867 mmol) were combined in toluene (10 mL) at 23 °C, resulting in a pale yellow solution. The reaction solution was magnetically stirred for 3 h at 23 °C and then concentrated in vacuo to dryness. The resultant white solid was triterated with hexane (5 mL) and dried under vacuum (395 mg, 0.625 mmol, 73%). Crystals suitable for X-ray crystallography were grown from $CH_2Cl_2$/pentane. $^1$H NMR (200 MHz, $C_6D_6$): $\delta$ 8.55 (m, 2 H, DMAP Ar), 7.56 (d, $J$ = 5.8 Hz, 2 H, Ph), 7.03 (m, 10 H total, Ph + −C*H*), 5.71 (d, $J$ = 3.6 Hz, 1 H, −C*H*), 5.64 (m, 2 H, DMAP Ar), 5.08 (m, 2 H, −C*H*(CH$_3$)$_2$), 1.98 (s, 6 H, −N(C$H_3$)$_2$), 1.49 (d, $J$ = 4.6 Hz, 3 H, −CH(C$H_3$)$_2$), 1.39 (d, $J$ = 4.6 Hz, 6 H, −CH(C$H_3$)$_2$), 1.31 (d, $J$ = 4.6 Hz, 3 H, −CH(C$H_3$)$_2$). $^{13}$C{$^1$H} NMR (50.28 MHz, $CD_2Cl_2$): $\delta$ 155.9, 149.2 (DMAP Ar), 142.1, 140.6, 128.9, 127.8, 127.2, 126.8, 126.5 (Ph), 106.4 (DMAP Ar), 90.6, 74.6 (−*C*H), 82.1, 81.0 (−O*C*H(CH$_3$)$_2$), 39.5 (−N(*C*H$_3$)$_2$), 25.9 (−OCH(*C*H$_3$)$_2$; 4 are expected).[25,27] $^{19}$F NMR (282.33 MHz, $C_6D_6$): $\delta$ −75.0 (s, −C$F_3$). Anal. Calcd for $C_{28}H_{36}F_3N_3O_5STi$: C, 53.25; H, 5.75; N, 6.65. Found: C, 53.21; H, 5.53; N, 6.80.

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**Supporting Information Available:** Tables of crystallographic data collection parameters, bond distances, bond angles, bond torsion angles, atomic parameters, and isotropic and anisotropic (for non-hydrogen atoms) thermal parameters (46 pages). Ordering information is given on any current masthead page.

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