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Synthesis and Structure of Titanium(IV) Amido Complexes Containing C_2-Symmetric Bis(sulfonamide) Ligands

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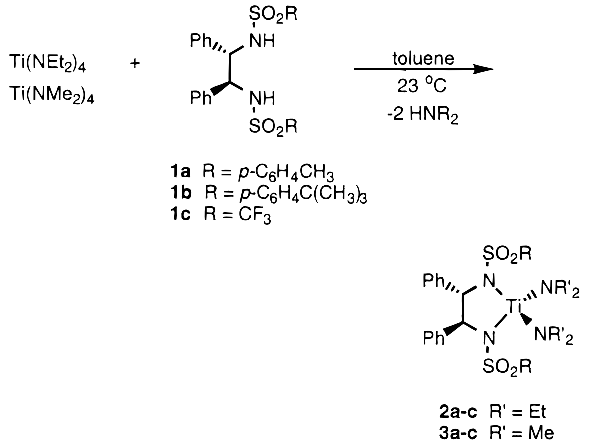
Mixed-amido Ti(IV) compounds of the type $Ti(NR'_2)_2[N(SO_2R)CHPhCHPhN(SO_2R)]$ (R′= Me, Et; R = p-$C_6H_4CH_3$, p-$C_6H_4C(CH_3)_3$, CF_3) were synthesized by the aminolysis of $Ti(NR'_2)_4$ with bis(sulfonamide) ligands **1a**−**c**. The structure of compound **3b**, determined by X-ray crystallography, indicates that one oxygen from a single SO_2 group binds to the metal center in the solid state, breaking the C_2 symmetry. These Ti−bis(sulfonamide) complexes, when treated with 2,6-dimethylphenol, generate putative $Ti(OAr)_2$(bis(sulfonamide)) intermediates which display unorthodox disproportionation behavior.

Group IV organometallic compounds containing bidentate bis(amido) ligands are generating increased interest of late, especially in the area of catalysis. *In situ* generated titanium(IV) bis(sulfonamide) complexes of the type $TiX_2[(RSO_2)N^*N(SO_2R)]$ (X = halide, alkoxide; R = Ar, CF_3; N*N = chiral diamine) have been used as catalysts for the asymmetric alkylation of aldehydes[1] and the cyclopropanation of allylic alcohols with dialkylzinc reagents.[2,3] Other non-titanium Lewis acid catalysts utilizing the same class of chiral bis(sulfonamide) ligands are also known to stereospecifically catalyze the Diels−Alder,[4] Claisen,[5] [2 + 2] cycloaddition,[6] and enolization−amination reactions.[7]

We report herein the synthesis and structure of Ti(IV) mixed-amido compounds of general formula $Ti(NR'_2)_2$-$[N(SO_2R)CHPhCHPhN(SO_2R)]$ and their reactivity with 2,6-dimethylphenol (**4**). The described mixed-amido compounds are derived from the aminolysis of $Ti(NR'_2)_4$ (R′ = Me, Et)[8] and chiral bis(sulfonamides) derived from (1*S*,2*S*)-1,2-diphenylethylenediamine (eq 1).[9] The products from reactions with $Ti(NEt_2)_4$ (**2a**−**c**) could be isolated in good yields (65−85%) as pure compounds, except for fractional amounts of $HNEt_2$ and solvent that were consistently and tenaciously retained. Compounds **3a**−**c**, also retaining fractional amounts of $HNMe_2$ and solvent, were consistently isolated in lower purity (80−95% pure, 55−88% yield). When reactions of $Ti(NMe_2)_4$ and **1a**−**c** were monitored by ^1H NMR (in C_6D_6 or CD_2Cl_2), clean conversion to the desired products **3a**−**c** (100%) and concomitant $HNMe_2$ was observed. However, concentration of the reaction solutions to solids leads to the production of secondary materials of unknown composition.[10] Pure, crystalline **3b** could be isolated after repeated recrystallizations from toluene/hexane, albeit with a reduced yield (≤20%). All of the mixed-amido compounds (**2a**−**c** and **3a**−**c**) are air-, water-, and temperature-sensitive, showing considerable decomposition at room temperature over a 24 h period, both in solution and in the solid state. However, when stored under an inert atmosphere at −35 °C, isolated solids are stable for months.



(1)

The ^1H NMR spectra of these compounds support an overall C_2 symmetry, as evidenced by the two sets of diastereotopic $-CH_2-$ resonances in **2a**−**c** and the

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[⊗] Abstract published in *Advance ACS Abstracts*, December 15, 1997.

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[2] (a) Denmark, S. E.; O'Connor, S. P. *J. Org. Chem.* **1997**, *62*, 584−594. (b) Denmark, S. E.; Christenson, B. L.; Coe, D. M.; O'Connor, S. P. *Tetrahedron Lett.* **1995**, *36*, 2215−2218.

[3] For general references on chiral Ti complexes and their utility in catalysis see: (a) Duthaler, R. O.; Hafner, A. *Chem. Rev.* **1992**, *92*, 807−832. (b) Narasaka, K. *Synthesis* **1991**, 1−11.

[4] (a) Corey, E. J.; Letavic, M. A. *J. Am. Chem. Soc.* **1995**, *117*, 9616−9617 and references therein. (b) Mikami, K.; Kotera, O.; Motoyama, Y.; Sakaguchi, H. *Synlett* **1995**, 975−977. (c) Motoyama, Y.; Mikami, K. *J. Chem. Soc., Chem. Commun.* **1994**, 1563−1564.

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[7] Evans, D. A.; Nelson, S. G. *J. Am. Chem. Soc.* **1997**, *119*, 6452−6453.

[8] Bradley, D. C.; Thomas, I. M. *J. Chem. Soc.* **1960**, 3857−3861.

[9] Pikul, S.; Corey, E. J. *Org. Synth.* **1992**, *71*, 22−29, 30−37.

[10] These secondary products are consistently the same, appearing to be unsymmetric Ti−bis(sulfonamide) compounds by ^1H NMR spectroscopy.

S0276-7333(97)00939-4 CCC: $15.00

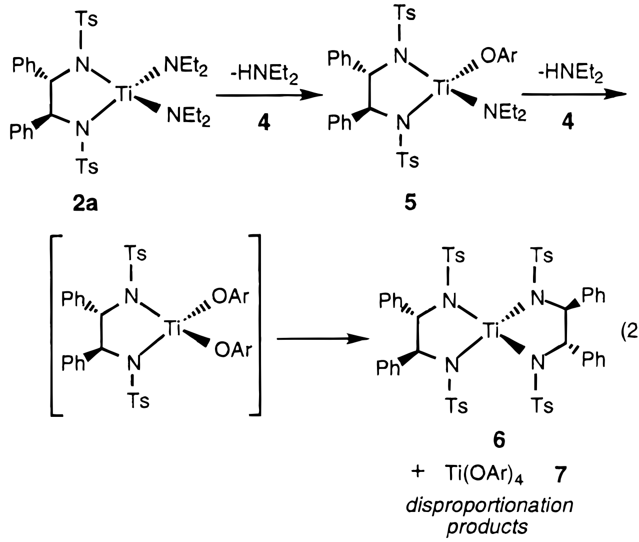
single set of bis(sulfonamide) ligand resonances for **2a**−**c** and **3a**−**c**. The amido methyl groups (NEt_2 and NMe_2 ligands) are equivalent to −70 °C, consistent with rapid rotation about the Ti−NR_2 bonds. Hindered rotation would otherwise result in inequivalent methyl groups.

Yellow crystals of compound **3b** suitable for X-ray crystallography were grown from a saturated toluene solution with slow diffusion of hexanes at room temperature.[11] The ^1H NMR spectra of these crystals show them to be identical with the major product from the aforementioned reaction ($Ti(NMe_2)_4$ + **1b** → **3b**). ORTEP diagrams of this compound with selected bond distances and angles are shown in Figure 1. The overall symmetry of this molecule is best described as a distorted tetrahedron, with the gross features of a C_2 axis clearly identifiable. A careful examination of potential bonding interactions, however, indicates that one sulfonamide group is distorted in such a way as to accommodate the coordination of a single oxygen atom to the titanium center, thus breaking the C_2 symmetry of the molecule. This interaction results in a net reduction of the Ti−O distance relative to the pseudo-symmetry-related sulfonamide oxygen (2.26 and 2.62 Å for Ti−O12 and Ti−O22, respectively), as well as a lengthening of the S=O bond (1.48 vs 1.45 Å for S1−O12 and S2−O22, respectively). An additional perturbation is observed in the Ti−N−S angles for the bound and unbound sulfonamides (99.1 and 107.5°, respectively). Moreover, the oxygen coordination results in a noticeable pyramidalization of the sulfonamide nitrogen (sums of the bond angles for S1 and S2 are 343.8 and 353.7°, respectively). The net C_2 symmetry for **2a**−**c** and **3a**−**c** that is observed in solution by ^1H NMR spectroscopy suggests that the two SO_2 groups in these compounds are either rapidly interconverting between bound and free states or do not coordinate to an appreciable extent.

Similar secondary bonding interactions are observed in the X-ray structure of $Ti[N(SO_2Ar)C_6H_{10}N(SO_2Ar)](NMe_2)_2$, where the chiral bis(sulfonamide) ligand is derived from *trans*-1,2-diaminocyclohexane.[12,13] In this case, a single sulfonamide oxygen binds to the titanium center when enantiomerically pure ligand is used, and two oxygens—one from each sulfonamide group—coordinate to the titanium center when a racemic mixture of the ligand is used.

Inspection of metrical parameters in the present system highlights the differences between the bonding in Ti−$NR(SO_2Ar)$ and Ti−NR_2, especially in comparison to Ti−N bond lengths of similar Ti−amide compounds.[14] The majority of the Ti−N bond lengths reported to date, including the Ti−NR_2 bonds in compound **3b** (1.87 Å), fall between 1.80 and 1.93 Å. The Ti−$NR(SO_2Ar)$ bonds, however, are 2.08 Å in length and reflect the poor donor character of an amide substituted with the strongly electron-withdrawing $-SO_2Ar$ group.[15] The strong inductive effect of these substituents effectively decreases the degree of π-donation from the filled nitrogen p_z orbital to an empty Ti d_π orbital.[16]

When compounds **2a**−**c** were treated with 2,6-dimethylphenol, an unusual *disproportionation* reaction of the putative $Ti(OAr)_2$(bis(sulfonamide)) intermediate was observed.[17] For example, when **2a** was treated with 2 equiv of **4**, the disproportionation products **6** and **7**[18] were observed, presumably via the intermediacy of the spectroscopically observable (^1H NMR) mono(aryloxide) **5** (eq 2). We hypothesize that $Ti(OAr)_2$(bis(sulfonamide)) initially forms from **5** but rapidly disproportionates into **6** and **7**. Consistent with this notion are the unsuc-



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[11] X-ray data for **3b**: data were collected at −100 °C on a Siemens SMART diffractometer using graphite-monochromated Mo Kα radiation. A total of 27 098 reflections were collected in the 2θ range 3.0−60°, of which 10 843 were unique (R_{int} = 0.023). The structure was solved by direct methods, and non−hydrogen atoms were refined anisotropically. In the final least-squares refinement cycle on *F*, the model converged at $R = 0.047$, $R_w = 0.039$, and GOF = 1.90 for 9317 reflections with $I_{net} > 2.5\sigma(I_{net})$ and 642 parameters. Crystal data are a = 14.8712(7) Å, b = 15.5436(7) Å, c = 16.7789(8) Å, V = 3878.5(3) Å^3, space group $P2_12_12_1$, Z = 4, mol wt 738.85, and ρ(calcd) = 1.265 g/cm^3.

[12] For the first evidence of this type of interaction in early-metal complexes, see: Walsh, P. J.; Gantzel, P., Pritchett, S.; Ho, D. *Abstracts of Papers*, 213th National Meeting of the American Chemical Society, San Francisco, CA; American Chemical Society: Washington DC, 1997; INOR 208.

[13] Pritchett, S.; Gantzel, P.; Walsh, P. J. *Organometallics* **1997**, *16*, 5130−5132.

[14] (a) Tsuie, B.; Swenson, D. C.; Jordan, R. F. *Organometallics* **1997**, *16*, 1392−1400. (b) Johnson, A. R.; Davis, W. M.; Cummins, C. C. *Organometallics* **1996**, *15*, 3825−3835. (c) Aoyagi, K.; Gantzel, P. K. *Organometallics* **1996**, *156*, 923−927. (d) Clark, H. C. S.; Cloke, F. G. N.; Hitchcock, P. B.; Love, J. B.; Wainwright, A. P. *J. Organomet. Chem.* **1995**, *501*, 333−340. (e) Lappert, M. F.; Power, P. P.; Sanger, A. R.; Srivastava, R. C. *Metal and Metalloid Amides*; Ellis Horwood: Chichester, U.K., 1980; Chapter 8.

[15] The pK_a's of triflamide and benzenesulfonamide are 9.7 and 16.1, respectively, in DMSO. The pK_a of $HNEt_3^+$ in DMSO is 9.0. See: Bordwell, F. G. *Acc. Chem. Res.* **1988**, *21*, 456−463.

[16] Hillhouse, G. L.; Bulls, A. R.; Santarsiero, B. D.; Bercaw, J. E. *J. Am. Chem. Soc.* **1988**, *7*, 1309−1312.

[17] Typically, *comproportionation*-type behavior is observed for TiX_4 + TiY_4 reactions. For example:

$$Ti(OiPr)_4 + TiCl_4 \rightarrow 2Ti(OiPr)_2Cl_2{}^{17a}$$

$$Ti(OiPr)_4 + Ti(NMe_2)_2 \rightarrow 2Ti(OiPr)_2(NMe_2)_2{}^{17b}$$

$$Ti(NR_2)_4 + TiCl_4 \rightarrow 2Ti(NR_2)_2Cl_2{}^{17b}$$

$$Ti(OAr)_4 + TiCl_4 \rightarrow 2Ti(OAr)_2Cl_2{}^{17c}$$

(a) *Encyclopedia of Organic Reagents*; Paquette, L. A., Ed.; Wiley: Chichester, U.K., 1995; Vol. 3, pp 1732−1733. (b) Renzinger, E.; Kornicker, W. *Chem. Ber.*, **1961**, 2263−2267. (c) Reactivity observed when ArOH is 2,6-dimethylphenol.

[18] The compound **7** was independently synthesized by the aminolysis reaction pathway: $Ti(NR_2)_4 + 4ArOH \rightarrow Ti(OAr)_4 + 4HNR_2$. For another synthetic route to **7**, see: Durfee, L. D.; Latesky, S. L.; Rothwell, I. P.; Huffman, J. C.; Folting, K. *Inorg. Chem.* **1985**, *24*, 4569−4573.

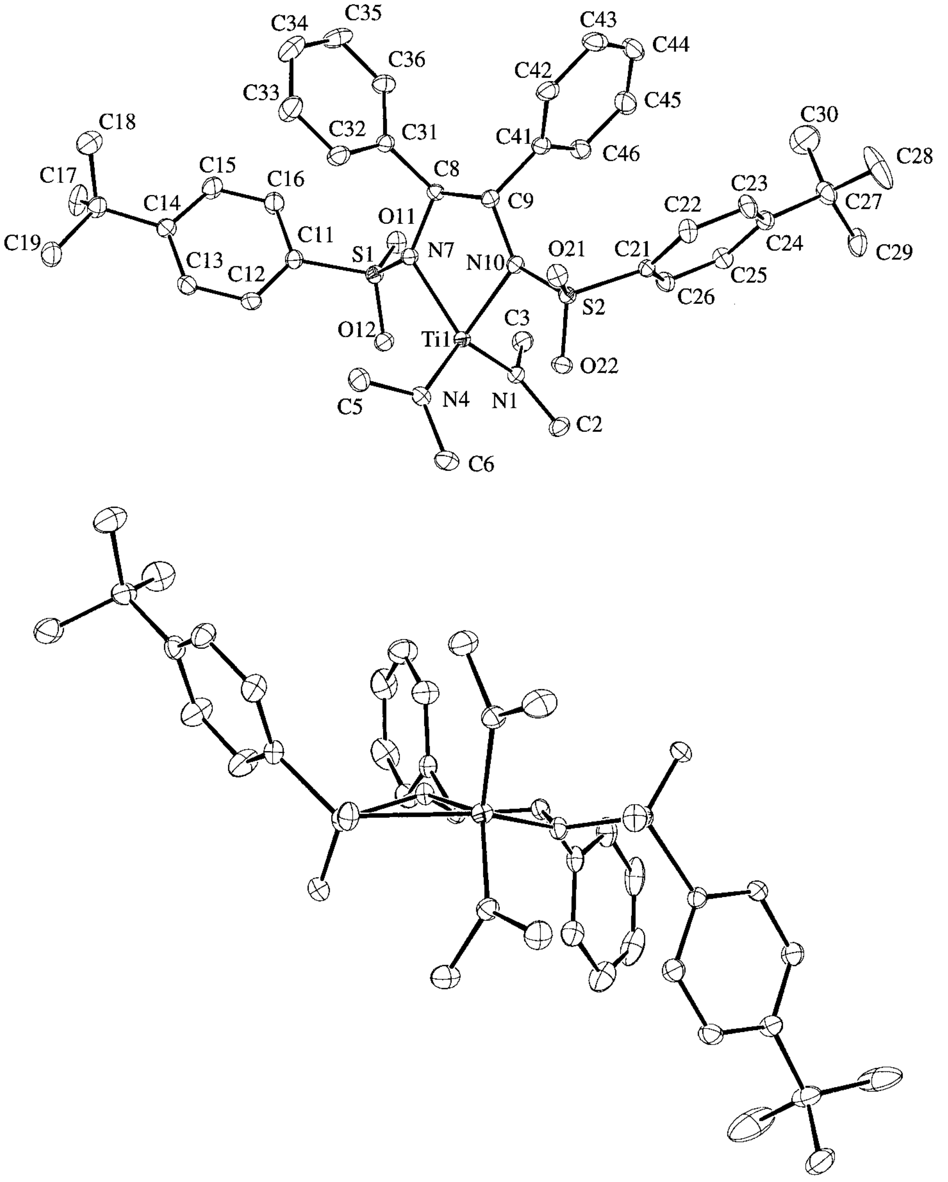
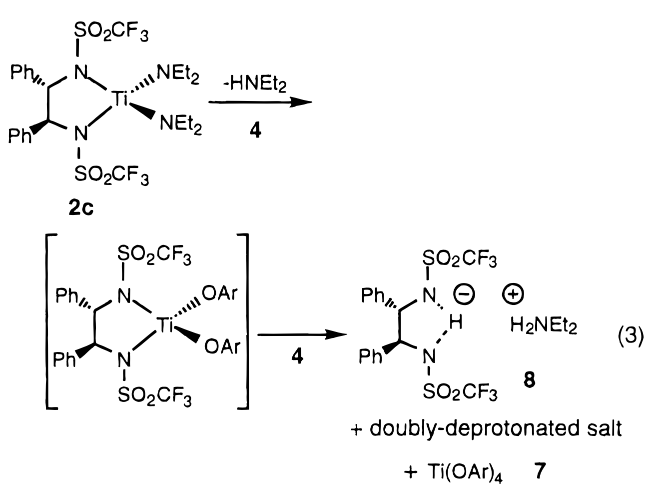


Figure 1. ORTEP drawings of **3b**: (top) top view; (bottom) front view. Selected bond distances (Å) and angles (deg): Ti1−N1 = 1.8711(2), Ti1−N4 = 1.8732(7), Ti1−N7 = 2.0755(2), Ti1−N10 = 2.0771(2), Ti1−O12 = 2.2643(2), S1−O12 = 1.4772(2), S2−O22 = 1.4543(2); Ti1−N7−S1 = 99.05(9), Ti1−N10−S2 = 107.50(9).

cessful attempts to thermally convert mixtures of **6** and **7** to Ti(OAr)$_2$(bis(sulfonamide)) through a *comproportionation* pathway and the kinetic stability of **5** formed in the presence of 1 equiv of **4**.

Although **7** could be prepared independently,[18] attempts to synthesize **6** via the direct aminolysis pathways were unsuccessful. However, the latter could be purified from the crude reaction mixture by removing the soluble **7** byproduct with a hexane wash. Additional evidence for the structure of **6** exists in the unpublished work of Walsh wherein a similiar bis(bis(sulfonamide)) Ti(IV) compound derived from *trans*-1,2-diaminocyclohexane has been crystallographically characterized.[19]



(3)

In contrast to the sulfonamide complexes, the triflamide-based complex **2c** generated **7** and triflamide−diethylammonium salts **8** upon treatment with **4** (eq 3). The solubility of **7** again allowed the triflamide−ammonium salts to be isolated by a hexane wash. Formation of singly and doubly deprotonated triflamide−ammonium salts is not unreasonable on the basis of the pK_a of triflamide.[15] In fact, authentic material

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[19] Walsh, P. J. Personal communication (manuscript in preparation).

could be directly synthesized from bis(triflamide) ligand **1c** and either 1 or 2 equiv of diethylamine.

In summary, we have synthesized and characterized several C_2-symmetric Ti(IV) complexes containing chiral bis(sulfonamide) ligands. Although the goal of the described experiments was the synthesis of $(ArO)_2Ti$-(bis(sulfonamide))-type complexes, the evidence suggests that these materials are unstable towards an unorthodox disproportionation reaction for aryl-substituted ligands and salt formation for CF_3-substituted ligands.

Experimental Details

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 (toluene, hexanes, CH_2Cl_2) were dried by running them through a column of activated alumina and stored under argon prior to use. All deuterated solvents (C_6D_6, CD_2Cl_2, and THF-d_8) were vacuum-transferred from sodium/benzophenone ketyl and stored under an argon atmosphere. All solvents (protonated and deuterated) were also freeze−pump−thaw-degassed before use. All $Ti(NR_2)_4$ compounds and bis(sulfonamide) ligands were prepared according to literature procedures,[20] or modifications thereof.[21] Diethylamine was distilled from CaH_2, while all other reagents were used as obtained from commercial sources.

^1H and ^{13}C NMR spectra were recorded in C_6D_6, CD_2Cl_2, or THF-d_8 at ambient temperature on a Bruker AC200 spectrometer. All ^{19}F NMR spectra were recorded on a Varian Gemini 2000 spectrometer (300 MHz, ^1H) with $CFCl_3$ as an external reference. Infrared spectra were obtained on a Nicolet Magna-IR 560 FT-IR spectrometer and optical rotation measurements on a Jasco DIP-1000 digital polarimeter. Elemental analyses were performed by Atlantic Microlab, Inc., Norcross, GA.

$Ti(NEt_2)_2[N(Ts)CHPhCHPhN(Ts)]$ (2a). $Ti(NEt_2)_4$ (576 mg, 1.71 mmol) and **1a** (888 mg, 1.71 mmol) were combined in toluene (20 mL) at 23 °C, resulting in a dark red homogeneous solution. The reaction solution was magnetically stirred for 2.5 h and then concentrated in vacuo to several milliliters. Hexane was added via syringe (10 mL), precipitating an orange solid from the red solution. The slurry was cooled to 0 °C for 1 h and then filtered via cannula to isolate the orange solid (1.01 g, 1.41 mmol, 83%). ^1H NMR (200 MHz, C_6D_6): δ 7.39, 7.04, 6.80, 6.57 (m, 18 H total, Ar), 5.33 (s, 2 H, $-CH$), 4.38, 4.29 (m, 8 H, $-CH_2CH_3$), 1.82 (s, 6H, $-CH_3$), 1.34 (t, 12 H, $-CH_2CH_3$). $^{13}C\{^1H\}$ NMR (50.28 MHz, CD_2Cl_2): δ 142.6, 139.7, 139.2, 129.0, 128.8, 128.0, 127.7, 127.1 (Ar), 72.2 ($-CH$), 46.3 ($-CH_2CH_3$), 21.5 ($-CH_3$), 14.5 ($-CH_2CH_3$). IR (KBr, CH_2Cl_2): 2976 (m), 2930 (w), 2863 (w), 1276 (s), 1147 (m), 1106 (m), 938 (s), 815 (m), 677 (s) cm^{-1}. $[\alpha]_D^{27.9} = -55.9$ ($c = 1.34$, CH_2Cl_2). CHN analyses for this compound were routinely low, even in the presence of a combustion aid. Anal. Calcd for $C_{36}H_{46}N_4O_4S_2Ti$: C, 60.83; H, 6.52; N, 7.88. Found: C, 58.42; H, 6.30; N, 7.17. This compound consistently retains fractional amounts of $HNEt_2$ and solvent according to ^1H NMR.

$Ti(NEt_2)_2[N(SO_2\text{-}4\text{-}^tBuC_6H_4)CHPhCHPhN(SO_2\text{-}4\text{-}^tBuC_6H_4)]$ (2b). $Ti(NEt_2)_4$ (373 mg, 1.11 mmol) and **1b** (668 mg, 1.10 mmol) were combined in toluene (20 mL) at 23 °C, resulting in a dark red homogeneous solution. The reaction solution was magnetically stirred for 1.5 h and then concentrated in vacuo to several milliliters. Hexane was added via syringe (8 mL), precipitating an orange solid from the red solution. The mixture was cooled to −78 °C for 1 h and then filtered via cannula. The resulting orange solid was then washed with hexanes (5 mL) at −78 °C and dried in vacuo to yield the product (554 mg, 0.697 mmol, 63%). ^1H NMR (200 MHz, C_6D_6): δ 7.47, 7.01, 6.90, 6.76 (m, 18 H total, Ar), 5.31 (s, 2 H, $-CH$), 4.39 (m, 8 H, $-CH_2CH_3$), 1.37 (t, 12 H, $-CH_2CH_3$), 1.03 (s, 18 H, $-C(CH_3)_3$). $^{13}C\{^1H\}$ NMR (50.28 MHz, CD_2Cl_2): δ 155.4, 139.4, 138.9, 128.6, 127.8, 127.5, 126.7, 125.2 (Ar), 72.1 ($-CH$), 46.1 ($-CH_2CH_3$), 35.0 ($-C(CH_3)_3$), 31.1 ($-C(CH_3)_3$), 14.3 ($-CH_2CH_3$). IR (KBr, CH_2Cl_2): 2966 (s), 2929 (w), 2904 (w), 2868 (w), 1598 (w), 1454 (w), 1275 (m), 1137 (m), 1096 (m), 940 (s), 652 (s) cm^{-1}. $[\alpha]_D^{28.3} = -62.8$ ($c = 1.01$, CH_2Cl_2). CHN analyses for this compound were routinely low. Anal. Calcd for $C_{42}H_{58}N_4O_4S_2Ti$: C, 63.46; H, 7.35; N, 7.05. Found: C, 60.91; H, 6.97; N, 6.04. This compound consistently retains fractional amounts of $HNEt_2$ and solvent according to ^1H NMR.

$Ti(NEt_2)_2[N(Tf)CHPhCHPhN(Tf)]$ (2c). $Ti(NEt_2)_4$ (532 mg, 1.58 mmol) and **1c** (752 mg, 1.58 mmol) were combined in toluene (20 mL) at 23 °C to give a dark red homogeneous solution. The solution was magnetically stirred for 2.5 h and then concentrated in vacuo to several milliliters. Hexane was added via syringe (8 mL) to precipitate an orange solid from the concentrated solution. The mixture was cooled to 0 °C for 1 h and then filtered via cannula to isolate the orange solid (936 mg, 1.40 mmol, 89%). ^1H NMR (200 MHz, C_6D_6): δ 7.23 (dd, 4 H, Ph), 7.02 (m, 6 H, Ph), 5.26 (s, 2 H, $-CH$), 4.08, 3.93 (m, 8 H, $-CH_2CH_3$), 0.98 (t, 12 H, $-CH_2CH_3$). $^{13}C\{^1H\}$ NMR (50.28 MHz, CD_2Cl_2): δ 139.5, 128.9, 128.2 (Ph), 119.9 (q, $-CF_3$, $^1J_{CF} = 325$ Hz), 71.5 ($-CH$), 46.4 ($-CH_2CH_3$), 13.7 ($-CH_2CH_3$). ^{19}F NMR (282.33 MHz, C_6D_6): δ −75.4 (s, $-CF_3$). IR (KBr, CH_2Cl_2): 2976 (w), 2930 (w), 2870 (w), 1451 (w), 1326 (s), 1197 (vs), 1142 (m), 1063 (w), 944 (m), 893 (w), 640 (m) cm^{-1}. $[\alpha]_D^{25.1} = -49.6$ ($c = 1.01$, CH_2Cl_2). Anal. Calcd for $C_{24}H_{32}F_6N_4O_4S_2Ti$: C, 43.25; H, 4.84; N, 8.41. Found: C, 43.01; H, 4.90; N, 8.27.

$Ti(NMe_2)_2[N(Ts)CHPhCHPhN(Ts)]$ (3a). $Ti(NMe_2)_4$ (103 mg, 0.460 mmol) and **1a** (237 mg, 0.456 mmol) were combined in toluene (10 mL) at 23 °C, resulting in a dark orange homogeneous solution. The reaction solution was magnetically stirred for 2.5 h and then concentrated in vacuo to several milliliters. Hexane was added via syringe (5 mL), precipitating an orange solid from the solution. The mixture was cooled to 0 °C for 1 h and then filtered via cannula to isolate the orange solid (170 mg, 90% pure by NMR, 57% yield). Attempts to further purify the product by recrystallization from toluene/hexane were unsuccessful. ^1H NMR (200 MHz, C_6D_6): δ 7.37, 7.00, 6.77, 6.55 (m, 18 H total, Ar), 5.25 (s, 2 H, $-CH$), 3.70 (s, 12 H, $-N(CH_3)_2$), 1.83 (s, 6H, $-CH_3$). ^{13}C NMR spectra were recorded of *in situ* generated product. Concomitant $HNMe_2$ was also present. $^{13}C\{^1H\}$ NMR (50.28 MHz, CD_2Cl_2): δ 142.9, 139.7, 139.2, 129.3, 128.4, 128.1, 127.7, 127.1 (Ar), 72.4 ($-CH$), 46.1 ($-N(CH_3)_2$), 39.1 ($HN(CH_3)_2$), 21.5 ($-CH_3$). This compound consistently retains fractional amounts of $HNMe_2$ and solvent according to ^1H NMR.

$Ti(NMe_2)_2[N(SO_2\text{-}4\text{-}^tBuC_6H_4)CHPhCHPhN(SO_2\text{-}4\text{-}^tBuC_6H_4)]$ (3b). $Ti(NMe_2)_4$ (285 mg, 1.27 mmol) and **1b** (768 mg, 1.27 mmol) were combined in toluene (10 mL) at 23 °C, resulting in a dark orange homogeneous solution. The reaction solution was magnetically stirred for 2.5 h, during which time a yellow solid precipitated from the solution. The mixture was concentrated in vacuo to several milliliters, cooled to −78 °C for 1 h, and then filtered via cannula to yield the yellow solid (672 mg, 88% pure by NMR, 71% yield). Several recrystallizations from toluene/hexane yielded pure crystals of **3b**. ^1H NMR (200 MHz, C_6D_6): δ 7.43, 6.90, 6.76 (m, 18 H total, Ar), 5.26 (s, 2 H, $-CH$), 3.75 (s, 12 H, $-N(CH_3)_2$), 1.04 (s, 18 H, $-C(CH_3)_3$). $^{13}C\{^1H\}$ NMR (50.28 MHz, CD_2Cl_2): δ 155.8, 139.5, 139.1, 128.4, 128.1, 127.6, 126.9, 125.7 (Ar), 72.3 ($-CH$), 46.1

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[20] For the synthesis of $Ti(NR_2)_4$ see: Bradley, D. C.; Thomas, I. M. *J. Chem. Soc.* **1960**, 3857−3861. For the synthesis of bis(triflamide) **1c**, see: Pikul, S.; Corey, E. J. *Org. Synth.* **1992**, *71*, 30−37.

[21] The bis(triflamide) ligand **1c** was prepared according to the literature procedure but further purified by recrystallization in CH_2Cl_2/hexanes. The bis(sulfonamide) ligands **1a** and **1b** were prepared according to the same procedure but purified by recrystallization from CH_2Cl_2/hexanes.

Table 1. Crystallographic Data and Collection Parameters for 3b

formula	$TiS_2C_{38}H_{50}N_4O_4$
fw	738.85
color, habit	yellow, crystal
cryst size, mm	0.30 × 0.30 × 0.25
cryst syst	orthorhombic
space group	$P2_12_12_1$
a, Å	14.8712(7)
b, Å	15.5436(7)
c, Å	16.7789(8)
V, Å^3	3878.5(3)
Z	4
T, °C	−100
D_c, g/cm^3	1.265
F(000)	1570.90
radiation (λ, Å)	Mo Kα (0.710 73)
μ, mm^{-1}	0.37
scan mode	ω
data collected	$\pm h, \pm k, \pm l$
$2\theta_{max}$, deg	60.0
total no. of rflns	27 098
no. of unique rflns	10 843
R_{merge}	0.023
no. of rflns with $I > 2.5\sigma(I)$	9325
no. of variables	642
R_F[a]	0.047
R_w[b]	0.039
GOF[c]	1.90
max Δ/σ	0.060
residual density, e/Å^3	−0.39, +0.40

[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.

($-N(CH_3)_2$), 35.2 ($-C(CH_3)_3$), 31.2 ($-C(CH_3)_3$). IR (KBr, CH_2Cl_2): 2966 (m), 2902 (m), 2869 (m), 2780 (w), 1595 (w), 1275 (s), 1145 (m), 1095 (m), 942 (s), 650 (s) cm^{-1}. $[\alpha]_D^{25} = -117.2$ ($c = 0.76$, CH_2Cl_2). This compound consistently retains fractional amounts of $HNMe_2$ and solvent according to ^1H NMR. Details of the X-ray study of **3b** are given in Table 1.

$Ti(NMe_2)_2[N(Tf)CHPhCHPhN(Tf)]$ (3c). $Ti(NMe_2)_4$ (374 mg, 1.67 mmol) and **1c** (793 mg, 1.66 mmol) were combined in toluene (10 mL) at 23 °C, resulting in a dark red homogeneous solution. The reaction solution was magnetically stirred for 2.5 h and then concentrated in vacuo to several milliliters. Hexane was added via syringe (5 mL), precipitating a red-brown solid from the red solution. The solution was cooled to −78 °C for 1 h and then filtered via cannula to yield the red-brown solid (905 mg, 87% pure by NMR, 89% yield). Attempts to further purify the product by recrystallization from toluene/hexane were unsuccessful. ^1H NMR (200 MHz, C_6D_6): δ 7.30, 7.10 (m, 10 H total, Ph), 5.33 (s, 2 H, $-CH$), 3.21 (s, 12 H, $-N(CH_3)_2$). ^{13}C NMR spectra were recorded of *in situ* generated product. Concomitant $HNMe_2$ was also present. $^{13}C\{^1H\}$ NMR (50.28 MHz, CD_2Cl_2): δ 141.3, 128.5, 127.9, 127.4 (Ar), 120.5 (q, $-CF_3$, $^1J_{CF}$ = 326 Hz), 71.6 ($-CH$), 47.1 ($-N(CH_3)_2$), 40.1 ($HN(CH_3)_2$). ^{19}F NMR (282.33 MHz, C_6D_6): δ −74.6 (s, $-CF_3$). This compound consistently retains fractional amounts of $HNMe_2$ and solvent according to ^1H NMR.

$Ti[N(Ts)CHPhCHPhN(Ts)]_2$ (6). **2a** (82 mg, 0.115 mmol) and **4** (29 mg, 0.237 mmol) were combined in toluene (10 mL) at 23 °C, resulting in an orange heterogeneous solution. The slurry was magnetically stirred for 2 h and then concentrated in vacuo to dryness. The orange solid, analyzed by ^1H NMR, was a mixture of **6**, **7**, and a third product which could not be isolated (postulated to be $Ti(OAr)_2$(bis(sulfonamide))). The solid was dissolved in toluene (10 mL), and this solution was heated at 80 °C for 2 h and then concentrated in vacuo to dryness. The resulting orange solid, analyzed by ^1H NMR, was a mixture of only **6** and **7**. Compound **6** was isolated in pure form after washing three times with hexane (5 mL) and once with toluene/hexane. ^1H NMR (200 MHz, THF-d_8): δ 7.42, 7.30, 6.98, 6.73 (m, 36 H total, Ar), 4.53 (d, 4 H, $-CH$), 2.28 (s, 12 H, $-CH_3$). $^{13}C\{^1H\}$ NMR (50.28 MHz, THF-d_8): δ 142.8, 139.9, 138.6, 129.6, 128.8, 128.2, 127.7, 127.6 (Ar), 63.3 ($-CH$), 21.2 ($-CH_3$). Anal. Calcd for $C_{56}H_{52}N_4O_8S_4Ti$: C, 61.98; H, 4.83; N, 5.16. Found: C, 61.91; H, 5.31; N, 5.06.

$Tf_2dpeda^-H_2NEt_2^+/Tf_2dpeda^{2-}(H_2NEt_2)^+_2$ (8). **2c** (355 mg, 0.533 mmol) and **4** (130 mg, 1.06 mmol) were combined in toluene (10 mL) at 23 °C, resulting in a red homogeneous solution. The reaction was magnetically stirred for 6 h and then concentrated in vacuo to dryness. The resulting yellow solid was washed twice with hexane and once with toluene/hexane, resulting in a pale yellow solid which was analyzed by ^1H NMR to be a 3:2 mixture of the singly and doubly deprotonated salts (1.4 equiv of $H_2HEt_2^+$ to one molecule of deprotonoted bis(triflamide)). ^1H NMR (200 MHz, C_6D_6): δ 7.79 (bs, 2.8 H, $H_2NEt_2^+$), 6.92 (m, 10 H total, Ar), 4.80 (s, 2 H, $-CH$), 2.43 (q, 5.6 H, $-N(CH_2CH_3)_2$), 0.94 (t, 8.4 H, $-N(CH_2CH_3)_3$). $^{13}C\{^1H\}$ NMR (50.28 MHz, CD_2Cl_2): δ 140.8, 128.8, 128.1, 128.0 (Ar), 121.1 (q, $-CF_3$, $^1J_{CF}$ = 327 Hz), 66.1 ($-CH$), 42.8 ($-CH_2CH_3$), 11.3 ($-CH_2CH_3$). ^{19}F NMR (282.33 MHz, C_6D_6): δ −77.7 (s, $-CF_3$). Anal. Calcd for $C_{21.6}H_{29.4}F_6N_{3.4}O_4S_2$ (3:2 single-/double-deprotonated salt): C, 44.82; H, 5.12; N, 8.22. Found: C, 44.72; H, 5.09; N, 7.83.

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Supporting Information Available: Tables of crystallographic data for **3b**, including bond distances, bond angles, torsion angles, atomic parameters, and isotropic and anisotropic (for non-hydrogen atoms) thermal parameters (8 pages). Ordering information is given on any current masthead page.

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