Articles

Synthesis and Structural Study of Titanium Bis(sulfonamido) Bis(amide) Complexes

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Reaction of the titanium tetraamide $Ti(NMe_2)_4$ with various bis(sulfonamide) ligands resulted in the clean formation of the bis(sulfonamido)$Ti(NMe_2)_2$ complexes and *N,N*-dimethylamine. We have characterized the resulting racemic and resolved bis(sulfonamido)-$Ti(NMe_2)_2$ complexes by X-ray crystallography to explore differences in the bonding and geometry of the ligand in these complexes. From the crystal structures, the ligand is found to bind through the sulfonyl oxygens as well as the sulfonamido nitrogens. The Ti−N distances of the sulfonamido groups range from 2.048(3) to 2.103(2) Å, while the Ti−N distances of the amides are significantly shorter, between 1.858(3) and 1.896(3) Å. The structures indicate that the bonding of the ligand to the metal can be either η^3 or η^4, with the Ti−O sulfonyl distances ranging from 2.167(2) to 2.447(4) Å. We have synthesized bis-(sulfonamido)$Ti(NMe_2)_2$ complexes with bis(sulfonamide) ligands of varying sizes and found that the bulk of the ortho substituent of the aryl groups (H vs Me vs *i*-Pr) dictates the position of the aryl rings in the solid state. The bis(sulfonamido)$Ti(NMe_2)_2$ complexes described here are related to the proposed catalysts in the asymmetric alkylation of aldehydes.

Introduction

Recent interest in early-transition-metal amide chemistry has been fueled by the remarkable reactivity of metals bearing amide ligands as well as by the synthetic utility of the amide group. These characteristics are exemplified by their extraordinary activation[1] and cleavage[2−4] of dinitrogen and by their stabilization of previously unknown bonding motifs (LV=NH,[5] LTa=PR,[6] and LW≡P,[7] L = triamidoamine[8]). Amides have also been essential supporting ligands in the activation of C−H bonds[9] and in the polymerization of terminal olefins.[10−14] As spectator ligands, amides allow a broad variability of electronic and steric properties.[15,16] Furthermore, due to the basic nature of the metal−nitrogen bond, they are very useful functional groups in organometallic and inorganic synthesis. One avenue through which functional group interconversion of metal amides can be directed is amine elimination reactions.[17−20] Improvements in the scope of this process have greatly increased the utility of metal−amide complexes as synthetic intermediates.

Our initial interest in titanium amide complexes was in their role as precursors in the synthesis of titanium bis(sulfonamido) bis(alkoxide) complexes (Figure 1).[21] These chiral Lewis acids are the proposed catalysts in

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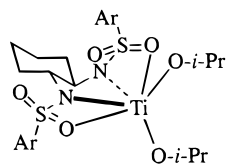
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Figure 1.

the asymmetric transfer of alkyl groups from dialkylzinc reagents to aldehydes (eq 1). The titanium bis(sulfona-

$$\text{(1)}$$
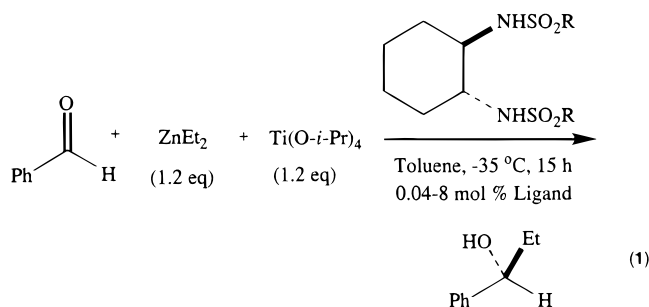
mide) based catalysts, which were developed by Ohno[22-24] and elegantly applied to asymmetric synthesis by Knochel,[25-32] comprise one of the most efficient and enantioselective[33] C—C bond forming reactions known.[34-39]

While exploring the synthesis of bis(sulfonamido)Ti-(NMe$_2$)$_2$ complexes, we,[40] and Gagné and co-workers,[41] found that these compounds are structurally very interesting. We determined that the bis(sulfonamido) ligand could adopt an η^3 or η^4 bonding mode[40] through coordination of the sulfonyl oxygens as well as through the sulfonamido nitrogens. The hapticity of the bis-(sulfonamido) ligand in the solid-state structure of a titanium bis(sulfonamido) bis(amide) complex differed

dramatically, depending on whether racemic or resolved bis(sulfonamide) ligand was employed.

We anticipate that the titanium bis(sulfonamido) bis-(amide) complexes bis(sulfonamido)Ti(NMe$_2$)$_2$ will be useful starting materials for other bis(sulfonamido)-titanium species. A reliable methodology has been developed for the efficient conversion of group IV metal amides directly into the corresponding halide[20] or alkyl complexes.[42] Thus, the titanium bis(sulfonamido) bis-(amide) complexes may serve as precursors in the synthesis of the dihalide and dimethyl compounds bis-(sulfonamido)TiX$_2$ and bis(sulfonamido)TiMe$_2$.[19] We expect that the dihalide derivatives will be strong Lewis acids and will be potentially useful in asymmetric Lewis-acid-catalyzed processes.[43] The bis(sulfonamido)-TiMe$_2$ compounds can be evaluated as precatalysts in the single-site cationic polymerization of olefins by C_2-symmetric group IV complexes.

The main goal of our research is to understand the details which control catalyst efficiency and enantiose-lectivity in asymmetric processes and to aid in building a foundation upon which future generations of catalysts can be designed and refined. In the present work, we extend our synthetic and solid-state structural study of titanium bis(sulfonamido) bis(amide) complexes. Due to the importance of titanium bis(sulfonamido) based titanium catalysts in asymmetric synthesis, we have focused on the influence of the size of the ligand on the chiral environment around the titanium center.

Results

We have prepared racemic (rac) and resolved (res) bis-(sulfonamide) ligands (**1rac**, Ar = C$_6$H$_5$; **2rac** and **2res**, Ar = 4-C$_6$H$_4$-Me; **3rac** and **3res**, Ar = 2,4,6-C$_6$H$_2$-Me$_3$; **4rac**, Ar = 2,4,6-C$_6$H$_2$-^{i}Pr$_3$) to examine the effect of ligand size on hapticity and conformation of the corresponding titanium complexes. The synthesis of the racemic C_2-symmetric bis(sulfonamide) ligands was accomplished through reaction of the racemic *trans*-1,2-diaminocyclohexane with the appropriate sulfonyl chloride in the presence of triethylamine (eq 2). The racemic

$$\text{(2)}$$

1rac Ar = C$_6$H$_5$

2rac, 2res Ar = 4-C$_6$H$_4$-Me

3rac, 3res Ar = 2,4,6-C$_6$H$_2$-Me$_3$

4rac Ar = 2,4,6-C$_6$H$_2$-^{i}Pr$_3$

diamine was easily resolved with tartaric acid and isolated from this procedure as the tartrate salt.[44-48]

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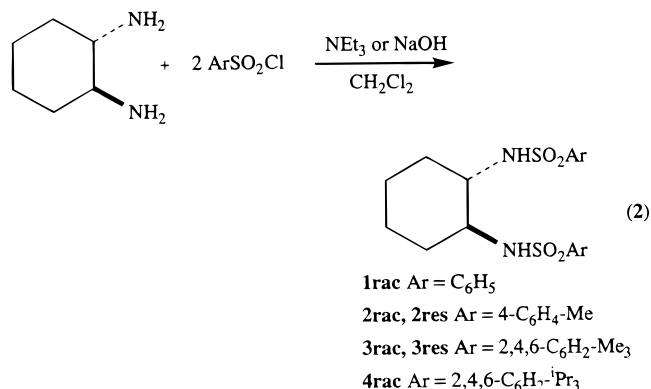
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The resolved diamine was liberated by dissolving the diammonium tartrate salt in a mixture of 2 M aqueous NaOH and CH_2Cl_2. Addition of the sulfonyl chloride to this biphasic mixture resulted in the formation of the bis(sulfonamide) ligand. In the ligand preparations, a slight excess of diamine was employed to ensure that all of the sulfonyl chloride was converted to bis(sulfonamide) product. The reactions were terminated with the addition of dilute acid to remove any traces of amine impurities from the organic layer. Both procedures are clean and rapid and can be easily performed on a large scale.

The bis(sulfonamido) titanium bis(amide) complexes **5rac**, **5res**, **6rac**, and **6res** were readily synthesized by addition of $Ti(NMe_2)_4$ to a heterogeneous mixture of the racemic or resolved bis(sulfonamide) ligand in diethyl ether (eq 3).[40,41,49] In the case of the bulky ligand **4rac**,

2rac, 2res
3rac, 3res
4rac

5rac, 5res
6rac, 6res
7rac

(3)
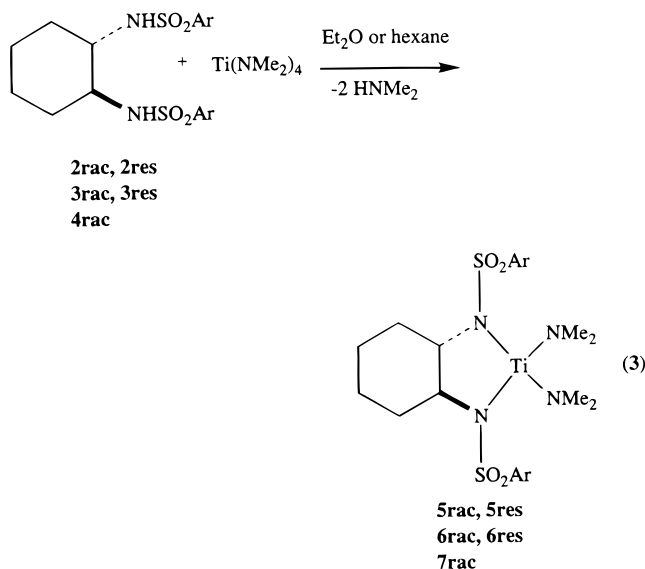
$Ti(NMe_2)_4$ was added to a heterogeneous mixture of the ligand in hexane. In all of these experiments, upon addition of $Ti(NMe_2)_4$, the ligand dissolved and the solution become red-brown. **5rac**, **5res**, **6rac**, and **6res** were crystallized from diethyl ether in 95, 89, 85, and 81% yield, respectively (Experimental Section). Bis-(amide) complex **7rac** was crystallized from hexanes at −25 °C in 58% yield. Although **7rac** is formed cleanly in the reaction (^{1}H NMR), the yield is lower due to the high solubility of this compound in hexanes.

Racemic and resolved compounds **5rac**, **5res**, **6rac**, **6res**, and **7rac** were characterized by ^{1}H and $^{13}C\{^1H\}$ NMR spectrometry in benzene-d_6. The *N*-methyl groups were equivalent in the ^{1}H NMR spectrum for each compound and fell in the range of 3.56−3.68 ppm. Likewise, a single resonance for the *N*-methyl groups was observed in the $^{13}C\{^1H\}$ NMR spectrum for each compound between 65.4 and 66.0 ppm. As described below, the compounds are monomeric in the solid state.

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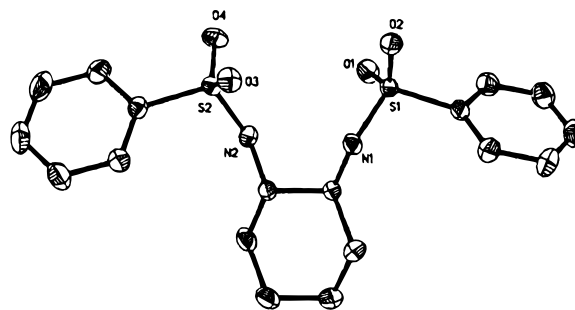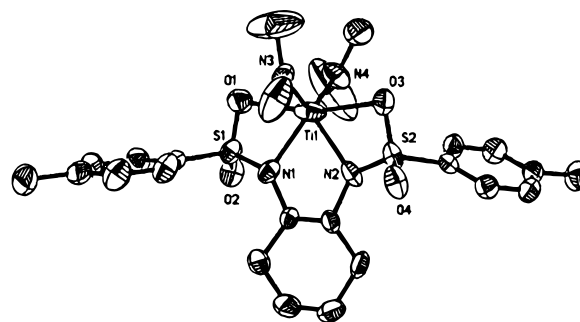
Figure 2. Structure of **1rac**.

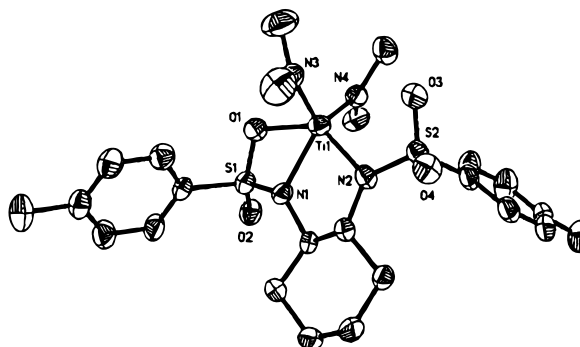**Figure 3.** Structure of **5rac**.

Figure 4. Structure of **5res**.

The solution NMR spectra for **5rac** and **5res** are identical, as they are for **6rac** and **6res.**

As outlined in the Experimental Section, X-ray-quality crystals of **1rac**, **5rac**, **5res**, **6rac**, **6res**, and **7rac** were grown and their structures were determined at low temperature. ORTEP diagrams for **1rac, 5rac**, **5res**, **6rac**, **6res**, and **7rac** are shown in Figures 2−7, along with bond distances in Table 1 and bond angles in Table 2. Crystallographic Data and Collection Parameters are given in Table 3. The structure of the ligand **1rac** was undertaken for the purpose of comparison with the titanium bis(sulfonamido) bis(amide) structures. The conformation of the free ligand **1rac** in the solid state (Figure 2) is different from that of the titanium-bound ligands (Figures 3−7). In **1rac**, the bonds between the sulfur and the phenyl groups are close to parallel to the plane of the paper. However, in the titanium complexes, the bonds between the S and the aryl group are opposite the axial methine C−H's of the cyclohexane moiety.

In the titanium complexes, the metal is bonded to two *N,N*-dimethylamide ligands with distances from 1.858(4) to 1.896(3) Å and to two sulfonamido nitrogens with bond lengths between 2.048(3) and 2.103(2) Å. The titanium is also bonded to one or two sulfonyl oxygens.

Table 1. Selected Bond Distances for 1rac, 5rac, 5res, 6rac, 6res, and 7rac (Å)

	1rac	5rac	5res	6rac	6res	7rac
Ti(1)−N(1)		2.068(3)	2.048(3)	2.096(3)	2.089(2)	2.103(2)
Ti(1)−N(2)		2.094(4)	2.073(3)	2.082(3)	2.087(2)	2.087(2)
Ti(1)−N(3)		1.858(3)	1.859(3)	1.881(3)	1.870(3)	1.867(2)
Ti(1)−N(4)		1.861(3)	1.896(3)	1.869(3)	1.875(3)	1.886(2)
Ti(1)−O(1)		2.447(4)	2.219(3)	2.167(2)	2.182(2)	2.181(2)
Ti(1)−O(3)		2.434(4)	2.901(4)	3.096(4)	3.147(4)	2.933(4)
S(1)−O(1)	1.443(2)	1.467(3)	1.486(3)	1.491(3)	1.497(2)	1.493(2)
S(1)−O(2)	1.443(2)	1.438(3)	1.436(3)	1.430(3)	1.435(2)	1.438(2)
S(2)−O(3)	1.443(2)	1.465(4)	1.449(3)	1.442(3)	1.447(2)	1.448(2)
S(2)−O(4)	1.437(2)	1.438(3)	1.435(3)	1.440(3)	1.440(2)	1.438(2)
S(1)−N(1)	1.607(2)	1.580(4)	1.559(3)	1.570(3)	1.567(2)	1.586(2)
S(2)−N(2)	1.613(2)	1.586(3)	1.592(3)	1.618(3)	1.614(2)	1.609(2)

In **5res**, **6rac**, **6res**, and **7rac** only one sulfonyl oxygen is interacting with the titanium center, with distances for the Ti(1)−O(1) bond ranging from 2.167(2) to 2.219(3) Å. The geometries in these five-coordinate titanium complexes are distorted from tetrahedral by coordination of one of the sulfonyl oxygens. The resulting geometries are highly distorted bipyramidal. In contrast, the titanium in **5rac** is interacting with two oxygens, one from each sulfonyl group. The Ti−O distances in **5rac** are longer (Ti(1)−O(1) = 2.447(4) Å and Ti(1)−O(3) = 2.434(4) Å), and the geometry about the titanium can be described as trigonal prismatic. The coordination of the two sulfonyl oxygens in **5rac** is similar to the bonding in the bis(sulfonamido)Ti(O-*i*-Pr)$_2$ complexes in the solid state. In these alkoxide complexes, the bis(sulfonamido) ligand is tetradentate and is bound through the oxygens and nitrogens.[21]

Inspection of the sulfonyl S−O bond distances in Table 1 indicates that coordination of oxygen to titanium results in a lengthening of the S−O relative to the uncoordinated sulfonyl oxygens in the titanium complexes and in the free ligand **1rac**. As is seen in **5res**, **6rac**, **6res**, and **7rac** the lengthening of the S−O bond distance is greatest when the titanium−oxygen distance is shortest. In **5rac**, where the titanium is interacting with two sulfonyl oxygens, the lengthening of the S−O bonds on coordination of the oxygen to titanium is less pronounced. The S(1) sulfur compensates for the loss of electron density from the interaction of O(1) with the titanium center by shortening the bond to the sulfonamido nitrogen, N(1). In the structures of **5res**, **6rac**, **6res**, and **7rac** the S(1)−N(1) distance is shorter than the S(2)−N(2) distance (on average by 0.037 Å). This effect is less prominent in the structure of **7rac** and is most likely due to the more sterically demanding nature of the bulky aryl groups of the ligand with the Ti(NMe$_2$)$_2$ moiety. The disparity in the S(1)−N(1) and S(2)−N(2) distances is not observed in the structure of **5rac**, where the S−N distances are intermediate between the S(1)−N(1) and S(2)−N(2) distances of **5res**, **6rac**, and **6res**. The S(1)−N(1) and S(2)−N(2) distances in the free ligand **1rac** are similar to the S(2)−N(2) distances found in the titanium complexes.

The effect of coordination of the sulfonyl oxygen to the titanium is also evident from the bond angles about S(1) and S(2) in the titanium complexes (Table 2). In **5res**, **6rac**, **6res**, and **7rac**, coordination of O(1) causes a compression of the N(1)−S(1)−O(1) angles, which range from 97.2 to 97.9°, while the N(1)−S(1)−O(2) angles open to 112.4−115.0°. A similar, but less dramatic, behavior is observed in the N(2)−S(2)−O(3) and

N(2)−S(2)−O(4) bond angles. The N(2)−S(2)−O(3) bond angles fall between 104.6 and 106.1°, with the N(2)−S(2)−O(4) bond angles being between 109.5 and 113.2°. Intermediate angles are found for the six-coordinate complex **5rac** relative to complexes **5res**, **6rac**, **6res**, and **7rac**. Coordination of both O(1) and O(3) to titanium results in a decrease in the N(1)−S(1)−O(1) and N(2)−S(2)−O(3) bond angles to 101.1 and 100.3°, respectively. The N(1)−S(1)−O(2) and N(2)−S(2)−O(4) angles are opened more than their counterparts in **5res**, **6rac**, **6res**, and **7rac**. N(1)−S(1)−O(2) and N(2)−S(2)−O(4) were determined to be 115.3 and 115.7°. In the free ligand **1rac**, N−S−O bond angles show the least variance, ranging from 105.76(10) to 109.87(10)°. For all the structures the N(1)−Ti(1)−N(2) angles fall into the range of 73.0−75.0°, while the N(3)−Ti(1)−N(4) angles are larger (105.4−115.8°).

Discussion

The bis(sulfonamide) ligands are easily prepared by reaction of sulfonyl chlorides with the diamines in the presence of base (eq 2). Due to the large number of sulfonyl chlorides which are commercially available[50] and the continual development and optimization of routes to chiral diamines,[46,51−56] a wide variety of bis(sulfonamide) ligands can be easily prepared. We have chosen to work with *trans*-1,2-diaminocyclohexane because it is inexpensive and is readily resolved on large scales.[44−48] Derivatization of the diamine as sulfonamides results in a decrease of the pK_a of the N−H to about 10,[57] rendering it as acidic as phenol. The electron-withdrawing nature of the sulfonyl group also affects the ability of the deprotonated sulfonamide, the sulfonamido group, to donate electron density to metals. As a result, metals bearing sulfonamido groups exhibit enhanced Lewis acidity relative to traditional metal amides (M−NR$_2$).[15] Finally, sulfonamides are remarkably robust, being stable under hydrolytic, oxidative, and reductive conditions.[58] These qualities are ideal for the development of inert ligands.

Reaction of Ti(NMe$_2$)$_4$ with racemic and resolved bis(sulfonamide) ligands (**2rac**, **2res**, **3rac**, **3res**, and **4rac**) resulted in a rapid change in color of the reaction mixture from the yellow of Ti(NMe$_2$)$_4$ to the red-brown of bis(sulfonamido)Ti(NMe$_2$)$_2$ (eq 3). Spectroscopic data indicate that the products are the titanium bis(sulfonamido) bis(amide) complexes **5rac**, **5res**, **6rac**, **6res**, and **7rac** and the volatile *N*,*N*-dimethylamine.

We have reported the synthesis and characterization of the titanium bis(sulfonamido) bis(alkoxide) complexes

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Table 2. Selected Bond Angles for 5rac, 5res, 6rac, 6res, and 7rac (deg)

	1rac	5rac	5res	6rac	6res	7rac
N(1)−S(1)−O(1)	109.87(10)	101.1(2)	97.9(1)	97.23(14)	97.22(12)	97.92(10)
N(1)−S(1)−O(2)	105.76(10)	115.3(2)	116.9(2)	114.9(2)	114.97(13)	112.46(10)
N(2)−S(2)−O(3)	108.13(10)	100.3(2)	104.6(2)	106.09(13)	106.07(11)	105.48(11)
N(2)−S(2)−O(4)	106.98(10)	115.7(2)	113.2(2)	110.17(14)	110.50(12)	109.49(11)
N(1)−Ti(1)−N(2)		73.0(1)	73.9(1)	74.96(11)	74.37(9)	74.98(8)
N(3)−Ti(1)−N(4)		115.8(2)	114.0(1)	106.53(13)	105.36(11)	113.18(11)

Table 3. Crystallographic Data and Collection Parameters for 1rac, 5rac, 5res, 6rac, 6res, and 7rac

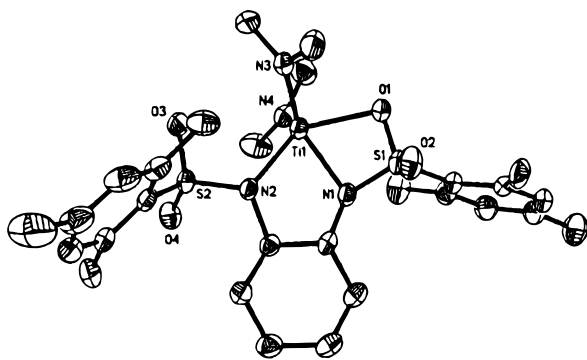|	1rac	5rac	5res	6rac	6res	7rac
empirical formula	$C_{18}H_{20}N_2O_2S_2$	$C_{24}H_{36}N_4O_4S_2Ti$	$C_{24}H_{36}N_4O_4S_2Ti$	$C_{28}H_{44}N_4O_4S_2Ti$	$C_{28}H_{44}N_4O_4S_2Ti$	$C_{40}H_{68}N_4O_4S_2Ti$
fw	392.48	556.6	556.6	612.7	612.7	781.0
cryst size (mm³)	1.3 × 0.25 × 0.20	0.45 × 0.45 × 0.32	1.0 × 1.0 × 0.4	0.5 × 0.3 × 0.2	1.0 × 0.8 × 0.5	1.0 × 1.0 × 0.7
color/shape	clear/blocks	brown/prism	brown/prism	brown/prism	brown/prism	brown/prism
space group	$P2_1/c$	$P\bar{1}$	$P2_12_12_1$	$P2_1/c$	$P2_12_12_1$	$P\bar{1}$
a (Å)	9.412(5)	9.556(4)	9.123(6)	8.879(6)	8.722(3)	9.217(4)
b (Å)	9.116(4)	11.915(7)	13.579(7)	24.746(13)	14.317(9)	12.745(5)
c (Å)	21.358(11)	13.390(7)	22.412(9)	14.158(14)	24.465(11)	19.110(11)
α (deg)		76.94(3)				76.81(4)
β (deg)	94.76	73.67(3)		98.40(7)		82.28(4)
γ (deg)		75.18(3)				88.80(4)
V (Å³)	1826(2)	1394.8(11)	2776(2)	3077(4)	3055(3)	2166(2)
Z	4	2	4	4	4	2
T (K)	190	193	189	195	188	187
diffractometer			Siemens R3m/V			
radiation, λ (Å)			Mo Kα, 0.710 373			
2θ range (deg)	1.91−27.5	3.0−55.0	3.0−55.0	1.65−22.50	1.65−27.50	1.64−25.0
data collected: hkl	0−12, 0−11, −27 to +27	0−12; −14 to +15; −14 to +15	0−11, −1 to +17, 0−29	−9 to +9, −26 to 0, 0−15	0−11, −1 to +18, 0−31	−2 to +10, −15 to +15, −22 to +22
no. of rflns	4425	6605	3852	4223	4225	7813
no. of unique rflns	4188	6418	3841	4032	4214	7611
R_{int} (%)	1.23	1.25	1.24	2.55	2.27	5.61
no. of obsd rflns	3396	4081	3439	3344	3942	6632
abs cor			semiempirical			
structure soln			direct methods			
GOF	1.113	1.44	1.30	0.805	1.035	1.042
R (%)	4.45	6.04	3.72	3.83	3.25	4.56
R_w (%)	11.81	7.33	5.40	10.01	8.96	11.74
max resid density (e/Å³)	0.872	0.47	0.73	0.294	0.385	1.080

Figure 5. Structure of **6rac**.

Figure 6. Structure of **6res**.

bis(sulfonamido)Ti(O-*i*-Pr)$_2$ (Figure 1) and have found that, in each case, the titanium coordinates two of the sulfonyl oxygens, one from each of the sulfonyl groups.[21] The titanium−sulfonyl oxygen distances range from 2.249 to 2.390 Å. Given the ability of the amide to donate electron density to metal centers,[15] we were curious as to how the amide groups would affect the Lewis acidity of the titanium center and influence the coordination of the sulfonyl oxygens of the bis(sulfona-mido) ligand. We therefore determined the structures of the titanium bis(sulfonamido) bis(amide) complexes **5rac** and **5res**. As previously communicated,[40] X-ray-quality crystals were obtained from diethyl ether and the structures were determined at low temperature. ORTEP diagrams of **5rac** and **5res** are illustrated in
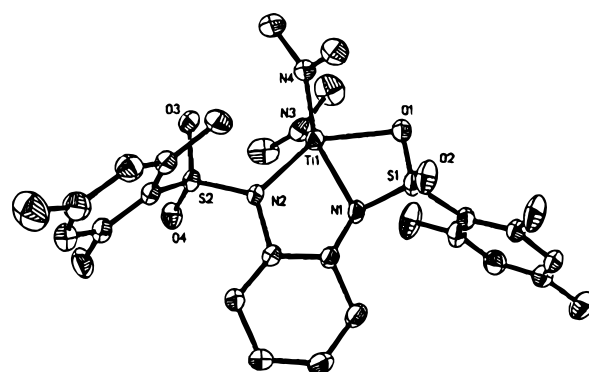
Figures 2 and 3, respectively. Selected bond distances and angles are listed in Tables 1 and 2. Each titanium is bonded to two *N,N*-dimethylamide ligands, which have distances ranging from 1.858(3) to 1.896(3) Å. These values are typical of titanium−amide bond lengths.[15] The Ti−N distances of the sulfonamido groups are significantly longer, falling between 2.048(3) and 2.094(4) Å. The large disparity in the titanium amide and sulfonamido distances is a result of the delocaliza-tion of the nitrogen lone pairs of the sulfonamido nitrogen into the electron-withdrawing sulfonyl group. In contrast, the Ti−NMe$_2$ groups behave as π-donors to titanium. To offset the poor donor ability of the sulfonamido nitrogens, the titanium forms intramolecu-
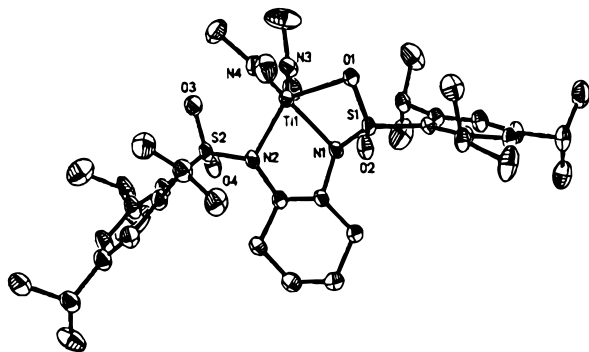
Figure 7. Structure of **7rac**.

Figure 8. Overlay of **5rac** (solid lines) and **5res** (dashed lines).

lar dative interactions with one or two of the sulfonyl oxygens. In the case of **5rac**, the titanium interacts weakly with one oxygen of each sulfonyl group, as observed with the bis(sulfonamido)titanium bis(isopropoxide) complexes. The Ti(1)−O(1) and Ti(1)−O(3) distances are very similar at 2.447(4) and 2.434(4) Å, respectively.[14] In contrast, the structure of the resolved titanium complex **5res** indicates that the titanium is interacting more strongly with only one of the sulfonyl oxygens. The Ti(1)−O(1) distance of 2.219(3) Å is markedly shorter than either of the titanium−sulfonyl oxygen interactions found in **5rac**. The distance between Ti(1) and O(3) of 2.901(4) Å in **5res** indicates that there is no interaction between these two atoms.

The impact of coordination of one or two sulfonyl oxygens to the titanium center is evident on examination of the bond angles of the sulfonamido groups in Table 2. Larger dissimilarities in the geometry about sulfur are observed for unsymmetrical **5res**. Specifically, on coordination of the sulfonyl oxygen O(1) to titanium in **5res**, the N(1)−S(1)−O(1) angle is compressed to 97.9(1)°, while the N(1)−S(1)−O(2) angle opens to 116.9-(2)°. In contrast, the N−S−O bond angles about S(2) are closer, with N(2)−S(2)−O(3) and N(2)−S(2)−O(4) angles of 104.6(2) and 113.2(2)°, respectively. The corresponding differences in bond angles in **5rac** are less pronounced, due to the weaker interaction of the sulfonyl oxygens with the titanium center. The bond angles involving the titanium-bound oxygens, N(1)−S(1)−O(1) and N(2)−S(2)-O(3), are 101.1(2) and 100.3(2)°, while N(1)−S(1)−O(2) and N(2)−S(2)−O(4) are 115.3(2) and 115.7(2)°, respectively. To aid in the visualization of the differences in the bonding between complexes prepared with racemic and resolved bis(sulfonamido) ligands, we have performed a series of overlays. As shown for **5rac** and **5res** in Figure 8, we have overlaid the structures by superimposing Ti(1), N(1), and N(2). The structure depicted with solid lines is that of **5rac**, while the structure with broken lines is **5res**. The fit of the atoms in the cyclohexane portion is quite good. The differences in the bonding of the sulfonyl oxygens and the positions and conformations of the aryl groups are also clearly illustrated in the overlay diagram.

These results strongly support the different bonding modes of the bis(sulfonamido) ligands in the derivatives **5rac** and **5res**. The differences in hapticity of the bis(sulfonamido) ligands in **5rac** and **5res** suggest that the titanium center can moderate the effect of the weakly donating sulfonamido groups by interacting loosely with two sulfonyl oxygens or more intimately with only one.
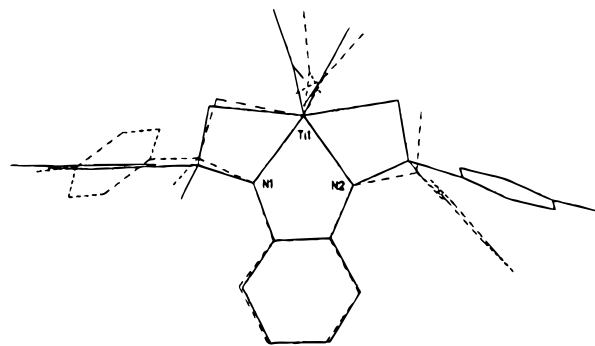
Unlike the structures of **5rac** and **5res**, which show dramatic differences in the solid state, the ¹H and ¹³C-{¹H} NMR spectra indicate that the solution structures are the same. In solution, the complexes maintain their C_2 symmetry on the NMR time scale. We have been unable to detect any loss of symmetry in the ¹H NMR spectra of **5rac** on cooling to −60 °C. This indicates that either the symmetric η^4 coordination mode of the ligand is lower in energy or that the interconversion of the η^3 and η^4 bonding modes is rapid on the NMR time scale.

The unexpected differences in the hapticities of the bis(sulfonamido) ligand in **5rac** and **5res** can be explained by considering the interactions in the solid state. It is observed that crystals of racemic and resolved materials have different properties, such as melting point and solubility. The lattice energies will vary depending on the how the molecules must pack in the crystal.[59] The structures of **5rac** and **5res** represent a rare example of the crystal-packing forces directly and dramatically affecting the bonding mode of a ligand. The origin of the structural differences between **5rac** and **5res** is not clear.

Given the peculiarity of the structures of **5rac** and **5res**, we were curious as to how crystal-packing forces would influence the hapticity of other titanium bis-(sulfonamido) bis(amide) complexes in the solid state. We therefore prepared the racemic and resolved titanium bis(sulfonamido) bis(amide) complexes **6rac** and **6res**, as illustrated in eq 3. X-ray-quality crystals of **6rac** and **6res** were grown from diethyl ether, and the ORTEP diagrams are shown in Figures 5 and 6, respectively. Unlike the racemic and resolved complexes **5rac** and **5res**, the structures of **6rac** and **6res** are almost identical, as can be determined by comparison of the gross structural features as well as the bond lengths and angles listed in Tables 1 and 2. In both, the titanium is five-coordinate, bonding to the four nitrogens of the bis(sulfonamido) and amide ligands and to one of the sulfonyl oxygens. Like the structure of **5res**, the structures **6rac** and **6res** are distorted from C_2 symmetry by coordination of one of the sulfonyl oxygens. To highlight the similarities, two overlay diagrams of **6rac** and **6res** are illustrated in Figure 9. In the diagrams, the solid-line structure is **6rac** and the broken-line structure is **6res**. The fit of the two structures is remarkably good, with small differences in the positions of the aryl rings observed.

We have also prepared the bis(amide) complex **7rac**, containing the bulky isopropyl-substituted aryl ligand

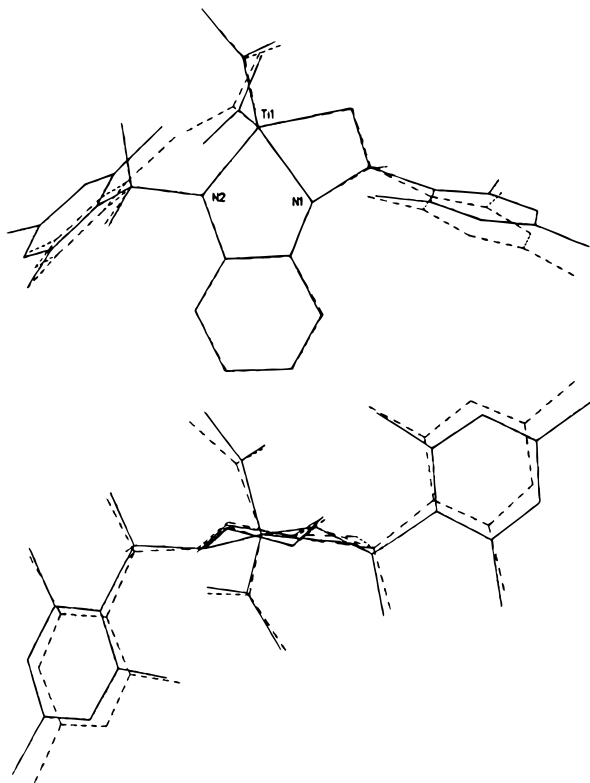(59) Desiraju, G. R. *Crystal Engineering*; Elsevier: New York, 1989.

Figure 9. Overlays of **6rac** (solid lines) and **6res** (dashed lines).

Figure 10. Overlay of **5res** (hollow lines), **6res** (dashed lines), and **7rac** (solid lines).

Figure 11.

4rac (eq 3). **7rac** is very soluble but can be crystallized from concentrated hexanes to give large blocklike deep amber crystals. Because of the considerable size of the 2,4,6-triisopropyl ligand, we thought it would be interesting to examine the effect of the bulky aryl groups on the bonding of the bis(sulfonamido) ligand. Accordingly, the structure was determined at −86 °C, and an ORTEP diagram is illustrated in Figure 7. The structure consists of a five-coordinate titanium with the fifth position occupied by one of the sulfonyl oxygens (Ti(1)−O(1) = 2.181(2) Å). The Ti(1)−N(1) and Ti(1)−N(2) distances are, on average, slightly longer than the corresponding bond distances in **5rac, 5res, 6rac**, and **6res**. This is most likely a result of steric interactions of the bulky bis(sulfonamido) ligand with the Ti(NMe₂)₂ moiety. To minimize the interaction of the isopropyl substituents with the Ti(NMe₂)₂ group, the methyls of the isopropyl groups are directed away from the titanium center. The Ti−N distances of the titanium *N,N*-dimethylamide groups are slightly longer than those in the other bis-(sulfonamido) titanium complexes. This difference is most likely due to interaction of the bis(amide) groups with the isopropyl substituents of the ligand.

To better illustrate the influence of the size of the bis-(sulfonamido) ligand on the geometry of the structures of the titanium bis(sulfonamido) bis(amide) complexes, we have superimposed the structures of **5res**, **6res**, and **7rac** (Figure 10). In Figure 10, complex **7rac** is drawn with bold bonds, **6res** with dashed bonds, and **5res** with hollow bonds. The gross features of the structures, such as the positions of the cyclohexane ring and the amide groups, are quite similar. However, the distances of the aromatic groups from the titanium are a function of the size of the substituents on aryl rings. This observation
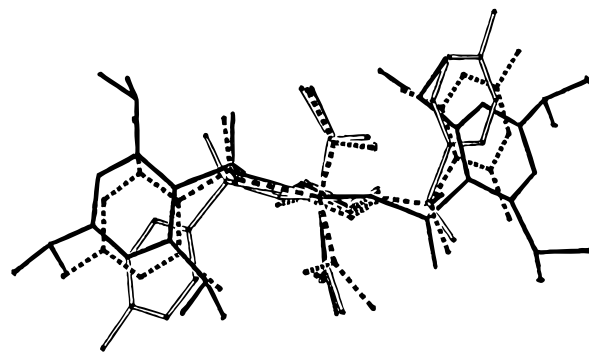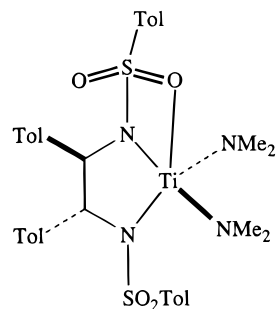
can be attributed to the interaction of the ortho substituents with the Ti(NMe₂)₂ group.

A similar trend in the positioning of the aryl groups was observed with the bis(sulfonamido)titanium bis-(isopropoxide) complexes.[21] The ligands **2res** and **3res** were used to make the bis(sulfonamido)Ti(O-*i*-Pr)₂ complexes, which were part of a structure/enantio-selectivity study. An overlay of these complexes showed that the smaller tolyl groups were closer to the metal center than the mesityl groups. The tolyl derivative gave 97% ee in the asymmetric alkylation of aldehydes (eq 1), while the mesityl compound gave only 18% ee.

The structures described here can be compared to the related titanium bis(sulfonamido) bis(amide) complex derived from 1,2-di-4-tolyl-1,2-diaminoethane prepared by Gagné and co-workers (Figure 11).[41] In this structure, the titanium is also five-coordinate, bonded to the amide and bis(sulfonamido) nitrogens and one sulfonyl oxygen as observed with **5res**, **6rac**, **6res**, and **7rac**. The titanium−sulfonyl oxygen distance is 2.26 Å, while the Ti−N distances to the sulfonamido and amide groups are 2.08 and 1.87 Å, respectively. Similar distortions of the angles about sulfur to **5res**, **6rac**, **6res**, and **7rac** also are observed. Recently, Anwander and co-workers described the synthesis of rare-earth bis(sulfonamido) compounds.[49] Using the ligand **4rac** and the yttrium amide Y[N(SiMe₃)₂]₃, they were able to prepare the yttrium bis(sulfonamido) amide complex [bis(sulfona-mido)YN(SiMe₃)₂]₂ by amine elimination (Figure 12). The solid-state structure is that of the heterochiral dimer with sulfonyl groups bridging the yttrium centers. Each ligand is $\mu^2,\eta^4{:}\eta^1$ with Y−O sulfonyl interactions ranging from 2.23 Å for the intermolecular bond distance to 2.60 Å for the intramolecular Y−O bond length (Figure 12). The greater size and unsaturation at the metal center, in combination with the oxophilicity of Y, is most likely responsible for dimer formation. The
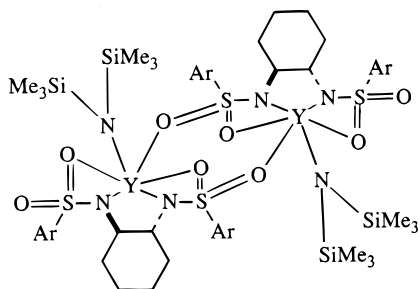
Figure 12.

structures of **5rac**, **5res**, **6rac**, **6res**, and **7rac** can also be compared to those of the titanium bis(silylamide) bis-(amide) complexes prepared by Jordan and co-workers employing *trans*-1,2-diaminocyclohexane. The Ti−N distances of the titanium−silylamide ligands range from 1.836(2) to 1.879(1) Å.[60]

In conclusion, we have synthesized bis(sulfonamido)-Ti(NMe$_2$)$_2$ complexes and examined their solid-state and solution structures. It is necessary to understand the relationship between ligand size and metal complex geometry in order to more efficiently develop catalytic asymmetric reactions. The bis(sulfonamido) ligand system is important, due to its use in the asymmetric addition of dialkylzinc reagents to aldehydes. From this work, it is clear that the chiral environment about the titanium center is highly dependent on the steric properties of the ligand. Furthermore, from the structures of **5rac** and **5res**, we are reminded that care must be exercised in drawing conclusions about geometries and bonding modes in structures which involve weak metal−ligand interactions.

Experimental Section

General Considerations. Unless otherwise noted, all manipulations were carried out under an inert atmosphere in a Vacuum Atmospheres drybox with an attached MO-40 Dritrain or by using standard Schlenk or vacuum-line techniques. Solutions were degassed as follows: they were cooled to −196 °C, evacuated under high vacuum, and thawed. This sequence was repeated three times in each case.

^{1}H NMR spectra were obtained on either the Varian Gemini 2000-BB 200 MHz Fourier transform spectrometer or a Varian Unity 500 MHz Fourier transform spectrometer at the San Diego State University NMR facility. ^{1}H NMR spectra were recorded relative to residual protiated solvent. ^{13}C{^{1}H} NMR spectra were obtained at either 50 or 125 MHz on the 200 or 500 MHz instrument, respectively, and chemical shifts were recorded relative to the solvent resonance. Chemical shifts are reported in units of parts per million downfield from tetramethylsilane, and all coupling constants are reported in Hz. IR spectra were obtained on a Perkin-Elmer 1600 series spectrometer.

Unless otherwise specified, all reagents were purchased from Aldrich Chemical Co. and used without further purification. Bis(sulfonamide) ligands[22−24] were prepared by following literature procedures.

Hexanes (UV grade, alkene free) was distilled from sodium benzophenone ketyl/tetraglyme under nitrogen. Benzene, toluene, diethyl ether, and THF were distilled from sodium benzophenone ketyl under nitrogen. Deuterated solvents (purchased from Cambridge Isotopes) for use in NMR experiments were dried in the same manner as their protiated

(60) Tsuie, B.; Swenson, D. C.; Jordan, R. F.; Peterson, J. L. *Organometallics* **1997**, *16*, 1392−1400.

analogues but were vacuum-transferred from the drying agent. CDCl$_3$ was dried over calcium hydride and vacuum-transferred.

Synthesis and Characterization of 5rac, 5res, 6rac, and 6res. The procedure for the preparation of **5rac, 5res, 6rac,** and **6res** was identical in all cases and is described for the synthesis of **5rac**. The conditions under which crystals of these compounds were grown and the characterization of the compounds are listed separately below.

Under an inert atmosphere, the insoluble ligand **2rac** (451 mg, 1.06×10^{-3} mol) was stirred in 10 mL of diethyl ether at room temperature. To this mixture was added Ti(NMe$_2$)$_4$ (2.39 mg, 1.06×10^{-3} mol, 1 equiv) as a solution in 1 mL of diethyl ether. On addition of the titanium complex, the ligand solution turned red-brown and the ligand **2rac** dissolved to give a clear solution. (If necessary, the solution was filtered after the ligand had dissolved.) When no undissolved ligand remained, stirring was discontinued and the solution was allowed to stand. After standing at room temperature (usually 1−2 h), dark amber crystals began to form. The solution was decanted, the crystals were washed with cold diethyl ether (−25 °C) and the product was allowed to dry. In this manner **5rac** was isolated in 95% yield (572 mg, 1.03×10^{-3} mol).

Data for **5rac**: mp 190° C dec; ^{1}H NMR (C$_6$D$_6$, 200 MHz) δ 7.99 (d, J = 8.2 Hz, 4H), 6.95 (d, J = 8.2 Hz, 4H), 3.68 (s, 12H), 3.55 (m, 2H), 2.32 (m, 2H), 2.07 (s, 6H), 1.41 (m, 2H), 1.24 (m, 4H) ppm; ^{13}C{^{1}H} NMR (C$_6$D$_6$, 50 MHz) δ 142.6, 129.9, 128.7, 127.5, 66.0, 46.1, 32.6, 24.9, 21.4 ppm; IR (C$_6$D$_6$) 2932, 2882, 2777, 1598, 1277, 1206, 1178, 1134, 1111, 1088, 1038, 982, 843, 887, 813, 679, 586, 554 cm^{-1}. Anal. Calcd for C$_{24}$H$_{36}$N$_4$O$_4$S$_2$Ti: C, 51.79; H, 6.52; N, 10.06. Found: C, 51.38; H, 6.48; N, 10.01.

Data for **5res**: yield 89%; melting range 170−172 °C. The solution data for **5res** are identical with those for **5rac**.

Data for **6rac**: yield 85%; ^{1}H NMR (C$_6$D$_6$, 500 MHz) δ 6.64 (s, 4H), 3.68 (m, 2H), 3.56 (s, 12H), 2.71 (s, 12H), 1.93 (s, 6H), 1.87 (m, 2H), 1.18 (m, 2H), 0.92 (m, 4H) ppm; ^{13}C{^{1}H} NMR (C$_6$D$_6$, 125 MHz) δ 141.6, 140.7, 139.3, 132.4, 65.4, 46.4, 32.5, 25.0, 23.8, 21.1 ppm; IR (C$_6$D$_6$) 2935, 2859, 2824, 2778, 1419, 1286, 1271, 1130, 1089, 1073, 1054, 1035, 1015, 976, 944, 893, 881 cm^{-1}.

Data for **6res**: yield 81%. The solution data for **6res** are identical with those for **6rac**. Anal. Calcd for C$_{28}$H$_{44}$N$_4$O$_4$S$_2$-Ti: C, 54.89; H, 7.23; N, 9.14. Found: C, 54.77; H, 7.36; N, 9.24.

Synthesis and Characterization of 7rac. Under a nitrogen atmosphere, the ligand **4rac** (258 mg, 4.20×10^{-4} mol) was suspended in 4 mL of hexanes at room temperature and the mixture stirred. To this mixture was added Ti(NMe$_2$)$_4$ (94.1 mg, 4.20×10^{-4} mol, 1 equiv) as a solution in 1 mL of hexanes. On addition of the titanium complex, the ligand solution turned amber and the ligand **4rac** dissolved to give a solution with a trace of a flocculent material. The solution was filtered, the solvent volume reduced to 2 mL under reduced pressure, and the solution cooled to −25 °C. Amber crystals formed on standing and were isolated by decanting the solvent to give **7rac** in 58% yield (191 mg, 2.44×10^{-4} mol).

Data for **7rac**: ^{1}H NMR (C$_6$D$_6$, 200 MHz) δ 7.20 (s, 4H), 4.66 (sep, J = 6.7 Hz, 4H), 3.77 (m, 2H), 3.63 (s, 12H), 2.67 (sep, J = 7.0 Hz, 2H), 1.93 (m, 2H), 1.38 (d, J = 6.7 Hz, 12H), 1.33 (d, J = 6.8 Hz, 12H), 1.16 (m, 2H), 1.12 (d, J = 6.8 Hz, 12H), 1.03 (m, 2H), 0.93 (m, 2H) ppm; ^{13}C{^{1}H} NMR (C$_6$D$_6$, 125 MHz) δ 152.6, 150.7, 140.1, 124.4, 65.7, 47.1, 34.8, 33.1, 30.1, 26.0, 25.5, 25.0, 24.2, 24.1 ppm; IR (C$_6$D$_6$) 2955, 2925, 2774, 1599, 1423, 1356, 1277, 1247, 1127, 1077, 1051, 1016, 976, 941, 891 cm^{-1}. Anal. Calcd for C$_{40}$H$_{68}$N$_4$O$_4$S$_2$Ti: C, 61.52; H, 8.78; N, 7.17. Found: C, 61.20; H, 8.81; N, 7.34.

X-ray Crystallographic Procedures. Crystals were isolated from the mother liquor and immediately immersed in Paratone under a nitrogen atmosphere in a drybox (except for **1rac**, which was studied in air). A crystal was selected for the

X-ray diffraction study and mounted in Paratone on a quartz fiber and rapidly placed in a nitrogen gas cold stream of the cryostat of the Siemens P3/PC diffractometer. The crystal was indexedd, and data were collected at low temperature. Corrections for the effects of absorption anisotropy were done. Structure solutions were performed by direct methods, and structure refinement was carried out with the programs SHELXS and SHELXL.[25] Crystallographic parameters are given in Table 3, and selected bond distances and angles are provided in Tables 1 and 2, respectively.

Supporting Information Available: X-ray crystal structure data for **1rac**, **5rac**, **5res**, **6rac**, **6res**, and **7rac**, including tables of crystal data and structure refinement details, positional and thermal parameters, and bond distances and angles and figures giving the structures with expanded atom labeling. This material is available free of charge via the Internet at http://pubs.acs.org.

OM9807755