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Synthesis and Crystal Structures of Chiral Titanium Bis(sulfonamido) Bis(amide) Complexes: Differences in Ligand Hapticity Caused by Crystal Packing Forces

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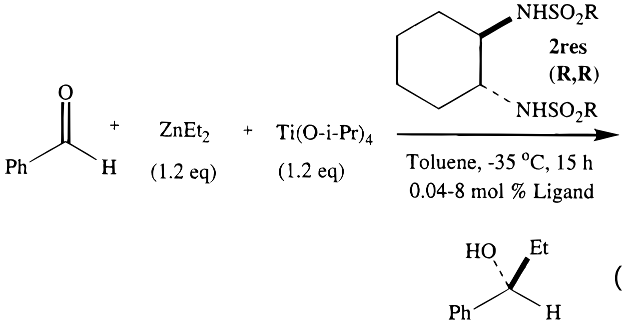
Summary: Titanium bis(sulfonamido) bis(amide) complexes ***3rac*** *and* ***3res*** *were prepared by the reaction of racemic and resolved bis(sulfonamide) ligands* ***2rac*** *and* ***2res*** *with* $Ti(NMe_2)_4$ *and have been crystallographically characterized. For both* ***3rac*** *and* ***3res****, the bis(sulfonamido) ligand binds through the oxygens of the sulfonyl group as well as through the nitrogen atoms. Coordination of the ligand in* ***3rac*** *and* ***3res*** *(*η^4 *or* η^3*) is different due to the crystal packing forces.*

The use of chiral transition metal complexes in the enantioselective synthesis of organic compounds is an important area of chemistry due to the demand for optically pure materials.[1−6] One of the most successful and significant asymmetric processes is the enantioselective formation of C−C bonds through the nucleophilic addition of alkyl groups to aldehydes.[7] The additions are efficiently catalyzed by a combination of titanium complexes with bis(sulfonamide)-[8−14] or diol-[15−18] based ligands. The bis(sulfonamide) system (eq 1), which was introduced by Ohno and co-workers,[8−10] is the most efficient at catalyzing this reaction; giving exceptionally high enantioselectivities at low catalyst loadings. Knochel and co-workers have further developed the scope of this process by employing a variety of aldehydes and functionalized dialkylzinc reagents to provide elaborate secondary alcohols with high optical purities.[19−30] The proposed catalysts for this process are the bis(sulfonamido) titanium bis(isopropoxide) complexes (**1**, Figure 1).[31]



(1)

In an effort to more thoroughly examine bis(sulfonamido) complexes related to the proposed titanium catalysts **1**, we have prepared the bis(amide) derivatives (bis(sulfonamido))$Ti(NMe_2)_2$. We have found that the bis(sulfonamido) ligand is bound to the titanium through the sulfonyl oxygens and the sulfonamido nitrogens. Furthermore, the structures of the titanium complexes with racemic and resolved bis(sulfonamide) ligands reveal that the hapticity of the ligand is highly dependent on the crystal packing forces.

Chiral bis(sulfonamide) ligands of the type employed in eq 1 are easily prepared from *trans*-1,2-diaminocy-

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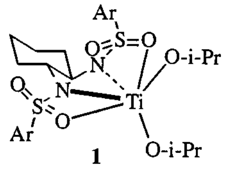
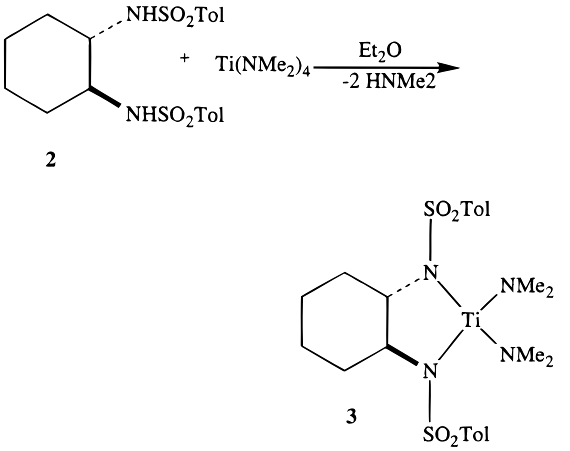


Figure 1.

clohexane[13,32,33] and *p*-toluene sulfonyl chloride in the presence of base (NaOH or Et_3N). The N−H of the sulfonamide is acidic due to the highly electron-withdrawing nature of the sulfonyl group.[34] Therefore, unlike traditional metal amides[35] ($M-NR_2$), the sulfonamido nitrogen is a poor electron donor and the resulting complexes are Lewis acidic.

The bis(sulfonamido) titanium bisamide complexes **3rac** and **3res** were easily synthesized by addition of $Ti(NMe_2)_4$ to a heterogeneous mixture of the racemic or resolved bis(sulfonamide) ligand **2rac** or **2res**, respectively, in diethyl ether (eq 2).[36] Upon addition of the titanium tetraamide to the solution of the ligand, the ligand rapidly dissolved and the color of the solution become red-brown. Within minutes at room temperature, the reaction mixture was homogeneous and stirring was discontinued. On standing, large amber crystals of the bis(sulfonamido) titanium bis(amide) complexes **3rac** or **3res** formed and were isolated in 85–96% yield.



(2)

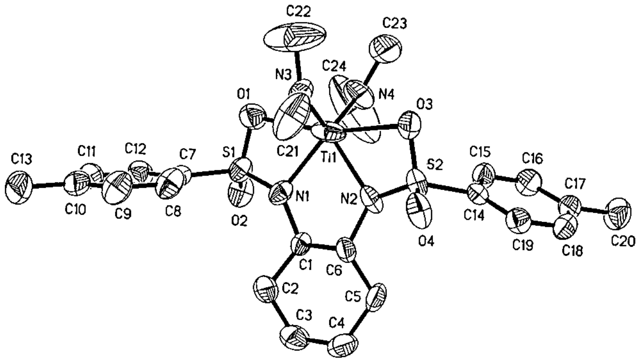


Figure 2. Crystal structure of **3rac**. Selected bond distances (Å) are as follows: Ti(1)−N(1) = 2.068(3), Ti(1)−N(2) = 2.094(4), Ti(1)−N(3) = 1.858(3), Ti(1)−N(4) = 1.861(4), Ti(1)−O(1) = 2.447(4), Ti(1)−O(3) = 2.434(4).

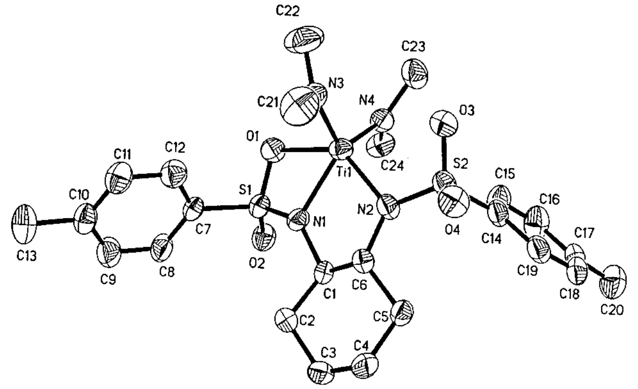


Figure 3. Crystal structure of **3res**. Selected bond distances (Å) are as follows: Ti(1)−N(1) = 2.048(3), Ti(1)−N(2) = 2.073(3), Ti(1)−N(3) = 1.859(3), Ti(1)−N(4) = 1.896(3), Ti(1)−O(1) = 2.219(3), Ti(1)−O(3) = 2.901(4).

We have determined the structures of **3rac**[37] and **3res**[38] at low temperature, and the ORTEP diagrams are illustrated in Figures 2 and 3, respectively. The geometry about the titanium in **3rac** can be described as trigional prismatic. In **3res**, the five-coordinate titanium is distorted from tetrahedral by coordination of one of the sulfonyl oxygens resulting in a highly distorted bipyramidal geometry. Both structures show titanium bonded to two *N*,*N*-dimethylamides. The Ti−N distances for the amides range from 1.858(3) to 1.896(3) Å. These values are typical of titanium−amide bond lengths.[35] The Ti−N distances of the sulfonamidos are considerably longer, ranging from 2.048(3) to 2.094(4) Å due to the delocalization of the nitrogen lone pair into the electron-withdrawing sulfonyl group. These distances can be compared to the Ti−N distances of titanium complexes of bis(silylamide) ligands derived from *trans*-1,2-diaminocyclohexane which range from 1.836(2) to 1.879(1).[39] To compensate for the decreased donor ability of the sulfonamido nitrogens, the titanium also forms intramolecular dative interactions with the sulfonyl oxygens. In the case of **3rac**, the titanium interacts weakly with both sulfonyl oxygens.[40] The Ti(1)−O(1) distance is 2.447(4) Å, while the Ti(1)−O(3)

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(37) **X-ray data for 3rac**: Data were collected at 193 K using highly oriented graphite-crystal-monochromated Mo Kα radiation. There were 6605 reflections collected in the 2θ range from 3.0° to 55.0° of which 6418 were unique (R_{int} = 1.25%). The structure was solved by direct methods, and non-hydrogen atoms were refined anisotropically. In the final least-squares refinement cycle on *F*, R = 6.04%, R_w = 7.33%, and GOF = 1.44 for 4081 reflections with $F > 4.0\sigma(F)$ and 319 parameters. The crystal data are a = 9.556(4) Å, b = 11.915(7) Å, c = 13.390(7) Å, α = 76.94(3)°, β = 73.67(3)°, γ = 75.18(3)°, V = 1394.8(11) Å^3, space group $P\bar{1}$, Z = 2, MW = 556.6, and ρ(calcd)1.325 g/cm^3.

(38) **X-ray data for 3res**: Data were collected at 189 K using highly oriented graphite-crystal-monochromated Mo Kα radiation. There were 3852 reflections collected in the 2θ range from 3.0° to 55.0° of which 3841 were unique (R_{int} = 1.24%). The structure was solved by direct methods, and non-hydrogen atoms were refined anisotropically. In the final least-squares refinement cycle on *F*, R = 3.72%, R_w = 5.23%, and GOF = 1.30 for 3439 reflections with $F > 4.0\sigma(F)$ and 326 parameters. The crystal data are a = 9.123(6) Å, b = 13.579(7) Å, c = 22.412(9) Å, V = 2776(2) Å^3, space group $P2_12_12_1$, Z = 4, MW = 556.6, and ρ(calcd)1.332 g/cm^3.

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distance is very similar at 2.434(4) Å. In contrast, the structure of the resolved titanium complex **3res** indicates that the titanium is interacting more strongly with just one of the sulfonyl oxygens. Specifically, the Ti(1)−O(1) distance of 2.219(3) Å is significantly shorter than either of the titanium—sulfonyl oxygen interactions found in **3rac**. However, the distance between Ti(1) and O(3) is 2.901(4) Å in **3res**, indicating that there is no interaction between these two atoms. Sigma bond distances for Ti−O have been predicted from the covalent radii to range from 1.99 to 2.05 Å.[41] It appears that the electrophilicity of the Ti(IV) center is compensated by the presence of two weak Ti−O(sulfonyl) dative interactions in **3rac** and by a single stronger Ti−O(sulfonyl) bonding interaction in **3res**. The ^{1}H and $^{13}C\{^{1}H\}$ NMR spectra of **3rac** and **3res** are the same in benzene-d_6 at room temperature, as expected for monomeric species. We have been unable to detect any changes in the ^{1}H NMR spectra of **3rac** 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 fast on the NMR time scale.

It is well-known that the crystals of racemic and resolved materials have different properties, such as melting point and solubility, due to the different ways the molecules must pack in the crystal.[42] Therefore, the lattice energies of the crystals will also be different. The structures of **3rac** and **3res** represent a rare example of the crystal packing forces directly and dramatically effecting the bonding mode of a ligand. There are no obvious interactions in the packing diagrams, which could be responsible for the differences in the bonding in **3rac** and **3res**.

In conclusion, we have synthesized (bis(sulfonamido))-Ti(NMe_2)$_2$ complexes and examined their solid-state and solution structures. From this introductory work, it is apparent that care must be exercised in drawing conclusions about the geometries and even bonding modes in structures which involve weak metal−ligand interactions. We are continuing to explore the use of bis(sulfonamide) ligands in early transition metal systems.

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Supporting Information Available: Tables of final atomic coordinates for the non-hydrogen atoms, anisotropic thermal parameters, complete list of bond distances and angles, and complete crystallographic data and characterization data for **3rac** and **3res** (17 pages). Ordering information is given on any current masthead page.

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