Mechanism of Asymmetric Dialkylzinc Addition to Aldehydes Catalyzed by Titanium(IV) Complexes of *N*-Sulfonylated *β*-Amino Alcohols

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A series of dimeric complexes $[TiL^*X_2]_2$ (H_2L^* = (1*R*,2*S*)-2-(4-methylbenzenesulfonylamino)-1,3-diphenyl-1-propanol (**5**); X = O-*i*-Pr (**4**), NMe_2 (**6**), or O-*t*-Bu (**7**)) were prepared, and the asymmetric Et_2Zn additions to benzaldehyde catalyzed by the complex **4**, **6**, or **7** with the addition of excess Ti(O-*i*-Pr)$_4$ give excellent enantioselectivities up to 96.3% ee. The ^{1}H NMR study shows that the catalytic systems of these complexes involve a common active intermediate. The reaction of **4** with 2 molar equiv of Ti(O-*i*-Pr)$_4$ afforded another dimeric complex, **9**, with the structure (*i*-PrO)$_2$TiL*Ti(O-*i*-Pr)$_4$. Complex **9** is demonstrated to provide a suitable environment, achieving an enantioselectivity of 95.6% ee. Complex **9** in solution is shown as a mixture of complexes **4**, **9**, and Ti(O-*i*-Pr)$_4$, and the equilibrium among these three complexes is solvent and temperature dependent. The reaction of complex **4** or **9** with MeTi(O-*i*-Pr)$_3$ furnished the complex (*i*-PrO)$_2$TiL*Ti(O-*i*-Pr)$_3$Me (**10**), which reacted stoichiometrically with benzaldehyde to afford the complex (*i*-PrO)$_2$TiL*Ti(O-*i*-Pr)$_3$(OCHMePh) (**11**), which dissociates to give a mixture of the complexes **4**, **11**, and Ti(O-*i*-Pr)$_4$. A complete scope of the mechanism is clearly deduced from stepwise reactions starting from complex **4** to **9**, **10**, **11** and then back to **4**. This is an example of a mechanism with all intermediates confirmed structurally or spectroscopically except complex **12**, which proceeds directly to complex **11**. This mechanism is also suggested to apply for the reactions catalyzed by the titanium complexes of BINOLs and diols. One of the roles of excess Ti(O-*i*-Pr)$_4$ is to facilitate removal of the product from the metal center. However, more importantly, the two major roles of Ti(O-*i*-Pr)$_4$ are to exchange an alkyl group with the dialkylzinc reagent and to regenerate complex **9** from complex **11** for next cycles of reactions.

Introduction

The asymmetric dialkylzinc addition to aldehydes[1] is one of the most important carbon−carbon bond formation reactions and has been studied extensively in the past decade. In the reactions catalyzed by zinc complexes of chiral ligands, the mechanistic details are well established experimentally and theoretically by Noyori[2] and Norrby.[3] For reactions catalyzed by chiral titanium(IV) complexes, numerious chiral ligands of C_2 symmetry such as chiral diols,[4] BINOLS,[5] and disulfonamides[6] were reported to give the desired chiral alcohols in excellent enantioselectivities. Recently, ligands derived from C_1-symmetric *β*-amino alcohols[7] and others[8] had also been developed to achieve also excellent stereocontrols. In contrast, the titanium-catalyzed reactions are more complicated due to the general requirement of excess Ti(O-*i*-Pr)$_4$ to achieve the best enantioselectivity with the use of different types of chiral ligands. The role of excess Ti(OR)$_4$ has been suggested to facilitate removal of the product from the resulting titanium metal complexes after transferring the alkyl group to aldehydes.[9] In the titanium−BINOL complex

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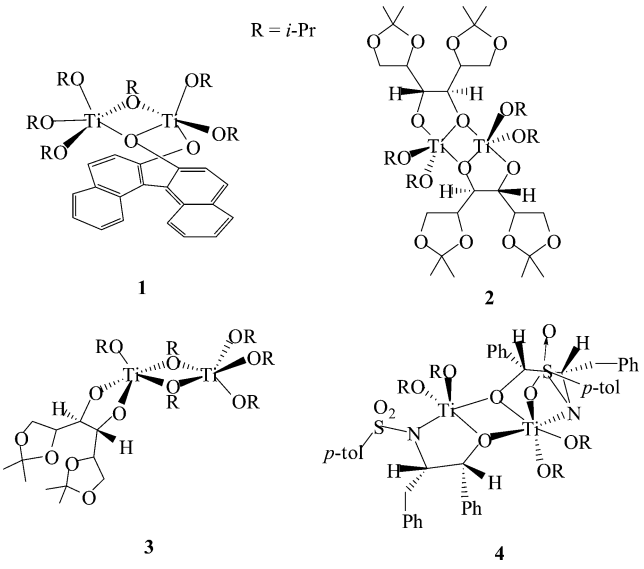
system, Nakai first suggested a bimetallic titanium catalyst containing only one BINOLate ligand.[10] In the past 5 years, a number of chiral titanium complexes have been prepared for X-ray structural analyses.[11] A mechanistic insight was reported in a delicate study by Walsh et al., and from the racemic BINOL, they were able to prepared a bimetallic titanium−BINOLate complex, **1**.[12] The molecular structure of **1** shows that the two metal centers are bridged by one 2-propoxide ligand and one BINOLate oxygen donor instead of two 2-propoxide bridging ligands suggested by Nakai. The chiral bimetallic complex **1** is considered as the active catalyst in the asymmetric dialkylzinc addition reactions to aldehydes. Our recent study on the titanium complexes of D-mannitol derivatives shows that the reaction of the chiral diol with 1 molar equiv of Ti(O-*i*-Pr)$_4$ gives a dimeric complex, **2**, having a Ti/chiral diol ratio of 1:1.[13] In the presence of excess Ti(O-*i*-Pr)$_4$, complex **2** reacts further with Ti(O-*i*-Pr)$_4$ to afford another dinuclear titanium complex, **3**, with a Ti/chiral diol ratio of 2:1. The structure of complex **3** is proposed on the basis of ^{1}H NMR and FAB-mass evidence, and complex **3** is suggested to be effective in the asymmetric reactions. For ligands of *N*-sulfonylated amine alcohols, Yus et al. suggested an active bimetallic species having a structure similar to the structure **3**, and the catalytic cycle was proposed involving species of charged metal centers.[14] In our study of titanium complexes of *N*-sulfonylated *β*-amino alcohols, the dimeric complex **4** was prepared, and complex **4** alone was proven ineffective as a catalyst.[15] However, with the addition of excess Ti(O-*i*-Pr)$_4$ to complex **4**, the resulting system catalyzes the reactions with excellent enantioselectivities up to 96% ee. The same requirement of excess Ti(O-*i*-Pr)$_4$ strongly suggests that the asymmetric diethylzinc addition reactions catalyzed by titanium complexes of *N*-sulfonylated *β*-amino alcohols should proceed in a mechanism similar to that of titanium complexes of chiral diols or BINOLs. However, the questions raised are as follows: (1) why do the titanium complexes of *N*-sulfonylated *β*-amino alcohols provide a suitable environment for achieving excellent stereocontrols; and (2) how do the catalytic reactions proceed? Thus it is important to establish a mechanism for this prototype of reactions.



Following our studies of asymmetric reactions catalyzed by chiral titanium complexes[16] and for exploring the active intermediate and the role of excess Ti(O*i*-Pr)$_4$ in the asymmetric additions of dialkylzinc to aldehydes, we here report the synthesis of bimetallic complexes [TiL*X$_2$]$_2$ (X = O-*i*-Pr (**4**),[15] NMe$_2$ (**6**), or O-*t*-Bu (**7**)) and (*i*-PrO)$_2$TiL*TiR(O-*i*-Pr)$_3$ (R = O-*i*-Pr (**9**), Me (**10**), or OCHMePh (**11**)). With the addition of excess Ti(O-*i*-Pr)$_4$, complexes **4**, **6**, and **7** are demonstrated to be effective in stereocontrol, indicating a common intermediate involved in the catalytic reactions. The structure of complex **9** shows an open pocket after dissociation of the weak Ti−O(sulfonyl) bond for accommodation of the incoming aldehyde, and **9** is proven to provide a suitable environment for achieving excellent enantioselectivities. Complex **9**, **10**, or **11** is shown to exist as an equilibrium mixture of itself, complex **4**, and the Ti(O-*i*-Pr)$_4$ or Ti(O-*i*-Pr)$_3$(OCHMePh) in solution. Stepwise reactions starting from complex **4** to **9**, **10**, **11**, and then back to the complex **4** complete a catalytic cycle of the mechanism. This is a titanium-catalyzed mechanism with all intermediates confirmed.

Results and Discussion

Synthesis of Titanium Complexes 6 and 7 and the Molecular Structure of 7. For studying the effects of nonchiral supporting ligands, the reaction of Ti(NMe$_2$)$_4$ with 1 molar equiv of *N*-sulfonylated *β*-amino alcohol **5** was carried out, affording the dimeric complex

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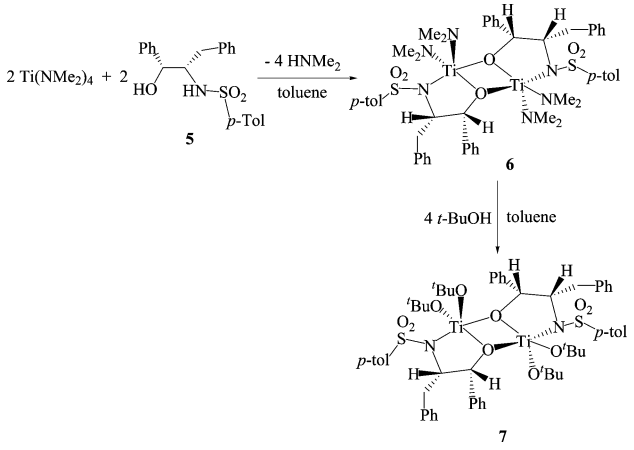
Scheme 1



6 (Scheme 1). For complex **6**, a dimeric structure bridging through the alkoxide donor of the chiral *N*-sulfonylated *β*-amido alcoholato ligand is proposed according to the literature.[11d,e] Treatment of **6** with 4 molar equiv of *t*-BuOH furnished another dimeric complex, **7**, with the two titanium metal centers bridged also by the chiral alcoholato donors. Both complexes are characterized by ^{1}H NMR spectroscopy. Colorless crystals of **7** were grown from a solution of toluene/*n*-hexane, and the molecular structure is shown in Figure 1.

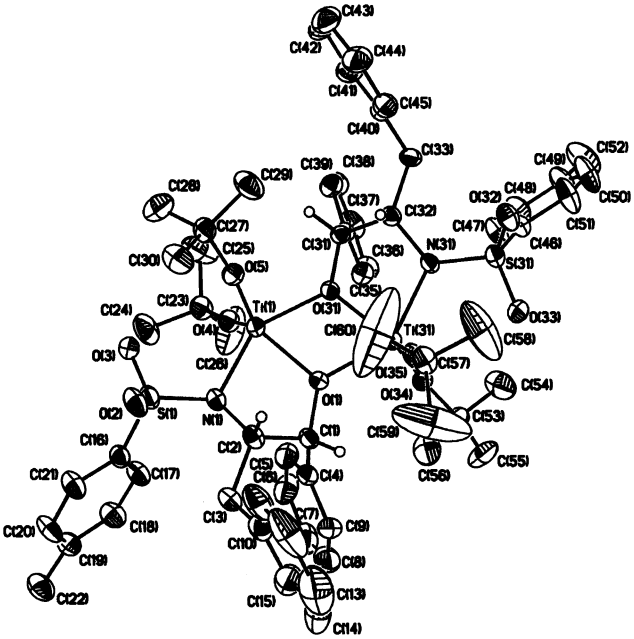
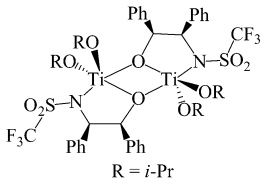


Figure 1. Molecular structure of **7**. Hydrogen atoms, except those attached to chiral carbon atoms, are omitted for clarity. Bond lengths (Å): Ti(1)−O(1), 2.013(3); Ti(1)−N(1), 2.083(4); Ti(1)−O(4), 1.732(3); Ti(1)−O(5), 1.734(3); Ti(1)−O(31), 2.036(3); Ti(31)−O(31), 2.003(3); Ti(31)−N(31), 2.079(4); Ti(31)−O(34), 1.740(3); Ti(31)−O(35), 1.731-(3); Ti(31)−O(1), 2.025(3); Ti(1)···Ti(31), 3.3219(12). Bond angles (deg): N(1)−Ti(1)−O(31), 144.12(15); O(1)−Ti(1)−O(4), 120.88(16); O(1)−Ti(1)−O(5), 124.45; O(4)−Ti(1)−O(5), 113.62(18); O(1)−Ti(1)−O(31), 68.68(11); Ti(1)−O(1)−Ti(31), 110.71(13); Ti(1)−O(31)−Ti(31), 110.67(12); Ti(1)−O(4)−C(23), 168.9(4); Ti(1)−O(5)−C(27), 171.0(4); N(31)−Ti(31)−O(1), 144.75(14); O(31)−Ti(31)−O(34), 119.32-(14); O(31)−Ti(31)−O(35), 124.77(15); O(34)−Ti(31)−O(35), 115.12(16); Ti(31)−O(34)−C(53), 160.4(4); Ti(31)−O(35)−C(57), 169.0(4).

Complex **7** is a symmetric dimeric compound bridging through the chiral alcoholato alkoxide donors, and its structure is the same as that of the complex **8**,[11e] with both metal centers adopting a distorted trigonal-bipyramidal geometry. Structural data around both metal centers in **7** are nearly identical. For example, the axial N(1)−Ti(1)−O(31) and N(31)−Ti(2)−O(1) angles are observed to be 144.12(15)° and 144.75(14)°, respectively. All bonds attached to titanium metals in **7** are found slightly shorter than corresponding distances in **8**, indicating slightly better bonding of ligands in complex **7**. For comparison between complexes **4** and **7**, the only difference is the *tert*-butoxide instead of isopropoxide ligands in **4**. However, it is interesting to note that the solid state structure of **7** is different from the complex **4**.[15] The bonding parameters in the five-coordinate titanium metal center in **4** reveal slight variations relative to those for **7**. However, due to the coordination of the sulfonyl oxygen in one metal center in the solid state structure of **4**, Ti−OR and one of Ti−O(*μ*) bond distance are much longer while Ti−N and another Ti−O(*μ*) bond length are shorter. For complex **7**, the bulkier and better *π*-donating characteristics of *tert*-butoxide ligands hinder a further coordination of the sulfonyl oxygens and thus result in a dimeric structure having both metal centers of five coordination. The structures of **4**, **7**, and **8** clearly demonstrate structural variations in terms of variations of alkoxides and chiral *N*-sulfonylated *β*-amido alcoholato ligands.



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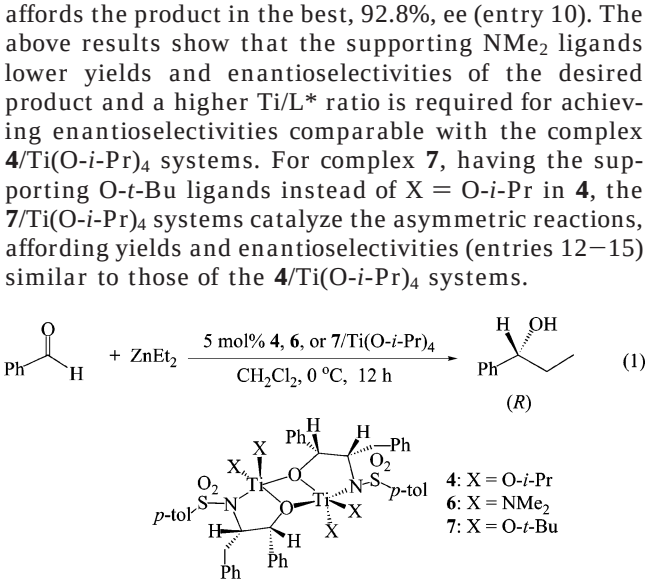
Asymmetric $ZnEt_2$ Addition to Benzaldehyde Catalyzed by Titanium(IV) Complexes 4, 6, or 7/Ti(O-*i*-Pr)$_4$ Systems. For exploring the effects of supporting nonchiral ligands X, the asymmetric diethylzinc additions to benzaldehyde employing the titanium(IV) complex **4**, **6**, or **7** without/with the addition of Ti(O-*i*-Pr)$_4$ were conducted (eq 1), and results are listed in Table 1. The reaction catalyzed by 5 mol % **4** (10 mol % chiral liand) is sluggish with only 9.2% yield of the desired product (entry 1). With the addition of 6 molar equiv of Ti(O-*i*-Pr)$_4$ to complex **4**, the resulting system has a Ti/L* (L* = *N*-sulfonylated *β*-amino alcoholate) ratio of 4 and the yield and the enantioselectivity of the product improve dramatically to 80.7% and 86.7% ee (entry 2), respectively. Further increasing the Ti/L* ratio to 8, the yield reaches 100% and the best enantioselectivity of 96.3% ee is achieved (entry 3). With a Ti/L* ratio of 10, a comparable enantioselectivity of 95.5% ee is observed (entry 4). For 5 mol % complex **6** alone, a slightly better reactivity of 18% yield is obtained (entry 5). Increasing the Ti/L* ratio to 4 gives the product in only 34% yield (entry 6), which is much lower than 80.7% for the **4**/Ti(O-*i*-Pr)$_4$ system with the same Ti/L* ratio. Increasing the Ti/L* ratio to 8 and 10 increases the yields to 89.3 and 95.0% and the enantioselectivities increase to 75.9 and 79.2% ee (entries 7 and 8), respectively. Further increasing the Ti/L* ratio to 16

Table 1. Asymmetric Diethylzinc Addition to Benzaldehyde Catalyzed by Complex 4, 6, or 7/Ti(O-*i*-Pr)$_4$ Systems[a−c]

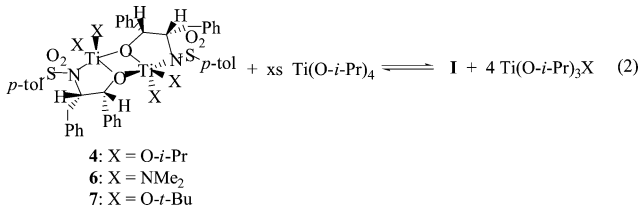
entry	complex	X	Ti(O-*i*-Pr)$_4$ (equiv)	Ti/L*	yield (%)	ee (%)
1[d]	**4**	O-*i*-Pr	0	1	9.2	
2[d]	**4**	O-*i*-Pr	6	4	80.7	86.7
3[d]	**4**	O-*i*-Pr	14	8	100	96.3
4[d]	**4**	O-*i*-Pr	18	10	99.0	95.5
5	**6**	NMe_2	0	1	18.0	
6	**6**	NMe_2	6	4	34.0	
7	**6**	NMe_2	14	8	89.3	75.9
8	**6**	NMe_2	18	10	95.0	79.2
9	**6**	NMe_2	22	12	95.8	89.6
10	**6**	NMe_2	30	16	95.8	92.8
11	**6**	NMe_2	38	20	99.0	91.9
12	**7**	O-*t*-Bu	0	1	8.5	
13	**7**	O-*t*-Bu	6	4	90.3	58.6
14	**7**	O-*t*-Bu	14	8	100	91.5
15	**7**	O-*t*-Bu	18	10	100	94.0

[a] Reaction conditions: PhCHO/$ZnEt_2$/complex = 1:1.5:0.1; solvent, CH_2Cl_2; reaction temperature, 0 °C; reaction time, 12 h. [b] Yields (%) were determined by ^{1}H NMR. [c] ee (%) values were determiend by HPLC using a Chiralcel OD column from Daicel. [d] Reference 15.

affords the product in the best, 92.8%, ee (entry 10). The above results show that the supporting NMe_2 ligands lower yields and enantioselectivities of the desired product and a higher Ti/L* ratio is required for achieving enantioselectivities comparable with the complex **4**/Ti(O-*i*-Pr)$_4$ systems. For complex **7**, having the supporting O-*t*-Bu ligands instead of X = O-*i*-Pr in **4**, the **7**/Ti(O-*i*-Pr)$_4$ systems catalyze the asymmetric reactions, affording yields and enantioselectivities (entries 12−15) similar to those of the **4**/Ti(O-*i*-Pr)$_4$ systems.



The above results demonstrate that complex **4**, **6**, or **7** alone is not an effective catalyst. However, upon addition Ti(O-*i*-Pr)$_4$ to the complex, a general feature of increasing yields and enantioselectivities with increasing Ti/L* ratios is observed, strongly suggesting the common intermediate **I** generated in the catalytic solutions from reactions of complex **4**, **6**, or **7** with Ti(O-*i*-Pr)$_4$ (eq 2). For complex **6**, with X = NMe_2, a higher ratio of Ti(O-*i*-Pr)$_4$ is required to push the equilibrium toward the formation of the complex **I** in solution.



^{1}H NMR Study of the Complexes 4 and 6/Ti(O-*i*-Pr)$_4$ Systems. For verifying if the common complex **I** is generated in solution, a ^{1}H NMR study of complex **6** in CD_2Cl_2 at 0 °C was conducted, and the spectra in the C*H*(O−)Ph methine region along with the spectra of the complex **4**/Ti(O-*i*-Pr)$_4$ systems are shown in Figure 2. Figure 2c shows the spectrum of complex **6** having only one C*H*(O−)Ph doublet at δ 4.989 ppm. With the addition of 38 equiv of Ti(O-*i*-Pr)$_4$ to complex **6**, the ^{1}H NMR spectrum exhibits a new doublet at δ 5.460 ppm in addition to the original doublet as shown in Figure 2d. This resonance is exactly at the same chemical shift of the major doublet for the complex **4** with the addition of 18 equiv of Ti(O-*i*-Pr)$_4$ as shown in Figure 2b. For complex **4** alone, the major peak appears relatively downfield at δ 5.642 ppm without the observation of the resonance at δ 5.460 ppm (Figure 2a). The above study clearly demonstrates the formation of the common complex **I** with the C*H*(O−)Ph methine doublet appearing at δ 5.460 ppm from mixing either complex **6** or complex **4** with excess Ti(O-*i*-Pr)$_4$.

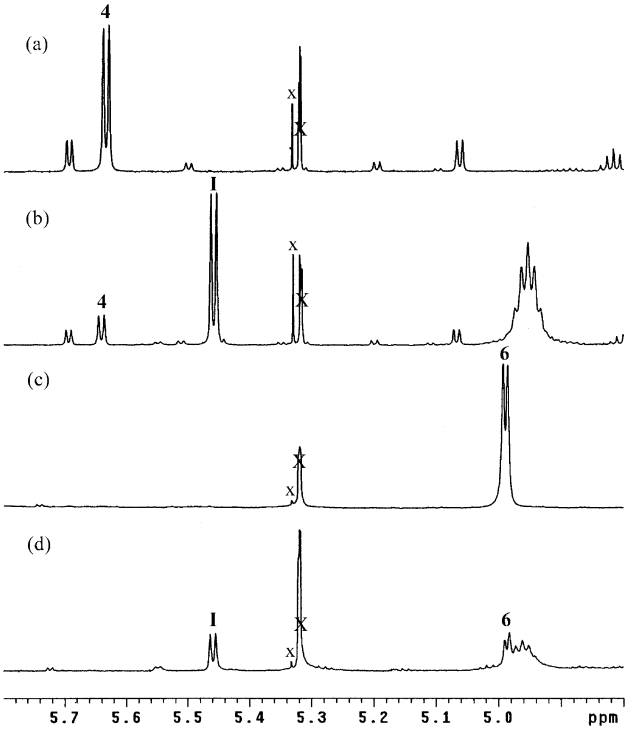


Figure 2. ^{1}H NMR Spectra from δ 5.80 to 4.80 ppm for complexes **4** and **6** in CD_2Cl_2 at 600 MHz at 0 °C: (a) **4**; (b) **4** + 18 equiv of Ti(O-*i*-Pr)$_4$; (c) **6**; and (d) **6** + 38 equiv of Ti(O-*i*-Pr)$_4$. X: CD_2Cl_2 solvent; x: impurity.

Synthesis and Molecular Structure of the Dimeric Titanium(IV) Complex 9. For further exploring the structure of **I**, treatment of 2 molar equiv of Ti(O-*i*-Pr)$_4$ with complex **4** in *n*-hexane furnished colorless crystals of **9** in 67.5% yield after concentrating and cooling the solution. Complex **9** was subjected to an X-ray analysis, and the molecular structure of **9** is confirmed as a dimeric species having a Ti/L* ratio of 2 (Figure 3). Since complex **9** contains only one chiral ligand, the two metal centers are inequivalent to six and five coordinations, respectively. The six-coordinate metal center has a structure similar to the six-coordinate metal moiety in **4** except for replacing one of the bridging chiral alcoholate oxygen donors with the nonchiral 2-propoxide ligand. In **9**, the Ti−O(sulfonyl) bond is trans to the strong 2-propoxide ligand, and this bond is weak, with a bond length of 2.473(3) Å, which is comparable to the

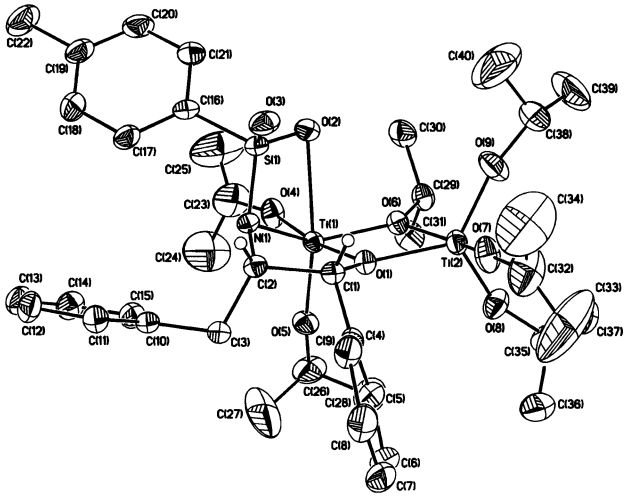


Figure 3. Molecular structure of **9**. Hydrogen atoms, except those attached to chiral carbon atoms, are omitted for clarity. Bond lengths (Å): Ti(1)−O(1), 2.083(2); Ti(1)−N(1), 2.093(3); Ti(1)−O(2), 2.474(3); Ti(1)−O(4), 1.761(3); Ti(1)−O(5), 1.775(3); Ti(1)−O(6), 1.918(2); Ti(2)−O(1), 1.983(3); Ti(2)−O(6), 2.079(4); Ti(2)−O(7), 1.768(3); Ti(2)−O(8), 1.772(3); Ti(2)−O(9), 1.777(3); Ti(1)···Ti(2), 3.2639(10). Bond angles (deg): O(1)−Ti(1)−O(4), 170.04(14); O(2)−Ti(1)−O(5), 167.65(11); N(1)−Ti(1)−O(6), 136.69(11); O(1)−Ti(1)−O(6), 74.47(10); Ti(1)−O(1)−Ti(2), 106.75(10); Ti(1)−O(6)−Ti(2), 106.91(11); N(1)−Ti(1)−O(2), 63.00(10); Ti(1)−O(4)−C(23), 166.2(5); Ti(1)−O(5)−C(26), 149.0(4); O(7)−Ti(2)−O(6), 162.59(13); O(1)−Ti(2)−O(8), 115.05(14); O(1)−Ti(2)−O(9), 129.35(16); O(8)−Ti(2)−O(9), 110.91(19); O(1)−Ti(2)−O(6), 71.87(9); Ti(2)−O(7)−C(32), 166.4(5); Ti(2)−O(8)−C(35), 150.2(5); Ti(2)−O(9)−C(38), 146.1(5).

distance of 2.486(5) Å in **4**. All bonding parameters in the six-coordinate moiety in **9** are comparable to the correspondent data in **4** except for the slightly shorter Ti(1)−O(6) distance of 1.918(2) Å (1.961(4) Å in **9**) and the much smaller Ti(1)−O(5)−C(26) angle of 149.0(4)° (>160° in **4**). For the five-coordinate moiety, in contrast, the Ti(2)−O(6) distance of 2.079(4) Å is slightly longer than the correspondent distance of 2.025(4) Å in **4**. Due to the donation of three terminal 2-propoxide ligands instead of two 2-propoxide ligands in **4**, the three Ti−OR distances are nearly identical, ranging from 1.768(3) to 1.777(3) Å, and are longer than the two bond lengths of 1.721(6) and 1.745(5) Å in **4**. The Ti(2)−O(1) distance of 1.983(3) Å is shorter than the distance of 2.031(4) Å (Ti(2)−O(31)) in **4**. Differences are observed for other bonding parameters due to differences of bonding ligands in the five-coordinate moiety.

The structure of **9** clearly reveals a pocket on the same side of the sulfonyl oxygen bond. Since the Ti−O(sulfonyl) bond is very weak, the benzaldehyde is expected to access the six-coordinate metal center from the top of the pocket for replacing the sulfonyl oxygen donor. Apparently, this pocket locks the benzaldehyde substrate into suitable position for achieving the best enantioselectivity. For the ineffective complex **4**, the structure is much more congested to prevent the substrate from accessing the metal centers. For the Ti−BINOLate complex **1**, a similar pocket is also observed.

^{1}H NMR Study of Solvent Effects of Complex 9. Although the X-ray analysis shows a dimeric structure having a Ti/L* ratio of 2 for the complex **9**, the ^{1}H NMR spectrum of complex **9** in $CDCl_3$ reveals the existence

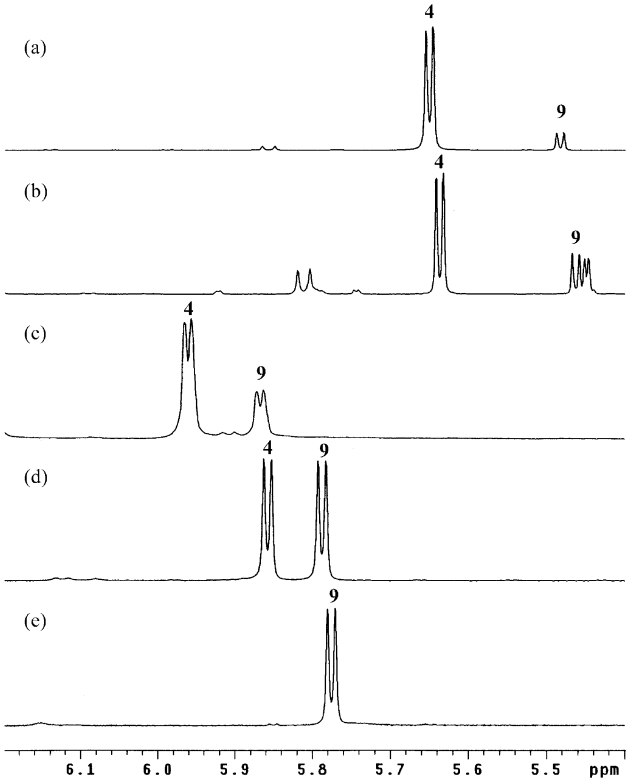
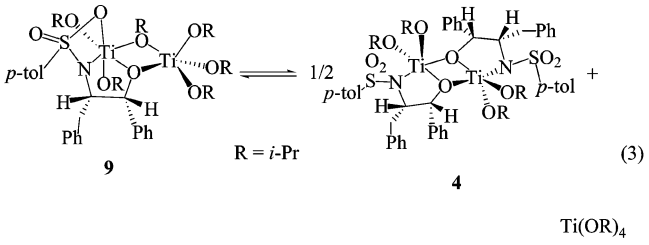


Figure 4. ^{1}H NMR spectra in the −C*H*(O−)Ph methine region of complex **9** at 600 MHz at 0 °C in (a) $CDCl_3$, (b) CD_2Cl_2, (c) toluene-d_8, (d) *n*-hexane-d_{14}, and (e) + 18 equiv of Ti(O-*i*-Pr)$_4$ in *n*-hexane-d_{14}.

of mainly the dimeric complex **4** and a minor species. This finding prompted us to investigate solvent effects of complex **9** in solution, and the spectra in the C*H*-(O−)Ph methine region in $CDCl_3$, CD_2Cl_2, toluene-d_8, and *n*-hexane-d_{14} are shown in Figure 4. In $CDCl_3$ (Figure 4a), the major doublet at δ 5.651 ppm of 88.6% intensity is the resonance for complex **4**, and the minor peak at δ 5.483 ppm of 11.4% intenisty is considered as the resonance of complex **9**. Complex **4** is a dimeric species containing two chiral ligands, and complex **9** contains only one chiral ligand. On the basis of the relative intensities of 8:1 of the methine doublets, the relative abundance of **4**/**9** is 4:1. Figure 4b shows the spectrum of complex **9** in CD_2Cl_2, and four major doublets are observed along with a couple of minor doublets of lower intensities. Our previous ^{1}H NMR study of complex **4** in CD_2Cl_2 shows a complicated spectrum with a major peak at δ 5.634 ppm, and with the addition of Ti(O-*i*-Pr)$_4$ to the complex **4**, a new major species is formed with the resonance appearing at δ 5.459 ppm. The spectrum in Figure 4b shows a pattern very similar to that of the **4**/Ti(O-*i*-Pr)$_4$ system, and the doublet at δ 5.637 ppm is the peak of complex **4**. The doublet at δ 5.463 ppm is the resonance of complex **9**, and in CD_2Cl_2, the relative abundance of these two species decreases to ∼1.5:1. When the spectrum is taken in the less polar toluene-d_8, two doublets at δ 5.962 and 5.868 ppm are observed, as shown in Figure 4c. The downfield peak is suggested to be the resonance of complex **4**, and the upfield resonance belongs to the peak of complex **9**. The relative abundance of **4**/**9** further decreases to ∼1.15:1. When the spectrum is recorded in nonpolar *n*-hexane-d_{14}, as shown in Figure 4d, two

doublets of equal intensities are observed at δ 5.857 and 5.788 ppm, respectively. The upfield peak is confirmed as the resonance of complex **9** from the ^{1}H NMR experiment of addition of Ti(O-*i*-Pr)$_4$ to complex **9**, which shows only one species with the resonance appearing at δ 5.776 ppm. In *n*-hexane-d_{14}, the relative abundance of **4**/**9** becomes 1:2. Although complex **9** is obtained from the solution of *n*-hexane as colorless crystals, the above results show that complex **9** dissociates in solution to give a mixture of complexes **4**, **9**, and Ti(O-*i*-Pr)$_4$, which are in equilibrium as illustrated in eq 3. The equilibrium process is solvent dependent, with the polar solvent resulting in higher abundance of complex **4**, and the order of dissociation is established as $CDCl_3$ > CD_2Cl_2 > toluene-d_8 > *n*-hexane-d_{14}. Since this dissociation process gives a positive ΔS (2 molecules of **9** dissociate to 1 molecule of **4** and 2 molecules of Ti(O-*i*-Pr)$_4$), it is perceivable that more polar solvents favor the dissociation process of complex **9**.



(3)

^{1}H Variable-Temperature NMR Study of Complex 9. The temperature effect of complex **9** in *n*-hexane-d_{14} is also studied, and selected spectra are shown in Figure 5. It is interesting to note that the equilibrium described in eq 3 is also temperature dependent. The spectra clearly reveal the existence of two species of complexes **4** and **9**, and the relative ratios of **4**/**9** increase with increasing temperature. For example, at −40.0 °C, the relative ratio is determined to be 1:8 based on the −C*H*(−O)Ph methine resonances for the two complexes. The ratios increase to 1:3, 1:2, 3:4, and 5:4 at −20.0, 0.0, 20.0, and 40.0 °C, respectively.

Asymmetric ZnEt$_2$ Addition to Benzaldehyde Mediated or Catalyzed by Complex 9. For showing the effectiveness of complex **9** in stereocontrol in the asymmetric diethylzinc addition reactions, a stoichiometric reaction of complex **9** with benzaldehyde and diethylzinc was first examined in *n*-hexane at 0 °C in 12 h. (*R*)-1-Phenylpropanol is obtained in 100% yield and 95.6% ee. For this reaction, it should be kept in mind that complex **9** in solution exists as an equilibrium of the complexes **4**, **9**, and Ti(O-*i*-Pr)$_4$. Nevertheless, the stoichiometric reaction gives the same enantioselectivity as that of the in situ-formed **4**/Ti(O-*i*-Pr)$_4$ system having a Ti/L* ratio of 10:1. This result clearly demonstrates that complex **9** indeed provides a suitable environment for the best enantioselectivity. The catalytic activity of 10 mol % complex **9** was also tested, and the result shows a yield of 100% and a lower enantioselectivity of 42.8% ee. Without the addition of Ti(O-*i*-Pr)$_4$ to remove the (*R*)-1-phenylpropoxide from the resulting complex for regenerating complex **9** for next cycles, the resulting chiral alkoxide still resides on the titanium metals after the first cycle. As the reaction proceeds, more chiral alkoxides accumulate on the titanium metals, giving complexes with different environments from that in complex **9**. Apparently, the sterically bulkier (*R*)-1-phenylpropoxide ligands on the metals have a negative effect on stereocontrol in the asymmetric reactions.

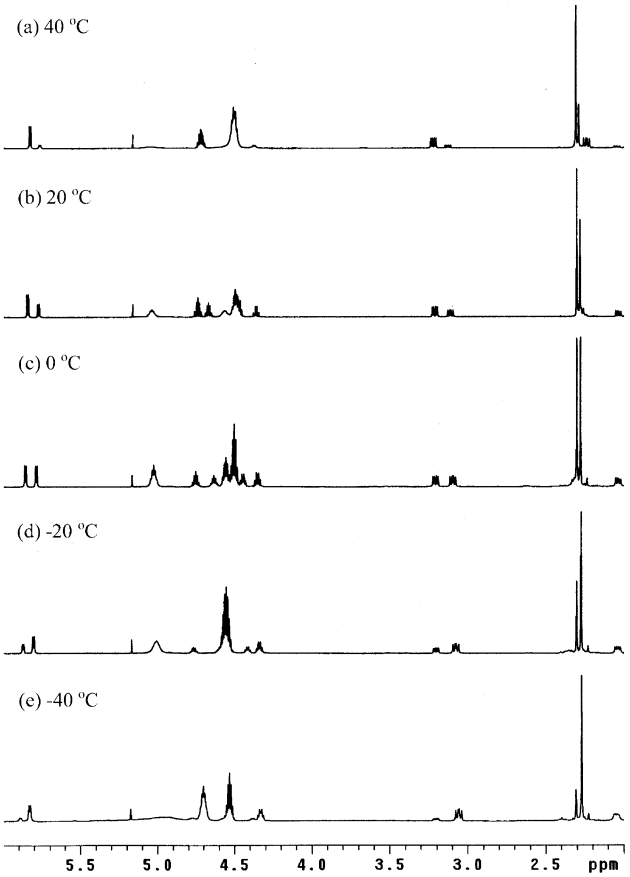
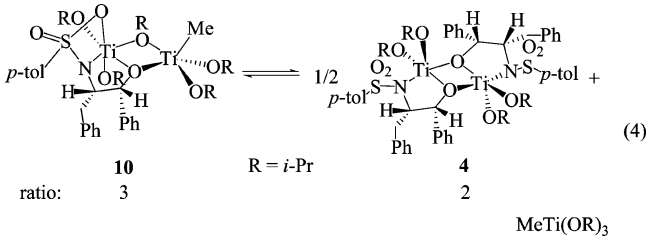


Figure 5. Selected ^{1}H variable-temperature NMR spectra of complex **9** in the region from δ 6.00 to 2.00 ppm at 600 MHz in *n*-hexane-d_{14}.

Asymmetric ZnMe$_2$ or MeTi(O-*i*-Pr)$_3$ Addition to Benzaldehyde Mediated or Catalyzed by the Titanium(IV) Complex 9 or 10. Up to this point, a question raised is whether the alkyl source is from dialkylzinc directly or from RTi(O-*i*-Pr)$_3$, which is obtained by transferring an alkyl group from ZnR_2 to Ti(O-*i*-Pr)$_4$. The study by Yoshioda et al. demonstrates a complicated equilibrium system containing EtTi(O-*i*-Pr)$_3$ species from the reaction of Ti(O-*i*-Pr)$_4$ with $ZnEt_2$.[17] In the work by Walsh, the extent of transferring a methyl group from Me_2Zn to Ti(O-*i*-Pr)$_4$ to give the MeTi(O-*i*-Pr)$_3$ complex is 2−3%.[12] For verifying the requirement of transferring an alkyl group to the excess Ti(O-*i*-Pr)$_4$ in advance, MeTi(O-*i*-Pr)$_3$ was prepared from a reaction of ClTi(O-*i*-Pr)$_3$ with 1 molar equiv of LiMe.[18] The reaction of complex **4** with 2 molar equiv of MeTi(O-*i*-Pr)$_3$ gave a quantitative yield of dimeric complex **10**. The reaction of complex **9** also resulted in the formation of complex **10**. Complex **10** is stable for several days as long as the complex is shielded from light and stored in a refrigerator. However, complex **10** in solution is highly unstable and decomposes into unidentified products in 24 h. The ^{1}H NMR spectrum of the complex reveals an equilibrium of the complexes

(17) Yoshioda, M.; Kawakita, T.; Ohno, M. *Tetrahedron Lett.* **1989**, *30*, 1657.
(18) Reetz, M. T.; Westermann, J.; Steinbach, R.; Wenderoth, B.; Peter, R.; Ostarek, R.; Maus, S. *Chem. Ber.* **1985**, *118*, 1421.

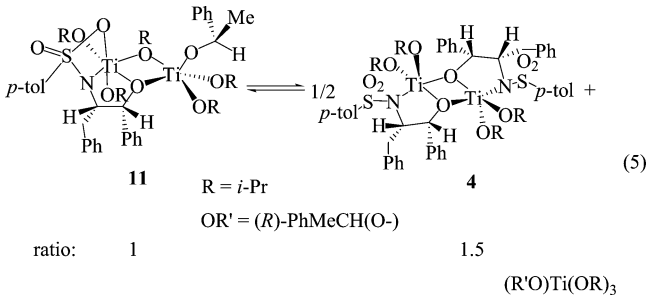
4, **10**, and Ti(O-*i*-Pr)$_4$ as described in eq 4, and the relative abundance of **4**/**10** is 2:3. A stoichiometric reaction of complex **9** with 1.5 molar equiv of Me_2Zn followed by the addition of 1.0 molar equiv of benzaldehyde was conducted, affording the chiral alcohol in 100% yield and 91.6% ee. For comparison, the stoichiometric reaction of complex **10** with 1.0 molar equiv of benzaldehyde gives the product in a somewhat lower yield of 78.0% and a comparable enantioselectivity of 94.0% ee. For the similar enantioselectivities of these two reactions, two possible reasons can account for the observations: (1) the stereoselectivity for transferring a methyl group from Me_2Zn to the attached benzaldehyde directly is comparable to that from the methyl group in **10**; and (2) a common methyl source of MeTi(O-*i*-Pr)$_3$ gives similar enantioselectivities. MeTi(O-*i*-Pr)$_3$ has been shown to react easily with **4** to give the active intermediate **10** as the reverse reaction shown in eq 4. However, the reaction catalyzed by 10 mol % **9** alone suggests incapability of Et_2Zn for transferring the ethyl group to the dimeric complex directly, and thus, the first reason for transferring the alkyl group directly to the active dimeric complex containing the benzaldehyde ligand can be ruled out.



(4)

For further supporting the preliminary requirement of transferring the alkyl group to Ti(O-*i*-Pr)$_4$, an asymmetric catalytic reaction was carried out employing 10 mol % complex **9** and 1.5 molar equiv of Me_2Zn, and the result shows no observable chiral alcohol product. In constrast, the catalytic reaction with the addition of 1 molar equiv of MeTi(O-*i*-Pr)$_3$ as the alkyl source gave the product in 92.0% yield and 86.6% ee, indicating the requirement of the RTi(O-*i*-Pr)$_3$ species for the reactions.

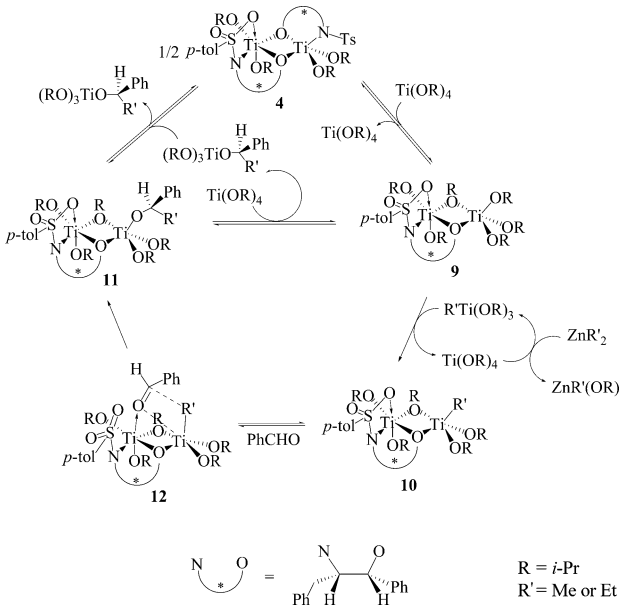
Reactions of Complex 10 with Benzaldehyde. For demonstrating the effect of the resulting chiral (*R*)-1-phenylethoxide ligand, complex **10** was reacted with 1 molar equiv of benzaldehyde to give a supposed complex **11** containing the (*R*)-1-phenylethoxide ligand. The ^{1}H NMR spectrum in CD_2Cl_2 in the region from δ 5.80 to 5.20 ppm shows several −C*H*(O−)Ph methine doublets and two PhC*H*(O−)Me methine quartets. The doublet observed at δ 5.658 ppm is the resonance of complex **4**, and the quartet at δ 5.490 ppm and the doublet at δ 5.406 ppm, which is overlapped with the methine quartet of (PhCHMeO)Ti(O-*i*-Pr)$_3$, are the resonances of complex **11**. The relative abundance of **4**/**11** is ∼1.5:1, and the equilibrium among complexes **4**, **11**, and (PhCHMeO)Ti(O-*i*-Pr)$_3$ is shown in eq 5. The above results show that complex **11** formed after the alkyl addition partially dissociates into the dimeric complex **4** and (PhCHMeO)Ti(O-*i*-Pr)$_3$. As shown in eq 4, MeTi(O-*i*-Pr)$_3$ is then reacted with complex **4** or even **11** to afford the active intermediate **10** for next cycles of the reactions.



(5)

Mechanism of the Asymmetric Alkyl Addition Reaction to Aldehydes. All the above studies provide a clear scope of the mechanistic details for the asymmetric alkyl addition reactions, and the mechanism is given in Scheme 2. The reaction of the chiral *N*-sulfonylated β-amino alcohol **5** with 1 molar equiv of Ti(O-*i*-Pr)$_4$ affords the dimeric complex **4**. The complex **4** further reacts with 1 molar equiv of Ti(O-*i*-Pr)$_4$, giving another dimeric complex, **9**, having a Ti/L* ratio of 2. The ^{1}H NMR study shows that complex **9** dissociates into complex **4** and Ti(O-*i*-Pr)$_4$ in solution, and the complexes **4**, **9**, and Ti(O-*i*-Pr)$_4$ are in equilibrium. This equilibrium is demonstrated to be solvent and temperature dependent. Both structures of the complexes **4** and **9** were determined from the X-ray analyses. Complex **9** is shown to react with MeTi(O-*i*-Pr)$_3$, giving complex **10**, which is demonstrated to be in equilibrium with complex **4** and (PhCHMeO)Ti(O-*i*-Pr)$_3$ in solution from the ^{1}H NMR study. Here MeTi(O-*i*-Pr)$_3$ can be generated from a reaction of excess Ti(O-*i*-Pr)$_4$ with $ZnMe_2$. Due to the very weak Ti−O(sulfonyl) bond suggested from the long bond distance of 2.474(3) Å in **9**, the dissociation is facile to open up a coordination site for accommodation of the incoming benzaldehyde. To achieve the right configuration of the chiral alcohol product, the benzaldehyde should be locked into a position with the phenyl group pointing toward the same side of the bridging oxygen donor of the chiral ligand, giving the intermediate **12**. The attached Me then moves to the carbonyl carbon and the benzaldehyde oxygen is proposed to

Scheme 2



move simultaneously toward the second titanium metal center having the alkyl group attached, giving complex **11**. Complex **11** is also demonstrated to exist as an equilibrium mixture of complexes **4** and **11**. The regeneration of the starting complex **4** completes the catalytic cycle for the next asymmetric reactions. It is also highly likely that complex **11** reacts with the excess Ti(O-*i*-Pr)$_4$ or MeTi(O-*i*-Pr)$_3$ to give complex **9** or **10** for the next cycles of reactions. In the mechanism, all intermediates, except the intermediate **12**, are confirmed on the basis of the X-ray structures or from ^{1}H NMR spectroscopic evidence.

Conclusions

A series of dimeric complexes [TiX$_2$L*]$_2$ (X = O-*i*-Pr (**4**); NMe$_2$ (**6**); O-*t*-Bu (**7**)) were prepared and demonstrated to be effective catalysts with the addition of excess Ti(O-*i*-Pr)$_4$. Another series of dimeric complexes [X$_2$TiL*TiX$_3$R] (**9**, X = O-*i*-Pr, R = O-*i*-Pr; **10**, X = O-*i*-Pr, R = Me; **11**, X = O-*i*-Pr, R = OCHMePh) were also prepared. The structural and ^{1}H NMR studies were carried out to deduce the complete cycle for the mechanism of the asymmetric additions of alkyl to aldehydes catalyzed by chiral titanium complexes. This is an example with all intermediates confirmed. The active intermediate is shown to be the bimetallic titanium complexes having a Ti/L* ratio of 2. This mechanism is also applied to titanium complexes of chiral diols or BINOLs in terms of the observations of the similar feature of excess Ti(O-*i*-Pr)$_4$ required and the similar open pocket as shown in structures **1** and **9**. One of the roles of excess Ti(O*i*-Pr)$_4$ is to react with complex **11** to remove the resulting chiral alkoxide from the bimetallic complex **11** or to react with the dimeric complex **4** to give complex **9**. However, the major role of excess Ti(O*i*-Pr)$_4$, strictly said, is to exchange the alkyl group from dialkylzinc reagents, affording the RTi(O-*i*-Pr)$_3$ complex, which reacts easily with the dimeric complex **4**, **9**, or **11**, giving the active complex **10**. Since the aldehyde is locked into the pocket in the intermediate **12**, this mechanism also suggests that the same excellent enantioselectivities can be achieved with R in RTi(O-*i*-Pr)$_3$ other than methyl.

Experimental Section

Reagent and General Techniques. (1*R*,2*S*)-2-Amino-1,3-diphenyl-1-propanol was prepared on the basis of modified procedures reported by Reetz et al.[19] The complex **4**,[15] MeTi(O-*i*-Pr)$_3$,[17] and (1*R*,2*S*)-2-(4-methylbenzenesulfonylamino)-1,3-diphenyl-1-propanol (**5**)[15] were prepared according to the literature procedures. Ti(NMe$_2$)$_4$ (Aldrich), dimethylzinc (2.0 M in toluene, Aldrich), and diethylzinc (1.0 M in hexane, Fluka) were used directly. Benzaldehyde (dried over MgSO$_4$), *t*-BuOH (dried over CaH$_2$), and Ti(O-*i*-Pr)$_4$ were freshly distilled prior to use. Solvents were dried by refluxing for at least 24 h over P$_2$O$_5$ (dichloromethane) or sodium/benzophenone (*n*-hexane or toluene) and were freshly distilled prior to use. Deuterated solvents (CDCl$_3$, C$_6$D$_6$, CD$_2$Cl$_2$, toluene-d_8, *n*-hexane-d_{14}) were dried over molecular sieves. All syntheses and manipulations were carried out under a dry dinitrogen atmosphere.

Physical Measurements. ^{1}H NMR spectra were obtained with a Varian Inova Unity-600 (600 MHz) or a Varian Mercury-400 (400 MHz), and chemical shifts were measured relative to tetramethylsilane as the internal reference. Melting points were taken on a Mel-Temp II instrument and were not corrected. Elemental analyses were performed using a Heraeus CHN-OS-RAPID instrument.

Synthesis of Complex 6. To a solution of (1*R*,2*S*)-2-(*p*-tolylsulfonylamino)-1,3-diphenyl-1-propanol (**5**) (0.381 g, 1.00 mmol) in 25 mL of toluene at room temperature was added slowly Ti(NMe$_2$)$_4$ in 5 mL of toluene in 30 min. The resulting mixture was stirred for 12 h, and the solvent was removed completely, to give a quantitative yield of a dark red solid with a trace of impurities. ^{1}H NMR (400 MHz, C$_6$D$_6$): δ 8.29 (d, J = 8.0 Hz, 4H, Ph), 7.41−7.04 (m, 24H, Ph), 5.41 (d, J = 4.8 Hz, 2H, PhC*H*O), 4.58 (m, 2H, C*H*N), 3.62 (dd, J = 2.4, 14.0 Hz, 2H, PhCH_AH_B), 3.48 (s, 12H, NCH_3), 2.81 (dd, J = 9.6, 14.0 Hz, 2H, PhCH_AH_B), 2.18 (s, 6H, CH_3C$_6$H$_4$) ppm.

Synthesis of Complex 7. To a solution of complex **6** (0.515 g, 0.500 mmol) in 25 mL of toluene was added slowly *tert*-butyl alcohol (0.19 mL, 2.00 mmol) in 5 mL of toluene at room temperature. The mixture was stirred for 12 h, and the solvent was removed under reduced pressure to give a quantitative yield of a light yellow solid. Colorless crystals of **7**·(C$_7$H$_8$)$_2$ were obtained from a solution of *n*-hexane/toluene for an X-ray structural analysis and an elemental analysis. ^{1}H NMR (400 MHz, CDCl$_3$): δ 8.29 (J = 8.0 Hz, 4H, Ph), 7.41−7.04 (m, 24H, Ph), 5.41 (d, J = 4.8 Hz, 2H, PhC*H*O), 4.58 (m, 2H, C*H*N), 3.62 (dd, J = 2.4, 14.0 Hz, 2H, PhCH_AH_B), 3.48 (s, 12H, NCH_3), 2.81 (dd, J = 9.6, 14.0 Hz, 2H, PhCH_AH_B), 2.18 (s, 6H, CH_3C$_6$H$_4$), 7.71−6.88 (m, 24H, Ph), 5.33 (d, J = 5.2 Hz, 2H, PhC*H*O), 4.63 (m, 2H, C*H*N), 3.16 (d, J = 12.4 Hz, 2H, PhCH_2), 2.22 (s, 6H, CH_3C$_6$H$_4$), 1.40 (s, 18H, C*Me*$_3$), 0.89 (s, 18H, C*Me*$_3$) ppm. Anal. Calcd for C$_{60}$H$_{78}$N$_2$O$_{10}$S$_2$Ti$_2$·(C$_7$H$_8$)$_2$: C, 66.76; H, 7.12; N, 2.10. Found: C, 65.85; H, 7.13; N, 2.15.

Synthesis of Complex 9. To a solution of complex **4** (1.64 g, 1.50 mmol) in 50 mL of *n*-hexane was added Ti(O-*i*-Pr)$_4$ (0.744 g, 3.00 mmol), and the mixture was stirred at room temperature for 12 h. The solution was concentrated to ∼30 mL and was cooled to 5 °C for 3 days to afford colorless crystals (1.68 g, 67.5%), mp 89.0−91.0 °C. Anal. Calcd for C$_{40}$H$_{63}$NO$_2$STi$_2$: C, 57.90; H, 7.65; N, 1.69. Found: C, 57.79; H, 7.32; N, 2.15.

Preparation of Complex 10. To a solution of **4** (1.09 g, 1.00 mmol) in 10 mL of *n*-hexane was added MeTi(O-*i*-Pr)$_3$ (0.480 g, 2.00 mmol) in 3 mL of *n*-hexane at room temperature. The mixture was allowed to react for 1 h, and the solvent was removed completely under reduced pressure to give a yellowish brown residue. The spectrum of this residue in CD$_2$Cl$_2$ at 0 °C shows an equilibrium mixture of the complexes **4**, **10**, and MeTi(O-*i*-Pr)$_3$. **10**: ^{1}H NMR (CD$_2$Cl$_2$, 600 MHz): δ 5.557 (d, J = 4.8 Hz, C*H*(O−)Ph, 1H), 5.016 (sept, J = 6.0 Hz, C*H*Me$_2$, 3H), 4.669 (sept, J = 6.0 Hz, C*H*Me$_2$, 1H), 4.216 (m, C*H*N, 1H), 4.111 (sept, J = 6.0 Hz, C*H*Me$_2$, 1H), 3.014 (dd, J = 3.6, 14.4 Hz, PhCH_AH_B, 1H), 2.356 (s, C$_6$H$_4$CH_3, 3H), 2.221 (dd, J = 9.6, 14.4 Hz, PhCH_AH_B, 1H), 1.421 (d, J = 6.0 Hz, C*Me*$_2$, 18H), 1.196 (d, J = 6.0 Hz, C*Me*$_2$, 3H), 1.172 (d, J = 6.0 Hz, C*Me*$_2$, 3H), 0.996 (d, J = 6.0 Hz, C*Me*$_2$, 3H), 0.919 (d, J = 6.0 Hz, C*Me*$_2$, 3H), 0.569 (s, Ti*Me*, 3H) ppm (^{1}H resonances of phenyl groups are not assigned).

Preparation of Complex 11. To a solution of **10** (1.57 g, 2.00 mmol) in 15 mL of *n*-hexane at 0 °C was added benzaldehyde (0.20 mL, 2.0 mmol). The mixture was stirred at 0 °C for 15 h, and the solvent was removed under reduced pressure to give a yellowish brown residue. The spectrum of the residue in CD$_2$Cl$_2$ shows the existence of the complexes **4**, **11**, Ti(O-*i*-Pr)$_3$(OCHMePh), and other species of minor intensities. **11**: ^{1}H NMR (CD$_2$Cl$_2$, 400 MHz): δ 5.490 (q, J = 7.8 Hz, OC*H*MePh, 1H), 5.402 (d, J = 9.0 Hz, C*H*(O-)Ph, 1H), 4.474 (sept, J = 9.0 Hz, C*H*Me$_2$, 5H; overlapped with Ti(O-*i*-Pr)$_3$(OCHMePh), 4.276 (m, C*H*N, 1H; overlapped with **4**), 3.044

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(dd, $J = 7.2$, 16.2 Hz, PhCH_AH_B, 1H; overlapped with **4**), 2.470 (dd, $J = 7.2$, 18.0 Hz, PhCH_AH_B, 1H; overlapped with **4**), 2.355 (s, $C_6H_4CH_3$, 3H), 1.223 (d, $J = 8.4$ Hz, CHMe_2, 30H; overlapped with Ti(O-*i*-Pr)$_3$(OCHMePh)) ppm (^{1}H resonances of phenyl groups and Me protons of OCHMePh group are not assigned).

General Procedures for the Addition of Et_2Zn to Benzaldehyde Catalyzed by the Titanium(IV) Complex 6, 7, or 9/Ti(O-*i*-Pr)$_4$ Systems. Under a dry dinitrogen atmosphere, the complex (10 mol % in chiral ligand) and Ti(O-*i*-Pr)$_4$ were mixed in 1.5 mL of dry dichloromethane at room temperature. After 1 h, 0.75 mmol of Et_2Zn (1.0 M solution in hexane) was added at 0 °C. After the mixture was stirred for 30 min, the orange-colored solution was treated with benzaldehyde (0.5 mmol) at 0 °C. The mixture was allowed to react at 0 °C for 12 h and then was quenched with 1 N HCl (5 mL). The aqueous phase was extracted with ethyl acetate (3 × 5 mL). The combined organic phase was dried over $MgSO_4$, filtered, and concentrated. Chromatography of the residue on silica gel (elution with 5:1 hexane/ethyl acetate) gave 1-phenylpropanol. The enantiomeric purity of the product was determined by HPLC with a Chiralcel-OD column from Daicel.

General Procedures for the Addition of Et_2Zn or MeTi(O-*i*-Pr)$_3$ to Benzaldehyde Mediated by the Complex 9 or 10 System. Under a dry dinitrogen atmosphere, a solution of complex **9** or **10** (0.375 mmol) and Et_2Zn (0.563 mmol) or MeTi(O-*i*-Pr)$_3$ (0.375 mmol) in 1.5 mL of dry dichloromethane was stirred for 1 h at 0 °C. After 30 min, the orange-colored solution was treated with benzaldehyde (0.038 mL, 0.375 mmol) at 0 °C, stirred at this temperature for 12 h, and quenched with 1 N HCl (5 mL). The aqueous phase was extracted with ethyl acetate (3 × 5 mL), and the combined organic phases were dried over $MgSO_4$, filtered, and concentrated. Chromatography of the residue on silica gel (elution with 5:1 hexane/ethyl acetate) gave 1-phenylpropanol as a colorless oil. The enantiomeric purity of the product was determined by HPLC.

General Procedures for the Addition of MeTi(O-*i*-Pr)$_3$ to Benzaldehyde Catalyzed by the Complex 9 or 10 System. Under a dry dinitrogen atmosphere, a solution of complex **9** or **10** (0.025 mmol, 10 mol %) and MeTi(O-*i*-Pr)$_3$ (0.5 mmol) in 1.5 mL of dry dichloromethane was stirred for 1 h and then was treated with benzaldehyde (0.05 mL, 0.50 mmol) at 0 °C, stirred at this temperature for 12 h, and quenched with 1 N HCl (5 mL). The aqueous phase was extracted with ethyl acetate (3 × 5 mL), and the combined organic phases were dried over $MgSO_4$, filtered, and concentrated. Chromatography of the residue on silica gel (elution with 5:1 hexane/ethyl acetate) gave 1-phenylpropanol as a colorless oil. The enantiomeric purity of the product was determined by HPLC.

Crystal Structure Determinations. Colorless crystals of **7** of size 0.68 × 0.61 × 0.30 mm and **9** of size 0.54 × 0.47 × 0.27 mm in sealed capillaries under dinitrogen atmosphere were used for X-ray diffraction studies. Diffraction intensities were collected on a Bruker CCD Smart-1000 diffractometer equipped with graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å). All refinements and calculations were carried out with the Bruker AXS SHELXTL software package on a P4 2.4 GHz computer. Positions of heavy atoms were determined by direct methods, and remaining non-hydrogen atoms were located from successive difference Fourier map calculations. Refinements were carried out using full-matrix least-squares techniques. All non-hydrogen atoms were refined as individual anisotropic atoms. Hydrogen atoms were considered as the riding atom on carbon atoms with a C−H bond length of 0.96 Å, and hydrogen atom temperature factors were fixed at 0.08 Å. Hydrogen atoms were included for refinements in the final cycles. The crystal structure of **7** contains two disordered toluene molecules, and positions of atoms for toluene molecules are not well-defined.

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Supporting Information Available: X-ray crystallographic data including final coordinates, bond lengths, bond angles, and anisotropic displacement coefficients for the complexes **7** and **9** are available free of charge via the Internet at http://pubs.acs.org.

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