Facile Syntheses of $TiCl_2$(TADDOLate)(L_2), Efficient Asymmetric Ethylation of PhCHO, and an Unexpected Rearrangement of the Tetramethyl Analogue of the TADDOL Ligand

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Facile syntheses of $TiCl_2$(TADDOLate)L_2 (TADDOL = α,α,α′,α′-tetraphenyl-1,3-dioxolane-4,5-dimethanol; L = THF (**1**), AcOEt (**2**)) were developed from reactions of $TiCl_4$ with the TADDOL ligand in coordinating solvent L. The labile solvent ligands L can be replaced by a neutral bidentate ligand such as 1,2-bis(diphenylphosphino)ethane (dppe) or 3,3-dimethyl-2,4-pentanedione (diketone) to give $TiCl_2$(TADDOLate)(L_2) (L_2 = dppe (**3**), diketone (**4**)). The molecular structure of complex **3** shows a structure with two chlorides in trans positions, and the dppe ligand is trans to the strong alkoxide ligands. The most significant features of the structure are the long Ti−P(phosphine) bond distances observed, indicating considerable steric hindrance arising from the TADDOLate ligand in the complex. In a reaction of the TADDOL analogue α,α,α′,α′-tetramethyl-1,3-dioxolane-4,5-dimethanol with $TiCl_4$ in Et_2O, the unexpected complex **6** derived from rearrangement of the chiral diol ligand was obtained. This rearrangement is apparently mediated by $TiCl_4$ with the conversion of the 2,3-ketal-1,4-diol into the isomeric 3,4-ketal-1,2-diol. The asymmetric ethylations of benzaldehyde catalyzed by the complex **1**, **2**, or **3**/Ti(O-*i*-Pr)$_4$ system are efficient, and the enantioselectivities are good, with values of enantiomeric excess up to 89%.

Introduction

Though titanium(IV) species had been extensively used in mediating many types of organic reactions, the incorporations of the Lewis acidities of titanium(IV) species and of the enantioselectivities with the addition of chiral ligands had not gained much attention before the discovery of asymmetric epoxidation of allylic alcohols by Sharpless and co-workers in 1980.[1] Since then, asymmetric catalysis using chiral titanium complexes has become an intensely studied subject, mainly due to diversified asymmetric reaction types provided by chiral titanium complexes. The systems studied include asymmetric epoxidations,[2] asymmetric Diels−Alder reactions,[3] asymmetric aldol condensation reactions,[4] asymmetric synthesis of cyanohydrins,[5] and asymmetric allylations[6] or alkylations.[7] Among numerous chiral ligands used in the asymmetric syntheses, the α,α,α′,α′-tetraaryl-1,3-dioxolane-4,5-dimethanols (TADDOLs) are interesting and had been studied extensively[8] due to excellent enantioselectivities obtained and due to the adjustible electronic state or steric environments through the replacements of α-phenyl substituents. In general, the active catalytic species are generated in situ from mixing $Ti(OR)_xCl_{4-x}$ with a TADDOL ligand. In terms of synthetic approaches, besides the synthesis of Ti(TADDOLate)$_2$[9] and Cp′TiCl(TADDOLate)[10] complexes, much attention had focused on the synthesis of the $TiCl_2$(TADDOLate) catalysts[11] used in the asymmetric Diels−Alder reactions developed by Narasaka and coworkers.[3b]

To explore the Ti−TADDOLate complex systems, we here report facile syntheses of $TiCl_2$(TADDOLate)L_2 from reactions of the TADDOL ligand with $TiCl_4$ in coordinating solvent L. In these complexes, the weakly coordinated L ligands can be replaced easily by neutral bidentate ligands such as 1,2-bis(diphenylphosphino)-ethane (dppe) and 3,3-dimethyl-2,4-pentanedione (di-

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ketone) with the formation of $TiCl_2$(TADDOLate)(L_2). In a reaction of the tetramethyl analogue of the TADDOL ligand with $TiCl_4$, an unexpected rearrangement of the chiral diol ligand mediated by $TiCl_4$ was observed. In this study, asymmetric ethylations of benzaldehyde with the catalytic system **1**, **2**, or **3**/Ti(O-*i*-Pr)$_4$ were conducted to give good enantioselectivities of (*S*)-1-phenylpropanol.

Experimental Section

Reagents and General Techniques. α,α,α′,α′-Tetraphenyl-1,3-dioxolane-4,5-dimethanol[12] (TADDOL), α,α,α′,α′-tetramethyl-1,3-dioxolane-4,5-dimethanol,[12] and 3,3-dimethyl-2,4-pentanedione[13] were prepared according to literature procedures. $TiCl_4$ (Merck) was freshly distilled prior to use, and bis(diphenylphosphino)ethane (Aldrich) was used without further purification. Benzaldehyde and ethyl acetate were distilled and stored over molecular sieves. Solvents were dried by refluxing for at least 24 h over P_2O_5 (dichloromethane) or sodium/benzophenone (diethyl ether, tetrahydrofuran) and were freshly distilled prior to use. Deuterated solvents (Aldrich) were dried over molecular sieves. All syntheses and manipulations were carried out under a dry dinitrogen atmosphere.

Synthesis of $TiCl_2$(TADDOLate)(THF)$_2$ (1). To a solution of TADDOL (0.466 g, 1.00 mmol) in 20 mL of Et_2O at room temperature was added $TiCl_4$ (0.247 g, 1.30 mmol) with stirring. After the solution was stirred for 30 min, 5.0 mL of THF was added. The resulting yellowish brown solution was stirred further for 1 h and then the solution was concentrated to ∼10 mL. The concentrated solution was cooled to −25 °C to give colorless crystals (0.503 g, 62.7%), mp 81.3−83.0 °C. The second crop (0.225 g, 28.0%) was obtained with further concentration of the filtrate and cooling. **1·OEt$_2$**: ^{1}H NMR ($CDCl_3$) δ 7.59 (m, 4H), 7.46 (m, 4H), 7.21−7.34 (m, 12H), 5.35 (s, 2H), 4.10 (m, 8H), 3.48 (q, 4H), 1.87 (br, 8H), 1.21 (t, 6H), 0.64 (s, 6H) ppm; ^{13}C{^{1}H} NMR ($CDCl_3$) δ 144.3, 142.7, 129.7, 127.7, 127.5, 127.2, 127.0, 111.2, 101.3, 80.1, 71.8, 65.8, 27.2, 25.4, 15.2 ppm. Anal. Found: C, 64.86; H, 6.62. Calcd for $C_{43}H_{54}O_7Cl_2Ti$: C, 64.42; H, 6.79.

Synthesis of $TiCl_2$(TADDOLate)(AcOEt)$_2$ (2). To a solution of TADDOL (0.466 g, 1.00 mmol) in 30 mL of ethyl acetate at room temperature was added $TiCl_4$ (0.247 g, 1.30 mmol). The resulting solution was stirred for 1 h and then was cooled to 4.0 °C to afford colorless crystals (0.347 g, 45.7%), mp 119.0−121.4 °C dec. ^{1}H NMR ($CDCl_3$): δ 7.51 (m, 8H), 7.25−7.36 (m, 12H), 5.21 (s, 2H), 4.19 (q, 4H), 2.12 (s, 6H), 1.26 (t, 6H), 0.71 (s, 6H) ppm. ^{13}C{^{1}H} NMR ($CDCl_3$): δ 174.1, 144.5, 141.1, 129.2, 127.9, 127.5, 127.3, 111.1, 102.4, 80.6, 77.2, 62.0, 27.1, 21.1, 14.1 ppm. Anal. Found: C, 61.65; H, 5.85. Calcd for $C_{39}H_{44}O_8Cl_2Ti$: C, 61.67; H, 5.84.

Synthesis of $TiCl_2$(TADDOLate)(dppe) (3). To a solution of TADDOL (0.466 g, 1.00 mmol) in 20 mL of Et_2O at room temperature was added $TiCl_4$ (0.247 g, 1.30 mmol), and the solution was stirred for 30 min. Then 5.0 mL of THF was added and the resulting solution was stirred for 1 h to give a yellowish brown solution. The solvent was removed and was subsequently replaced with 30 mL of CH_2Cl_2. Then dppe (0.40 g, 1.00 mmol) was added and the reaction mixture was stirred for 1 h. The solution was filtered and dried completely to give the product in quantitative yield. Colorless crystals could be obtained from crystallization of the product in CH_2Cl_2 at −25.0 °C; mp 92.8−94.0 °C. ^{1}H NMR ($CDCl_3$): δ 7.09−7.71 (m, 40H), 5.52 (s, 2H), 2.72 (br, 2H), 2.46 (br, 2H), 0.66 (s, 6H) ppm. ^{13}C{^{1}H} NMR ($CDCl_3$): δ 144.7, 143.0, 133.5, 132.8, 130.5, 129.3, 128.2, 127.8, 127.3, 127.1, 126.8, 111.1, 100.9, 80.5, 27.3, 20.9 ppm. Anal. Found: C, 70.35; H, 5.31. Calcd for $C_{57}H_{52}O_4P_2Cl_2Ti$: C, 69.73; H, 5.34.

Synthesis of $TiCl_2$(TADDOLate)(3,3-dimethyl-2,4-pentanedione) (4). To a solution of complex **2** (0.76 g, 1.00 mmol) in 20 mL of CH_2Cl_2 was added 3,3-dimethy-2,4-pentanedione (0.14 mL, 1.00 mmol) at room temperature. The resulting solution changed color from colorless to orange and was stirred for 1 h. The solution was dried in vacuo to remove any volatile materials to give a pale yellow product containing traces of impurities. Attempts to further purify the product by recrystallization gave little improvement. ^{1}H NMR ($CDCl_3$): δ 7.20−7.58 (m, 20H), 5.21 (s, 2H), 2.21 (s, 6H), 1.43 (s, 6H), 0.71 (s, 6H) ppm. ^{13}C{^{1}H} NMR ($CDCl_3$): δ 212.29, 144.53, 141.30, 129.10, 127.73, 127.59, 127.24, 127.12, 127.05, 111.06, 102.28, 80.99, 60.56, 27.21, 27.11, 21.83 ppm. Anal. Found: C, 63.87; H, 6.03. Calcd for $C_{38}H_{40}O_6Cl_2Ti$: C, 64.15; H, 5.67.

Synthesis of 6·OEt$_2$. To a solution of α,α,α′,α′-tetramethyl-1,3-dioxolane-4,5-dimethanol (0.980 g, 4.50 mmol) in 30 mL of Et_2O was added $TiCl_4$ (0.865 g, 4.50 mmol) at room temperature. The yellowish brown solution was stirred for 1 h, filtered, and cooled to −25.0 °C to afford colorless crystals (1.25 g, 62.5%), mp 103.8−104.1 °C dec. **6·OEt$_2$**: ^{1}H NMR ($CDCl_3$) δ 8.89 (br, 1H), 4.37 (br, 1H), 4.03 (br, 1H), 3.54 (q, 4H), 1.71 (s, 3H), 1.61 (s, 3H), 1.57 (s, 3H), 1.49 (s, 3H), 1.28 (s, 3H), 1.27 (s, 3H), 1.19 (t, 6H) ppm; ^{13}C{^{1}H} NMR ($CDCl_3$) δ 112.9, 89.9, 87.3, 83.4, 80.6, 66.0, 28.8, 27.7, 26.4, 25.7, 23.7, 22.4, 14.8 ppm. Anal. Found: C, 40.47; H, 7.23. Calcd for $C_{15}H_{31}O_5Cl_3Ti$: C, 40.53; H, 7.04.

General Procedures for Ethylation of Benzaldehyde. To a solution of 0.1 mmol of complex **1**, **2**, or **3** and 0−1.5 mmol of Ti(O-*i*-Pr)$_4$ in 2.5 mL of toluene at 0 °C was added with vigorous stirring 0.1 mL (1.0 mmol) of PhCHO followed by addition of 1.2 mmol of $ZnEt_2$. The solution was warmed to room temperature. After a total reaction time of 3 h, the solution was quenched with saturated aqueous NH_4Cl solution (5 mL), ethyl acetate (5 mL) was added, and the mixture was filtered with the aid of Celite. The filtrate was extracted with ethyl acetate (3 × 5 mL), dried over $MgSO_4$, filtered and concentrated. The sample was chromatographed through a short column containing silica gel to remove any nonvolatile material, and the solvent was removed to give a crude sample for HPLC analysis.

Physical Measurements. ^{1}H NMR spectra were obtained with a Varian Gemini-200 (200 MHz) or a Varian VXR-300 (300 MHz) spectrometer, and ^{13}C NMR spectra were recorded with the Varian VXR-300 (75.43 MHz) spectrometer. The ^{1}H and ^{13}C chemical shifts were measured relative to tetramethylsilane as the internal reference. Melting points were measured with a Büchi 535 instrument, and the temperatures were not calibrated. Elemental analyses of complexes were performed using a Heraeus CHN-O-RAPID instrument.

Crystal Structure Determinations. Crystals of **3** and **6** in sealed capillaries were used for X-ray diffraction studies. The diffraction intensities were collected on a Siemens P4 diffractometer equipped with graphite-monochromated Mo Kα radiation (λ = 0.710 73 Å). An absorption correction was performed on the sample of complex **3**. All refinements and calculations were carried out with the Siemens SHELXTL PLUS software package on an SGI Indigo computer. Absolute structure determinations were performed on both samples. The positions of heavy atoms for the structures were determined by direct methods, and the remaining non-hydrogen atoms were located from successive difference Fourier map calculations. The refinements were carried out using full-matrix least-squares techniques. All non-hydrogen atoms were refined as individual anisotropic atoms. The hydrogen atoms, except the hydroxy hydrogen of complex **6**, which was also located from the successive difference Fourier map calcula-

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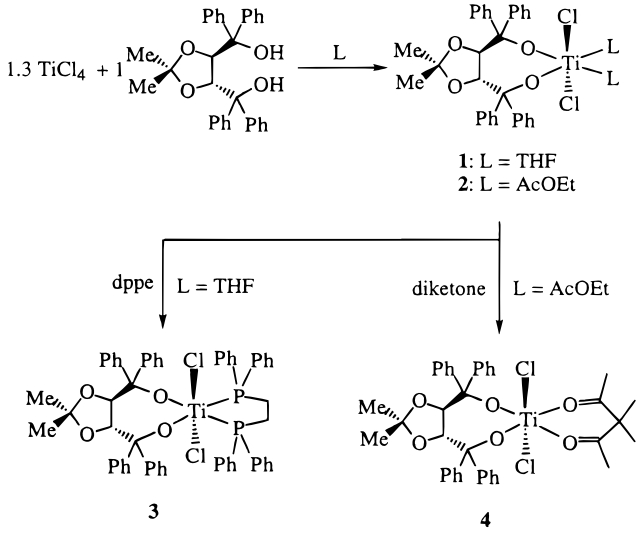
Table 1. Crystallographic Data for Complexes 3 and 6

	3	6
formula	$C_{57}H_{52}O_4P_2Cl_2Ti$	$C_{11}H_{21}O_4Cl_3Ti{\cdot}OEt_2$
fw	981.7	445.6
cryst syst	monoclinic	orthorhombic
space group	$P2_1$	$P2_12_12_1$
a (Å)	9.767(2)	8.498(2)
b (Å)	23.389(3)	15.026(2)
c (Å)	11.796(2)	18.120(2)
β (deg)	107.07(2)	
V (Å^3)	2465.8(7)	2313.8(7)
Z	2	4
D_{calcd} (g cm^{-3})	1.322	1.279
abs coeff (mm^{-1})	0.394	0.734
range (deg)	4.0−50.0	4.0−45.0
scan type	$2\theta-\theta$	$2\theta-\theta$
no. of rflns collected	9334	3457
no. of indep rflns	8608 (R_{int} = 3.53%)	2995 (R_{int} = 1.82%)
no. of obsd rflns	7681 ($\sigma > 2.0\sigma(I)$)	2577 ($\sigma > 2.0\sigma(I)$)
absolute structure	1.02(5)	1.00(10)
no. of refined params	595	218
R^a for significant rflns	0.040	0.045
$R_w{}^b$ for significant rflns	0.053	0.058
goodness of fit^c	1.22	1.31

^{a} $R = [\sum(F_o - F_c)/\sum F_o]$. ^{b} $R_w = [\sum w(F_o - F_c)^2/\sum wF_o^2]^{1/2}$. ^{c} The goodness of fit equals $[\sum w(F_o - F_c)^2/(N_{rflns} - N_{params})]^{1/2}$.

Scheme 1



tions, were considered as riding on the carbon atoms with a C−H bond length of 0.96 Å; the hydrogen atom temperature factors were fixed at 0.08 Å. The hydrogen atoms were included for refinements in the final cycles. The crystallographic data for complexes **3** and **6** are summarized in Table 1.

Results and Discussion

Synthesis and Characterizations of Complexes 1−4. Reactions of $TiCl_4$ with a TADDOL ligand in the coordinating solvent THF or ethyl acetate (AcOEt) and further reactions with neutral bidentate ligands such as dppe and diketone are outlined in Scheme 1. Unlike the usual preparation of Ti−TADDOLate complexes from reactions of the TADDOL ligand with titanium alkoxides, it was found in our laboratory recently that the TADDOL ligand reacts easily with 1.3 molar equiv of $TiCl_4$ in a coordinating solvent such as THF or AcOEt (EA) to give clean and quantitative yields of titanium(IV)−TADDOLate complexes, $TiCl_2$(TADDOLate)L_2 (L = THF (**1**), EA (**2**)), after removing the solvent completely. In these reactions, a 30% excess of $TiCl_4$ is required to secure the complete consumption of the TADDOL ligand. The coordinating solvent L ligands in complexes **1** and **2** are rather facile and can be replaced easily by various neutral bidentate ligands which are more coordinative than the coordinating L ligands such as a bidentate dppe (bis(diphenylphosphino)ethane) and diketone (3,3-dimethyl-2,4-pentanedione) ligand.[14] When 1 molar equiv of dppe reacted with complex **1**, the complex $TiCl_2$(TADDOLate)(dppe) (**3**) was isolated in nearly quantitative yield. However, 3,3-dimethyl-2,4-pentanedione, which is a more weakly bonding ligand than THF, is not able to replace the coordinated THF's in complex **1** completely. Fortunately, it easily replaces the coordinating ethyl acetates in complex **2** to afford the complex $TiCl_2$(TADDOLate)(diketone) (**4**) after removing the solvent and AcOEt in vacuo. Unlike the $TiCl_2$(TADDOLate) catalysts, which are unstable and need to be stored at low temperatures, complexes **1**−**4** are stable at room temperature under a dinitrogen atmosphere for at least 1 week. Besides, all of these complexes except complex **4** crystallize easily from suitable solvents to afford suitable crystals for structural studies.

Reaction of α,α,α′,α′-Tetramethyl-1,3-dioxolane-4,5-dimethanol with $TiCl_4$. To further study the steric effect of the chiral titanium complexes, the structurally less steric α,α,α′,α′-tetramethyl-1,3-dioxolane-4,5-dimethanol was reacted with $TiCl_4$ in Et_2O to afford the unexpected product **6**. Instead of the two methyl signals expected for the chiral ligand in a complex with a structure similar to that of complex **1** or **2**, ^{1}H NMR of complex **6** reveals six distinct methyl signals, indicating a structure having all six methyl groups magnetically inequivalent. The solid-state structure of **6** reveals a surprisingly rearranged product mediated apparently by $TiCl_4$. On the basis of this structure, a likely mechanism (Scheme 2) for this rather unique reaction is proposed. To give complex **6**, the chiral ligand needs to coordinate to $TiCl_4$ in a bidentate fashion through one hydroxy and one ketal group for the formation of the six-coordinate intermediate **5**. Due to the activation by the Ti(IV) metal, the ketal O−CMe_2 bond breaks heteroleptically to give a strong Ti−O(alkoxide) bond and subsequently a ring-closure process proceeds by the attack of the dangling $^+CMe_2$ on the uncoordinated hydroxy group to form a new ketal ring. Finally, the other ketal oxygen attaches to the titanium metal with simultaneous evolution of 1 molar equiv of HCl to give the monomeric titanium complex **6**. Thus, the rearranged chiral ligand bonds to the Ti metal center in a tridentate fashion through one hydroxy, one alkoxy, and one ketal oxygen. Though a similar rearrangement had been reported by Cotton et al.[15] in a reaction of a Re(III) derivative with a chiral diop ligand having a similar 1,3-dioxolane skeleton, to our knowledge this is the first example of the rearrangement of the 1,3-dioxolane-4,5-dimethanol skeleton mediated by an early Ti group metal. In this unique reaction, the preferential bonding of a ketal oxygen to

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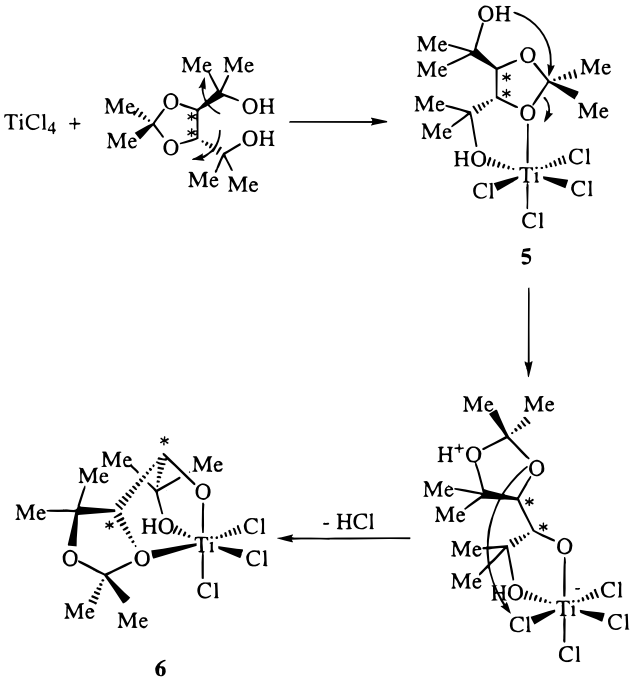
Scheme 2



a hydroxy group is demonstrated. In addition, this reaction feature provides a way to convert 2,3-ketal-1,4-diol into 3,4-ketal-1,2-diol.

Molecular Structure of Complex 3. The dppe complex **3** was subjected to an X-ray structural analysis, and the solid-state structure (Figure 1) shows that the relative positions of bonding ligands in the six-coordinate complex are governed exclusively by the relative bonding abilities of the ligands, in which the weakest dppe ligand is trans to the strongest alkoxide donors, leaving two chlorides trans to each other with a molecular symmetry of C_2. The Ti−O distances at 1.771(2) and 1.782(2) Å are about normal compared to those in other titanium alkoxides containing two or more alkoxide ligands. Although the Ti−Cl distances (2.325(1) and 2.345(1) Å) are also normal, the chloride ligands bend significantly away from the alkoxide ligands with a Cl−Ti−Cl angle of 157.2(1)°. This structural distortion is likely due to the bonding effect of the strong O−Ti multiple bonds and/or due to the steric effect of the bulky TADDOLate ligand. The most significant structural feature about complex **3** is the unusually long Ti−P distances at 2.801(1) and 2.813(1) Å, which are about 0.20−0.30 Å longer than the distances in Ti-phosphine complexes.[16] These bond distances are the longest Ti−P(phosphine) distances so far observed, and they are even longer than the distances in many phosphine complexes of the much larger 4d zirconium or 5d hafnium metal.[17] The long Ti−P distances can be attributed primarily to the mutual repulsion of the steric bulk of the TADDOLate and the dppe ligands. As

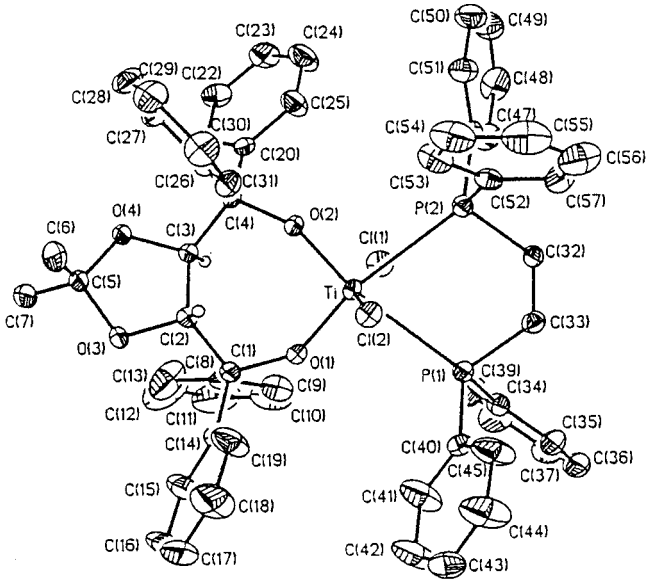


Figure 1. Molecular structure of **3**. The hydrogens, except the hydrogens attached to chiral carbons, are omitted for clarity. Bond lengths (Å): Ti−Cl(1), 2.325(1); Ti−Cl(2), 2.345(1); Ti−P(1), 2.813(1); Ti−P(2), 2.801(1); Ti−O(1), 1.782(2); Ti−O(2), 1.771(2). Bond angles (deg): O(1)−Ti−O(2), 98.7(1); P(1)−Ti−P(2), 75.3(1); Cl(1)−Ti−Cl(2), 157.2(1); Ti−O(1)−C(1), 146.0(2); Ti−O(2)−C(4), 153.0(2).

a result, the weaker phosphorus donors are pushed away from the metal center and the stronger alkoxide donors of the TADDOLate ligand remain insensitive or shorten slightly in order to compensate for the weak Ti(IV)−P bonds. The structural features in complex **3** strongly suggest that the $TiCl_2$(TADDOLate) moiety already provides steric environments suitable for achieving high enantioselectivities in asymmetric catalysis.

Molecular Structure of Complex 6. The molecular structure of complex **6** with selected bond lengths and bond angles is shown in Figure 2. The complex **6** is a six-coordinate titanium(IV) complex containing three chlorides, one alkoxide, one hydroxide, and one ether donor. Relative to the dialkoxide complex **3**, the Ti−O(alkoxide) bond in complex **6** is somewhat weaker, with a Ti−O(3) distance of 1.816(3) Å. This weak bond is mainly due to the constraint of the five-membered chelate ring formed from the rearranged chiral ligand with titanium metal. In general, a strong Ti−O(alkoxide) bonding requires a large Ti−O−C angle in order to achieve better oxygen to metal π donation. However, the Ti−O(3)−C(2) angle at 116.0(3)° is only slightly larger than the sp^3 angle and is substantially smaller than the usual angles of 140−160° for titanium alkoxides. In contrast, the Ti−Cl distances are shorter by ∼0.07 Å for complex **6** than the Ti−Cl distances for complex **3**. The hydroxy hydrogen is located from the successive Fourier difference map in the X-ray structural analysis and is found to hydrogen-bond to a diethyl ether oxygen with an H···OEt_2 distance of 1.516 Å and a close to linear O(1)−H···OEt_2 angle of 158.2°. The Ti−O(hydroxy) distance at 2.104(3) Å is substantially longer

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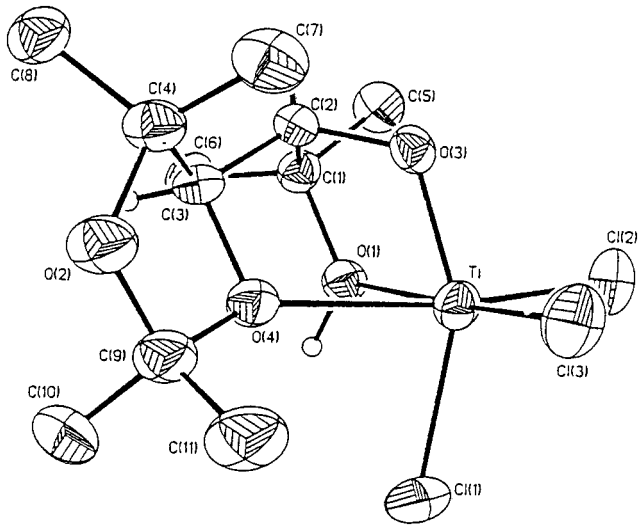
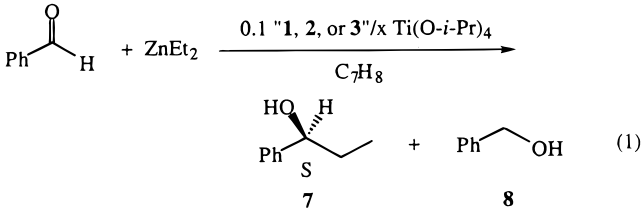


Figure 2. Molecular structure of **6·OEt$_2$**. The solvated diethyl ether and the hydrogens, except those attached to chiral carbons C(2) and C(3) and the hydroxy hydrogen, are omitted for clarity. Bond lengths (Å): Ti−Cl(1), 2.284(2); Ti−Cl(2), 2.246(2); Ti−Cl(3), 2.261(2); Ti−O(1), 2.104(3); Ti−O(3), 1.816(3); Ti−O(4), 2.369(5); O(1)−H, 1.105; H···OEt$_2$, 1.516. Bond angles (deg): Cl(1)−Ti−Cl(2), 101.1(1); Cl(1)−Ti−Cl(3), 98.2(1); Cl(2)−Ti−Cl(3), 96.2(1); Cl(1)−Ti−O(3), 153.3(1); O(1)−Ti−O(3), 77.1(2); O(3)−Ti−O(4), 72.5(1); O(1)−Ti−O(4), 74.5(1); Ti− O(1)−C(1), 114.6(3); Ti−O(3)−C(2), 116.0(3); O(1)−H···OEt$_2$, 158.2.

by 0.3 Å than the Ti−O(alkoxide) bond distance. Though the Ti−O(ketal) bond is considered to be a type of Ti−OR$_2$ bonding, the Ti−O(ketal) distance at 2.369(5) Å is extremely long compared to the usual Ti−OR$_2$ distances from 2.1 to 2.20 Å. The rearranged chiral ligand bonds to the titanium metal in a facial tridentate bonding mode, and the two five-membered chelate rings have a O(1)−Ti−O(3) angle of 77.1(2)° and a O(3)−Ti−O(4) angle of 72.5(1)°.

Asymmetric Ethylation of Benzaldehyde. Ethylation reactions of benzaldehyde in the presence of complexes **1**, **2**, or **3** with or without the addition of Ti(O-*i*-Pr)$_4$ were carried out (eq 1), and the results are



(1)

shown in Table 2. When the reactant was mixed with 10 mol % of complex **2** at 0 °C for 3 h without the addition of Ti(O-*i*-Pr)$_4$ and the reaction solution was warmed to room temperature (entry 1), 86% of the benzaldehyde was found to be converted to the desired 1-phenylpropanol (**7**) along with the reduction product PhCH$_2$OH (**8**) in a ratio of 95:5. The enantiomeric excess of (*S*)-1-phenylpropanol was only 19%. However, with the addition of Ti(O-*i*-Pr)$_4$ to the reaction system (entries 2−4), the enantioselectivities improved dramatically. The best result was obtained with an ee value of 87% in a system with the addition of 1.5 molar equiv of Ti(O-*i*-Pr)$_4$. Besides the dramatic improvement of enantioselectivities, the addition of Ti(O-*i*-Pr)$_4$ to the reaction systems speeded up the asymmetric reaction to a point of 100% conversion in 3 h. It was found that the addition of Ti(O-*i*-Pr)$_4$ also suppressed the formation of the reduction product **8** to a negligible amount. The use of a higher ratio of Ti(O-*i*-Pr)$_4$ relative to the chiral ligand has been previously reported in other systems.[7,18] The asymmetric ethylation reaction was also carried out using complex **1** as catalyst under conditions otherwise identical with those for entry 4, and the ee value improved slightly from 87% to 89% (entry 5). When the catalytic system and the reagent were mixed and reacted at ambient temperature (entry 6), the ee value decreased to 78%. It appeared that mixing the reactants with the catalyst at 0 °C gave better enantioselectivities. With the use of 10 mol % of complex **3** and 1.5 molar equiv of Ti(O-*i*-Pr)$_4$, the asymmetric ethylation (entry 7) gave the chiral product with an ee value of 85%.

Table 2. Asymmetric Addition of Diethylzinc to Benzaldehyde[a]

entry no.	complex (amt, mmol)	Ti(O-*i*-Pr)$_4$ (amt, mmol)	temp	conversion (%)	selectivity (%)	ee (%)
1	**2** (0.1)		0 °C−rt	86	95	19
2	**2** (0.1)	0.5	0 °C−rt	100	>99	74
3	**2** (0.1)	1.0	0 °C−rt	100	100	84
4	**2** (0.1)	1.5	0 °C−rt	100	100	87
5	**1** (0.1)	1.5	0 °C−rt	100	100	89
6	**1** (0.1)	1.5	rt	100	100	78
7	**3** (0.1)	1.5	0 °C−rt	100	100	85

[a] The complex, Ti(O-*i*-Pr)$_4$, benzaldehyde (1.0 mmol), and Et$_2$Zn (1.2 mmol) were mixed at 0 °C (except entry 6) and the reaction mixture was warmed to room temperature (rt). The conversions and the selectivities are based on the ^{1}H NMR spectra. The ee values were determined by HPLC with a Chiralcel-OD column from Daicel. The configuration is *S* in all cases.

Conclusions

In summary, facile and high-yield syntheses of TiCl$_2$(TADDOLate)L$_2$ (L = THF, AcOEt) have been demonstrated. The weakly coordinating solvent ligands can be replaced easily by any neutral ligands, and this synthetic approach provides ways to prepare diversified TiCl$_2$(TADDOLate)L$_2$ complexes containing all sorts of monodentate or bidentate ligands as long as the replacing ligands are better bonding than the coordinated solvents. In this study, the reactions of complex **1** or **2** with bidentate ligand dppe or diketone are demonstrated. The surprising, first reported rearrangement of the α,α,α′,α′-tetramethyl-1,3-dioxolane-4,5-dimethanol ligand mediated by TiCl$_4$ is also reported. A similar rearrangement is not observed for the TADDOL moiety containing bulky α-phenyl groups. In the asymmetric ethylation of benzaldehyde, the reactions with catalytic systems of 10 mol % of complex **1**, **2**, or **3** and 1.5 molar equiv of Ti(O-*i*-Pr)$_4$ very cleanly efficiently give (*S*)-1-phenylpropanol with good enantioselectivities. It seems likely that better enantioselectivities can be achieved through the adjustment of the catalytic systems either on the TADDOLate substituents or on the supplementary nonchiral ligands. Further investigations on the

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synthesis of monomeric or higher nuclear titanium–TADDOLate complexes and on the studies of the catalytic behaviors of these complexes are currently underway.

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Supporting Information Available: Tables giving X-ray crystallographic data, including final coordinates, bond lengths, bond angles, and anisotropic displacement coefficients for complexes **3** and **6** (19 pages). Ordering information is given on any current masthead page.

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