Pergamon

Tetrahedron 54 (1998) 727–734

TETRAHEDRON

Novel Cationic Titanium(IV) Lewis Acids and Their Use in Asymmetric Aldol Reactions

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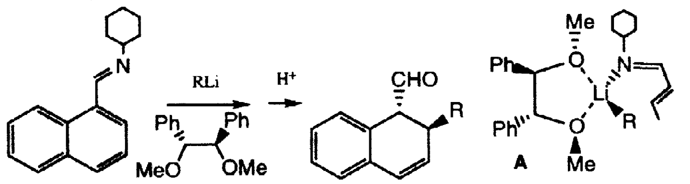
Received 11 June 1997; accepted 30 October 1997

Abstract: Novel cationic Lewis acids were generated by the addition of silver hexafluoroantimonate to titanium complexes **7** ($TiCl_4$•(*R*,*R*)-1,2-diphenylethane-1,2-diol dialkyl ether) or **8** ($TiCl_3(OR)$•(*R*,*R*)-1,2-diphenylethane-1,2-diol dialkyl ether) at -20 °C. Interestingly, the titanium complexes **7** or **8** could be isolated and the structures of **7c** ($TiCl_4$•(*R*,*R*)-1,2-diphenylethane-1,2-diol di-*n*-propyl ether) and **8a** ($TiCl_3(O\text{-}i\text{-}Pr)$•(*R*,*R*)-1,2-diphenylethane-1,2-diol dimethyl ether) were determined by X-ray analysis. Asymmetric aldol reaction using the cationic Lewis acids is also described. © 1997 Elsevier Science Ltd. All rights reserved.

INTRODUCTION

Considerable recent researches have been focused on asymmetric induction reactions by using various chiral Lewis acids such as titanium(IV) halides or alkoxides bearing chiral diols, diamines, and aminoalcohols.[2] In these cases, the Lewis acidity of the complexes are not so strong but stereochemically stable chiral centers at carbon atoms in the ligands control the stereoselectivity of reactions. Recently, Tomioka et. al. reported novel enantioselective conjugate addition of organolithium reagents to an α,β-unsaturated aldimine by use of a C_2 symmetric chiral diether,[3] and the corresponding aldehyde in >99 % ee was obtained by using (*R*,*R*)-1,2-diphenylethane-1,2-diol dimethyl diether (Scheme 1). They proposed the model **A** for the structure of the active species where the diether formed a five-membered chelate complex with the organolithium reagent and the lone pair of the nitrogen atom of the aldimine coordinated to the lithium atom.



Scheme 1

It was assumed that four substituents of the ligand would take an all-*trans* arrangement because of the steric factors which would lead chirality transfer from chirality of the carbon atoms on the backbone to the oxygen atoms.

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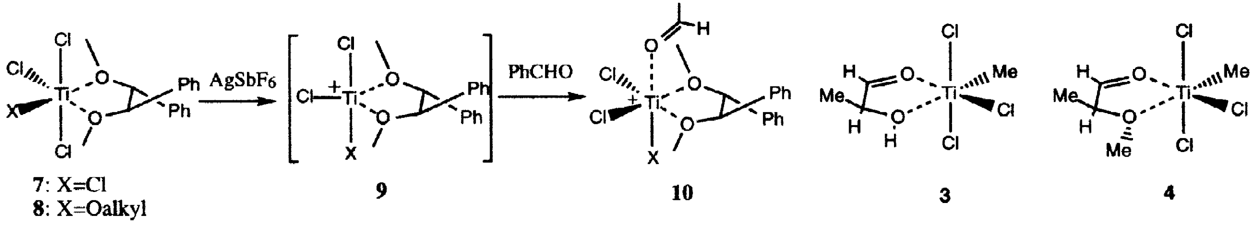
PII: S0040-4020(97)10296-4

In spite of these interests, stronger Lewis acids with chiral diether ligands have not been reported yet. Here we describe the generation of cationic Lewis acids **9** as shown in Scheme 2 hoping that these will be reactive enough to employ unactivated substrates or reactants. In the Lewis acids, the coordinating diether as shown in **10** suppresses polymerization of the cationic species and coordination site for the substrate in octahedral geometry should be available by abstraction of a chloride ion from **7** or **8** with silver hexafluoroantimonate.

However, chelation of the ether oxygen to Lewis acidic central atoms such as Ti(IV) usually renders the hybridization of the oxygen to an sp^2 mode from sp^3, thus losing the chirality at the oxygen. For example, recently reported X-ray structures of $Ti(O\text{-}i\text{-}Pr)Cl_3(Et_2O)(PhCHO)$ (**1**) and $Ti(O\text{-}i\text{-}Pr)Cl_3(THF)_2$ (**2**) clearly showed that the oxygen atoms of diethyl ether and THF coordinating to the Ti(IV) center were almost sp^2 hybridized (the sum of the bond angles of the oxygen atoms: 359.3 ° in **1**, 359.8 ° in **2**).[4] On the other hand, *ab initio* calculations of chelate complexes of CH_3TiCl_3 with (*S*)-2-hydroxypropionaldehyde (**3**) and (*S*)-2-methoxypropionaldehyde (**4**) showed the oxygen atom of the hydroxy group in **3** was practically sp^2 hybridized whereas some chiral induction on the oxygen atom from the carbon center was observed in **4**.[5]

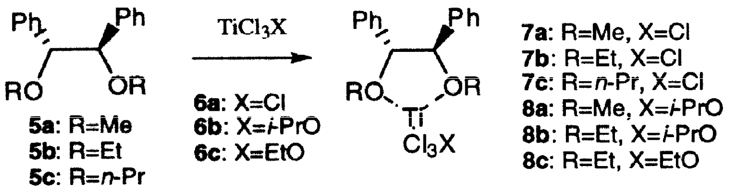


Scheme 2

Therefore, it is interesting to confirm the structures of complexes **7** and **8** experimentally whether chirality transfer from the chiral carbon backbone to a coordinating oxygen atom is possible. In addition, the applicability of the cationic Lewis acids for some reactions is also quite important. Here we report on the X-ray structures of six-coordinate titanium complexes **7c** and **8a** bearing diethers derived from (*R*,*R*)-1,2-diphenylethane-1,2-diol and asymmetric aldol reactions by using the novel cationic Lewis acids.

RESULTS AND DISCUSSION

The chiral diether-titanium (IV) complexes were prepared as shown in Scheme 3. To a stirred solution of the chiral diether in dry dichloromethane was added $TiCl_4$ very slowly at -20 °C. Then dry *n*-hexane was added to the solution and the resulting precipitates were filtered through glass wool under argon. The precipitates were washed with *n*-hexane and were dried in vacuo. The $TiCl_4$-diether complexes **7** were thermally very unstable and quite moisture sensitive so that careful manipulation was necessary. The $TiCl_3$(O-alkyl)-diether complexes **8** were not thermally unstable but moisture sensitive. Complexes **7** and **8** were prepared and used under argon. In the ^1H NMR of **7**, the signal of the benzyl protons in **5** (for example, δ 4.55 in **5b**) shifted to lower fields as a singlet (for example, δ 5.46 in **7b**) when the diether-$TiCl_4$ complex was formed.



Scheme 3

The facts suggest that the diethers are symmetrically coordinated to $TiCl_4$ although polymeric structures are not to be excluded. In the case of $TiCl_3$(Oalkyl)-diether complexes **8**, the signals of two benzyl protons appeared as one pair of doublets but one cannot determine the exact structure.

To confirm these structures, the crystals suitable for X-ray analysis were prepared by recrystallization from dichloromethane and *n*-hexane in a freezer (-20 °C). The crystals of **7** were thermally unstable as mentioned above but could be handled under argon in a glove bag at room temperature for a short period. A single crystal of **7c** in a sealed capillary was used for X-ray diffraction measurement at ca. -5 °C, but even at this low temperature significant decomposition (ca. 10 %) took place during the measurement. Thus, the obtained data were not quite good (R=9.5%) but the position of the atoms could be determined. In contrast, crystals of **8a** were stable at room temperature and X-ray structural analysis of **8a** could be carried out at room temperature in a sealed capillary without any problem. The obtained data showed very good quality (R=3.8 %). The ORTEP drawings of **7c** and **8a** are shown in Figure 1, and the selected bond distances and angles are listed in Table 1. These structures show six-coordinated geometry around the titanium center. To our delight the substituents (*n*-propyl in **7c** and methyl in **8a**) on the ether oxygen atoms are oriented *trans* to the phenyl group on the neighboring carbon although these oxygen atoms are not completely sp^3 hybridized (the sum of the bond angles around the oxygen atoms are 347.4° and 355.6° in **7c**, and 345.7° and 347.1° in **8a**).

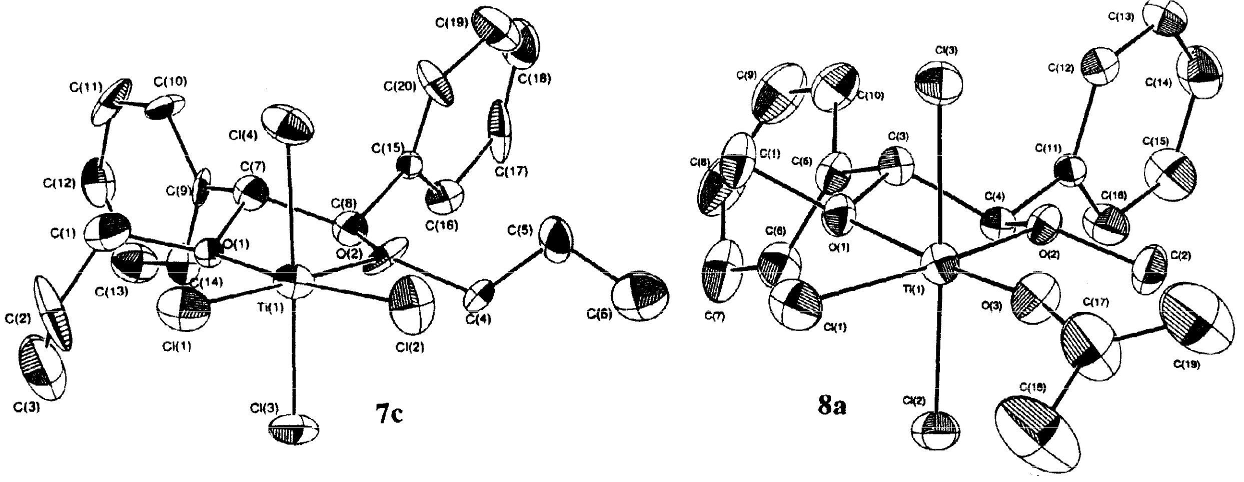
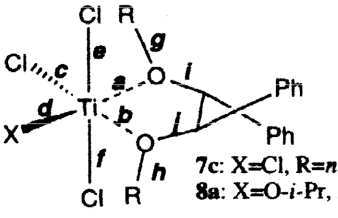


Figure 1. ORTEP diagrams (30% probability ellipsoids) for 7c and 8a.

Table 1. Selected Bond Lengths and Bond Angles for 7c and 8a.



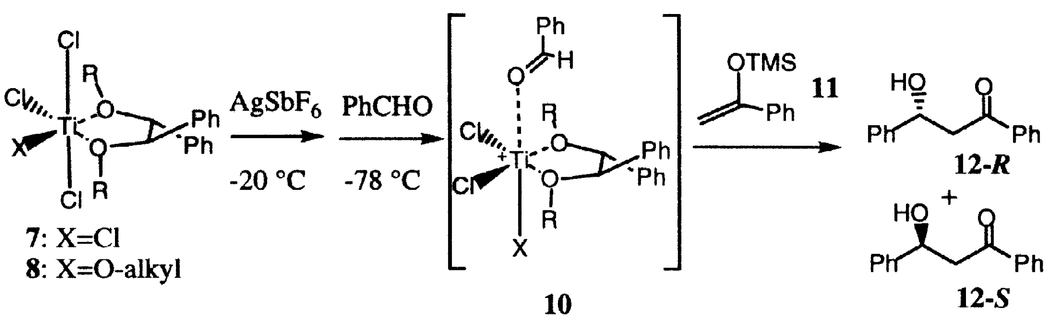
7c: X=Cl, R=*n*-Pr
8a: X=O-*i*-Pr, R=Me

	7c	8a
	bond lengths (Å)	
a	2.140(16)	2.226(5)
b	2.087(18)	2.138(4)
c	2.211(9)	2.267(3)
d	2.223(10)	1.707(5)
e	2.297(9)	2.315(3)
f	2.274(9)	2.339(3)

	7c	8a
	bond angles (deg)	
ab	74.2(7)	73.6(2)
ac	99.2(6)	91.8(2)
ad	164.9(6)	169.0(2)
ae	84.6(5)	83.3(2)
af	84.8(5)	83.7(2)
ag	119.7(17)	119.8(4)
ai	116.6(13)	115.3(4)
gi	111.1(19)	110.6(5)
bc	173.4(6)	165.0(2)
bd	90.7(6)	95.5(2)
be	87.8(6)	86.3(2)
bf	85.1(6)	83.3(2)
bj	120.0(14)	115.6(4)
bh	125.1(16)	117.9(4)
jh	110.5(20)	113.6(5)

The structure of **8a** is consistent with the reported principle that the strongest ligand (Ti-O-*i*-Pr in **8a**) prefers a trans position to the weakest ligand (Ti-O(ether)).[4] The bond distance of Ti-O(isopropoxide) (1.707(5) Å, **d** in Table 1) is comparable to the reported distances such as 1.742(6) Å in $[Ti(O\text{-}i\text{-}Pr)Cl_5]^{2-}$, 1.726(4) Å in $Ti(O\text{-}i\text{-}Pr)Cl_3(THF)_2$, 1.721(2) Å in $Ti(O\text{-}i\text{-}Pr)Cl_3(Et_2O)(PhCHO)$, and 1.702(4) Å in $[Ti(O\text{-}i\text{-}Pr)Cl_2(\mu\text{-}Cl)(OC(OMe)C_6H_5)]_2$.[4] The distance between Ti and the ether oxygen (2.226(5) Å, **a** in Table 1) trans to the isopropoxide was longer than that between Ti and the cis ether oxygen (2.138(4) Å, **b** in Table 1). The strong trans influence of the isopropoxide ligand has also been pointed out in **1** and **2**.[4]

With these results in hand, asymmetric aldol reaction of benzaldehyde with silyl enol ether (**11**) was conducted by using the cationic complexes prepared from **7** and **8** (Scheme 4). The results are shown in Table 2.



Scheme 4

Table 2. Aldol Reactions of Benzaldehyde and Silyl Enol Ether (11) By Using 7 or 8.

entry	X	R	12-*R*:12-*S*[a]	yield (%)
1[c]	O-*i*-Pr	Me	58 : 42	96
2[c]	O-*i*-Pr	Et	61 : 39	95
3[c]	OEt	Et	61 : 39	93
4[b,d]	Cl	Et	75:25	81
5[b,d]	Cl	*n*-Pr	76.5:23.5	76
6[c]	Cl	Me	76.5:23.5	80
7[c]	Cl	Et	77:23	86
8[c]	Cl	*n*-Pr	78:22	82

[a] Enantioselectivity was determined by HPLC analysis (Daicel AS column, *i*-PrOH:*n*-hexane=5:95).
[b] The complexes were prepared *in situ*.
[c] **7** (or **8**) 1.3 mmol, molecular sieves 4A 30 mg, 2,6-di-*tert*-butyl-4-methylpyridine 1 drop (see note 6), dichloromethane 5 mL, $AgSbF_6$ 1.9 mmol; then benzaldehyde 1.3 mmol, silyl enol ether 2.5 mmol.
[d] $TiCl_4$ 1.0 mmol, diether 1.5 mmol, molecular sieves 4A 30 mg, 2,6-di-*tert*-butyl-4-methyl-pyridine 1 drop (see note 6), $AgSbF_6$ 1.5 mmol, dichloromethane 3 mL; then benzaldehyde 1.3 mmol, silyl enol ether 2.5 mmol.

The reactions using the complexes **7** and **8** without abstraction of a chloride ion by silver hexafluoroantimonate proceeded to give aldol products in high yields but without selectivity. It is necessary to abstract a chloride ion by silver salts for stereoselection.[7] Even by use of the silver salt the reaction with $TiCl_3(OR)$-diether complexes **8** afforded the products in high yields, but the selectivities were rather low (Table 2). Bulky alkoxy substituents such as neopentyloxy or diisopropylmethoxy group did not give the products with higher selectivity (**12-*R***:**12-*S***=57:43 - 52:48) than the case with the isopropoxy or ethoxy substituents (entries 2 and 3, Table 2, **12-*R***:**12-*S***=61:39). Very small effects of the diether substituents on the selectivity were observed (entries 1 and 2, Table 2). However, **12** could be obtained selectively in ratios of 75:25-78:22 when $TiCl_4$-diether complexes were used with silver hexafluoroantimonate (entries **4-8**, Table 2). There were little effects of the diether substituents on the selectivity, but we reasoned the chain-like ether substituents (*n*-alkyl substituents) extended toward the quasi-equatorial direction in the coordinated conformation and did not affect the chiral environments. To overcome the problem, bulkier dibenzyl diether was used but its $TiCl_4$ complex was very unstable and decomposition occurred even at -20 °C. In addition to the reactions with the isolated complexes, we also investigated the reactions with the complexes prepared *in situ* (entries 4 and 5, Table 2) and found that there was no change of the selectivity compared with the case of the isolated complexes (entries 7 and 8, Table 2). Thus the reaction will proceed selectively by the use of the complexes prepared *in situ* without isolation of the complexes.

In conclusion, we could generate *in situ* cationic titanium Lewis acids bearing chiral diethers and show promising utility for asymmetric reactions. The starting neutral titanium-diether complexes **7** and **8** were isolated and some of which were characterized by X-ray analyses. Now we are applying the novel Lewis acids to other systems and are improving the ligand system.

EXPERIMENTAL

General.

^1H NMR spectra were recorded at 400 MHz (JEOL EX400) in $CDCl_3$. Chemical shifts (δ) are reported in ppm downfield from internal tetramethylsilane or from residual chloroform (δ=7.26).

General Procedures for the Preparation of Chiral Diethers.

(*R*,*R*)-1,2-Diphenylethane-1,2-diol[8] and (*R*,*R*)-1,2-diphenylethane-1,2-diol dimethyl ether (**5a**)[3] were prepared according to the literatures. Other diethers were prepared by modified Johnstone's method[9] as follows; To DMSO (100 mL) was added powdered KOH (22 g) at room temperature. After stirring for ca. 5 min, (*R*,*R*)-1,2-diphenylethane-1,2-diol (10.6 g, 50 mmol) in DMSO (50 mL) and alkyl halide (199 mmol) were added to the solution successively (alkyl halide was added very slowly because of the exothermic reaction). The reaction mixture was stirred for 1 day at room temperature and was treated with H_2O. The mixture was extracted with dichloromethane, and the combined organics were washed with water. After the solvents were evaporated, the crude products were purified by column chromatography (Merck silica gel 7734: ether / *n*-hexane = 1 / 5).

(*R*,*R*)-1,2-Diphenylethane-1,2-diol Diethyl Ether (5b): colorless oil (yield 80 %)

^1H NMR 1.26 (t, 6 H, *J* = 6.8 Hz), 3.50-3.59 (m, 4 H), 4.55 (s, 2 H), 7.17-7.40 (m, 10 H). HRMS(FAB+) 271.1675 (M+1, calcd for $C_{18}H_{23}O_2$ 270.1698).

(*R*,*R*)-1,2-Diphenylethane-1,2-diol Di-*n*-propyl Ether (5c): colorless oil (yield 71 %)

^1H NMR 0.99 (t, 6 H, *J* = 7.2 Hz), 1.65-1.72 (m, 4 H), 3.39-3.49 (m, 4 H), 4.53 (s, 2 H), 7.16-7.50 (m, 10 H). HRMS(FAB+) 299.1986 (M+1, calcd for $C_{20}H_{27}O_2$ 299.2011).

General Procedures for the Preparation of $Ti(OR)_4$.

$Ti(OR)_4$ were prepared according to the literature.[10] $TiCl_3(OR)$ were prepared by Bradley's method.[11]

$TiCl_3$(O-*i*-propyl) (6b).

^1H NMR 1.55 (d, 6 H, *J* = 5.8 Hz), 5.16-5.20 (m, 1 H).

$TiCl_3$(OEt) (6c).

^1H NMR 1.64 (t, 3 H, *J* = 7.0 Hz), 4.90-4.95 (m, 2 H).

General Procedures for the Preparation of $TiCl_4$-Diether Complexes.

To a stirred solution of diether (19 mmol) in dry dichloromethane (15 mL) was added $TiCl_4$ (12.7 mmol) very slowly at -20°C. After stirring for a few minutes, dry *n*-hexane (ca. 50-100 mL) was added to the solution. The yellow precipitates were filtered by using glass wool and washed with dry *n*-hexane. The (*R*,*R*)-1,2-diphenylethane-1,2-diol dialkyl diether (yellow powder) was collected under argon and was dried in vacuo (the powder was unstable at room temperature and moisture sensitive so that rapid manipulation was necessary). Identification of these complexes could be carried out by ^1H NMR but the thermal instability and moisture sensitivity of these complexes prevented precise characterization based on elemental analyses and HRMS.

$TiCl_4$-(*R*,*R*)-1,2-Diphenylethane-1,2-diol Dimethyl Ether Complex (7a).

^1H NMR 3.81 (s, 6 H), 5.20 (s, 2 H), 7.20-7.40 (m, 10 H).

$TiCl_4$-(*R*,*R*)-1,2-Diphenylethane-1,2-diol Diethyl Ether Complex (7b).

^1H NMR 0.87 (t, 6 H, J = 6.6 Hz), 4.12-4.16 (m, 2 H), 4.61-4.64 (m, 2 H), 5.46 (s, 2 H), 7.25-7.40 (m, 10 H).

$TiCl_4$-(*R*,*R*)-1,2-Diphenylethane-1,2-diol Di-*n*-propyl Ether Complex (7c).

^1H NMR 0.56 (t, 6 H, J = 7.4 Hz), 1.43-1.51 (m, 2 H), 1.88-1.91 (m, 2 H), 3.81-3.89 (m, 2 H), 4.42-4.48 (m, 2 H), 5.42 (s, 2 H), 7.18-7.31 (m, 10 H).

General procedures for the preparation of $TiCl_3(OR)$-diether complexes were similar to those for $TiCl_4$-diether complexes.

$TiCl_3$(O-*i*-Pr)-(*R*,*R*)-1,2-Diphenylethane-1,2-diol Dimethyl Ether Complex (8a).

^1H NMR 1.56 (d, 3 H, J = 5.8 Hz), 1.59 (d, 3 H, J = 5.8 Hz), 3.56 (s, 3 H), 3.79 (s, 3 H), 5.01 (d, 1 H, J = 9.9 Hz), 5.10 (d, 1 H, J = 9.9 Hz), 5.38-5.45 (m, 1 H), 7.09-7.24 (m, 10 H). Anal. Calcd for $C_{19}H_{25}O_3Cl_3Ti$: C, 50.08; H, 5.53. Found: C, 50.16; H, 5.60.

$TiCl_3$(O-*i*-Pr)-(*R*,*R*)-1,2-Diphenylethane-1,2-diol Diethyl Ether Complex (8b).

^1H NMR 1.20-1.28 (m, 6 H), 1.57-1.66 (m, 6 H), 3.85-3.88 (m, 1 H), 4.14-4.17 (m, 1 H), 4.39-4.42 (m, 1 H), 4.61-4.64 (m, 1 H), 5.29 (d, 1 H, J = 9.7 Hz), 5.40 (d, 1 H, J = 9.7 Hz), 5.44-5.48 (m, 1 H), 7.25-7.30 (m, 10 H). Anal. Calcd for $C_{21}H_{29}O_3Cl_3Ti+CH_2Cl_2$: C, 47.81; H, 5.65. Found: C, 47.87; H, 5.87.

$TiCl_3$(OEt)-(*R*,*R*)-1,2-Diphenylethane-1,2-diol Diethyl Ether Complex (8c).

^1H NMR 1.20-1.28 (m, 6 H), 1.64 (t, 3 H, J = 6.8 Hz), 3.81-3.85 (m, 1 H), 4.15-4.19 (m, 1 H), 4.39-4.43 (m, 1 H), 4.61-4.66 (m, 1 H), 5.15 (q, 2 H, J = 6.8 Hz), 5.29 (d, 1 H, J = 10.3 Hz), 5.39 (d, 1 H, J = 10.3 Hz), 7.10-7.40 (m, 10 H). Anal. Calcd for $C_{20}H_{27}O_3Cl_3Ti$: C, 51.15; H, 5.79. Found: C, 51.15; H, 5.94.

General Procedures for Aldol Reactions of Benzaldehyde with Silyl Enol Ether (11) by Using Isolated Titanium Complexes.

To a stirred solution of the titanium complex (1.3 mmol), molecular sieves 4A (30 mg), and 2,6-di-*tert*-butyl-4-methylpyridine (1 drop) in dry CH_2Cl_2 (3 mL) was added silver hexafluoroantimonate (1.9 mmol) in dry CH_2Cl_2 (2 mL) at -20 °C. After stirring for 15 min, the temperature was cooled to -78 °C and the mixture was stirred for 20 min. Benzaldehyde (1.3 mmol) and silyl enol ether (2.5 mmol) were added to the solution successively and the mixture was stirred overnight at the same temperature. The reaction mixture was quenched with 1M HCl, and the mixture was extracted with ether. The organics were dried over Na_2SO_4, and the solvents were evaporarted to give crude aldol products. The products were purified by column chromatography (Merck silica gel 7734: gradient elution, CH_3COOEt / *n*-hexane = 1 / 5 -100 / 0). The products were identified according to the literature.[12] The enantioselectivity was determined by HPLC (Daicel Chiralcel AS, *i*-PrOH:*n*-hexane = 5:95).

General Procedures for Aldol Reactions of Benzaldehyde with Silyl Enol Ether (11) by Using Titanium Complexes Prepared *in situ*.

To a stirrded solution of diether (1.5 mmol), molecular sieves 4A (30 mg), and 2,6-di-*tert*-butyl-4-methylpyridine (1 drop) in dry CH_2Cl_2 (3 mL) was added 1 mmol of titanium tetrachloride at -20°C. After stirring for 2 min, silver hexafluoroantimonate (1.5 mmol) in dry CH_2Cl_2 (2 mL) was added dropwise to the solution at -20 °C. After the mixture was stirred for 15 min, the temperature was cooled to -78°C and the reaction mixture was stirred for 20 min. The procedures of the aldol reaction were the same as above.

X-ray Structure Determination of 7c and 8a. Crystal data and numeric details of the structure determinations are given in Table 3. Crystals in sealed capillaries suitable for X-ray structure determination were mounted on a Mac Science MXC3 diffractometer and irradiated with graphite-monochromated Cu Kα radiation (λ = 1.54178 Å) for data collection. Lattice parameters were determined by least-squares fitting of 31 reflections with $44° < 2\theta < 50°$ and $40° < 2\theta < 50°$ for **7c** and **8a**, respectively. Data were collected with the 2θ/ω-scan mode. All data were corrected for absorption.[13] The structures were solved by a direct method with the SIR 92 program[14] in the Crystan-GM package. Refinement on *F* was carried out by full-matrix least squares. All non-hydrogen atoms were refined with anisotropic thermal parameters except for C(7) and C(8) in **7c**. These carbon atoms were refined with isotropic thermal parameters. All hydrogen atoms in **7c** and **8a** were included in the refinement on calculated positions (C-H = 1.0 Å) riding on their carrier atoms with isotropic thermal parameters. All the computations were carried out on a Indigo 2 computer.

Table 3. Selected Crystallographic Data for 7c and 8a.

No	7c	8a
formula	$C_{20}H_{26}O_2Cl_4Ti$	$C_{19}H_{25}O_3Cl_3Ti$
mol wt	488.1	455.7
crystal system	orthorhombic	orthorhombic
space group	$P2_12_12_1$	$P2_12_12_1$
a, Å	13.42 (1)	13.656 (2)
b, Å	15.84 (1)	14.748 (3)
c, Å	10.982 (9)	11.047 (2)
V, Å^3	2334 (3)	2225 (7)
Z	4	4
D_{calc}, g cm^{-3}	1.39	1.36
abs. coeff.; μ, cm^{-1}	75.58	68.105
F(000)	1008	944
radiation; λ, Å	Cu Kα, 1.54178	Cu Kα, 1.54178
temperature, °C	-5±1	23±1
cryst. dimens., mm	0.85 x 0.55 x 0.25	0.55 x 0.50 x 0.35
2θ max, deg	130	130
scan rate, deg/min	2.5	1.0
linear decay,%	10	-
data collected	$+h,+k,+l$	$+h,-k,+l$
total data collcd., obsd.	2219, 1138 (I>3σ(I))	2177, 1662 (I>3σ(I))
R int	0.189	0.023
no. of params. refined	234	260
R, R_w, S^a	0.095, 0.107, 4.356	0.038, 0.039, 1.230
max shift in final cycle	0.4495	0.975
final diff map, max, e/Å^3	0.81	0.36

[a] Function minimized was sum $[\omega(|Fo|-|Fc|)^2]$ which $\omega=1.0/[(\sigma|Fo|^2+0.0003|Fo|^2]$. $R=\Sigma[(||Fo|-|Fc||)/\Sigma|Fo|$. $Rw=[\Sigma\omega(|Fo|-|Fc|)^2/\Sigma|Fo|^2]^{1/2}$. $S=(\Sigma\omega(|Fo|-|Fc|)^2/n-m)^{1/2}$, where n and m are the no. of reflections used and variables refined, respectively.

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6) Somewhat lower ee was observed when the reaction was carried out without molecular sieves 4A and 2,6-di-*tert*-butyl-4-methylpyridine.

7) The cationic species could not be characterized because of their thermal instability and moisture sensitivity. However, quantitative formation of AgCl, which was characterized by powder X-ray analysis of a precipitate formed in the reaction of **7** (or **8**) with silver hexafluoroantimonate, might suggest the generation of the cationic species. We are grateful to professor Koji Yamada and professor Tsutomu Okuda for measurement of powder X-ray diffraction.

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