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

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Abstract: Novel cationic Lewis acids were generated by the addition of silver hexafluoroantimonate to titanium complexes 7 (TiCl₄•(R,R)-1,2-diphenylethane-1,2-diol dialkyl ether) or 8 (TiCl₃(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 (TiCl₄•(R,R)-1,2-diphenylethane-1,2-diol dialkyl ether) at 6 diol dial. 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 C₂ 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.

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 sp² mode from sp³, thus losing the chirality at the oxygen. For example, recently reported X-ray structures of Ti(O-*i*-Pr)Cl₃(Et₂O)(PhCHO) (1) and Ti(O-*i*-Pr)Cl₃(THF)₂ (2) clearly showed that the oxygen atoms of diethyl ether and THF coordinating to the Ti(IV) center were almost sp² 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 CH₃TiCl₃ with (*S*)-2-hydroxypropionaldehyde (3) and (*S*)-2-methoxypropionaldehyde (4) showed the oxygen atom of the hydroxy group in 3 was practically sp² hybridized whereas some chiral induction on the oxygen atom from the carbon center was observed in 4.⁵



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 TiCl4 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 TiCl4-diether complexes 7 were thermally very unstable and quite moisture sensitive so that careful manipulation was necessary. The TiCl3(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-TiCl4 complex was formed.



The facts suggest that the diethers are symmetrically coordinated to TiCl4 although polymeric structures are not to be excluded. In the case of TiCl3(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 sp³ 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.

				the second s	
c	L B	•		7c	8a
			_	bond angles (deg)	
Cl _{M,C}			ab	74.2(7)	73.6(2)
	· a · · ·	_Ph	ac	99.2(6)	91.8(2)
v ger			ad	164.9(6)	169.0(2)
^	1 9		ae	84.6(5)	83.3(2)
	'_/h_7c:X:	$= \bigcup_{i \in \mathbb{N}} K = n - M_{i}$	af	84.8(5)	83.7(2)
(CIR MARIN	=0- <i>i</i> -Pf, K=me	ag	119.7(17)	119.8(4)
			ai	116.6(13)	115.3(4)
	7c	8a	gi	111.1(19)	110.6(5)
	bond length	ıs (Å)	bc	173.4(6)	165.0(2)
a	2.140(16)	2.226(5)	bd	90.7(6)	95.5(2)
b	2.087(18)	2.138(4)	be	87.8(6)	86.3(2)
c	2.211(9)	2.267(3)	bf	85.1(6)	83.3(2)
d	2.223(10)	1.707(5)	ЪJ	120.0(14)	115.6(4)
e	2.297(9)	2.315(3)	bh	125.1(16)	117.9(4)
f	2.274(9)	2.339(3)	jh	110.5(20)	113.6(5)

110.5(20)

113.6(5)

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

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-*i*-Pr)Cl₅]²⁻, 1.726(4) Å in Ti(O-*i*-Pr)Cl₃(THF)₂, 1.721(2) Å in Ti(O-*i*-Pr)Cl₃(Et₂O)(PhCHO), and 1.702(4) Å in [Ti(O-*i*-Pr)Cl₂(μ -Cl)(OC(OMe)C₆H₅)]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-Sa	yield (%)
10	O-i-Pr	Me	58 : 42	96
2^c	O-i-Pr	Et	61 : 39	95
3 ^c	OEt	Et	61 : 39	93
4 <i>b</i> , <i>d</i>	Cl	Et	75:25	81
5 ^{b,d}	Cl	<i>n</i> -Pr	76.5:23.5	76
6 ^c	Cl	Me	76.5:23.5	80
7¢	Cl	Et	77:23	86
8 ^c	Cl	<i>n</i> -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, AgSbF6 1.9 mmol; then benzaldehyde 1.3 mmol, silyl enol ether 2.5 mmol.

d TiCl4 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), AgSbF6 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 TiCl₃(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 TiCl4-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 TiCl4 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 CDCl₃. 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-diol⁸ 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 method⁹ 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 H₂O. 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 C₁₈H₂₃O₂ 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 C₂₀H₂₇O₂ 299.2011).

General Procedures for the Preparation of Ti(OR)4.

Ti(OR)4 were prepared according to the literature.¹⁰ TiCl₃(OR) were prepared by Bradley's method.¹¹ TiCl₃(O-*i*-propyl) (6b).

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

TiCl3(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 TiCl4-Diether Complexes.

To a stirred solution of diether (19 mmol) in dry dichloromethane (15 mL) was added TiCl4 (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.

TiCl4-(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).

TiCl₄-(*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).

TiCl4-(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 TiCl₃(OR)-diether complexes were similar to those for TiCl₄-diether complexes.

TiCl3(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 C₁₉H₂₅O₃Cl₃Ti: C, 50.08; H, 5.53. Found: C, 50.16; H, 5.60.

TiCl3(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 C₂₁H₂₉O₃Cl₃Ti+CH₂Cl₂: C, 47.81; H, 5.65. Found: C, 47.87; H, 5.87.

TiCl3(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 C₂₀H₂₇O₃Cl₃Ti: 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 CH₂Cl₂ (3 mL) was added silver hexafluoroantimonate (1.9 mmol) in dry CH₂Cl₂ (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 Na₂SO₄, and the solvents were evaporarted to give crude aldol products. The products were purified by column chromatography (Merck silica gel 7734: gradient elution, CH₃COOEt / *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-4methylpyridine (1 drop) in dry CH₂Cl₂ (3 mL) was added 1 mmol of titanium tetrachloride at -20°C. After stirring for 2 min, silver hexafluoroantimonate (1.5 mmol) in dry CH₂Cl₂ (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 K α radiation ($\lambda = 1.54178$ Å) for data collection. Lattice parameters were determined by least-squares fitting of 31 reflections with $44^{\circ} < 2\theta < 50^{\circ}$ and $40^{\circ} < 2\theta < 50^{\circ}$ for 7c and 8a, respectively. Data were collected with the $2\theta/\omega$ -scan mode. All data were corrected for absorption.¹³ The structures were solved by a direct method with the SIR 92 program¹⁴ 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	<u>Crystallographic Data</u>	for 7c and 8a.
No	7c	8a
formula	C ₂₀ H ₂₆ O ₂ Cl ₄ Ti	C ₁₉ H ₂₅ O ₃ Cl ₃ Ti
mol wt	488.1	455.7
crystal system	orthorhombic	orthorhombic
space group	<i>P</i> 2 ₁ 2 ₁ 2 ₁	<i>P</i> 2 ₁ 2 ₁ 2 ₁
<i>a</i> , Å	13.42 (1)	13.656 (2)
<i>b</i> , Å	15.84 (1)	14.748 (3)
<i>c</i> , Å	10.982 (9)	11.047 (2)
V. Å ³	2334 (3)	2225 (7)
Z	4	4
$D_{\rm calc} {\rm g} {\rm cm}^{-3}$	1.39	1.36
abs. coeff.: $\mu_{\rm c}$ cm ⁻¹	75.58	68.105
F(000)	1008	944
radiation; λ, Å	Cu Ka, 1.54178	Cu Ka, 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
20 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 $\omega = 1.0/[(\sigma|Fo|^2 + 0.0003|Fo|^2]$. $R = \Sigma[(||Fo|-|Fc|])/\Sigma|Fo|$. $Rw = [\Sigma\omega(|Fo|-|Fc|)/\Sigma|Fo|$. $|F_{\rm C}|^2/\Sigma|F_0|^2|^{1/2}$. $S=(\Sigma\omega(|F_0|-|F_{\rm C}|)^2/n-m)^{1/2}$, where n and m are the no. of reflections used and variables refined, respectively.

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- 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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