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Modification of alkoxo ligands of BINOL–Ti ladder: Isolation and X-ray crystallographic analysis

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Abstract

The stable binaphthol–titanium ladder complexes have been successfully prepared by using bulky alkoxo ligands. From the secondary OR ligand (cyclohexyloxo, 2,4-dimethyl-3-pentyloxo or 2-adamantyloxo) and terially OR ligand (*tert*-butyloxo, 1-adamantyloxo), partial hydrolysis proceeded to give the μ^3-oxo titanium complexes. The use of $[Ti(BINOLato)(OEt)_2]_n$ made it possible to prepare the $Ti(BINOLato)(OR)_2$ complexes using alcohols (ROH) of high boiling point (R = cyclohexyl, 2-adamantyl, 1-adamantyl). X-ray analyses of [(*R*)-1,1′-bi-2-naphtholato]bis(O-2,4-dimethyl-3-pentyloxo)titanium and [(*R*)-3,3′-dimethyl-1,1′-bi-2-naphtholato]bis(2-adamantyloxo)titanium showed a good agreement with the estimated ladder complexes. The catalytic activity of BINOL–Ti catalyst analogues, obtained by partial hydrolysis of $Ti(BINOLato)(OR)_2$ with wet MS 4A was studied in asymmetric glyoxylate-ene reaction by two methods. Moderate to good chemical yields and enantioselectivities were obtained.

Keywords: Alkoxo ligands; BINOL–Ti ladder; X-ray crystallographic analysis; Asymmetric glyoxylate-ene reaction

1. Introduction

Binaphthol–titanium diisopropoxide complex, $Ti(BINOLato)(OPr^i)_2$, is the pre-catalyst for the BINOL–Ti catalyst [1], which is one of the most important catalysts for a number of highly enantioselective carbon–carbon bond forming processes [2], including the cyanosilylation of aldehydes [12b], Diels-Alder cycloadditions [3], hetero Diels-Alder cycloaddition [4], carbonyl-ene reaction [5], Mukaiyama aldol coreaction [6], nitro-aldol reaction [7], asymmetric allylation of aldehydes [8,11] and ketones [9], and asymmetric sulfide oxidation [10]. Sharpless has already reported the X-ray structure analysis of $Ti(BINOLato)(OPr^i)_2$ (**1**), synthesized via the reaction of BINOL with $Ti(OPr^i)_4$ [12e]. $Ti(BINOLato)(OPr^i)_2$ (**1**) has been reported to be dimeric in solution, though trimeric as a crystal. Heppert has also reported the X-ray analysis of more stable 3,3′-dimethyl-2-binaphthol–titanium diisopropoxide, $Ti(DMBINOLato)(OPr^i)_2$ (**2**), in which one of the oxygens of DMBINOLato ligand is coordinated to the two titanium centers [13].

We have also estimated the structure of μ^3-oxo titanium complex $Ti_4(BINOLato)_4(OPr^i)_4(\mu\text{-}O)_4$ (**3**), obtained during the preparation of the BINOL–Ti catalyst via partial hydrolysis of $Ti(BINOLato)(OPr^i)_2$ (Scheme 1) [14,15]. This complex is unstable and hence, the single crystal is not obtained yet. In an estimated structure of this complex (**3**) (Fig. 1), the upper side of the ladder structure is sterically less demanding. Water is assumed to attack the titanium center from this less hindered side and cause hydrolysis of μ^3-oxo titanium complex. We thus set up the present work to stabilize this ladder complex by introducing bulky alkoxo ligands in order to isolate the ladder complex for X-ray analysis.

2. Results and discussion

$Ti(BINOLato)(OR)_2$ complexes were prepared by an analogous method to that of $Ti(BINOLato)(OPr^i)_2$. Preparation of other $Ti(BINOLato)(OR)_2$ complexes via

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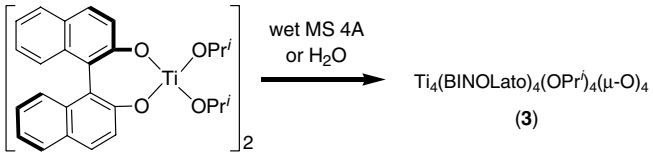


Scheme 1.

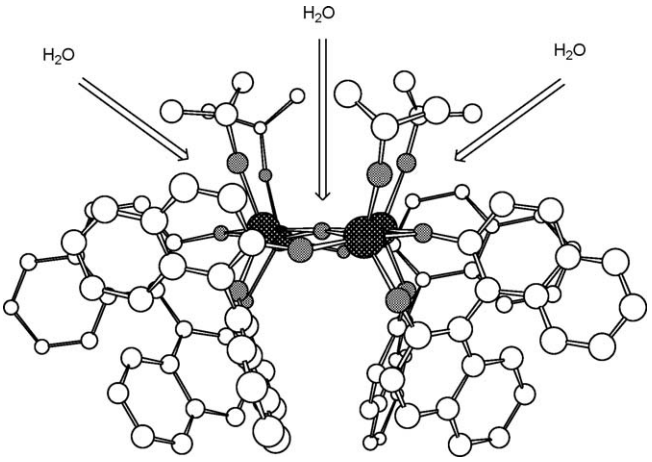
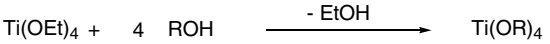


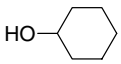
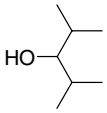
Fig. 1. Three-dimensional computer modeling structure of Ti_4(BINOLato)$_4$(OPr^i)$_4$(μ_3-O)$_4$ (**3**).

[Ti(BINOLato)(OEt)$_2$] was also examined. Partial hydrolysis of Ti(BINOLato)(OR)$_2$ complex and X-ray structure analysis of tetra-nuclear oxo complex were executed (Scheme 2).

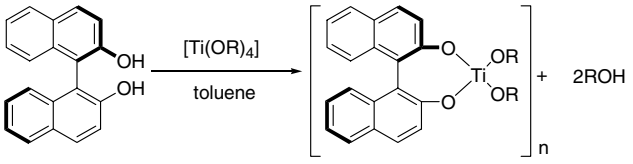
3. Synthesis of Ti(BINOLato)(OR)$_2$ complex from Ti(OR)$_4$

The reaction of Ti(OR)$_4$ (R = Et, *t*-Bu, cyclohexyl, 2,4-dimethyl-3-pentyl) and (*R*)-BINOL was examined. Ti(OBu^t)$_4$ and Ti(OEt)$_4$ were commercially available. Ti(O-cyclohexyl)$_4$ (**4**) and Ti(2,4-dimethyl-3-pentyloxo)$_4$ (**5**) were prepared from the reaction of Ti(OEt)$_4$ with 4 equiv of cyclohexanol and 2,4-dimethyl-3-pentanol, respectively (at room temperature for 1 h, without solvent), and then EtOH was removed under reduced pressure (Scheme 3). The ^{1}H NMR analyses of the products suggested that the reaction with cyclohexanol and 2,4-dimethyl-3-pentanol proceeded quantitatively to give the corresponding Ti(OR)$_4$ complex.



ROH	Product	Yield
	**4**	quant. (80% after recrystallization)
	**5**	quant.

Scheme 3.



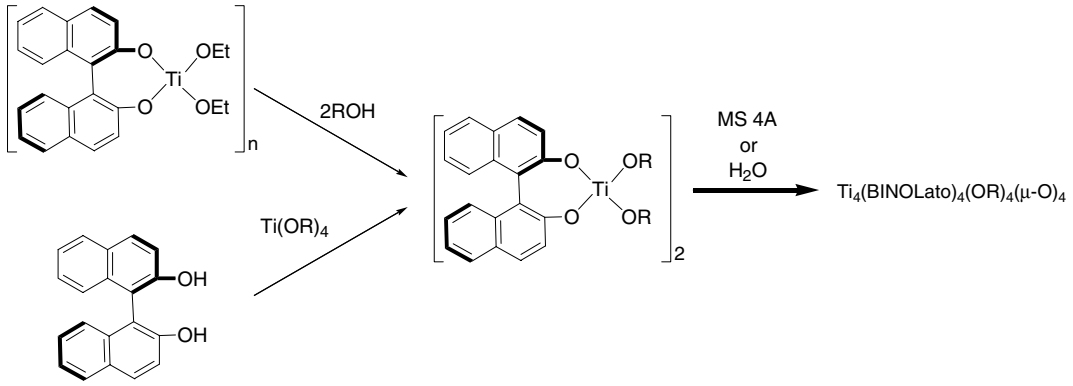
Entry	R	Product	Yield
1	Et	**6**	complex mixture
2	Pr^i	**1**	quant.[a]
3	Bu^t	**7**	quant.
4	cyclohexyl	**8**	quant.[b]
5	2,4-dimethyl-3-pentyloxo	**9**	quant.[c]

[a] dimer reported by Sharpless[12]; [b] mixture with cyclohexanol; [c] oxo complex

Scheme 4.

The synthetic method for Ti(BINOLato)(OR)$_2$ complexes was similar to that of Ti(BINOLato)(OPr^i)$_2$ (**1**) (Scheme 4). Ti(OR)$_4$ was added to BINOL in toluene at room temperature, and then azeotropic removal of ROH gave brown solid at 100 °C, 0.5 Torr.

Chart 1 showed ^{1}H NMR data of the Ti(BINOLato)(OR)$_2$ complexes. In the case of R = *t*-Bu (Chart 1. a) or cyclohexyl (Chart 1. b), the ^{1}H NMR data of BINO-



Scheme 2.

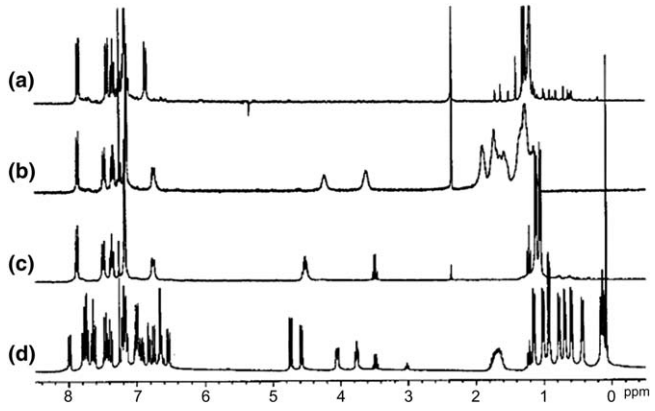


Chart 1. (a) Ti(BINOLato)(O-*t*-Bu)$_2$ (**7**); (b) Ti(BINOLato)(O-cyclohexyl)$_2$ (**8**); (c) Ti(BINOLato)(OPr^i)$_2$ (**1**); (d) Ti(BINOLato)(O-2,4-dimethyl-3-pentyl)$_2$ (**9**).

Lato parts were analogous to those of Ti(BINOLato)(OPr^i)$_2$ (**1**) (Chart 1. c). The reaction of BINOL and Ti(OEt)$_4$ gave the complicated product unfortunately. Stereochemically less demanding OEt moiety might cause oligomerization of Ti(BINOLato)(OEt)$_2$ (**6**). The formation of Ti(BINOLato)(2,4-dimethyl-3-pentyloxo)$_2$ (**9**) was not observed. However, the ladder complex, analogous to Ti$_4$(BINOLato)$_4$(OPr^i)$_4$(μ-oxo)$_2$, was observed. This complex was supposed to be formed by partial hydrolysis of Ti(BINOLato)(2,4-dimethyl-3-pentyloxo)$_2$.

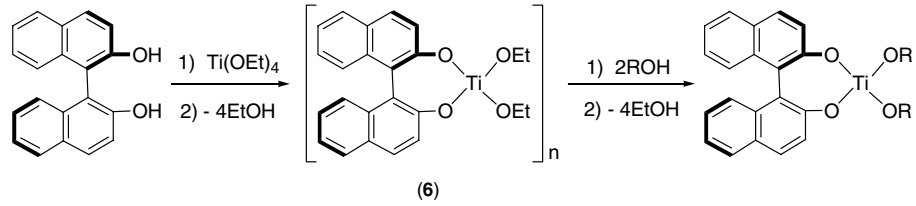
However, in the preparation of Ti(BINOLato)(O-cyclohexyl)$_2$ (**8**), 2 equiv of cyclohexanol produced could not be evacuated at 170 °C, 0.5 Torr. Such a high temperature treatment might promote epimerization of BINOLato ligand, and this method turned out to be not effective for the preparation of the Ti(BINOLato)(O-cyclohexyl)$_2$ and other complexes obtained from alcohols of high boiling point.

4. Synthesis of Ti(BINOLato)(OR)$_2$ complex from [Ti(BINOLato)(OEt)$_2$]$_n$

For these reasons, Ti(BINOLato)(OR)$_2$ analogues with sterically bulky alcohols of high boiling point were desired to be introduced. As a starting material, [Ti(BINOLato)(OEt)$_2$]$_n$ (**6**) was thus used (Scheme 5). The use of low boiling point of EtOH made this method advantageous. It is effective in the case of ROH with high boiling point, and only 2 equiv of ROH are required.

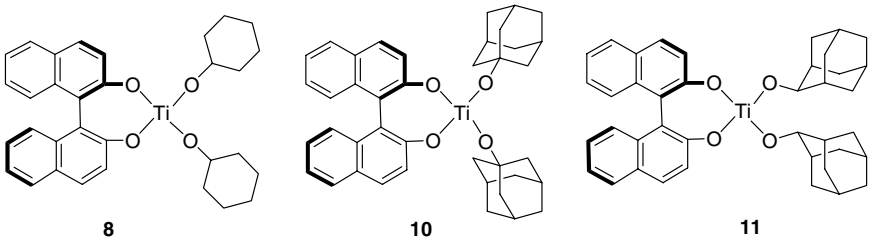
To the solution of BINOL and Ti(OEt)$_4$ in toluene, 2 equiv of alcohols (cyclohexanol, 2-adamantanol, or 1-adamantanol) were added at room temperature. Then EtOH and toluene were evaporated under reduced pressure to give brown solids.

In the case of R = cyclohexyl, 2-adamantyl, 1-adamantyl, ^{1}H NMR analysis (Chart 2) showed an analogous chart to that of Ti(BINOLato)(OPr^i)$_2$ (**1**) to suggest that the reaction proceeded quantitatively. [Ti(BINOLato)(O-cyclohexyl)$_2$] (**8**) gave good agreement with the complex obtained from the reaction of BINOL and Ti(O-cyclohexyl)$_4$ (**4**). However, the single crystal for X-ray analysis



(**6**)

ROH	Product	Yield
HO—	**8**	quant.
HO	**10**	quant.
HO	**11**	quant.



8 **10** **11**

Scheme 5.

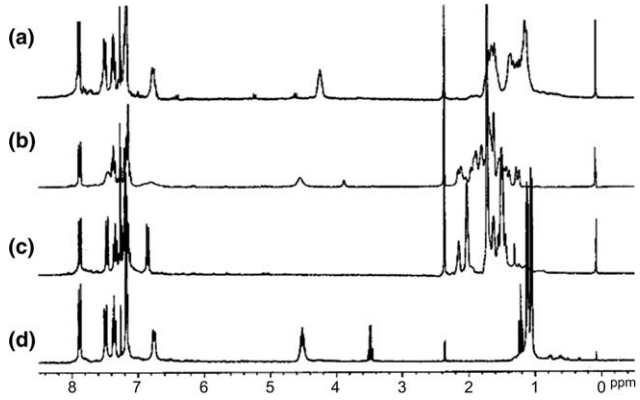


Chart 2. (a) Ti(BINOLato)(O-cyclohexyl)$_2$ (**8**); (b) Ti(BINOLato)(O-2-adamantyl)$_2$ (**11**); (c) Ti(BINOLato)(O-1-adamantyl)$_2$ (**10**); (d) Ti(BINOLato)(OPr^i)$_2$ (**1**).

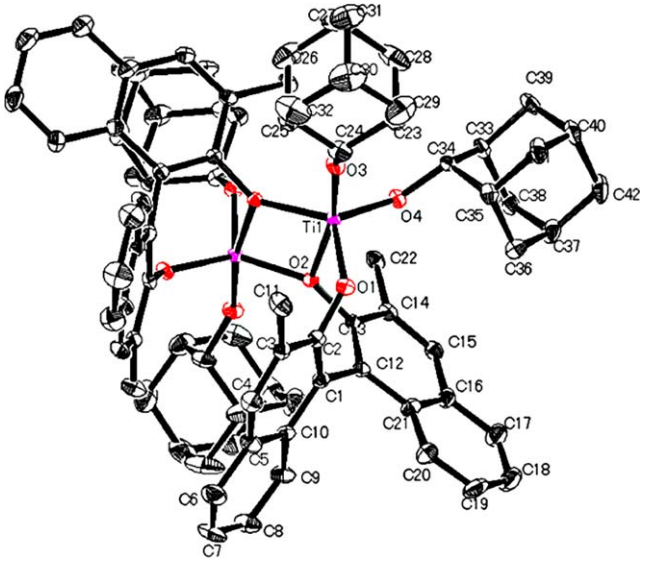


Fig. 2. ORTEP of [Ti(DMBINOLato)(O-2-adamantyl)$_2$]$_2$ [**13**]$_2$.

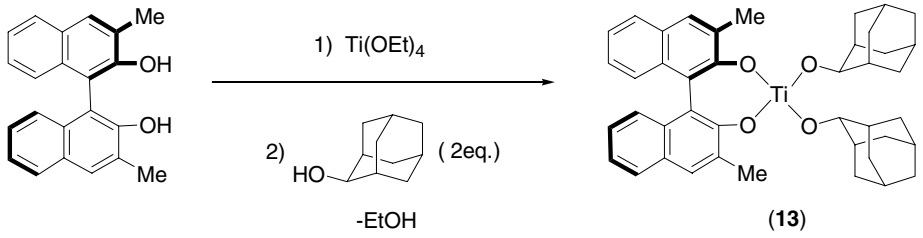
was not obtained in all cases. In order to obtain the X-ray data for the complex prepared by this method, DMBINOL was used. Similar to Heppert's work [13c], Ti(DMBINOLato)(OPr^i)$_2$ (**12**) complex was more stable than [Ti(BINOLato)(OPr^i)$_2$] (**1**) and easy to be crystallized. Ti(DMBINOLato)(O-2-adamantyl)$_2$ (**13**) was thus synthesized by the reaction of DMBINOL, Ti(OEt)$_4$, and 2 equiv of 2-adamantanol (Scheme 6).

The reaction proceeded quantitatively and the complex was recrystallized from toluene. Crystal system was monoclinic and space group was *C2*. The structure was determined by direct method (SIR92) and optimized by full-matrix least-square method. $R(I > 0.10\sigma(I))$ and $Rw(I > 0.10\sigma(I))$ were 0.099 and 0.114, respectively. Two independent Ti(DMBINOLato)(O-2-adamantyl)$_2$ units were observed and each unit was symmetrically expanded to give two dimeric [Ti(DMBINOLato)(O-2-adamantyl)$_2$]$_2$. Fig. 2 shows the ORTEP representation of one Ti(DMBINOLato)(O-2-adamantyl)$_2$ molecule, bond lengths and bond angles of major atoms are listed in Table 1. The bond lengths and angles of **13** are quite similar to those of **12** [13c].

5. Synthesis of μ^3-oxo titanium complex analogue

Ti$_4$O$_2$(BINOLato)$_4$(2,4-dimethyl-3-pentyloxo)$_4$ was obtained by the reaction of BINOL and Ti(2,4-dimethyl-3-pentyloxo)$_4$. Other Ti$_4$(BINOLato)$_4$(OR)$_4$(μ-O)$_2$ complexes were thus synthesized (Scheme 7). Partial hydrolysis of various Ti(BINOLato)(OR)$_2$ complexes was carried out. As secondary OR ligands, cyclohexyloxo and 2-adamantyloxo were used to generate Ti(BINOLato)(OR)$_2$ (R = cyclohexyl, 2,4-dimethyl-3-pentyl and 2-adamantyl) (0.05 mmol). After MS 4A (0.5 g containing 0.6 equiv. of water) was added and stirred for 1 h, the suspension was filtrated and analyzed by ^{1}H NMR.

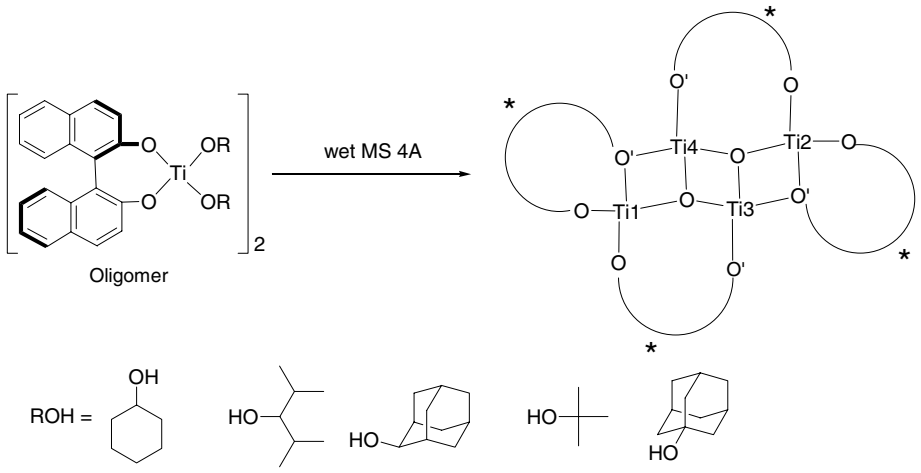
Chart 3 showed the ^{1}H NMR data of the product derived from 2-adamantanol. In the case of R = cyclohexyl or 2-adamantyl, partial hydrolysis of Ti(BINOLato)(OR)$_2$ proceeded to give new complexes. These new complexes gave the same pattern in ^{1}H NMR peaks and were considered to be isostructural to μ^3-oxo titanium ladder complex as compared with Ti(BINOLato)(OPr^i)$_2$ reported by Heppert [13a]. In the case of R = 2,4-dimethyl-3-pentyl, isostructural μ^3-oxo titanium complex was formed by the reaction of BINOL and Ti(2,4-dimethyl-3-pentyloxo)$_4$. Adventitious water in solvent might cause this partial hydrolysis. These complexes were more stable than the original ladder complex, Ti$_4$(BINOLato)$_4$(OPr^i)$_4$(μ^3-O)$_2$. The single crystal of μ^3-oxo titanium ladder complex of 2,4-dimethyl-3-pentyloxo was obtained by using (*S*)-BINOL in diethyl ether. Then, X-ray analysis of μ^3-oxo titanium complex of 2,4-dimethyl-3-pentyloxo analogue was carried out. The single crystal, obtained at room temperature, was



Scheme 6.

Table 1
Selected bond distance and bond angles

Bond	Distance (Å)	Bond	Distance (Å)	Angle	Degree	Angle	Degree
Ti(1)–O(1)	1.844(4)	Ti(1)–O(2)	2.181(3)	O(1)–Ti(1)–O(2)	85.4(1)	O(1)–Ti(1)–O(3)	99.5(2)
Ti(1)–O(3)	1.768(3)	Ti(1)–O(4)	1.795(4)	O(1)–Ti(1)–O(4)	112.5(2)	O(2)–Ti(1)–O(3)	167.8(2)
Ti(2)–O(6)	2.159(3)	Ti(2)–O(5)	1.832(4)	O(2)–Ti(1)–O(4)	87.4(2)	O(3)–Ti(1)–O(4)	100.9(2)
O(1)–C(2)	1.353(6)	O(2)–C(13)	1.377(5)	C(2)–O(1)–Ti(1)	133.0(4)	C(13)–O(2)–Ti(1)	116.4(3)
O(3)–C(24)	1.427(6)	O(4)–C(34)	1.426(7)	C(24)–O(3)–Ti(1)	150.0(4)	C(34)–O(4)–Ti(1)	132.6(3)



Scheme 7.

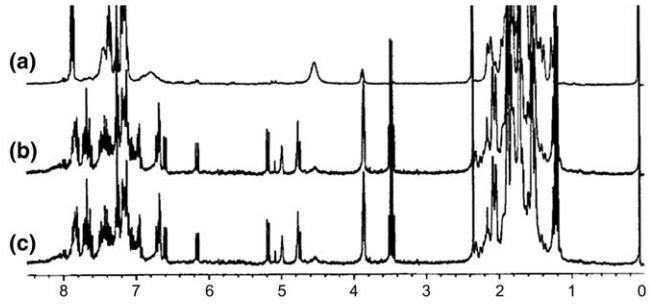


Chart 3. (a) Ti(BINOLato)(O-2-adamantyl)$_2$ (**11**); (b) 1 h after treatment of Ti(BINOLato)(O-2-adamantyl)$_2$ with MS 4A; (c) 24 h after treatment of Ti(BINOLato)(O-2-adamantyl)$_2$ with MS 4A.

red plate shaped. The crystal was monoclinic system and space group was *C2*. The positions of four titanium atoms were fixed by direct method and optimized by Full-Matrix least square ($2\theta = 29.99$, $R = 0.1020$, $Rw = 0.1390$) (Fig. 3).

The ORTEP figure of 2,4-dimethyl-3-pentyloxo analogue showed that the molecular equation of the complex was Ti$_4$(BINOLato)$_4$(2,4-dimethyl-3-pentyloxo)$_4$(μ-O)$_2$ of which the structure was similar to Ti$_4$(BINOLato)$_4$(OPr^i)$_4$(μ-O)$_2$ proposed. Crystal system was monoclinic and space group was *C2*. The skeleton of the complex was composed of four titanium centers and four μ^3-oxo ligands. All BINOLato ligands were bonded to two titanium centers. Two of four BINOLato ligands coordinated to two titanium

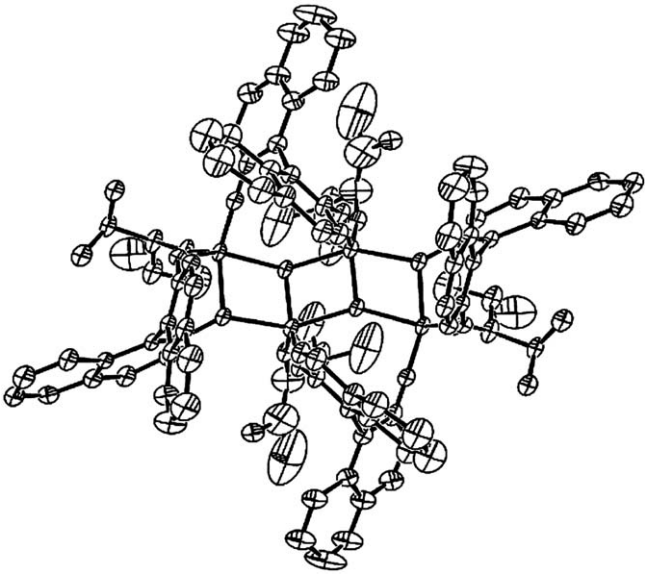


Fig. 3. ORTEP of Ti$_4$[(*S*)-(BINOLato)$_4$(2,4-dimethyl-3-pentyloxo)$_4$(μ-O)$_2$] (**9**).

centers. All four 2,4-dimethyl-3-pentyloxo ligands were bonded on the same side (see Table 2).

6. Catalytic activity of BINOL–Ti catalyst analogues

The catalytic activity of BINOL–Ti catalyst analogues was examined. In the preparation of BINOL–Ti analogues,

Table 2
Selected bond distance and bond angles

Bond	Distance (Å)	Bond	Distance (Å)	Angle	Degree	Angle	Degree
Ti(1)–O(1)	1.970(8)	Ti(1)–O(2)	1.846(9)	O(1)–Ti(1)–O(2)	132.7(4)	O(1)–Ti(1)–O(3)	71.0(4)
Ti(1)–O(3)	2.122(9)	Ti(1)–O(4)	1.730(10)	O(1)–Ti(1)–O(4)	113.7(5)	O(1)–Ti(1)–O(5)	93.8(4)
Ti(2)–O(6)	1.805(9)	Ti(2)–O(7)	1.768(10)	O(2)–Ti(1)–O(5)	96.3(5)	O(3)–Ti(1)–O(4)	95.6(5)
O(2)–C(2)	1.380(2)	O(3)–C(12)	1.390(2)	C(2)–O(2)–Ti(1)	132.7(8)	C(12)–O(3)–Ti(1)	118.8(7)
O(4)–C(41)	1.440(2)	O(5)–C(32)	1.290(2)	C(41)–O(4)–Ti(1)	164.0(1)	C(32)–O(5)–Ti(1)	175.0(1)

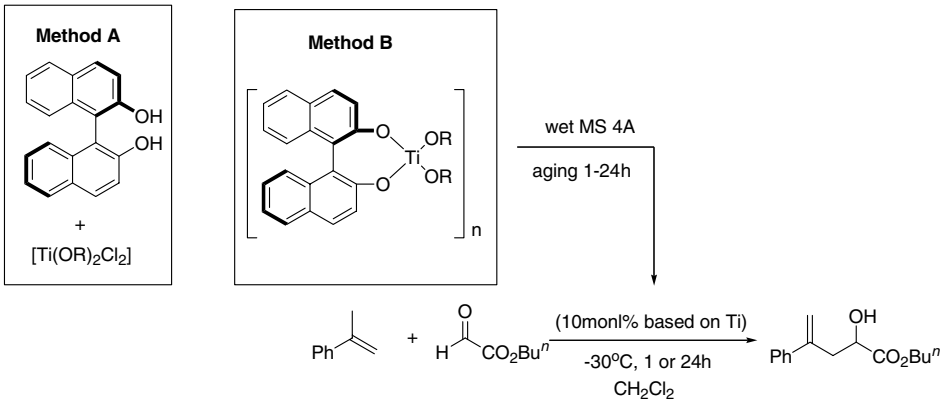
two methods were employed (Methods A and B). In the method A, the mixture of (*R*)-BINOL (1.0 mmol) and $Ti(OR)_2Cl_2$ (1.0 mmol) was treated with MS 4A (0.5 g) in CH_2Cl_2 (4 mL) for 1 h. In the method B, Ti(BINOLato)$(OR)_2$ (1.0 mmol) was treated with MS 4A (0.5 g) in CH_2Cl_2 (4 mL) for 1 h. The reaction of α-methylstyrene (1.0 mmol) and *n*-butyl glyoxylate (1.2 mmol) in CH_2Cl_2 (4 mL) (for 1 h at −30 °C) was used as a probe reaction (Table 3). Ti(O-cyclohexyl)$_2Cl_2$ was synthesized from the reaction of Ti(O-cyclohexyl)$_4$ and $TiCl_4$ in hexane.

The catalytic activity of all the complexes turned out to be lower than that of the original BINOL–Ti catalyst obtained by the method A and B (R = Pr^i). In the case of R = cyclohexyl, the reaction gave the ene-product highly enantioselectively, but chemical yield was moderate (73%, 98% ee). Such low catalytic activity of complex was due to the stability of Ti(BINOLato)$(OR)_2$ complex. Stabilization by steric bulkiness of alkoxo ligands led to retardation of the formation of the BINOL–Ti catalysts. The catalytic activity of the samples treated by MS 4A for 24 h (Method B) was also low in the case of R = cyclohexyl, 2,4-dimethyl-3-pentyl and 2-adamantyl. Increase in chemical yield was observed only in the case of R = *t*-Bu. However, steric bulkiness of alkoxo ligands was considered to interfere the approach of substrate, and hence lower the catalytic activity of the complexes.

7. Summary

The stabilization of the ladder complex has thus been attained by using bulky alkoxo ligands. From the secondary OR ligand (cyclohexyloxo, 2,4-dimethyl-3-pentyloxo or 2-adamantyloxo) and tertially OR ligand (*tert*-butyloxo, 1-adamantyloxo), partial hydrolysis proceeded to give the μ^3-oxo titanium complexes. The X-ray analysis of Ti_4(BINOLato)$_4$(2,4-dimethyl-3-pentyloxo)$_4$(μ-O)$_4$ successfully showed the ORTEP figure of 2,4-dimethyl-3-pentyloxo analogue, Ti_4(BINOLato)$_4$(2,4-dimethyl-3-pentyloxo)$_4$(μ-O)$_4$.

Table 3
BINOL–Ti analogues catalyzed asymmetric glyoxylate-ene reaction



Entry	ROH	Method	Aging time (h)	Yield (%)	Ee (%)
1	Pr^iOH	**A**	1	97	98
2	Pr^iOH	**B**	1	97	98
3	Bu^tOH	**B**	1	38	94
4	Bu^tOH	**B**	24	63	91
5	cyclohexanol	**A**	1	73	98
6	cyclohexanol	**A**	24	16	97
7[a]	2,4-dimethyl-3-pentanol	**B**	1	2	93
8[a]	2,4-dimethyl-3-pentanol	**B**	24	1	42
9	1-adamantanol	**B**	1	17	93
10	1-adamantanol	**B**	24	10	85

[a] [Ti_4(BINOLato)$_4$(2,4-dimethyl-3-pentyloxo)$_4$(μ3-O)$_2$] was used, in spite of Ti(BINOLato)(2,4-dimethyl-3-pentyloxo)$_2$.

The structure was similar to the estimated ladder complex, $Ti_4(BINOLato)_4(OPr^i)_4(\mu\text{-}O)_4$. The pre-catalysts, Ti(BINOLato)$(OR)_2$, were prepared by the reaction of $Ti(OR)_4$ and (*R*)-BINOL (R = *t*-Bu, cyclohexyl). However, in the preparation of Ti(BINOLato)(O-cyclohexyl)$_2$ (**8**), 2 equiv of cyclohexanol produced could not be excluded even at high temperature and low pressure. The use of [Ti(BINOLato)$(OEt)_2]_n$ made it possible to prepare the Ti(BINOLato)$(OR)_2$ complexes with alcohols of high boiling point (R = cyclohexyl, 2-adamantyl, 1-adamantyl). [Ti(BINOLato)(O-cyclohexyl)$_2]_2$ showed good agreement with the complex synthesized from the reaction of BINOL and Ti(O-cyclohexyl)$_4$. The catalytic activity of BINOL–Ti catalyst analogues, obtained by partial hydrolysis of Ti(BINOLato)$(OR)_2$ with wet MS 4A, turned out to be lower than that of the original BINOL–Ti catalyst. In the case of R = cyclohexyl, the reaction gave the ene-product with high enantioselectivity, however, chemical yield was moderate (73%, 98% ee).

8. Experimental

General method: Melting points and boiling points were uncorrected. ^{1}H NMR and ^{13}C NMR were measured on a Varian Gemini 300 (300 Hz) spectrometers and ^{17}O NMR was measured on a GX-500 (500 Hz) spectrometers. Chemical shifts of ^{1}H NMR were expressed in parts per million downfield from tetramethylsilane as an internal standard ($\delta = 0$) in $CDCl_3$. Chemical shifts of ^{13}C NMR were expressed in parts per million downfield from $CDCl_3$ as an internal standard ($\delta = 77.0$) in $CDCl_3$. Chemical shifts of ^{17}O NMR were expressed in parts per million downfield from H_2O as an internal standard ($\delta = 0$) in C_7D_8. IR spectra were measured on a JASCO FT/IR-5000 spectrometer. Optical rotations were measured on a JASCO DIP-370. Liquid chromatographic analyses (LC) were conducted on a Shimadzu PU-980, LG-980-02, DG-980-50 and CO-966 instrument equipped with model UV-975 spectrometers as an ultra violet light. Peak areas were calculated by Shimadzu C-R6A as an automatic integrator. Molecular weight measurements were performed on Knauer vapor pressure someter. Analytical thin layer chromatography (TLC) was performed on a glass plates and/or aluminum sheets pre-coated with silica gel (Merck Kieselgal 60 F_{254}, layer thickness 0.25 and 0.2 mm). Visualization was accomplished by UV light (254 nm), anisaldehyde, $KMnO_4$ and phosphomolybdic acid. Column chromatography was performed on Merck Kieselgel 60 and KANTO Silica Gel 60N (spherical, neutral), employing hexane/ ethyl acetate mixture as eluent unless otherwise noted. Molecular sieves (MS 4A, activated powder and pelets) were purchased from Aldrich Chemical Co. All experiments were carried out under argon atmosphere unless noted. Diethyl ether (dehydrate), benzene (dehydrate), toluene (dehydrate), dichloromethane (dehydrate), chloroform-d_3 and hexane (dehydrate) were purchased from Kanto chemical Co. Inc. and dried over molecular sieves (MS 4A, pelets).

8.1. Tetrakis(cyclohexyloxo)titanium (IV) (**4**)

A 20 mL schlenk tube equipped with a magnetic stirring bar and argon inlet was charged with cyclohexanol (7.6 g, 76 mmol). To the solution was slowly added titanium ethoxide (3.2 mL, 15 mmol) at ambient temperature from a syringe. After stirring for 1 min, the solution was allowed to stand for 6 h at 70 °C. Non-reacted cyclohexanol was removed under reduced pressure (140 °C, 10 mmHg) and recrystallized from hexane to give tetrakis(O-cyclohexyl)titanium (IV) (5.3 g, 12 mmol) as a white crystal. ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.13–1.58 (m, 24H), 1.65–1.81 (m, 8H), 1.83–2.10 (m, 8H), 4.07–4.17 (m, 4H).

8.2. Tetrakis(2,4-dimethyl-3-pentyloxo)titanium (IV) (**5**)

A 20 mL schlenk tube equipped with a magnetic stirring bar and argon inlet was charged with 2,4-dimethyl-3-propanol (13 g, 115 mmol). To the solution was added titanium (IV) ethoxide (5.47 mL, 26 mmol) slowly at ambient temperature from a syringe. After stirring for 10 min, the solution was allowed to stand for 6 h at room temperature. Non-reacted 2,4-dimethyl-3-propanol was removed under reduced pressure to give tetrakis (2,4-dimethyl-3-pentyloxo)titanium (IV) (13 g, 26 mmol). The product was used without any purification. ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.91 (d, $J = 6.6$ Hz, 24H), 0.96 (d, $J = 6.6$ Hz, 24H), 1.72 (m, 8H), 3.69 (sept, $J = 6.0$ Hz, 4H).

8.3. [(*R*)-1,1′-Bi-2-naphtholato]bis(O-t-Bu)titanium (IV) (*7*)

To a suspension of dried (*R*)-1,1′-bi-2-naphthol (0.88 g, 3.1 mmol) in toluene (20 mL) was added dried Ti(O-*t*-Bu)$_4$ (1.2 mL, 3.1 mmol) at room temperature. After stirring for 1 h at that temperature, the reaction mixture was azeotroped until volume of the solution was reduced to 8 mL. Further concentration was continued under reduced pressure to give [(*R*)-1,1′-bi-2-naptholato]bis(O-*tert*-butyloxo)titanium (IV) (**7**) (1.5 g, 3.1 mmol, 99%) as an orange crystal. ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.19 (s, 18H), 6.86 (d, $J = 9.0$ Hz, 2H), 7.12–7.24 (m, 4H), 7.34 (ddd, $J = 8.4$, 6.3, 1.8 Hz, 2H), 7.43 (d, $J = 9.0$ Hz, 2H), 7.86 (d, $J = 8.1$ Hz, 2H).

8.4. [(*R*)-1,1′-Bi-2-naphtholato] bis(cyclohexyloxo)titanium (IV) (*8*)

To a suspension of dried (*R*)-1,1′-bi-2-naphthol (260 mg, 0.92 mmol) in toluene (10 mL) was added dried Ti(OEt)$_4$ (209 μL, 0.92 mmol) at room temperature. After stirring for 1 h at that temperature, the reaction mixture was added cyclohexanol (180 mg, 1.8 mmol) and stirred for 1 h at that temperature. The reaction mixture was azeotroped until volume of the solution was reduced to 1 mL. Further concentration was continued under reduced pressure to give [(*R*)-1,1′-bi-2-naptholato]bis(cyclohexyloxo) titanium (IV) (**8**) (480 mg, 0.90 mmol) as an

orange crystal. ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.0–1.8 (m, 20H), 4.24 (br, 2H), 6.76 (d, $J = 8.7$ Hz, 2H), 7.13–7.20 (m, 4H), 7.36 (m, 2H), 7.48 (d, $J = 8.7$ Hz, 2H), 7.88 (d, $J = 8.4$ Hz, 2H).

8.5. [(R)-1,1′-Bi-2-naphtholato]bis(2,4-dimethyl-3-pentyloxo)titanium (IV) (9)

To a suspension of dried (*R*)-1,1′-bi-2-naphthol (1.1 g, 3.9 mmol) in toluene (30 mL) was added dried titanium(2,4-dimethyl-3-pentyloxo)$_4$ (2.2 mL, 3.9 mmol) at room temperature. After stirring for 1 h at that temperature, the reaction mixture was azeotroped until volume of the solution was reduced to 1 mL. Further concentration was continued under reduced pressure. Orange solid was recrystallized to give [(*R*)-1,1′-bi-2-naptholato]bis(O-2,4-dimethyl-3-pentyloxo)titanium (IV) (**9**) (620 mg, 0.34 mmol, 35%) as an orange crystal. ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.17 (d, $J = 6.6$ Hz, 6H), 0.44 (d, $J = 6.6$ Hz, 6H), 0.60 (d, $J = 6.9$ Hz, 6H), 0.69 (d, $J = 6.6$ Hz, 6H), 0.78 (d, $J = 6.6$ Hz, 6H), 0.93 (d, $J = 6.6$ Hz, 6H), 1.01 (d, $J = 7.2$ Hz, 6H), 1.15 (d, $J = 6.6$ Hz, 6H), 1.60–1.80 (m, 8H), 3.76 (m, 2H), 4.04 (m, 2H), 4.58 (d, $J = 8.4$ Hz, 2H), 4.74 (d, $J = 8.7$ Hz, 2H), 6.54 (d, $J = 7.8$ Hz, 2H), 6.65 (d, $J = 5.7$ Hz, 2H), 6.67 (s, 2H), 6.74 (d, $J = 9.0$ Hz, 2H), 6.82 (d, $J = 9.0$ Hz, 2H), 6.92 (t, $J = 6.6$ Hz, 2H), 6.97–7.04 (m, 6H), 7.12–7.22 (m, 8H), 7.36–7.67 (m, 4H), 7.46 (d, $J = 9.0$ Hz, 2H), 7.60–7.70 (m, 4H), 7.70–7.77 (m, 4H), 7.79 (d, $J = 7.9$ Hz, 2H), 7.71 (d, $J = 8.4$ Hz, 2H).

8.6. [(R)-1,1′-Bi-2-naphtholato]bis(1-adamantyloxo)-titanium (IV) (10)

To a suspension of dried (*R*)-1,1′-bi-2-naphthol (950 mg, 3.3 mmol) in toluene (10 mL) was added dried Ti(OEt)$_4$ (700 μL, 3.3;mmol) at room temperature. After stirring for 1 h at room temperature, to the reaction mixture was added 2-adamantanol (280 mg, 1.8 mmol) and stirred for 1 h at that temperature. The reaction mixture was azeotroped until volume of the solution was reduced to 1 mL. Further concentration was continued under reduced pressure to give [(*R*)-1,1′-bi-2-naptholato]bis(1-adamantyloxo)titanium (IV) (2.0 g, 3.10 mmol, 94%) as an orange solid. ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.42–1.55 (m, 8H), 1.71(br, 12H), 2.02(s, 6H), 2.15(s, 6H), 6.85 (d, $J = 8.7$ Hz, 2H), 7.11 ~ 7.19 (m, 4H), 7.34 (ddd, $J = 8.1$, 6.9, 1.2 Hz, 2H), 7.46 (d, $J = 9.0$, 2H), 7.81 (d, $J = 8.1$ Hz, 2H).

8.7. [(R)-1,1′-Bi-2-naphtholato]bis(2-adamantyloxo)-titanium (IV) (11)

To a suspension of dried (*R*)-1,1′-bi-2-naphthol (260 mg, 0.91 mmol) in toluene (20 mL) was added dried Ti(OEt)$_4$ (190 μL, 0.91 mmol) at room temperature. After stirring for 1 h at that temperature, to the reaction mixture was added 2-adamantanol (280 mg, 1.8 mmol) and stirred for 1 h at that temperature. The reaction mixture was azeotroped until volume of the solution was reduced to 1 mL. Further concentration was continued under reduced pressure to give [(*R*)-1,1′-bi-2-naptholato]bis(2-adamantyloxo)titanium (IV) (470 mg, 0.75 mmol, 82%) as an orange crystal. ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.21–2.16 (m, 30H), 4.54 (br, 2H), 6.79 (br, 2H), 7.81–7.19 (m, 4H), 7.35 (ddd, $J = 7.5$, 6.0, 1.2 Hz, 2H), 7.43 (br, 2H), 7.86 (d, $J = 7.8$ Hz, 2H).

8.8. [(R)-3,3′-dimethyl-1,1′-bi-2-naptholato]bis(2-adamantyloxo)titanium (IV) (13)

To a suspension of dried (*R*)-3,3′-dimethyl-1,1′-bi-2-naphthol (180 mg, 0.57 mmol) in toluene (10 mL) was added dried Ti(OEt)$_4$ (120 μL, 0.57 mmol) at room temperature. After stirring for 1 h at that temperature, the reaction mixture was added 2-adamantanol (170 mg, 1.1 mmol) and stirred for 1 h at that temperature. The reaction mixture was azeotroped until volume of the solution was reduced to 1 mL. Further concentration was continued under reduced pressure and recrystallize in toluene to give [(*R*)-3,3′-dimethyl-1,1′-Bi-2-naptholato]bis(2-adamantyloxo) titanium (IV) (**13**) (160 mg, 0.25 mmol, 43%) was obtained as X-ray grade yellow-orange crystal. ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.90 (d, $J = 12.6$ Hz, 4H), 1.21–1.96 (m, 24H), 2.00 (s, 6H), 4.63 (br, 2H), 6.99 (d, $J = 7.8$ Hz, 2H), 7.03 (dd, $J = 8.1$, 7.8 Hz, 2H), 7.21–7.31 (m, 2H), 7.57 (s, 2H), 7.79 (d, $J = 8.1$ Hz, 2H).

8.9. General procedure for preparation of ladder complex

To a well-dried toluene (10 mL) was added 0.1 M ether (0.5 mL) solution of H_2O (0.05 mmol, 0.9 μL) at room temperature and stirred for 1 min (the amount of H_2O/Et_2O solution was optimized by try and error). Then, [Ti(OR)$_2${(*R*)-μ-BINOLato}] derivatives (1.0 mmol) was added at room temperature under an argon atmosphere. After stirring for 1 h, the solvent was removed under reduced pressure to give [Ti$_4$(OR)$_4${(*R*)-μ-BINOLato}$_4$(μ$_3$-O)$_2$] (>95%).

8.10. Ladder complex

[Ti$_4${(*R*)-μ-BINOLato}$_4$(*tert*-butyloxo)$_4$(μ$_3$-O)$_2$]: The titled compound was prepared from (*R*)-[Ti{(*R*)-μ-BINOLato}(O-*t*-Bu)$_2$] according to the general procedure (about 85% yield). ^{1}H NMR (300 MHz, $CDCl_3$): δ1.40 (s, 36H), 4.73 (d, $J = 8.4$ Hz, 2H), 5.25 (d, $J = 9.0$ Hz, 2H), 6.03 (d, $J = 8.7$ Hz, 2H), 6.18–6.33 (m, 2H), 6.67 (s, 2H), 6.71 (d, $J = 8.4$ Hz, 2H), 6.95–6.30 (m, 20H), 7.48 (t, $J = 6.6$ Hz, 2H), 7.63 (d, $J = 8.7$, 2H), 7.66 ~ 7.84 (m, 12H).

9. Supplementary data

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited

in the Cambridge Crystallographic Data Center as supplementary publication nos. CCDC-261195 and CCDC-261196. Copies of this information can be obtained free of charge from The Director, CCDC, 12, Union Road, Cambridge CB2 1EZ, UK (fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

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