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Tetrahedron: *Asymmetry* 17 (2006) 2149–2153

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A novel trinuclear titanium(IV) complex with a C_3 axis along Ti1–Ti2–Ti3 containing 3-[(1*H*-1,2,4-triazol-1-yl)methyl]-BINOLate ligands: synthesis, structure, and reactivity

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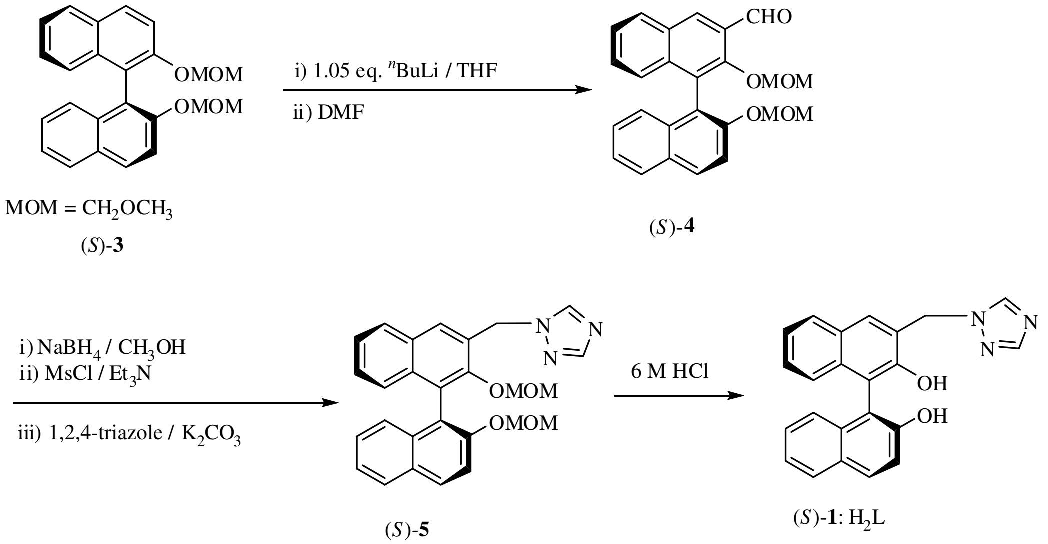
Received 6 July 2006; accepted 28 July 2006

Abstract—A new modified BINOL, (*S*)-3-[(1*H*-1,2,4-triazol-1-yl)methyl]-1,1′-binaphthol, was prepared. In the presence of titanium tetraisopropoxide, this ligand showed moderate catalytic properties for the asymmetric addition of diethylzinc to aldehydes. By treating *rac*-3-[(1*H*-1,2,4-triazol-1-yl)methyl]-1,1′-binaphthol with excess titanium tetraisopropoxide, a novel trinuclear titanium(IV) complex was obtained. A C_3 axis along Ti1–Ti2–Ti3 is present in the molecule.

1. Introduction

Chiral 1,1′-binaphthol (BINOL) has been successfully applied in a wide range of catalytic asymmetric reactions in the presence of various metals.[1] Titanium BINOLate complexes have also been successfully used to catalyze many asymmetric processes.[2] Nakai[3] and Chan[4] reported addition of diethylzinc to aldehydes catalyzed by chiral titanium BINOLate complexes. Ding[5] and Chan[6] reported the catalytic asymmetric addition of diethylzinc to alde-



Scheme 1. Synthesis of (*S*)-3-[(1*H*-1,2,4-triazol-1-yl)methyl]-1,1′-binaphthol.

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doi:10.1016/j.tetasy.2006.07.043

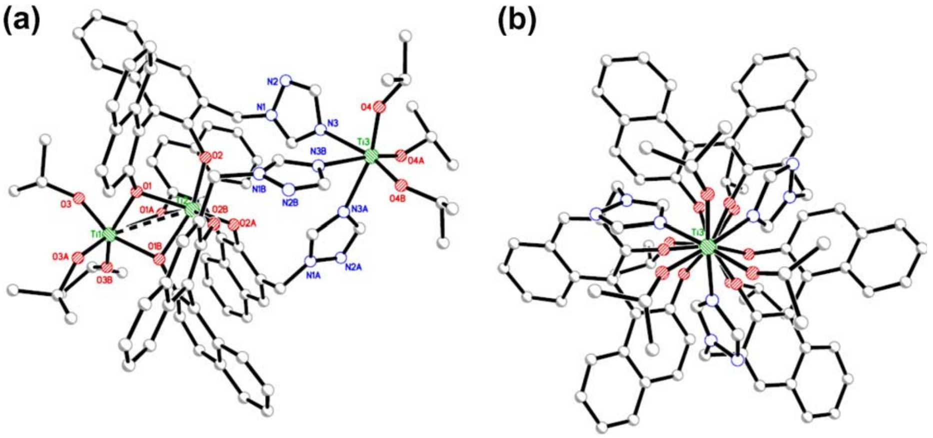


Figure 1. (a): The molecular structure of $[Ti_3L_3(OPr^i)_6]$ **2**, (b): view along the C_3 axis Ti3–Ti2–Ti1.

hydes using chiral titanium H_4-BINOLate and H_8-BINOLate complexes, respectively. Walsh et al.[7] reported in detail the crystal structures of some titanium BINOLate and H_8-BINOLate complexes to investigate the mechanisms of the reactions. However, only a few titanium 3- or 3,3′-substituted BINOLate complexes have been synthesized and studied.[2c,7,8] Herein, we report the synthesis of a new 3-substituted BINOL ligand (*S*)-3-[(1*H*-1,2,4-triazol-1-yl)-methyl]-1,1′-binaphthol **1** and its titanium complex $[Ti_3L_3(O^iPr)_6{\cdot}3CH_2Cl_2]$ **2** and the effectiveness of the ligand (*S*)-**1** in the titanium complex-catalyzed enantioselective addition of diethylzinc to aldehydes.

2. Results and discussion

Ligand (*S*)-**1** was synthesized as shown in Scheme 1. The lithium salt of (*S*)-2,2′-bis(methoxymethyl)-1,1′-binaphthol **3** reacted with DMF to afford (*S*)-3-formyl-2,2′-bis(methoxymethyl)-1,1′-binaphthol **4** in 57% yield after purification by column chromatography on silica gel.[9] By the reduction, methanesulfonylation and reaction with 1*H*-1,2,4-triazole, (*S*)-**4** was transformed into (*S*)-**5**.[10] After deprotection, (*S*)-**1** was obtained. By treating 2 equiv of titanium tetraisopropoxide with *rac*-3-[(1*H*-1,2,4-triazol-1-yl)-methyl]-BINOL, a nice C_3-symmetric trinuclear titanium complex **2** was obtained and its crystal structure was determined by X-ray diffraction.[11]

The molecule of **2** consists of a trinuclear titanium center bonded to three 3-[(1*H*-1,2,4-triazol-1-yl)methyl]-BINOLate ligands (Fig. 1(a)). All titanium atoms are six-coordinate while the stereochemistry of the three titanium centers are all distorted octahedral geometry. The middle titanium (Ti2) is bonded to the six oxygens of three BINOLates, among which three (O2, O2A, O2B) are terminal and the others (O1, O1A, O1B) are bridging to Ti1. In addition, Ti1 is still bonded to three isopropoxide groups. Ti3 is bonded to the three nitrogens at the 4-position of 1,2,4-triazoles and three isopropoxide groups. The formation of the three Ti3–N bonds makes the whole molecule orderliness. The crystallographic data show that there is a C_3 axis along Ti1–Ti2–Ti3 in the molecule (Fig. 1(b)).

Selected bond distances and angles are listed in Table 1. The Ti1–Ti2 distance is 3.116(4) Å. The Ti–O or Ti–N bond distances are particularly noteworthy. With regard to Ti3, the three Ti3–O distances are equal to 1.757(7) Å and the three Ti3–N distances are equal to 2.288(9) Å. The situation of the Ti1–O or Ti2–O distances is fully similar to the Ti3–O distances. The three bridging aryloxide Ti1–O distances are 2.167(7) Å while the three isopropoxide Ti1–O distances are 1.779(7) Å. Likewise, the three bridging aryloxide Ti2–O distances are 2.034(6) Å while the three terminal aryloxide Ti2–O distances are 1.857(6) Å. At the same time, the three O–Ti3–O angles are equal to 101.2(3)° and the three N–Ti3–N angles are equal to 80.3(3)°. For Ti1 and Ti2 every three corresponding O–Ti–O angles are also equal.

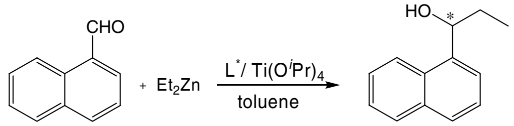
Table 1. Selected bond distances (Å) and angles (deg)

Bond	Distances (Å)	Bond	Angles (deg)
Ti1–Ti2	3.116(4)	Ti1–Ti2–Ti3	180
Ti1–O3	1.779(7)	O3A–Ti1–O3	100.4(3)
Ti1–O3A	1.779(7)	O3B–Ti1–O3	100.4(3)
Ti1–O3B	1.779(7)	O3A–Ti1–O3B	100.4(3)
Ti1–O1	2.167(7)	O1–Ti1–O1A	68.5(3)
Ti2–O2	1.857(6)	O2A–Ti2–O2	96.0(2)
Ti2–O1	2.034(6)	O1A–Ti2–O1B	73.6(3)
Ti3–O4	1.757(7)	O4B–Ti3–O4A	101.2(3)
Ti3–N3	2.288(9)	N3A–Ti3–N3B	80.3(3)
		C9–C10–C11–C20	118.2(10)
		C1–C10–C11–C12	123.0(10)

As shown in Figure 1, the three 3-[(1*H*-1,2,4-triazol-1-yl)-methyl]-BINOLate ligands are homochiral [(*R*)-configuration]. The three-substituted naphthalene plane of one BINOLate ligand is parallel with the unsubstituted one of the adjacent ligand, clockwise along the Ti3–Ti2–Ti1 axis. Every dihedral angle between the two naphthalene units is 66.9°. Additionally, the three dihedral angles of the 1,2,4-triazole rings are all 103.0°. Therefore, the three triazole rings can be considered as a regular propeller blade, while the six naphthalene units can be considered as a double propeller blade along the C_3 axis.

Up until now, the asymmetric addition of diethylzinc to aldehydes is considered as a classical test for the design of new catalysts.[12] We examined the chiral ligand (*S*)-3-[(1*H*-1,2,4-triazol-1-yl)methyl]-1,1′-binaphthol in the enantioselective addition of diethylzinc to aldehydes.[13] Instantly, 1-naphthaldehyde was taken as the substrate for optimizing the reaction conditions. As shown in Table 2, when changing the amount of ligand from 20 mol % to 5 mol %, it led to a slight change in enantioselectivity, while from 5 mol % to 1 mol %, led to a large decrease in enantioselectivity (entries 1–5). The best molar ratio of the ligand to metal was set up to be 1–12 in the addition reaction (entries 3, 6, and 7).

Table 2. Optimization of reaction conditions for enantioselectivity of the addition of Et_2Zn to 1-naphthaldehyde



Entry	L* (mol %)	L*/Ti(O^{i}Pr)$_4$ (M/M)	Yield[a] (%)	ee[b] (%)	Configuration[c]
1	20	1/12	97.6	76.9	*S*
2	10	1/12	93.3	80.3	*S*
3	5	1/12	96.8	76.7	*S*
4	3	1/12	100.0	69.0	*S*
5	1	1/12	94.3	41.5	*S*
6	5	1/6	93.8	71.3	*S*
7	5	1/2	96.3	44.0	*S*

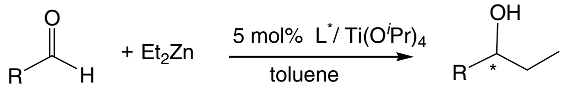
[a] Isolated yield.

[b] Data were determined by GC analysis using a chiral column (Chiral beta-DEX 120 capillary column).

[c] Based on the reported specific rotation (see Ref. 14).

Then, the addition of diethylzinc to a variety of aldehydes catalyzed by the titanium complex has been studied and the results are summarized in Table 3.

Table 3. Enantioselective addition of diethylzinc to aldehydes with the catalyst



Entry	R	Yield[a] (%)	ee[b] (%)	Configuration[c]
1	C_6H_5	69.0	69.2	*S*[15]
2	*p*-ClC_6H_4	79.6	70.3	*S*[16]
3	*p*-BrC_6H_4	83.3	67.3	*S*[17]
4	*p*-MeC_6H_4	64.7	68.1	*S*[18]
5	*p*-$MeOC_6H_4$	89.3	61.7	*S*[18]
6	*p*-$Me_2NC_6H_4$	77.2	70.4	*S*[19]
7	*o*-$MeOC_6H_4$	90.5	66.4	*S*[20]
8	1-Naphthyl	96.8	76.7	*S*[14]
9	PhCH=CH	89.1	72.4	*S*[21]

[a] Isolated yield.

[b] Data were determined by GC analysis using a chiral column (Chiral beta-DEX 120 capillary column).

[c] Based on the reported optical rotation.

3. Conclusion

In conclusion, we have synthesized (*S*)-3-[(1*H*-1,2,4-triazol-1-yl)methyl]-1,1′-binaphthol and a novel C_3-symmetric trinuclear titanium complex with the Ti1–Ti2–Ti3 axis containing three 3-[(1*H*-1,2,4-triazol-1-yl)methyl]-1,1′-BINOLate ligands. We used the chiral ligand in the asymmetric addition of diethylzinc to aldehydes to afford the corresponding secondary alcohols in high yields and moderate ee values.

4. Experimental

4.1. General

The ^1H and ^{13}C NMR spectra were recorded on a Bruker AC-300 instrument in $CDCl_3$ solution with TMS as the internal standard. Optical rotations were measured on a Perkin–Elmer 241 polarimeter. Elemental analysis was performed with a Yanaco CHN Corder MT-3 elemental analyzer. All experiments, which are sensitive to moisture or air, were carried out under argon atmosphere using standard Schlenk techniques. Diethylzinc was purchased from Aldrich. All anhydrous solvents were purified and dried by standard techniques just before use.

4.2. Synthesis of (*S*)-3-formyl-2,2′-bis(methoxymethyl)-1,1′-bi-naphthol (*S*)-4

To a stirred solution of MOM-protected (*S*)-binaphthol (*S*)-**3** (5.61 g, 15.1 mmol) in 60 mL of dry THF was added *n*-BuLi (8.4 mL, 15.8 mmol, 1.89 M in hexane) at −78 °C. The mixture was stirred overnight at room temperature. After cooling down to 0 °C, DMF (1.4 mL, 15.8 mmol) was added dropwise over 15 min. The mixture was then warmed up to room temperature and stirred for further 2 h. The reaction mixture was quenched with saturated aq NH_4Cl. The solution was then extracted with ethyl acetate, and the combined organic layer washed with water and brine, and then dried over Na_2SO_4. After removal of solvent, the residue was purified by column chromatography (hexane/ethyl acetate 5:1) to give (*S*)-**4** (3.75 g, 62%) as a yellow solid. Melting point: 110–112 °C. $[\alpha]_D^{25} = -83.3$ (*c* 0.4, $CHCl_3$).

4.3. Synthesis of (*S*)-3-[(1*H*-1,2,4-triazol-1-yl)methyl]-2,2′-bis(methoxymethyl)-1,1′-binaphthol (*S*)-5

To a solution of (*S*)-3-formyl-2,2′-bis(methoxymethyl)-1,1′-binaphthol (*S*)-**4** (3.77 g, 9.4 mmol) in methanol (50 mL) and THF (50 mL) was added $NaBH_4$ (0.45 g, 11.7 mmol) at 0 °C. After 30 min saturated aq NH_4Cl was added and the reaction mixture concentrated. The residue was extracted with ethyl acetate (50 mL × 3). The combined organic layer was washed with brine (50 mL) and dried over Na_2SO_4. Solvent was removed under reduced pressure and the crude product was directly used in the next reaction without purification. The solution of the crude product (1.78 g, 4.4 mmol) in ethyl acetate (50 mL) was cooled to 0 °C. To this solution, MsCl (0.70 mL, 8.8 mmol) and Et_3N (2.50 mL, 17.6 mmol) were added successively. After 1 h, the reaction mixture was filtered and the filtrate concentrated to dryness. The obtained pale-yellow oil was dissolved in 100 mL of acetone. 1*H*-

1,2,4-Triazole (0.30 g, 4.4 mmol) and anhydrous K_2CO_3 (0.61 g, 4.4 mmol) were added successively. The reaction mixture was refluxed for 7 h. The precipitate was filtered off and the solvent was removed under reduced pressure. The residue was chromatographed (hexane/ethyl acetate = 1:1) to afford compound (*S*)-**5** (1.14 g, 2.5 mmol) in 57% yield as a white solid. Anal. Calcd for $C_{27}H_{25}N_3O_4$ ($M_r = 455.51$): C, 71.19; H, 5.53; N, 9.22. Found: C, 71.21; H, 5.55, N, 9.01. Melting point: 109–110 °C. $[\alpha]_D^{25} = -56.6$ (*c* 1.4, CH_2Cl_2). ^1H NMR (300 MHz, $CDCl_3$) δ: 8.24 (s, 1H), 8.03 (s, 1H), 7.98 (d, $J = 9.12$ Hz, 1H), 7.88 (d, $J = 8.11$ Hz, 1H), 7.83 (d, $J = 8.16$ Hz, 1H), 7.72 (s, 1H), 7.59 (d, $J = 9.08$ Hz, 1H), 7.35–7.42 (m, 2H), 7.23–7.30 (m, 2H), 7.10–7.18 (m, 2H), 5.72 (dd, $J = 15.04$ Hz, 2H), 5.09 (dd, $J = 7.02$ Hz, 2H), 4.57 (d, $J = 5.70$ Hz, 1H), 4.44 (d, $J = 5.72$ Hz, 1H), 3.16 (s, 3H), 3.10 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 152.8, 152.1, 151.2, 143.3, 134.2, 133.7, 130.7, 130.3, 129.7, 129.5, 128.1, 128.0, 127.0, 126.9, 125.8, 125.6, 125.2, 124.3, 119.7, 116.3, 99.5, 94.8, 57.1, 56.0, 50.2.

4.4. Synthesis of (*S*)-3-[(1*H*-1,2,4-triazol-1-yl)methyl]-1,1-binaphthol (*S*)-1

(*S*)-**5** (1.14 g, 2.5 mmol) was dissolved in the mixed solvent of methanol/dichloromethane (30 mL/30 mL). At 0 °C HCl (6 M, 1.6 mL) was added dropwise. The reaction mixture was stirred at room temperature for 3 h and the solvent removed under reduced pressure. The residue was extracted with ethyl acetate (50 mL). The extract was washed with water, satd $NaHCO_3$, and brine in turn. After drying over Na_2SO_4 and removal of solvent, compound (*S*)-**1** (0.85 g, 2.3 mmol) was obtained in 90% yield as a white solid. Anal. Calcd for $C_{23}H_{17}N_3O_2$ ($M_r = 367.40$): C, 75.19; H, 4.66; N, 11.44. Found: C, 74.64; H, 5.12; N, 12.04. Melting point: 150–153 °C. $[\alpha]_D^{25} = -29.3$ (*c* 0.3, CH_2Cl_2). ^1H NMR (300 MHz, $CDCl_3$) δ: 8.23 (s, 1H), 7.96 (d, $J = 8.90$ Hz, 1H), 7.85 (m, 3H), 7.78 (s, 1H), 7.39 (m, 3H), 7.29 (m, 2H), 7.14 (d, $J = 8.08$ Hz 1H), 7.05 (d, $J = 8.26$ Hz 1H), 5.55 (dd, $J = 14.69$ Hz, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 152.9, 151.5, 150.7, 143.5, 133.8, 133.4, 131.5, 131.3, 129.4, 129.0, 128.5, 128.5, 128.0, 127.4, 124.7, 124.5, 124.1, 124.0, 123.5, 118.1, 113.2, 110.9, 49.7.

4.5. Synthesis of titanium complex 2

Under an argon atmosphere compound *rac*-**1** (0.410 g, 1.12 mmol) was suspended in dichloromethane (10 mL). To this suspension was added the solution of titanium isopropoxide (0.634 g, 2.23 mmol) in dichloromethane (10 mL) dropwise. The reaction mixture became clear deep red. After stirring at room temperature for 6 h, solvent and isopropanol were evaporated. Recrystallization of the resulting solid by dissolving it in dichloromethane at room temperature yielded X-ray quality red crystals of $[Ti_3L_3(O^iPr)_6\cdot 3CH_2Cl_2]$ in 76% yield (0.53 g, 0.28 mmol). Calcd for $C_{90}H_{93}N_9Cl_6Ti_3O_{12}$ ($M_r = 1849.13$): C, 58.46; H, 5.07; N, 6.81. Found: C, 59.27; H, 4.62, N, 7.26. Melting point: >240 °C dec ^1H NMR (300 MHz, $CDCl_3$) δ: 8.24 (s, 1H), 8.20 (s, 1H), 7.91 (d, $J = 8.07$ Hz, 1H), 7.86 (d, $J = 8.13$ Hz, 1H), 7.55 (s, 1H), 7.39 (s, 1H), 7.33 (m, 3H), 7.15 (m, 2H), 7.03 (m, 2H), 5.30 (s, 2H), 4.65 (m, 1H), 4.37 (m, 1H), 3.99 (d, $J = 13.72$ Hz, 1H), 3.45 (d, $J = 13.82$ Hz, 1H), 1.20 (d, $J = 6.13$ Hz, 1H), 1.17 (d, $J = 6.06$ Hz, 2H), 0.90 (d, $J = 6.10$ Hz, 3H), 0.67 (d, $J = 6.07$ Hz, 3H), 0.57 (d, $J = 6.10$ Hz, 3H).

4.6. A typical procedure for the asymmetric addition of diethylzinc to aldehydes

Titanium tetraisopropoxide (0.18 mL, 0.6 mmol) was added to a solution of (*S*)-**1** (0.018 g, 0.05 mmol) in 3 mL of toluene at room temperature. The reaction mixture was stirred for 30 min followed by the addition of diethylzinc (2.59 M in hexane, 1.16 mL) with continuous stirring for 15 min. The solution was cooled to 0 °C and 1-naphthaldehyde (0.14 mL, 1 mmol) was added via syringe. The reaction mixture was filtered through Celite to remove the insoluble material and the filtrate was extracted with 3 × 20 mL ethyl acetate. The combined organic layers were then dried over $MgSO_4$. The residue was purified by column chromatography on silica gel to afford 1-napthhyl-1-propanol as a light yellow liquid. The enantiomeric excess of the products was determined by GC on a Chiral beta-DEX 120 capillary column.

Acknowledgements

We thank the National Natural Science Foundation of China (Grant No. 20372037) for funding this project.

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11. Crystallographic data for titanium complex **2**: $C_{90}H_{93}Cl_6N_9O_{12}Ti_3$, formula weight 1849.13, Cubic, *Pa*-3, $a = b = c = 26.408(6)$ Å, $\alpha = \beta = \gamma = 90°$, $V = 18417(7)$ Å^3, $Z = 8$, $D_{\text{calcd}} = 1.334$ g/cm^3, $T = 294.2$ K, μ(Mo Kα) = 0.491 mm^{-1}, $R1$ ($wR2$) = 0.1138 (0.2777), crystal dimensions 0.20 × 0.18 × 0.10 mm. (CCDC 292400).
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