Synthesis, crystal structure and application in regio- and stereoselective epoxidation of allylic alcohols of a titanium binaphthyl-bridged Schiff base complex

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Abstract

A new octahedral titanium binaphthyl-bridged Schiff base complex (1) was synthesized and characterized. Analysis by ^{1}H and ^{13}C-NMR spectroscopy and X-ray crystallography indicated that the C_1-symmetric *cis*-β isomer is preferentially formed as one of the two possible enantiomeric couples of diasteroisomers. The catalytic behaviour of the complex **1** toward epoxidation of allylic alcohols was investigated. Using only 0.5% mol of the complex **1** the epoxyalcohols are obtained in very high regio-, chemo- and diastereoselctive way by the MW exposure of the mixture in solvent free-conditions.
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Keywords: Binaphthyl-bridged Schiff base ligands; Epoxidation; Ti(IV) complexes; Allylic alcohols; Microwave reactions

1. Introduction

Dianionic quadridentate Schiff bases such as *salen* and *acen* are ubiquitous ligands in organometallic chemistry. As well documented, N_2O_2 quadridentate ligands of this type can afford a variety of geometries: in particular, they can wrap around an octahedron according to the different configurations shown in Fig. 1. While for catalytic applications it is usually considered as a requirement that substrate and reagent ligands occupy mutually *cis* co-ordination sites, most complexes incorporating the above mentioned ligands preferentially adopt *trans* geometries (structure **a** in Fig. 1). Only in recent years, attention has been directed to the use of Schiff bases obtained from biaryldiamines providing conformationally constrained backbones which induce non-planar co-ordination and favor *cis* structures **b** (*cis*-β) and **c** (*cis*-α). [1]

Moreover, use of chiral non-racemic ligands can result in the preferential formation of "chiral-at-metal" complexes, which are of great potential interest for enantioselective catalysis.[2] Thus, complexes of this class have been employed in a variety of catalytic stereoselective organic transformations, including aldol reactions, alkene epoxidation, Bayer–Villiger oxidation, ring-opening lactide polymerization and Ziegler–Natta olefin polymerization.[1,2]

In this paper, we report the synthesis and the characterization of a new octahedral titanium complex bearing a bulky binaphthyl-bridged Schiff base ligand (*rac*-H$_2$L, Fig. 2), and some preliminary results concerning its catalytic activity in the epoxidation of allylic alcohols.

2. Experimental

2.1. General remarks

The manipulations of the titanium complex were carried out under dry nitrogen atmosphere using a Braun

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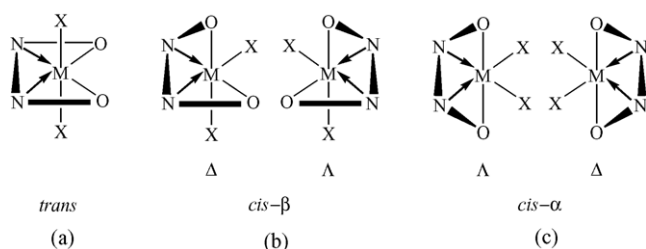   [1] Co-corresponding author.

Fig. 1. Structural classes of quadridentate Schiff base octahedral complexes.

Labmaster drybox or standard Schlenk line techniques. All solvents were dried by refluxing over an appropriate agent: dichlorometane was distilled over calcium hydride, toluene over sodium-benzophenone. 3-*tert*-butyl-2-hydroxy-benzaldehyde (Aldrich products) and (R,S)-2,2'-diamino-1,1'-binaphthyl (Strem product) were used as received.

MW-assisted epoxidation was conducted in an Ace pressure tube (Aldrich) using an unmodified domestic microwave oven (2450 MHz). Geraniol (**2a**), nerol (**2b**) *trans*-2-hexen-1-ol (**2c**), *cis*-2-hexen-1-ol (**2d**), were purchased from Aldrich. Secondary allylic alcohols **2e-2i** were prepared, according to Grignard method [3] from *n*-pentyl magnesium bromide and the corresponding aldehydes. Reactions were monitored by thin layer chromatography (TLC) on Merck silica gel plates (0.25 mm) and visualized by *p*-anysaldehyde spray test; column chromatographic purification of products was carried out using silica gel 60 (70–230 mesh, Merck). ^{1}H NMR and ^{13}C NMR spectra were recorded on solutions in CDCl$_3$ with Bruker DRX 400 (400.135 MHz for ^{1}H and 100.03 MHz for ^{13}C) spectrometers. Yields of products **3** refer to isolated pure compounds. Products **3** were identified by comparison with the data reported in literature [12,13,4] and *erythro/threo* ratios of epoxyalcohols were determined by integrating the characteristic peaks of the two diastereoisomers in the ^{1}H NMR spectra of the crude reaction mixtures.
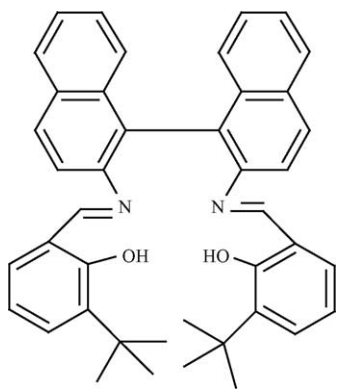

Fig. 2. Structure of 2,2'-bis(3-*t*-Bu-2-hydroxybenzylideneimino)-1,1'-binaphthyl (*rac*-H$_2$L).

2.2. Synthesis of complex 1

The ligand *rac*-H$_2$L was prepared by condensation of *rac*-N,N'-binaphthyldiammine and 3-*tert*-butylsalicyladehyde in 90% yield.[3]

Titanium tetrachloride (0.27 mL, 2.5 mmol) was added to a solution of *rac*-H$_2$L (1.5 g, 2.5 mmol) in toluene (50 mL). The mixture was stirred for 16 h and the toluene removed under reduced pressure. The dark red solid was extracted into methylene dichloride (60 mL). The solution was filtered through Celite, concentrated to ca. 10 mL in vacuo and cooled to −20 °C. This resulted in the precipitation of red solid. 1.37 g Yield = 76%.

^{1}H NMR (CD$_2$Cl$_2$): *cis*-β-**1**: δ 8.47 (s, 1H, N=CH), δ 8.21 (s, 1H, N=CH), 8.08 (d, *J* = 8.3 Hz, 1H), 8.01 (d, *J* = 8.3 Hz, 1H), 7.804 (d, *J* = 8.3 Hz, 1H), 7.798 (d, *J* = 8.3 Hz, 1H), 7.68 (dd, *J* = 7.4 Hz, J = 1.7 Hz, 1H), 7.67 (d, *J* = 8.3 Hz, 1H), 7.47 (m, 4H), 7.33 (t, *J* = 7.4 Hz, 1H), 7.22 (t, *J* = 7.4 Hz, 1H), 7.18 (d, *J* = 8.3 Hz, 1H), 7.10 (dd, *J* = 7.4 Hz, *J* = 1.7 Hz, 1H,), 7.06 (d, *J* = 7.4 Hz, 1H), 6.98 (d, *J* = 9.1 Hz, 1H,), 6.85 (t, *J* = 7.4 Hz, 1H,), 1.51 (s, 9H, *t*-Bu), 1.40 (s, 9H, *t*-Bu). A minor symmetric isomer is identified by eleven further resonances, some of which (in the aromatic region of the spectrum) are hidden by the signals of the more abundant species: δ 8.58 (s, 2H, N=CH), 1.53 (s, 18H, *t*-Bu).

^{13}C NMR (CD$_2$Cl$_2$): *cis*-β-**1**: δ 168.01 (C=N), 167.83 (C=N), 163.91 (q), 163.10 (q), 149.65 (q), 149.40 (q), 137.65 (q), 137.16 (q), 134.67, 134.49, 133.24, 133.02 (q), 132.97 (q), 132.89, 132.74 (q), 130.42, 129.68, 129.10, 128.70, 127.72, 127.37, 127.27, 127.16, 126.89 (q), 126.77, 126.48, 126.29 (q), 125.35 (q), 124.68, 124.50 (q), 124.16, 122.51, 122.27, 35.53 (*C*Me$_3$), 35.52 (*C*Me$_3$), 30.04 (CMe$_3$), 29.99 (CMe$_3$). The quaternary carbons (which are indicated with q) were identified comparing the DEPT 45 data with the ^{13}C NMR spectrum. Minor isomer: δ 169.93 (C=N), 36.04 (*C*Me$_3$), 30.32 (CMe$_3$). MS (EI): *m/z* 720 [M$^+$] and 685 [M$^+$ - Cl].

2.3. General procedure for the microwave-assisted epoxidation of allylic alcohols 2 catalyzed by 1

A mixture of allylic alcohol **2** (1 mmol), TBHP (1.1 mmol) and complex **1** (0.005 mmol) was placed in an Ace pressure tube and subjected to MW irradiation as reported in Tables 2 and 3. Then, the reaction was directly poured into the top of a silica gel chromatographic column. Eluition with light petroleum/ethyl acetate or diethyl ether mixtures afforded pure epoxyalcohols **3**.

2.4. X-ray crystallography

A suitable crystal of **1** (0.1 mm × 0.3 mm × 0.4 mm) was selected and sealed in a Lindemann capillary under nitrogen atmosphere. Diffraction measurements were performed at room temperature on a Rigaku AFC7S diffractometer (graphite monochromated Mo Kα radiation, λ = 0.71069 Å).

Lattice constants and crystal orientation were obtained from the setting angles of 25 centred reflections in the range $13° < 2\theta < 20°$.

Diffracted intensities were collected within $4° < 2\theta < 50°$, using $\omega-2\theta$ scan method. Intensity data were corrected for Lorentz and polarization, absorption correction was applied by means of ψ scan measurement ($T_{min} = 0.915$, $T_{max} = 0.999$), no decay correction was applied.

The structure was solved by direct methods using SIR92 [5] and refined on F^2 using SHELXL93 [6]. From the beginning a Fourier difference map showed the presence of a $CHCl_2$ molecule and a disordered pentane molecule. This consists in two pentane molecules in two different conformations. Any effort to consider two separate pentane molecules with half occupancy and refine them with a rigid body constraint gave unsatisfactory results. The present geometry has been obtained by applying the restraint condition that all bond distances should assume the same value. Hydrogen atoms were positioned geometrically and refined using a riding model. Anisotropic thermal factors were used for all non-hydrogen atoms except those belonging to the solvent molecule. A total of 474 refinable parameters were finally considered. Maximum and minimum residual density were, respectively, 0.84 and $-0.99 \, e\text{Å}^{-3}$. Final disagreement indices: $R_1 = 0.078$ for 1884 reflections with $F_o > 4\sigma(F_o)$, $_wR_2 = 0.1476$ for all 7850 data. Atomic coordinates, thermal factors, bond lengths and angles are provided as supplementary material. ORTEP drawings performed by means of the program ORTEP32 [7].

2.5. Crystallographic data

Formula: Ti Cl_2 O_2 N_2 C_{42} $H_{38} \cdot CH_2Cl_2 \cdot C_5H_{12}$, FW = 878.61, system: triclinic, space group P1bar, $Z = 4$, $a = 10.687(4)$ Å, $b = 15.302(4)$ Å, $c = 15.500(2)$ Å, $\alpha = 66.73(2)°$, $\beta = 73.02(2)°$, $y = 81.48(2)°$, $V = 2225(1)$ Å^3, $D_x = 1.311 \, \text{gcm}^{-3}$, $\mu_{calc} = 0.47 \, \text{mm}^{-1}$.

Crystallographic data (excluding structure factors) for the structure(s) reported in this paper have been with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-257235 copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: int. code +44 1223 336 033; E-mail: deposit@ccdc.cam.ac.uk).

3. Results and discussion

3.1. Synthesis and characterization of the complex

The Schiff base pro-ligand was synthesized from rac-N,N'-binaphthyldiamine and 3-tert-butylsalicyladehyde according to literature procedures. [8] The reaction of the ligand with $TiCl_4$ in toluene afforded after work-up complex **1** (Fig. 3) as a red microcrystalline powder in 76% yield. The ^1H and ^{13}C NMR spectra of **1** were measured in methylene dichloride–d$_2$. The ^1H NMR spectrum is consistent with the formation of a mixture of two out of the three possible isomeric forms (see Fig. 3), i.e. the C_1-symmetric cis-β-**1** and either the C_2-symmetric cis-α-**1** or the C_s-symmetric trans-**1**, the latter two isomers being not distinguishable by NMR analysis.

In fact, the aliphatic region of the ^1H spectrum contains three peaks, one assigned to the two equivalent tert-butyl groups of a symmetric isomer and the other two, with the same intensities, assignable to cis-β-**1** isomer. Similarly, three resonances are apparent for the imine protons. The ratio between the asymmetric cis-β and the symmetric isomer is about 9:1 in methylene dichloride–d$_2$ and it remains essentially unchanged after recrystallization from toluene. Single crystals suitable for X-ray analysis were obtained from a methylene dichloride/pentane solution of **1**. The molecular structure of complex **1** is shown in Fig. 4 and the corresponding selected interatomic distances and angles are reported in Table 1.

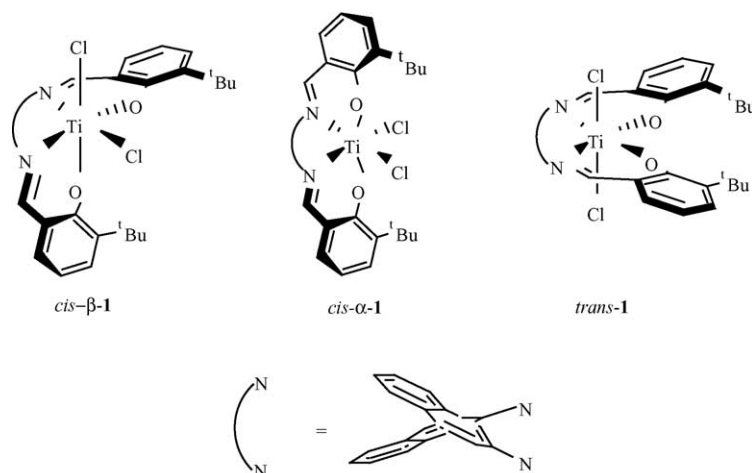cis–β-**1**   cis-α-**1**   trans-**1**

Fig. 3. Possible isomers of the binaphthyl-bridged Schiff base titanium complex **1**.
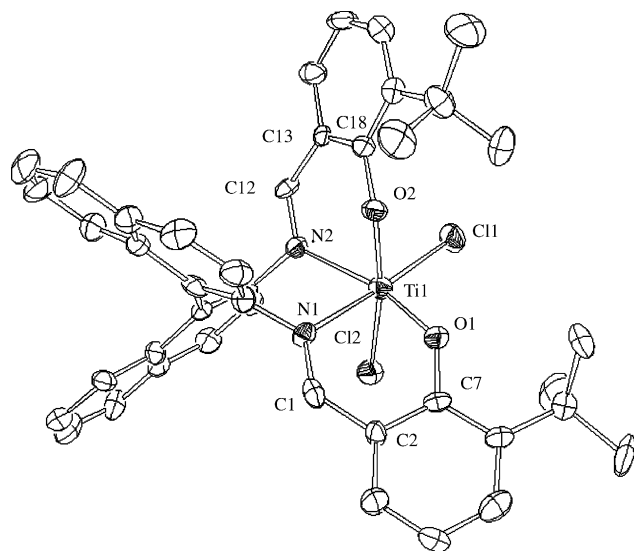
Fig. 4. X-ray molecular structure of one enantiomer ($R-\Delta$) of compound **1**. Thermal ellipsoids are drawn at 30% probability level. Hydrogen atoms have been omitted for clarity.

The coordination environment of the Ti atom is a distorted octahedron with two *cis* chlorine atoms and two *cis* oxygen atoms, indicating that the asymmetric *cis*-β isomer is selectively obtained by crystallization. The naphthyl rings result to be planar within a R.M.S.D. of 0.028 and 0.012 Å, respectively, the dihedral angle is 65.3(1)°. The two phenoxy rings (R.M.S.D. 0.004 and 0.020 Å) are *cis* to each other with a dihedral angle of 61.5(2)°.

The same configuration has been observed in the structures of manganese, iron and ruthenium analogues [3,9]. Notably the binaphthyl moiety displays a certain degree of flexibility in forming complex with metal ions, considering that the binaphthyl dihedral angle can range from 65.1(2)° (as in this case) to 85.5(3)° (for the manganese complex). Titanium complexes bearing closely related ligands with different stereorigid bridges, including cyclohexyl [10] and 6,6'-dimethylbiphenyl [11], have been previously reported. X-ray analysis, however, showed the preferential formation in the solid state of the *trans* isomer for the complex bearing the cyclohexyl-bridged ligand,[5] and of the *cis*-α isomer for the complex bearing the 6,6'-dimethylbiphenyl-bridged ligand. [6] The great potential of *cis*-β-metal-N_2O_2-Schiff base complexes for asymmetric catalysis has been recently addressed by Katsuki. [1a]

Table 1
Selected bond distances (Å) and angles (°) for **1**

Ti—O1	1.832 (6)	N1—Cl	1.312 (10)
Ti—O2	1.840 (5)	N2—Cl2	1.276 (9)
Ti—N2	2.170 (7)		
Ti—N1	2.206 (7)	O1—Ti—O2	101.0 (2)
Ti—Cl1	2.300 (3)	Cl1—Ti—Cl2	91.56 (1)
Ti—Cl2	2.336 (3)	N1—Ti—N2	81.8 (3)

Table 2
(*rac*-L)TiCl$_2$ catalyzed epoxidation of geraniol **2a** under conventional heating (CH) and microwave irradiation (MW)

Entry	Conditions	Time	Catalyst (% mol)	Yield (%)
1	CH (rt)	24 h	1	–
2	CH (40 °C)	24 h	1	38
3	MW (315 W)	15 min	–	–
4	MW (315 W)	15 min	1	87
5	MW (315 W)	15 min	0.5	75
6	MW (270 W)	15 min	0.5	29
7	MW (315 W)	3 × 15 min	0.1	37

Tetradentate ligands such as *rac*-H$_2$L can afford chiral-at-metal octahedral complexes having Δ- or Λ-configuration (except in the case of the *trans* isomer). When the racemic ligand is used, four isomers are possibly formed (i.e. the two enantiomeric couples of diastereoisomers $R-\Delta/S-\Lambda$, and $S-\Delta/R-\Lambda$). For the *cis*-β configuration, which is the predominant one in our case, the presence of just one pattern of signals in the NMR spectra suggests that only one enantiomeric couple is formed selectively, implicating that chirality at metal is induced by the ligand chirality. The X-ray diffraction analysis reveals the presence of the $R-\Delta$ and $S-\Lambda$ enantiomers in the crystal (in fact, the space group $P\bar{1}$ contains an inversion centre). This finding suggests that the use of a chiral diamine fragment should result in the selective formation of one enantiomeric complex [12].

3.2. Epoxidation of allylic alcohols catalyzed by complex 1

Several metal complexes of salen ligands have been found to serve as efficient catalysts for epoxidation of differently functionalized internal and terminal olefins [13]. A case in point is allylic alcohols for which the use of metal–salen complexes gives mainly the oxidation of the alcoholic functionality [14]. Adam et al. [15] reported that the exclusive epoxidation versus allylic oxidation occurs by using an achiral Mn^{III}(salen) complex and iodosyl benzene as oxygen source and high diastereoselectivity but poor regioselectivity were reported for alcohols with two double bonds. Herein, we report our study on the chemo-, regio-, and diastereoselective epoxidation of the allylic alcohols **2** to the corresponding epoxy alcohols catalyzed by the (*rac*-L) TiCl$_2$ complex (**1**).

In a preliminary screening, geraniol **2a**, chosen as model substrate, was treated with *t*-butyl-hydroperoxide (TBHP) in the presence of catalytic amounts of **1**. As shown by some preliminary experiments reported in Table 2, when the reaction was conducted at room temperature in CH$_2$Cl$_2$ (entry 1, Table 2) starting **2a** was recovered unchanged, and when the reaction was conducted under reflux conditions, even after one day (entry 2, Table 2) only a poor yield was achieved. It

is notable that no evidence of the competing reactions involving −OH functionality or 6,7-double bond oxidation could be detected by ^{1}H NMR analysis on the crude reaction mixtures.

In order to enhance the efficiency of the reaction we investigated the applicability of microwave heating to epoxidation of allylic alcohols. The use of microwave in enhancing chemical transformations is one of the most promising non-conventional methods used in organic synthesis due to several advantages such as rapid reaction rates, solvent-free conditions and easy work-up [16]. However, few examples of application of this technique to epoxide reaction are reported

in the literature: [17] in particular MW irradiation has been reported to accelerate epoxidation of α,β-unsaturated ketones and alkene [18] of allylic alcohols [19–20] and, more recently, of hindered homoallylic alcohols [21].

The epoxidation of **2a** was carried out in free-solvent conditions and under microwave irradiation (entry 3, Table 2) without catalyst but no product was observed after 15 min, while the same reaction performed in the presence of **1** (0.01 eq.) (entry 4, Table 2) gave the product **3a** in high yield and with complete regio- and chemoselectivity. A reduction of catalyst loading (entry 5, Table 2) caused a slight lowering of

Table 3

MW-assisted epoxidation of allylic alcohols **2** mediated by (*rac*-L)TiCl₂
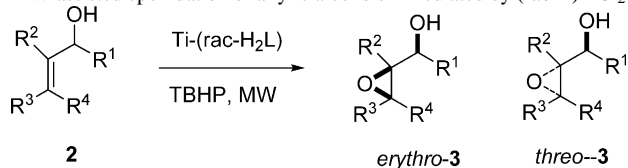
Entry	Substrate	Reaction time (min)/P (W)	Yield (%)[a]	*Erythro/threo* diastereomeric ratio[b]
1	**2a**	15 min/315 W	75	–
2	**2b**	15 min/315 W	75	–
3	**2c**	15 min/315 W	81	–
4	**2d**	15 min/315 W	63	–
5	**2e**	15 min/270 W	70	37/63
6	**2f**	15 min/270 W	96	10/90
7	**2g**	15 min/270 W	75	76/24
8	**2h**	15 min/270 W	99	77/23
9[c]	**2i**	15 min/315 W	26	50/50

[a] All the yields are referred to isolated chromatographically compounds. All the structures are confirmed by comparison of ^{1}H NMR data with the ones reported in literature [12,13,19].

[b] *Threo/erythro* diastereomeric ratio were determined by ^{1}H NMR analysis on the crude reaction mixture.

[c] The reaction was performed in the presence of 1 mol% of **1**.

yield, while a dramatic drop of efficiency was observed both under lower irradiation power (entry 6, Table 2) and further reducing the catalyst amount to 0.1 mol% (entry 7, Table 2).

To explore the synthetic potential of this microwave-assisted **1**-catalyzed epoxidation, the conditions of entry 5, Table 2 were applied to different primary and secondary allylic alcohols.

The primary allylic alcohols **2a–d** (Table 3, entries 1–4) were found to be less reactive than secondary ones **2e–h** (Table 3, entries 5–8) requiring a higher microwave power in order to obtain a satisfactory yields; however in all of the reported entries the oxidation proceeded almost chemoselectively to afford to the corresponding epoxy alcohols with <5% formation of the corresponding enals or enones.

Moreover as expected [22] because of the non-planar geometry of the catalytic complex (**1**) the primary *E*-allylic alcohol **2c** is more reactive than its *Z*-counterpart **2d** (cfr. entry 3 with entry 4); this difference proved to be absolutely negligible for geometrical isomer **2a** and **2b**, reasonably because of the enhanced reactivity of the more electron–rich trisubstituted 2,3-double bonds.

As reported [23] in literature, in metal-catalyzed epoxidation of allylic alcohols both 1,2- and 1,3-allylic strain operate a diastereoselective control (*threo* versus *erythro* epoxidation): thus, the allylic alcohol **2e** (Table 3, entry 5) without allylic strain was epoxidized in a low *threo* selectivity while the epoxidation of the β,β-disubstituted allylic alcohol **2f** (1,3-allylic strained alcohol) afforded the *threo*-epoxy alcohol quantitatively with high diastereoselectivity (10/90).

On the contrary, *erythro* epoxyalcohols were obtained as predominant stereoisomers starting from **2g–h** characterized by $A^{1,2}$-strain (Table 3, entries 7–8).

The monosubstitued alcohol **2i** (Table 3, entry 9), because of the poorer nucleophilicity of the terminal double bond, was found to be less reactive and to demand higher amount of catalyst in order to obtain an acceptable yield. Obviously the absence of allylic strain resulted in a complete lack of diastereoselectivity.

As regards the mechanistic aspects, the reported regio- and sterechemical control clearly point to a hydroxy-directing effect, as further confirmed by the absolute unreactivity showed by the acetate—protected geraniol under the usual reaction conditions.

Although the observed site-selectivity and stereochemical outcome seem to be in agreement with a Sharpless-type pathway based on the direct coordination of the allylic alcohol to the titanium center [24] the involvement of an oxo-titanium complex, acting according to the mechanism proposed by Adam [10a] cannot be excluded at this moment.

4. Conclusion

A new octahedral titanium complex, **1**, bearing a bulky binaphthyl-bridged Schiff base ligand, has been synthesized and characterized by NMR and X-ray analysis, showing that the C_1-symmetric *cis*-β isomer is preferentially formed. Interestingly, one out of the two possible enantiomeric couples of diasteroisomers is formed selectively ($R-\Delta/S-\Lambda$), implicating that chirality at metal is induced by the ligand chirality. Work is in progress to ascertain if use of a chiral non-racemic N,N'-binaphthyldiamine ligand precursor results in the selective formation of one enantiomeric complex.

In its first application in organic synthesis, complex **1** has shown to be an effective catalyst for the epoxidation of allylic alcohols. The epoxyalcohols can be obtained in very high regio- and chemoselective way by the MW exposure of the mixture in solvent free-conditions. Furthermore, high diastereoselectivities can be observed for secondary allylic alcohols.

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