

Note

## Titanium (IV) complexes based on substituted 2-[(2-hydroxyethyl)]aminophenols

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### Abstract

Novel substituted 2-[(2-hydroxyethyl)]aminophenols,  $\text{MeN}(\text{CHR}^1\text{CR}^2\text{R}^3\text{OH})(\text{C}_6\text{H}_4\text{-}o\text{-OH})$  (**2–5**), were synthesized by the reaction of 2-methylaminophenol with corresponding oxiranes. Titano-*spiro*-bis(ocanes)  $[\text{MeN}(\text{CHR}^1\text{CR}^2\text{R}^3\text{O})(\text{C}_6\text{H}_4\text{-}o\text{-O})]_2\text{Ti}$  **6–9** (**2, 6**,  $\text{R}^1 = \text{H}$ ,  $\text{R}^2 = \text{R}^3 = \text{Me}$ ; **3, 7**,  $\text{R}^1 = \text{R}^2 = \text{Ph}$  (*trans*),  $\text{R}^3 = \text{H}$ ; **4, 8**,  $\text{R}^1 = \text{Ph}$ ,  $\text{R}^2 = \text{R}^3 = \text{H}$ ; **5, 9**,  $\text{R}^1 = \text{R}^2 = \text{H}$ ,  $\text{R}^3 = \text{Ph}$ ) based on [ONO]-ligands have been synthesized. The obtained compounds were characterized by <sup>1</sup>H and <sup>13</sup>C NMR spectroscopy and elemental analysis data. The complex  $[\text{Ti}(\mu^2\text{-O})\{\text{O-}o\text{-C}_6\text{H}_4\}\{\mu^2\text{-CMe}_2\text{CH}_2\}\text{NMe}]_6$  (**10**) was obtained by controlled hydrolysis of **6**. Molecular structure of **10** was determined by X-ray structure analysis.

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### 1. Introduction

Currently a considerable efforts are being intended to develop the new chelating [OXO] (X = S, N, O) ligand systems for group IV metals, since their complexes have found widespread application as catalysts in various organic reactions. Indeed, Ti(IV) complexes based on polydentate ligands such as thiobisphenol [OSO] [1,2], aminobismethylphenols [ONO] [3,4] or dialkanolamines [ONO] [5–9] have been used as olefin polymerization catalysts or ring opening polymerization catalysts [10]. Both phenolate and aminoalkanoate ligands are important for construction of catalytic active Ti(IV) complexes and it is important to combine these functionalities in one ligand molecule to synthesize hybrid [ONO] alkanolaminophenols. There are only

a few publications concerned with related hybrid systems [11].

In continuation of our studies of Ti(IV) complexes with tri- and dialkanolamines [12–14], we present the synthesis and characterization of titanium complexes (**6–9**) – titano-*spiro*-bis(ocanes) – based on the new hybrid tridentate alkanolaminophenol ligands. Their structure in solution is discussed basing on NMR spectroscopy data. We established that crystalline compound **10** formed upon controlled hydrolysis of **6**. The structure of compound **10** was determined by single-crystal X-ray analysis.

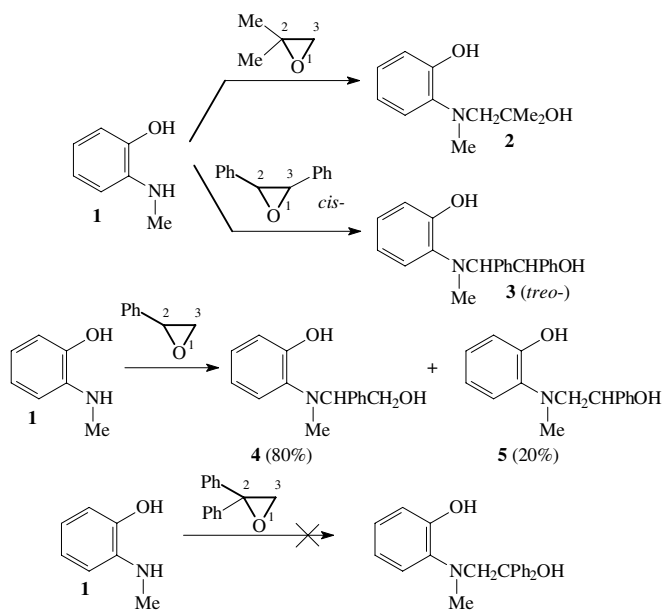
### 2. Results and discussion

#### 2.1. Synthesis

For synthesis of alkanolaminophenols **2–5** we investigated the reaction of 2-methylaminophenol (**1**) with the number of alkene oxides (Scheme 1). The reactions were

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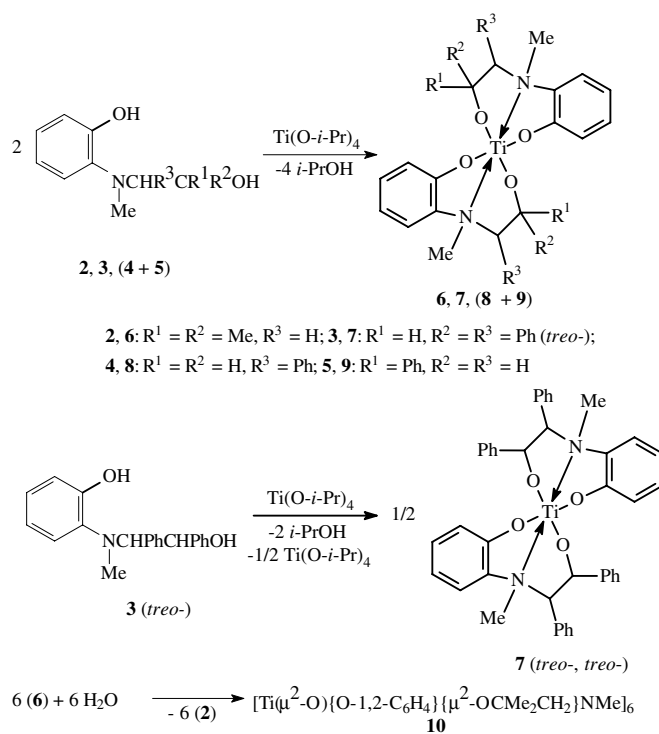
Scheme 1.

carried out by heating of reactants in the atmosphere of argon. In the case of isobutylene oxide the reaction proceeded regioselectively, only one expected product (**2**) formed. Only one diastereomer (**3**) formed in the reaction of **1** with *cis*-stilbene oxide. On the contrary, the reaction of **1** with styrene oxide resulted in the formation of both possible not separable products (**4** + **5**) in ratio **4**:**5** = 4:1 (according to NMR data). It is known from the literature that analogous reaction of alkanolamines with styrene oxide also led to the mixture of two compounds [15,16] with prevalence of the product formed under substitution on C<sub>3</sub>-O bond. That is contrasting to the case of **1** where the main product (**4**) formed under substitution on C<sub>2</sub>-O bond. To our opinion this fact may be explained by the more acidity of phenol OH-group in (**1**) in comparison with that in alkanolamines.

The reaction of **1** with 2,2-diphenyloxirane failed. In this case according to NMR data the reaction mixture contained only initial and unidentified compounds even after prolonged heating. Thus, the structures and yields of products of reaction of 2-methylaminophenol (**1**) with different alkene oxides depend on the substituent nature in the oxirane molecule.

According to the literature, the most suitable approach to the alkoxy titanium chelate complexes is the transalkoxylation reaction of Ti(OAlk)<sub>4</sub> with free ligand containing OH-groups. We have found that Ti(O-*i*-Pr)<sub>4</sub> readily reacted with two equivalents of corresponding alkanolaminophenols **2**–**5**. Compounds **6**–**9** were obtained at reflux in toluene in high yields (Scheme 2).

We also tried to prepare dialkoxytitanocanes [MeN(CHR<sup>1</sup>CR<sup>2</sup>R<sup>3</sup>O)(C<sub>6</sub>H<sub>4</sub>-*o*-O)]Ti(O-*i*-Pr)<sub>2</sub>, but the reaction of the equimolar amounts of **3** and Ti(O-*i*-Pr)<sub>4</sub> led to the corresponding titano-*spiro*-bis(ocane) (**7**) (Scheme 2). Analogous results were found for related RN(CH<sub>2</sub>-*o*-ArOH)<sub>2</sub>



Scheme 2.

ligands [17] and may be explained by the tendency of the titanium atom to adopt an octahedral geometry at the absence of the bulk substituent in the *ortho*-position of aromatic ring. Furthermore in the ligand **3** the phenolic OH-group is more acidic than the other, so in the process of synthesis the former may react with Ti(O-*i*-Pr)<sub>4</sub> more readily with obtaining of the titano-*spiro*-bis(ocane).

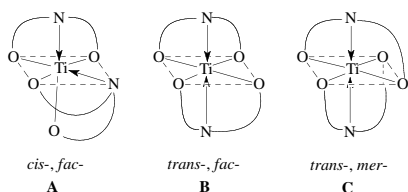
The obtained complexes **6**–**9** are very hydrolytically unstable. We carried out the controlled hydrolysis of **6** with forming of the polynuclear oxo complex **10** (Scheme 2). The main idea of such complexes preparation was to prepare more stable species which are also useful as above mentioned catalysts. Recently, related complex [Ti(μ<sup>2</sup>-O)-{OCH<sub>2</sub>CH<sub>2</sub>}<sub>2</sub>{μ<sup>2</sup>-OCH<sub>2</sub>CH<sub>2</sub>}NMe]<sub>6</sub> based on *N*-methyl-diethanolamine has been obtained in analogous conditions [18]. The molecular structure of **10** was investigated by X-ray analysis. Moreover, the close related tetranuclear titanatrane obtained from hydrolysis reaction was capable of polymerizing ethylene [19].

## 2.2. Solution structures (NMR spectroscopy data)

Compounds **6**–**9** which contain in coordination sphere of Ti atom two tridentate [ONO] ligands form octahedral monomeric complexes. The circumstantial evidence of the existence of two coordination Ti–N bonds in complexes is a shift of signals of NCH<sub>3</sub>-, NCH<sub>2</sub>- or NCH-groups to the weak field in comparison with the corresponding free ligands **2**–**5**.

Octahedral titanium complexes based on two identical [ONO] ligands may exist as three geometric isomers (A, B

and C) which differ in mutual positions of N atoms (*cis*-; *trans*-) and ligands (facial, *fac*-; meridional, *mer*-) in the coordination sphere of Ti atom.



Compounds **6–9** are prepared from the ligands containing three different substituents at N atom. So in **6–9** N atoms are asymmetric and each of the above mentioned geometric isomer (**A**, **B** and **C**) may exist as  $C_2$ - or  $C_1$ -symmetry complexes, where nitrogen atoms have correspondingly the same ((*R,R*) or (*S,S*)) or different absolute configurations ((*R,S*) or (*S,R*)).

$^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of **6** contain one set of signals corresponding to phenolate- and  $\text{NCH}_3$ -groups that indicated the formation of a single geometric isomer (**A**, **B** or **C**). The methyl groups in the  $\text{OCMe}_2$  fragment and protons in the  $\text{NCH}_2$  group are diastereotopic that accord with overall  $C_2$ -symmetry of the complex. Thus it may be assumed that **7–9** exist as single geometric isomer in solution, too. At the same time it is evident that **6** is monomeric in solution, so we may assume that the introduction of the phenyl substituents to the carbon atoms in **7–9** does not lead to dimerisation.

The complexes **7–9** were synthesized using the racemic mixtures of corresponding dialkanolamines. On the basis of our previous results [13] two ligands in coordination sphere of titanium are identical and the corresponding asymmetric carbon atoms have the same absolute configuration. According to the NMR spectra complexes **7–9** exist in solution ( $\text{CDCl}_3$ ) as a mixture of two diastereomers. We assume that these diastereomers differ in nitrogen configuration. In each case the dominant isomer (**7a**, **8a** and **9a**) contains one set of signals that corresponds to  $C_2$ -symmetry complex. On the contrary, the minor isomer (**7b**, **8b** and **9b**) contains two sets of signals that corresponds to  $C_1$ -symmetry complex. It is interesting to note that the ratio **7a/7b**, **8a/8b**, **9a/9b** exceeds 7:3 and does not change with time.

### 2.3. Solid-state structure (X-ray diffraction data)

The structure of **10** was studied by X-ray diffraction (Fig. 1). Table 1 lists selected geometrical parameters for this compound. Compound **10** possesses in the solid state polynuclear structure which is closely related to that described earlier for  $[\text{Ti}(\mu^2\text{-O})\{\text{OCH}_2\text{CH}_2\}\{\mu^2\text{-OCH}_2\text{CH}_2\}\text{-NMe}_6]$  [18]. The structure is pseudocentrosymmetric, each titanium atom tied to two neighbouring metal atoms by oxygen atoms of Ti–O–Ti bonds and  $\mu^2$ -bridging  $\text{NCH}_2\text{CMe}_2\text{O}$ -groups. In coordination sphere of titanium the alkanolaminophenol (**2**) behaves as a tridentate  $[\text{ONO}]$ -ligand with a *fac*-disposition of O, N atoms. So

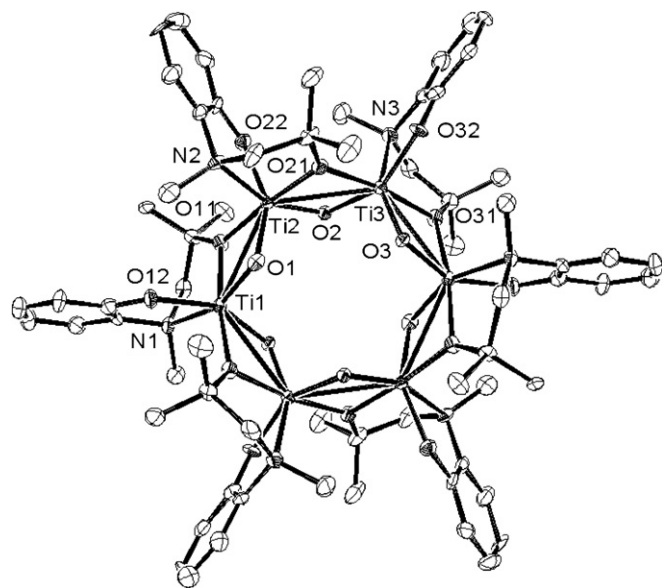


Fig. 1. Molecular structure of **10**; hydrogen atoms and solvated molecules are omitted for clarity.

central atoms are in a distorted octahedral coordination geometry such as the nitrogen atom and one of Ti–O–Ti–oxygen, another Ti–O–Ti–oxygen and phenolic oxygen, and two bridging  $\mu^2\text{-NCH}_2\text{CMe}_2\text{O}$ -groups occupy correspondingly the trans positions.

The titanium atoms form flat slightly distorted hexagon. In molecule there are six  $[\text{Ti}-\text{O}]_2$  fragments in which the torsion angle  $\text{TiOTiO}$  equal to  $167.5(2)^\circ$ ,  $170.39(2)^\circ$ ,  $172.02(2)^\circ$ . The angle formed by the two O–Ti–O fragments near one titanium atom is equal to  $73.2(2)^\circ$ ,  $74.2(2)^\circ$ ,  $75.1(2)^\circ$ .

The distance Ti–N in **10** [ $2.367(5)$  Å,  $2.362(6)$  Å,  $2.376(6)$  Å] is close to that previously found [ $2.310(2)$ – $2.471(2)$  Å] for hexacoordinated titanium complexes, based on dialkanolamines: titanospiro-bis(ocanes) [13], dimeric titanocanes [20] and  $[\text{Ti}(\mu^2\text{-O})\{\text{OCH}_2\text{CH}_2\}\{\mu^2\text{-OCH}_2\text{CH}_2\}\text{-NMe}_6]$  [18]. The phenolic ring conjugated with nitrogen atom does not significantly increase the Ti–N bond in complex **10** in comparison with that for Kemmitt's hexanuclear structure [18]. At the same time distances Ti–N in **10** are longer than those [ $2.248(2)$ – $2.308(4)$  Å] in related phenolic compounds  $[\text{RN}(\text{CH}_2\text{-}o\text{-ArO})_2]_2\text{Ti}$  [10,17]. This fact may be explained by trans disposition of nitrogen atoms in the coordination sphere of titanium in  $[\text{RN}(\text{CH}_2\text{-}o\text{-ArO})_2]_2\text{Ti}$ . The shortest Ti–O bond distances [ $\text{Ti}(1)\text{-O}(1)$   $1.781(5)$  Å,  $\text{Ti}(1)\text{-O}(3A)$   $1.904(4)$  Å] are observed for oxygen atom of Ti–O–Ti. The Ti–O bond distances involving the oxygen atom of the phenolic ring [ $1.921(5)$  Å,  $1.933(5)$  Å] are close to those previously found [ $1.871(5)$ – $1.930(3)$  Å] for related titanium complexes with chelating phenolic ligands [9,17,21]. At the same time this distance is somewhat longer than Ti–O bond distances in hexacoordinated titanium complexes of dialkanolamines [13] reflecting the greater polarity of this bond in titanium compounds with phenolic ligands.

Table 1  
Selected bond lengths (Å) and angles (°) for **10**

Ti(1)–O(1)	1.787(5)	Ti(1)–O(31A)	2.000(4)	Ti(1)–O(12)	1.921(5)
Ti(2)–O(2)	1.793(5)	Ti(2)–O(11)	2.032(4)	Ti(2)–O(22)	1.933(5)
Ti(2)–O(1)	1.880(5)	Ti(2)–O(11)	1.994(5)	Ti(3)–O(32)	1.921(5)
Ti(3)–O(3)	1.805(4)	Ti(3)–O(21)	1.993(5)		
Ti(3)–O(2)	1.901(4)	Ti(3)–O(31)	2.006(5)		
Ti(1)–O(3A)	1.904(4)	Ti(2)–O(21)	2.028(5)		
Ti(1)–Ti(2)	2.985(2)	Ti(1)–N(1)	2.367(5)	Ti(1)–O(1)–Ti(2)	109.0(2)
Ti(1)–Ti(3A)	2.993(2)	Ti(2)–N(2)	2.362(6)	Ti(1)–O(11)–Ti(2)	95.7(2)
Ti(2)–Ti(3)	2.993(2)	Ti(3)–N(3)	2.372(6)		
Ti(3)–Ti(1A)	2.993(2)				
Ti(2)–Ti(1)–Ti(3A)	118.24(5)	I(31A)–Ti(1)–N(1)	109.1(2)	I(12)–Ti(1)–O(3A)	150.0(2)
Ti(1)–Ti(2)–Ti(3)	122.12(5)	I(11)–Ti(1)–N(1)	75.6(2)	I(1)–Ti(1)–O(31A)	97.8(2)
Ti(2)–Ti(3)–Ti(1A)	119.56(5)	I(12)–Ti(1)–N(1)	75.8(2)	I(1)–Ti(1)–O(11)	77.9(2)

The five-membered chelating rings N–CH<sub>2</sub>–CMe<sub>2</sub>–O–Ti adopt an “envelope”-like conformation, the carbon atom in the  $\alpha$ -positions to the N atom occupy “flap” sites. On the contrary, chelating ring formed by the *o*-aminophenolic group are almost flat and lie in one plane with the phenolic ring.

In complex **10** there are very short Ti–Ti distances between two neighbouring titanium atoms, but it is obvious

Table 2  
Crystal data, data collection and refinement parameters for **10**

Compound	<b>10</b>
Empirical formula	C <sub>66</sub> H <sub>90</sub> N <sub>6</sub> O <sub>18</sub> Ti <sub>6</sub> · 2H <sub>2</sub> O · 0.66 CH <sub>2</sub> Cl <sub>2</sub>
Formula weight	1634.92
Colour, habit	Yellow, block
Crystal size (mm)	0.10 × 0.05 × 0.04
Crystal system	Monoclinic
Space group	<i>P</i> 2 <sub>1</sub> / <i>n</i>
<i>Unit cell dimensions</i>	
<i>a</i> (Å)	11.8058(18)
<i>b</i> (Å)	16.931(3)
<i>c</i> (Å)	19.713(3)
$\alpha$ (°)	90
$\beta$ (°)	96.439(4)
$\gamma$ (°)	90
Volume (Å <sup>3</sup> )	3915.4(10)
<i>Z</i>	2
<i>D</i> <sub>calc</sub> (g cm <sup>-3</sup> )	1.387
Absorption coefficient (mm <sup>-1</sup> )	0.697
<i>F</i> (000)	1703
Diffractometer	Bruker SMART 1K
Temperature (K)	120
Radiation ( $\lambda$ , Å)	0.71073
$\theta$ Range (°)	1.59–26.00
Index ranges	–14 ≤ <i>h</i> ≤ 5, –20 ≤ <i>k</i> ≤ 20, –22 ≤ <i>l</i> ≤ 23
Reflections collected	18377
Independent reflections	7381 [ <i>R</i> <sub>int</sub> = 0.1566]
Data/restraints/parameters	11 837/0/858
Goodness-of-fit on <i>F</i> <sup>2</sup>	0.895
Final <i>R</i> indices [ <i>I</i> > 2 $\sigma$ ( <i>I</i> )]	<i>R</i> <sub>1</sub> = 0.0837; <i>wR</i> <sub>2</sub> = 0.1441
<i>R</i> indices (all data)	<i>R</i> <sub>1</sub> = 0.1929; <i>wR</i> <sub>2</sub> = 0.1739
Largest difference peak/hole (e Å <sup>-3</sup> )	0.537/–0.459

Table 3  
Selected bond lengths (Å) and angles (°) for hydrogen bonds in the **10**

D–H···A	<i>d</i> (D–H)	<i>d</i> (H···A)	<i>d</i> (D···A)	DDHA
O(10)–H(2)···O(3)	0.76(8)	2.11(9)	2.851(8)	165(9)
O(10)–H(1)···O(2A)	0.79(11)	2.30(11)	2.882(9)	147(11)

that the intermetallic interaction does not exist. The space disposition of the atoms result in appearance of macrocyclic hole, the size of which may be determined by the distances between oxygen atoms [I(1)–I(11A) 5.491(6) Å, I(2)–I(21A) 5.400(6) Å, I(3)–I(31A) 5.574(6) Å]. Two molecules of water present in the crystal and form the hydrogen bonds with the oxygen atoms of the closest Ti–O–Ti fragment (Table 3).

In conclusion, we have synthesized a new type of polydentate [ONO]-ligands which we used for obtaining the titanium complexes. These complexes are hydrolytically unstable and may easily be converted to polynuclear Ti compounds.

### 3. Experimental

All manipulations were carried out under argon atmosphere using standard Schlenk techniques. Solvents were dried by standard methods and distilled before use. Ti(O*i*Pr)<sub>4</sub> (Aldrich) was distilled before use. Styrene oxide (Acros), isobutylene oxide (Acros) were used as supplied. 2-Methylaminophenol **1** [22], *cis*-stilbene oxide [23], 2,2-diphenyloxirane [24] were synthesized according to the literature procedures. CDCl<sub>3</sub> was obtained from Deutero GmbH and dried over CaH<sub>2</sub>. <sup>1</sup>H (400 MHz) and <sup>13</sup>C NMR (100 MHz) spectra were recorded on a Bruker Avance 400 spectrometer (in CDCl<sub>3</sub> at 295 K). Chemical shifts in the <sup>1</sup>H and <sup>13</sup>C NMR spectra are given in ppm relative to internal Me<sub>4</sub>Si. Mass spectra (EI-MS) were recorded on a VAR-IAN CH-7a device using electron impact ionization at 70 eV; all assignments were made with reference to the most abundant isotopes. Mass spectra (ESI) were recorded in acetonitrile for positive ions. Elemental analyses were carried out by the Microanalytical Laboratory of the Chemistry Department of the Moscow State University.

### 3.1. Synthesis of substituted ortho-aminophenols

#### 3.1.1. Synthesis of $\text{MeN}(\text{CH}_2\text{CMe}_2\text{OH})(\text{C}_6\text{H}_4\text{-o-OH})$ (**2**)

A mixture of **1** (1.50 g, 12.2 mmol) and isobutylene oxide (1.06 g, 14.6 mmol) was heated at 80 °C for 26 h in the Schlenk tube equipped with a J. Young valve. The residue was dried in vacuum to give 2.36 g (100%) of **2** as a yellowish oil.  $^1\text{H}$  NMR (400.1 MHz,  $\text{CDCl}_3$ , ppm):  $\delta = 7.09\text{--}7.04$  (m, 1H), 6.96–6.89 (m, 1H), 6.87–6.83 (m, 1H), 6.79–6.72 (m, 1H) (aromatic hydrogens), 5.27 (br s, 2 H, 2 OH), 2.84 (s, 2H,  $\text{NCH}_2$ ), 2.78 (s, 3H,  $\text{NCH}_3$ ), 1.17 (s), 1.18 (s) (6H, 2  $\text{CH}_3$ ).  $^{13}\text{C}$  NMR (100.61 MHz,  $\text{CDCl}_3$ , ppm):  $\delta = 151.09$ , 141.68, 125.21, 121.44, 119.79, 115.28 (aromatic carbons), 71.81 ( $\text{Me}_2\text{CO}$ ), 68.49 ( $\text{NCH}_2$ ), 43.51 ( $\text{NCH}_3$ ), 27.90 ( $\text{C}(\text{CH}_3)_2$ ). MS (EI,  $m/z$ , %): 195 (2) [ $\text{M}^+$ ], 162 (6) [ $\text{M}^+ - \text{CH}_3 - \text{H}_2\text{O}$ ], 136 (100) [ $\text{M}^+ - \text{H} - \text{Me}_2\text{CO}$ ], 120 (7) [ $\text{M}^+ - \text{CH}_3 - \text{H}_2\text{O} - \text{C}_3\text{H}_5 - \text{H}$ ], 93 (1) [ $\text{PhO}^+$ ], 65 (5) [ $\text{C}_5\text{H}_5^+$ ]. Anal. Calc. for  $\text{C}_{11}\text{H}_{17}\text{NO}_2$  (233.40): C, 67.66; H, 8.78; N, 7.17. Found: C, 67.08; H, 8.16; N, 6.84%.

#### 3.1.2. Synthesis of *treo*- $\text{MeN}(\text{CHPhCHPhOH})(\text{C}_6\text{H}_4\text{-o-OH})$ (**3**)

A mixture of **1** (0.79 g, 6.4 mmol) and *cis*-stilbene oxide (1.26 g, 6.4 mmol) was heated at 100 °C for 56 h. The residue was recrystallized from ether/hexane (1:2) mixture to give 1.12 g (55%) of **3** as a beige solid.  $^1\text{H}$  NMR (400.1 MHz,  $\text{CDCl}_3$ , ppm):  $\delta = 7.29\text{--}7.25$  (m, 2H), 7.18–7.11 (m, 6H), 7.03–6.96 (m, 2H), 6.86–6.83 (m, 2H), 6.70–6.65 (m, 1H), 6.48–6.47 (m, 1H) (aromatic hydrogens), 5.31 (d,  $^3J_{\text{HH}} = 12$  Hz, 1H, OCH), 4.25 (d,  $^3J_{\text{HH}} = 12$  Hz, 1H, NCH), 3.60 (br s, 2H, 2OH), 2.60 (s, 3H,  $\text{NCH}_3$ ).  $^{13}\text{C}$  NMR (100.61 MHz,  $\text{CDCl}_3$ , ppm):  $\delta = 151.49$ , 140.63, 138.47, 133.40, 129.66, 128.35, 128.04, 127.61, 127.53, 127.48, 125.28, 123.53, 119.25, 115.33 (aromatic carbons), 73.28 (OCH), 72.70 (NCH), 34.85 ( $\text{NCH}_3$ ). Anal. Calc. for  $\text{C}_{21}\text{H}_{21}\text{NO}_2$  (319.40): C, 78.97; H, 6.63; N, 4.39. Found: C, 78.00; H, 6.39; N, 4.12%.

#### 3.1.3. Synthesis of $\text{MeN}(\text{CHPhCH}_2\text{OH})(\text{C}_6\text{H}_4\text{-o-OH})$ (**4**) and $\text{MeN}(\text{CH}_2\text{CHPhOH})(\text{C}_6\text{H}_4\text{-o-OH})$ (**5**)

A mixture of **1** (4.04 g, 30.0 mmol) and styrene oxide (3.60 g, 30.0 mmol) was heated at 90 °C for 34 h. The residue was dried in vacuum to give 7.28 g (100%) of a mixture of **4** and **5** as a yellowish oil. The approximate ratio of isomers is **4**:**5** = 4:1 (according to  $^1\text{H}$  NMR). NMR data for  $\text{MeN}(\text{CHPhCH}_2\text{OH})(\text{C}_6\text{H}_4\text{-o-OH})$  (**4**):  $^1\text{H}$  NMR (400.1 MHz,  $\text{CDCl}_3$ , ppm):  $\delta = 7.36\text{--}7.28$  (m, 3H), 7.15–6.98 (m, 4H), 6.86–6.76 (m, 2H) (aromatic hydrogens), 5.75 (br s, 2H, 2OH), 4.19–4.14 (m, 1H, OCH(H)), 4.09–4.04 (m, 1H, OCH(H)), 3.80 (dd,  $^3J_{\text{HH}} = 4$  Hz,  $^3J_{\text{HH}} = 11$  Hz, 1H, NCH), 2.48 (s, 3H,  $\text{NCH}_3$ ).  $^{13}\text{C}$  NMR (100.61 MHz,  $\text{CDCl}_3$ , ppm):  $\delta = 151.96$ , 137.99, 136.72, 128.48, 128.32, 127.93, 125.85, 123.37, 119.54, 114.88 (aromatic carbons), 69.21 (NCH), 62.59 (OCH<sub>2</sub>), 37.57 ( $\text{NCH}_3$ ). NMR data for  $\text{MeN}(\text{CH}_2\text{CHPhOH})(\text{C}_6\text{H}_4\text{-o-OH})$  (**5**):  $^1\text{H}$  NMR (400.1 MHz,  $\text{CDCl}_3$ , ppm):  $\delta = 4.86$  (dd,

$^3J_{\text{HH}} = 2$  Hz,  $^3J_{\text{HH}} = 10$  Hz, 1H, OCH), 3.18–3.10 (m, 1H, NCH(H)), 3.00–2.94 (m, 1H) (NCH(H)), 2.80 (s, 3H,  $\text{NCH}_3$ ). Other proton resonances could not be located due to the overlap with those for major isomer.  $^{13}\text{C}$  NMR (100.61 MHz,  $\text{CDCl}_3$ , ppm):  $\delta = 151.17$ , 141.69, 139.60, 128.73, 126.73, 125.84, 125.18, 120.75, 119.78, 115.14 (aromatic carbons), 71.73 (OCH), 65.43 ( $\text{NCH}_2$ ), 41.45 ( $\text{NCH}_3$ ). MS (EI,  $m/z$ , %): 213(16) [ $\text{M}^+ - \text{CH}_2\text{O}$ ], 212 (100) [ $\text{M}^+ - \text{CH}_2\text{O} - \text{H}$ ], 136 (37) [ $\text{M}^+ - \text{CH}_2\text{O} - \text{Ph}$ ], 122 (12) [ $\text{M}^+ - \text{CH}_2\text{O} - \text{PhCH}_2$ ], 93 (2) [ $\text{PhO}^+$ ], 91 (27) [ $\text{PhCH}_2^+$ ], 77 (18) [ $\text{Ph}^+$ ], 65 (18) [ $\text{C}_5\text{H}_5^+$ ]. Anal. Calc. for  $\text{C}_{15}\text{H}_{17}\text{NO}_2$  (243.30): C, 74.05; H, 7.04; N, 5.76. Found: C, 73.78; H, 6.76; N, 5.34%.

#### 3.1.4. The reaction of $\text{MeN}(\text{H})(\text{C}_6\text{H}_4\text{-o-OH})$ (**1**) with 2,2-diphenyloxirane

A mixture of **1** (1.49 g, 12.1 mmol) and 2,2-diphenyloxirane (2.38 g, 12.1 mmol) was heated at 100 °C for 28 h. According to NMR spectroscopic data, the mixture of initial and unidentified compounds was formed.

### 3.2. Synthesis of complexes

#### 3.2.1. Synthesis of $[\text{MeN}(\text{CH}_2\text{CMe}_2\text{O})(\text{C}_6\text{H}_4\text{-o-O})]_2\text{Ti}$ (**6**)

$\text{Ti}(\text{O-}i\text{-Pr})_4$  (0.95 mL, 3.2 mmol) was added dropwise to a stirred solution of 1.24 g (6.4 mmol) of **2** in toluene (20 mL). After 7 h refluxing, the solvent was evaporated under reduced pressure. The residue was recrystallized from dichloromethane/heptane (1:1) mixture to give 1.15 g (83%) of **6** as a yellow solid.  $^1\text{H}$  NMR (400.1 MHz,  $\text{CDCl}_3$ , ppm):  $\delta = 7.20\text{--}7.08$  (m, 4H), 6.77–6.70 (m, 4H) (aromatic hydrogens), 3.85 (d, 2H), 3.32 (d, 2H) ( $^2J_{\text{HH}} = 12$  Hz, 2 $\text{NCH}_2$ ), 2.64 (s, 6H, 2 $\text{NCH}_3$ ), 1.27 (s, 6H), 0.83 (s, 6H) (4 $\text{CH}_3$ ).  $^{13}\text{C}$  NMR (100.61 MHz,  $\text{CDCl}_3$ , ppm):  $\delta = 162.59$ , 141.27, 138.48, 121.82, 118.44, 116.19 (aromatic carbons), 82.67 ( $\text{OCMe}_2$ ), 73.50 ( $\text{NCH}_2$ ), 49.51 ( $\text{NCH}_3$ ), 30.10, 28.73 (2  $\text{CH}_3$ ). MS (ESI,  $m/z$ ): 435.3 [ $\text{M}^+ + 1$ ]. Anal. Calc. for  $\text{C}_{22}\text{H}_{30}\text{N}_2\text{O}_4\text{Ti}$  (434.35): C, 60.83; H, 6.96; N, 6.45. Found: C, 60.60; H, 6.55; N, 6.24%.

#### 3.2.2. Synthesis of *treo*- $[\text{MeN}(\text{CHPhCHPhO})]_2\text{Ti}$ (**7**)

$\text{Ti}(\text{O-}i\text{-Pr})_4$  (0.36 mL, 1.2 mmol) was added dropwise to a stirred solution of 0.72 g (2.4 mmol) of **3** in toluene (20 mL). After 8 h refluxing, the solvent was evaporated under reduced pressure. The residue was recrystallized from dichloromethane/heptane (2:1) mixture to give 0.64 g (83%) of **7** as a yellow solid.  $^1\text{H}$  NMR spectroscopy of **7** in  $\text{CDCl}_3$  indicated it is a mixture of two diastereomers with  $\text{C}_2$ - (**7a**) and  $\text{C}_1$ -symmetry (**7b**), approximate ratio is **7a**/**7b** = 70:30. NMR data for **7a**:  $^1\text{H}$  NMR (400.1 MHz,  $\text{CDCl}_3$ , ppm):  $\delta = 7.31\text{--}6.95$  (m, 22H), 6.60–6.53 (m, 2H), 6.45–6.40 (m, 2H), 6.28–6.22 (m, 2H) (aromatic hydrogens), 6.05 (d,  $^3J_{\text{HH}} = 11$  Hz, 2H, 2OCH), 4.46 (d,  $^3J_{\text{HH}} = 11$  Hz, 2H, 2NCH), 3.23 (s, 6H, 2 $\text{NCH}_3$ ).  $^{13}\text{C}$

NMR (100.61 MHz, CDCl<sub>3</sub>, ppm):  $\delta$  = 162.59, 141.59, 139.94, 131.04, 129.03, 128.86, 128.16, 127.84, 126.28, 123.05, 117.78, 115.89 (aromatic carbons), 89.69 (OCH), 80.88 (NCH), 37.33 (NCH<sub>3</sub>). Two signals of aromatic carbons were not found probably due to coalescence of several signals. NMR data for **7b**: <sup>1</sup>H NMR (400.1 MHz, CDCl<sub>3</sub>, ppm):  $\delta$  = 6.52–6.48 (m, 2H), 6.40–6.33 (m, 2H), 6.20–6.15 (m, 2H) (aromatic hydrogens), 6.13 (d, <sup>3</sup>J<sub>HH</sub> = 11 Hz, 1H, OCH), 4.41 (d, <sup>3</sup>J<sub>HH</sub> = 11 Hz), 4.33 (d, <sup>3</sup>J<sub>HH</sub> = 14 Hz, 1H) (2NCH), 3.03 (s, 3H), 2.80 (s, 3H) (2NCH<sub>3</sub>). Other signals could not be located due to the overlap with those for major isomer or due to the low concentration in the sample. Anal. Calc. for C<sub>42</sub>H<sub>38</sub>N<sub>2</sub>O<sub>4</sub>Ti (682.63): C, 73.90; H, 5.61; N, 4.10. Found: C, 73.06; H, 5.25; N, 3.74%.

**B**: Ti(O-*i*-Pr)<sub>4</sub> (0.34 mL, 1.1 mmol) was added dropwise to a solution of 0.35 g (1.1 mmol) of **3** in toluene (20 mL). The reaction mixture was stirred for 14 h at room temperature, then the solvent was removed in vacuum. The crude product was recrystallized from dichloromethane/heptane (2:1) mixture to give 0.28 g (72%) of **7** as a yellow solid.

### 3.2.3. Synthesis of [MeN(CHPhCH<sub>2</sub>O)(C<sub>6</sub>H<sub>4</sub>-*o*-O)]<sub>2</sub>Ti (**8**) and [MeN(CH<sub>2</sub>CHPhO)(C<sub>6</sub>H<sub>4</sub>-*o*-O)]<sub>2</sub>Ti (**9**)

Ti(O-*i*-Pr)<sub>4</sub> (1.22 mL, 4.1 mmol) was added dropwise to a stirred solution of 2.00 g (8.2 mmol) of the mixture of 2-[(2-hydroxyethyl)aminophenols (**4** + **5**) in toluene (30 mL). After 5 h refluxing, the solvent was evaporated under reduced pressure. The residue was recrystallized from toluene/heptane (1:1) mixture to give 1.59 g (73%) of a mixture of **8** and isomeric **9** as a red solid. The approximate ratio of isomers is **8**:**9** = 3:1 (according to <sup>1</sup>H NMR). <sup>1</sup>H NMR spectroscopy in CDCl<sub>3</sub> indicated that **8** and **9** exist as a mixture of two diastereomers with C<sub>2</sub>- (**8a**, **9a**) and C<sub>1</sub>-symmetry (**8b**, **9b**); isomers **8a** and **9a** account for more than 80% of the total. NMR data for **8a**: <sup>1</sup>H NMR (400.1 MHz, CDCl<sub>3</sub>, ppm):  $\delta$  = 7.34–6.84 (m, 18H, aromatic hydrogens), 5.26–5.17 (m, 2H), 4.66 (dd, <sup>3</sup>J<sub>HH</sub> = 4 Hz, <sup>3</sup>J<sub>HH</sub> = 11 Hz, 2H), 4.41 (dd, <sup>3</sup>J<sub>HH</sub> = 7 Hz, <sup>3</sup>J<sub>HH</sub> = 12 Hz, 2H) (2 NCH, 2 OCH<sub>2</sub>), 2.96 (s, 6H, 2 NCH<sub>3</sub>). <sup>13</sup>C NMR (100.61 MHz, CDCl<sub>3</sub>, ppm):  $\delta$  = 161.98, 140.25, 137.74, 130.57, 128.94, 128.13, 125.20, 122.84, 118.03, 116.24 (aromatic carbons), 77.55, 74.41 (NCH, OCH<sub>2</sub>), 35.22 (NCH<sub>3</sub>). NMR data for **8b**: <sup>1</sup>H NMR (400.1 MHz, CDCl<sub>3</sub>, ppm):  $\delta$  = 5.58–5.53 (m, 1H), 4.99–4.95 (m, 1H), 4.91–4.86 (m, 1H), 4.53–4.48 (m, 1H) (2NCH, 2OCH<sub>2</sub>), 2.71 (s, 3H), 2.38 (s, 3H) (2NCH<sub>3</sub>). Other signals could not be located due to the overlap with those for major isomer or due to the low concentration in the sample. NMR data for **9a**: <sup>1</sup>H NMR (400.1 MHz, CDCl<sub>3</sub>, ppm):  $\delta$  = 6.22–6.18 (m, 2H, 2OCH), 4.03–3.95 (m, 2H) (NCH<sub>2</sub>), 2.54 (s, 6H, 2NCH<sub>3</sub>). <sup>13</sup>C NMR (100.61 MHz, CDCl<sub>3</sub>, ppm):  $\delta$  = 130.70, 127.81, 117.40 (aromatic carbons), 75.18 (OCH), 73.49 (NCH<sub>2</sub>), 45.58 (NCH<sub>3</sub>). Other signals could not be located due to the overlap with those for major isomer or due to the low concentration in the sample. NMR data for **9b**: <sup>1</sup>H NMR (400.1 MHz, CDCl<sub>3</sub>, ppm):  $\delta$  = 5.95–5.90 (m, 1H), 5.88–5.84 (m, 1H) (2OCH),

4.18–4.12 (m, 2H), 3.89–3.81 (m, 2H) (2NCH<sub>2</sub>), 2.84 (s, 3H), 2.50 (s, 3H) (2NCH<sub>3</sub>). Other signals could not be located due to the overlap with those for major isomer or due to the low concentration in the sample.

### 3.3. Synthesis of [Ti(μ<sup>2</sup>-O){O-*o*-C<sub>6</sub>H<sub>4</sub>}{μ<sup>2</sup>-OCMe<sub>2</sub>CH<sub>2</sub>}NMe]<sub>6</sub> (**10**)

A mixture (20 mL) of heptane and moist dichloromethane (1:2) was added to a saturated solution of **6** (0.2 g) in dichloromethane. The resulting mixture was stored at –78 °C over 7 days. The crystalline product precipitated from solution. X-ray quality crystals were formed on the side of the flask.

### 3.4. X-ray crystallographic study

Crystal data, data collection, structure solution and refinement parameters for **10** are listed in Table 2. The structure was solved by direct methods [25] and refined by full matrix least-squares on *F*<sup>2</sup> [26] with anisotropic thermal parameters for all non-hydrogen atoms (except solvent toluene molecules). Solvent toluene was found to be disordered over two positions with occupancies ratio 0.69/0.31. All hydrogen atoms of the main metal organic molecule were found from diff. Fourier synthesis and refined with isotropic thermal parameters, hydrogen atoms of solvent toluene molecules were placed in calculated positions and refined using a riding model.

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### Appendix A. Supplementary material

CCDC 612584 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif). Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2007.10.020.

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