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Titanium Complexes of Dialkanolamine Ligands: Synthesis and Structure

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Synthesis of the title compounds, viz. $[RN(CH_2CH_2O)(CHR^1CR^2R^3O)]Ti(OiPr)_2$ (**13**–**15**) and $[RN(CH_2CH_2O)(CHR^1CR^2R^3O)]_2Ti$ (**18**–**28**), by the reaction of one or two equivalents of the corresponding dialkanolamines $RN(CH_2CH_2OH)(CHR^1CR^2R^3OH)$ (**1**–**12**) with $Ti(OiPr)_4$ is reported. Other routes to $[RN(CH_2CH_2O)(CHR^1CR^2R^3O)]_2Ti$, such as the reaction of $Ti(CH_2Ph)_4$ with dialkanolamine and the reaction of $TiCl_4(THF)_2$ with dialkanolamine/Et_3N were also tested. Dimeric titanocane **16**, $[PhCH_2N(CH_2CH_2O)_2Ti(OMe)_2]_2$, was obtained from the reaction of one equivalent of dialkanolamine **3** with $CpTi(OMe)_3$. $PhCH_2N(CH_2CH_2O)_2Ti(OMenth)_2$ (**17**) was prepared from the transalkoxylation reaction of **15** with two equivalents of menthol. The composition and structures of all novel compounds were established by ^1H and ^{13}C NMR spectroscopy as well as elemental analysis data. The possible solution structure features of **13**–**28** are discussed. The single-crystal X-ray diffraction study of titanocane **16** clearly indicates a dimeric structure for this compound in the solid state. According to X-ray data, compounds $[PhCH_2N(CH_2CH_2O)_2]_2Ti$ (**19**), $[MeN(CH_2CH_2O)(CH_2CHPhO)]_2Ti$ (**20**), $[MeN(CH_2CH_2O)(CH_2CPh_2O)]_2Ti$ (**23**), *erythro*-$[MeN(CH_2CH_2O)(CHPhCHPhO)]_2Ti$ (**24**), *threo*-$[MeN(CH_2CH_2O)(CHPhCHPhO)]_2Ti$ (**25**), and $\{MeN(CH_2CH_2O)[CH(CH_2)_4CHO]\}_2Ti$ (**27**) possess a monomeric structure with a hexacoordinate titanium atom in the solid state. Among them complexes **19**, **20**, **23**, **25**, and **27** are characterized by a *cis* disposition of the nitrogen atoms in the coordination environment of the Ti atom, while nitrogen atoms in **24** occupy *trans* positions.

Introduction

Alkoxy- or aroxytitanium derivatives have attracted the attention of researchers during the last five decades because of their possible application as catalysts in various organic reactions,[1–8] as well as precursors for titanium sol-gel chemistry[9] and metal-organic chemical vapor deposition (MOCVD) processes.[10] Among these species, the compounds with different trialkanolamines, titanatranes, $N(CR^1R^4CR^2R^3O)_3TiX$, with different substituents at the carbon atoms of the atrane skeleton, have been investigated to a considerable extent because of their rich structural features and catalytic activities including polymerization reactions of alkenes (see key references and references cited therein).[11–19] At the same time the closely related derivatives of dialkanolamines, titanocanes, $RN(CR^1R^4CR^2R^3O)_2Ti(X)X'$, are less studied.[20–26] However, this class of compounds could be more promising for investigations because of their greater chemical and structural flexibility. In addition, some cyclic titanium alkoxides with transannular interactions were recently found to be good catalysts in olefin polymerization reactions.[27–33]

As a part of our program to investigate the structure and chemical behavior of metal complexes containing di- and trialkanolamine ligands,[34–43] we present the study of reactions of dialkanolamines **1**–**12** with $Ti(OiPr)_4$. In the case of the reaction of $RN(CH_2CH_2OH)_2$ with $Ti(OiPr)_4$ (1:1 ratio) novel titanocanes **13**–**15** formed (R = Ph, Me, $PhCH_2$). The dimer $[PhCH_2N(CH_2CH_2O)_2Ti(OMe)_2]_2$ (**16**), was obtained from the reaction of dialkanolamine **3** with $CpTi(OMe)_3$. The reaction of **15** with two equivalents of menthol led to $PhCH_2N(CH_2CH_2O)_2Ti(OMenth)_2$ (**17**). 1,1′-Spirobititanocanes **18**–**28** of type $[RN(CH_2CH_2O)(CHR^1CR^2R^3O)]_2Ti$ were prepared from the reaction of two equivalents of the corresponding dialkanolamines with $Ti(OiPr)_4$. The solid state and solution structures of prepared compounds are discussed on the basis of X-ray diffraction and NMR spectroscopic data. Once this work had been finished the report of Carpentier and coworkers was published where the synthesis and structural investigations of several closely related titanocanes and 1,1′-spirobititanocanes were reported.[44]

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Results and Discussion

Dialkanolamines **1**–**12** were involved in this study. The compounds **8**–**12** were obtained from the reaction of the corresponding alkene oxides with *N*-methylethanolamine in high yields (Scheme 1). The reaction with indene oxide was previously reported, but the structure of product **12** was not discussed.[45] Compound **7** was previously prepared by another method.[46] Compounds **8**–**11** are novel.

The reactions proceeded regiospecifically, only one expected product formed in the reactions with but-1-ene oxide, 1,1-diphenylethylene oxide, and indene oxide. Only one diastereomer formed in the reactions with *cis*- and *trans*-stilbene oxides, as well as cyclopentene and cyclohexene oxides.

Titanocanes: According to the literature, the most suitable approach to the dialkoxy complexes of titanium with chelate ligands is the transalkoxylation reaction of $Ti(OAlk)_4$ with the free ligand containing two OH groups. This method was used in the case of the closely related ligands $RN(CH_2\text{-}o\text{-}ArOH)_2$, where *o*-Ar is a benzene ring with different alkyl (methyl or *tert*-butyl) substituents and R is $CH_2CH_2NMe_2$.[27] When R is *n*Pr, the presence of an alkyl group in the other *ortho* position to the OH group of such ligands is required for the formation of bis(isopropoxide) complexes, otherwise the formation of bishomoleptic substances $[RN(CH_2\text{-}o\text{-}ArO)_2]_2Ti$ has been found.[27] Analogous results were found for other structurally close bis(phenols). The treatment of $Ti(OAlk)_4$ (Alk = *i*Pr, Me) with one equivalent of the bis(phenol), $CH_2[(3\text{-}t\text{Bu-}5\text{-}MeC_6H_2)\text{-}2\text{-}OH]_2$, gave monomeric complexes with a tetracoordinate Ti atom (NMR spectroscopic data), $CH_2[(3\text{-}t\text{Bu-}5\text{-}MeC_6H_2)\text{-}2\text{-}O]_2Ti(OAlk)_2$.[30] Reacting the thio-bis(phenol), $S[(3\text{-}t\text{Bu-}5\text{-}MeC_6H_2)\text{-}2\text{-}OH]_2$, with $Ti(OiPr)_4$ resulted in the dimeric $[S[(3\text{-}t\text{Bu-}5\text{-}MeC_6H_2)\text{-}2\text{-}O]_2Ti(OiPr)_2]_2$ (X-ray data) where dimerization ensues from the interaction of the oxygen atom of the isopropoxy group of one monomeric unit with the Ti atom of the other.[31] The diisopropoxy titanium complexes based on diamino-dialkoxide ligands, $[\text{-}CH_2N(Me)CH_2C(CF_3)_2OH]_2$ and $CH_2[CH_2N(Me)CH_2C(CF_3)_2OH]_2$, were also recently prepared by Carpentier and coworkers by the transalkoxylation reaction of $Ti(OiPr)_4$.[32]

To the best of our knowledge, the reactions of dialkanolamines with $Ti(OiPr)_4$ have only been published in a series of works by Kemmitt et al. and very recently in the report of Lavanant et al.[20–23,44] Kemmitt et al. noted that the reaction of two equivalents of dialkanolamine **2** with $Ti(OiPr)_4$ gave the bishomoleptic complex $[MeN(CH_2\text{-}CH_2O)_2]_2Ti$ (**29**). This transformation was supposed to proceed through a very reactive and unstable $MeN(CH_2\text{-}CH_2O)_2Ti(OiPr)_2$ but this suggestion was not confirmed by any analytical methods.[20] Increasing the amount of $Ti(OiPr)_4$ in the reaction mixture led to the unexpected $[Ti_2\{\mu_2\text{-}(OCH_2CH_2)_2NMe\}(\mu_2\text{-}OiPr)(OiPr)_5]$.[21] The analogous species, $Ti_2(OCH_2CH_2NMe)_2(OtBu)_6$, was prepared by the reaction of $Ti(OtBu)_4$ with **2**.[22] The treatment of $Ti(OiPr)_4$ with one equivalent of **2** in the presence of one equivalent of different diols led to dimeric titanium aminoalkoxydiolates, $[MeN(CH_2CH_2O)_2Ti(O\text{-}A\text{-}O)]_2$ (O-A-O = $OCMe_2CMe_2O$, $OCEt_2CEt_2O$, $OCMe_2CH_2CMe_2O$, $OCMe_2CH_2CHMeO$). Dimerization in latter complexes is realized by the interaction of the oxygen atom of one dialkanolamine "arm" of one monomeric unit with the Ti atom of the other.[23] Lavanant et al. have found that the reaction of one equivalent of $PhCH_2N(CH_2CMe_2OH)_2$ with $Ti(OiPr)_4$ gave the complex $PhCH_2N(CH_2CMe_2O)_2Ti(OiPr)_2$, which is monomeric in the solid state and in solution ($[D_8]$toluene).[44]

We have found that dialkanolamines **1**–**3** reacted readily with an equimolar amount of $Ti(OiPr)_4$ at room temperature in chloroform or toluene solution to give the corresponding titanocanes **13**–**15** in high yields (Scheme 2). We also tested two other reactions that may lead to the titanocanes, where X = X′. However, both reactions did not result in the desired products (Scheme 2). $CpSn\text{-}nBu_3$, one of the possible by-products in the reaction of Cp_2TiCl_2 with $MeN(CH_2CH_2OSn\text{-}nBu_3)_2$, was detected by NMR spectroscopy.

Our efforts to prepare titanocane with different substituents X and X′ by the transalkoxylation reaction of dialkanolamine **3** with $(MeO)_3TiCp$ failed. Only the dimer **16** was obtained. In contrast, Kim et al. synthesized $RN(CH_2CH_2O)_2Ti(Cl)Cp^*$ by the reaction of Cl_3TiCp^* (where Cp^* = pentamethylcyclopentadienyl) with $RN(CH_2CH_2OH)_2$ (R = Me, *n*Bu).[25] We believe that the difference in the behavior of $(MeO)_3TiCp$ and Cl_3TiCp^* (the rupture of Ti–Cp bond and the stability of Ti–Cp^* bond in the course of the reaction) is because of the different properties of these bonds.

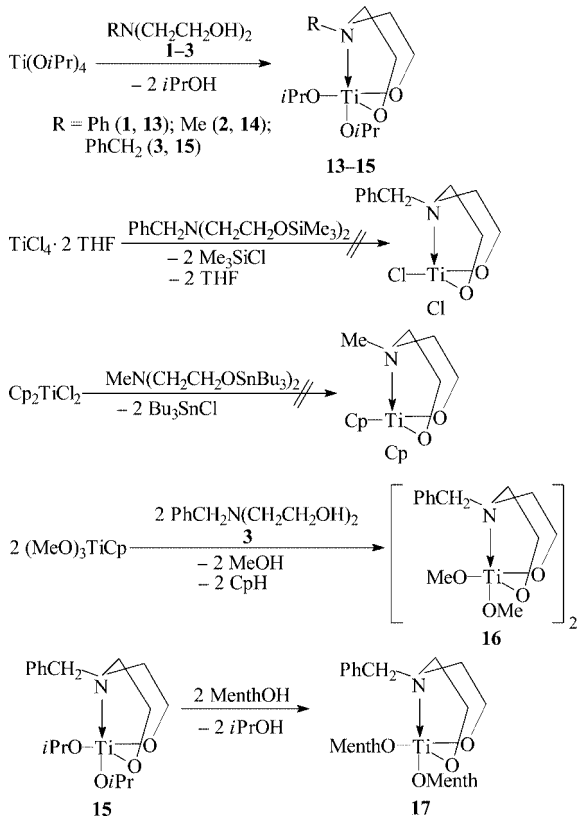
The possibility of alkoxy groups exchanging at the titanium atom was confirmed by the formation of complex **17** in the reaction of diisopropoxy derivative **15** with L-(–)-menthol (Scheme 2).

6–12

	R^1	R^2	R^3	
6	H	Et	H	
7	H	Ph	Ph	
8	Ph	Ph	H	*erythro*
9	Ph	Ph	H	*threo*

	R^1	R^2	R^3
10	$(CH_2)_3$		H
11	$(CH_2)_4$		H
12	$C_6H_4CH_2$		H

Scheme 1.



Scheme 2.

One of the most important questions in the chemistry of titanium is the coordination state of the Ti atom both in the solid state and in solutions. In our opinion the type of coordination environment around the titanium atoms is very important because of the potential ability of these compounds to catalyze different organic reactions where the stereochemistry of the catalytic center is significant.[3–8] Titanocanes prepared by us may possess monomeric structures with pentacoordinate titanium atoms or dimeric structures with hexacoordinate titanium atoms. There are two possibilities for dimerization: through the dialkanolamine moiety or through the alkoxy groups. According to the literature, most of the titanocanes prepared to date, $[MeN(CH_2CH_2O)_2Ti(O\text{-}A\text{-}O)]_2$ (O-A-O = $OCMe_2CMe_2O$, $OCEt_2CEt_2O$, $OCMe_2CH_2CMe_2O$, $OCMe_2CH_2CH$-MeO),[23] are dimeric in the solid state. The dimerization is realized by the additional contact of the oxygen atom of one diethanolamine "arm". In $CDCl_3$ solutions two compounds are also dimeric at room temperature (O-A-O = $OCMe_2CMe_2O$, $OCEt_2CEt_2O$) while two others are monomeric (O-A-O = $OCMe_2CH_2CMe_2O$, $OCMe_2CH_2CH$-MeO).[23] $PhCH_2N(CH_2CMe_2O)_2Ti(OiPr)_2$ is monomeric in the solid state and in solution (toluene-d_8).[44] As cited above, the closely related derivatives, nPrN{CH_2[3,5-bis(tBu)-C_6H_2]-2-O}$_2$Ti(OiPr)$_2$ and nPrN{CH_2[3,5-bis(Me)-C_6H_2]-2-O}$_2$Ti(OiPr)$_2$, are monomeric both in the solid state and in solution (C_6D_6).[27]

Among five dialkoxytitanocanes prepared by us only one compound **16**, the titanocane with two methoxy groups at the titanium atom, gave crystals suitable for an X-ray diffraction study. The molecular structure of **16** is shown in Figure 1. Table 1 lists selected geometrical parameters for **16**. The molecule of **16** represents a centrosymmetric complex with a Ti_2O_2 lozenge. The dimer results from μ_2-bridging by one methoxy group of one monomeric unit. The diethanolamine ligands in each dimer are bound meridionally to each titanium atom. Of interest, all previously studied alkoxytitanocanes except $PhCH_2N(CH_2CMe_2O)_2Ti(OiPr)_2$ are also dimeric, but the dimerization results from μ_2-bridging by one alkoxy "arm" of the diethanolamine ligand.[23,44] The coordination polyhedron of the Ti atoms in compound **16** represents a distorted octahedral geometry with the N(1) atom and O(4) atom (nonbridging methoxy group) in a *trans* orientation. The Ti(1)–N(1) distance in **16** [2.355(2) Å] is close to that previously found for $[MeN(CH_2CH_2O)_2$-Ti(O-A-O)]$_2$ [2.351(4)–2.431(4) Å].[23] The longest Ti–O distances in **16** [Ti(1)–O(3A) 2.024(1); Ti(1)–O(3) 2.066(1) Å] correspond to the bonds of titanium with both bridging methoxy groups, as expected. All five-membered rings of the ocane skeletons in **16** adopt an envelope-like conformation, all carbon atoms in the α positions to the N atom occupy "flap" sites, while the C-β atoms form the base of these envelope planes.

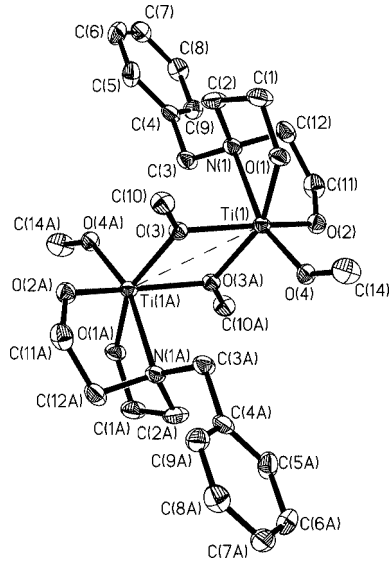


Figure 1. Molecular structure of **16**. Hydrogen atoms and solvate dichloromethane molecules are omitted for clarity.

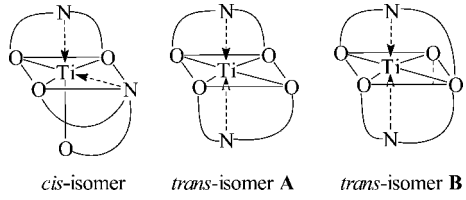
Table 1. Selected bond lengths [Å] and angles [°] for **16**.

Ti(1)–O(4)	1.808(1)	O(4)–Ti(1)–N(1)	162.26(6)
Ti(1)–O(1)	1.868(1)	O(1)–Ti(1)–N(1)	75.59(6)
Ti(1)–O(2)	1.873(1)	O(2)–Ti(1)–N(1)	76.79(6)
Ti(1)–O(3A)	2.024(1)	O(3A)–Ti(1)–N(1)	94.03(5)
Ti(1)–O(3)	2.066(1)	O(3)–Ti(1)–N(1)	92.07(5)
Ti(1)–N(1)	2.355(2)		

^{1}H and ^{13}C NMR spectroscopic data ($CDCl_3$ solution, room temperature) of **16** are in agreement with the centrosymmetric dimeric solid-state structure. In the ^{1}H NMR spectrum of **16** there are two singlets of methoxy groups.

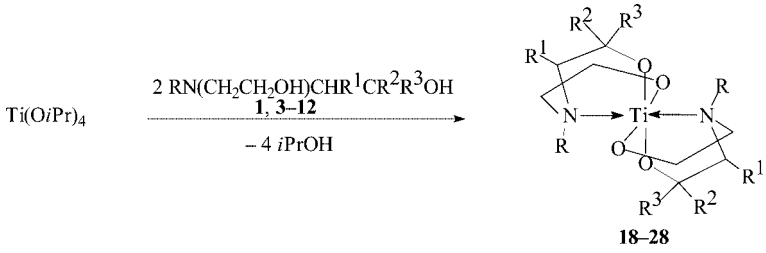
The signals of the methylene protons of one ocane skeleton appear as a set of multiplets resulting from the nonequivalence of all protons. Separate ^{13}C NMR signals were found for each carbon of the diethanolamine ligand in **16**. On the contrary, two other titanocanes with the benzyl group at the nitrogen atom (**15** and **17**) are monomeric in $CDCl_3$ solution at room temperature. This conclusion is based on the presence of one signal of the OCH_2 group and one signal of the NCH_2 group for the C atoms of the ocane skeleton of these compounds. Thus, these species (**15** and **17**) possess monomeric structures with trigonal-bipyramidal coordination environments of the titanium atom. These compounds may undergo exchange processes in solution (the exchange between equatorial and axial alkoxy groups).[44] Thus, the drastic difference in ^1H NMR spectra of **15** (OCH protons of the isoproxy group represent one broad singlet) and **17** (OCH protons of two menthoxy groups represent two spaced multiplets), to our opinion, resulted from the different dynamic behavior of these compounds in solution. While isopropoxy groups in **15** undergo fast position exchange around the Ti atom, more bulky menthoxy groups in **17** resulted in the rigid structure of the molecule. It should be noted that previously prepared $PhCH_2N(CH_2CMe_2O)_2Ti(OiPr)_2$ demonstrated the same trends in the NMR spectra as compound **15**.[44] The authors concluded that a monomeric structure of $PhCH_2N(CH_2CMe_2O)_2Ti(OiPr)_2$ occurs. This conclusion was also supported by variable temperature NMR spectroscopy.[44] The structure of diisopropoxytitanocane **14** is close to that of **15** according to the NMR spectroscopic data. In the ^{13}C spectrum of **13** the broadening of each signal is observed, probably because of possible monomer-dimer interconversion in this compound. Thus we can conclude that the steric bulkiness of alkoxy ligands in titanocanes is the determining factor that governs the coordination number in titanocanes.

Spirobititanocanes: Only two spirobititanocanes were reported by the beginning of our investigation, one of them is $[MeN(CH_2CH_2O)_2]_2Ti$ (**29**).[20] Very recently the synthesis of $[PhCH_2N(CH_2CMe_2O)_2]_2Ti$ from the reaction of $Ti(OiPr)_4$ with two equivalents of corresponding dialkanolamine was reported.[44] For synthesis of **29** the treatment of two equivalents of dialkanolamine **2** with $Ti(OiPr)_4$ or freshly prepared α-titanic acid was used. The structure of **29** was confirmed by X-ray diffraction, this species is monomeric in the solid state. The coordination polyhedron of the Ti atom represents a distorted octahedral geometry with two nitrogen atoms in a *cis* orientation (Scheme 3).[20] We have very recently found an analogous situation in spirobigermocanes. Both $[PhN(CH_2CH_2O)_2]_2Ge$ and $[MeN(CH_2CH_2O)(CH_2CHPhO)]_2Ge$ possess the structure of the *cis* isomer.[34] The bishomoleptic titanium derivative, $\{S[(3\text{-}tBu\text{-}5\text{-}MeC_6H_2)\text{-}2\text{-}O]_2\}_2Ti$, has an analogous structure.[47] Lavanant et al. supposed that the monomeric structure is present in solution for $[PhCH_2N(CH_2CMe_2O)_2]_2Ti$.[44]



Scheme 3.

The closely related spiro-bishomoleptic or spiro-bisheteroleptic complexes of titanium were prepared by Tshuva et al. by the reaction of $nPrN(CH_2\text{-}o\text{-}ArOH)_2$ or $RN(CH_2\text{-}o\text{-}Ar'OH)_2$ (R = *n*Pr or $CH_2CH_2NMe_2$) with $Ti(OiPr)_4$ lead-



	R	R^1	R^2	R^3
18	Ph	H	H	H
19	$PhCH_2$	H	H	H
20	Me	H	Ph	H
21	Me	H	Me	H
22	Me	H	Et	H
23	Me	H	Ph	Ph

	R	R^1	R^2	R^3	
24	Me	Ph	Ph	H	*erythro*
25	Me	Ph	Ph	H	*threo*
26	Me	$(CH_2)_3$		H	
27	Me	$(CH_2)_4$		H	
28	Me	$C_6H_4CH_2$		H	

$TiCl_4 \cdot 2\ THF$ —(2 $PhCH_2N(CH_2CH_2OH)_2$ (**3**) / 4 Et_3N; – 4 $Et_3N \cdot HCl$, – 2 THF)→ **19**

$Ti(CH_2Ph)_4$ —(2 $RN(CH_2CH_2OH)CHR^1CR^2R^3OH$, **3, 7**; – 4 $PhCH_3$)→ **19** or **23**

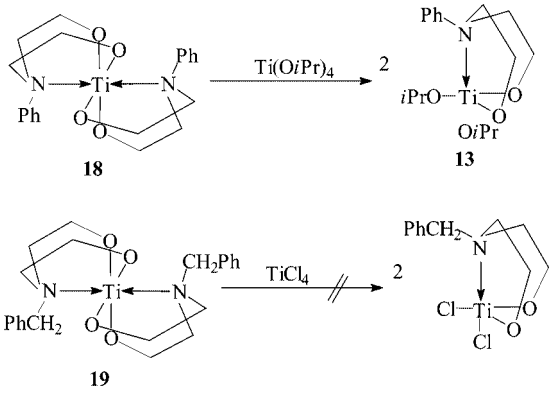
Scheme 4.

ing to [*n*PrN(CH$_2$-*o*-ArO)$_2$]$_2$Ti or [*n*PrN(CH$_2$-*o*-ArO)$_2$]Ti[(O-*o*-Ar′-CH$_2$)$_2$NR], respectively.[27] Three complexes were studied by X-ray diffraction and showed the structure of *trans*-isomer **A** (Scheme 3). The authors noted that the bulky substituents in the Ar groups prevent the formation of spiro-bishomoleptic species and the reaction stops at the titanocanes.[27] An analogous result in Zr chemistry has been found by Mountford and coworkers.[33] A very interesting result was found by Lavanant et al. for Zr derivatives of two dialkanolamines: [PhCH$_2$N(CH$_2$CMe$_2$O)$_2$]$_2$Zr and [PhCH$_2$N(CH$_2$C-*p*-Tol$_2$O)$_2$]$_2$Zr.[44] According to the NMR spectroscopic data both spirobizirconocanes are monomeric in solution while the X-ray diffraction study of [PhCH$_2$N(CH$_2$CMe$_2$O)$_2$]$_2$Zr showed the dimeric structure of this compound in the solid state resulting from the rupture of three of the four Zr–N bonds into two monomeric units.[44] Thus, one can conclude that the structure of the ligand is the main factor governing the coordination environment around the metal atom in spirobiocanes.

In order to clarify the structure of the ligand influence we explored the synthesis and structures of the number of novel spirobititanocanes. The compounds **18**–**28** were obtained in high yields from the reaction of Ti(O*i*Pr)$_4$ with two equivalents of corresponding dialkanolamines **1**, **3**–**12** at reflux in toluene (Scheme 4). Compound **19** was also prepared in 33% yield from the treatment of TiCl$_4$·(THF)$_2$ with **3** in the presence of Et$_3$N or in quantitative yield from the reaction of Ti(CH$_2$Ph)$_4$ with two equivalents of **3** (Scheme 4). The latter approach was also used for the synthesis of **23**.

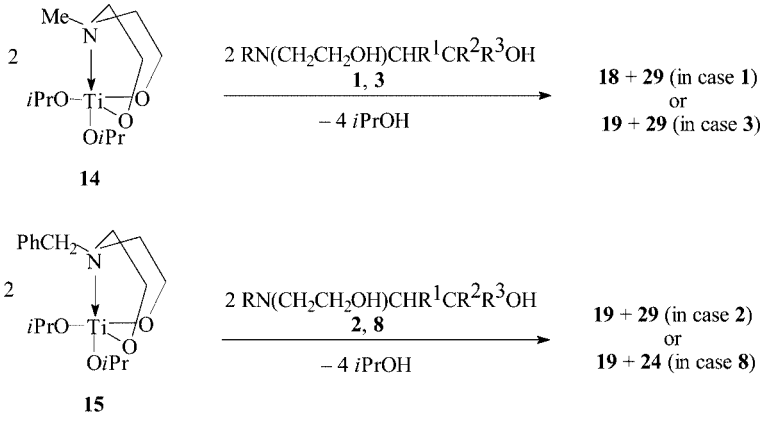
We also tried to prepare spiro-bisheteroleptic ocanes (Scheme 5), but in all of the studied cases equimolar mixtures of spiro-bishomoleptic ocanes were obtained (NMR spectroscopic data). This result contradicts that previously found for bis(aminophenol)-type ligands, where the bisheteroleptic species are stable.[27] We suppose that, on the one hand, the symmetric bis(ocanes) are more thermodynamically stable in the case of dialkanolamine type ligands. On the other hand, the unsymmetric bis(ocanes) are probably formed in the course of the reactions, but because of their higher flexibility in comparison with that for phenolic species[27] a mixture of symmetric compounds forms through a metathetical process.

One dialkanolamine ligand in spirobititanocane **18** can easily be exchanged by the treatment with equimolar amounts of Ti(O*i*Pr)$_4$ (Scheme 6). The reaction of **19** with one equivalent of TiCl$_4$ resulted in a mixture of unidentified products (Scheme 6).



Scheme 6.

According to the NMR spectroscopic data, spirobititanocane **19** possesses a monomeric structure in solution ($CDCl_3$) and exists as one isomer (Scheme 3). It should be noted that in the *trans* and *cis* isomers of **19** the two dialkanolamine groups are equivalent. Thus, in theory it is impossible to define what kind of isomer exists in $CDCl_3$ solution, but we can conclude that only one isomer is present under these conditions. We believe that spirobititanocane **18** is also monomeric in solution, but the broadening of



	R	R^1	R^2	R^3	
18	Ph	H	H	H	
19	$PhCH_2$	H	H	H	
24	Me	Ph	Ph	H	*erythro*
29	Me	H	H	H	

Scheme 5.

signals was found for its NMR spectra (like in closely related titanocane **13**). This indicates the presence of dynamic processes in solution of **18**, such as Berry pseudorotation, *cis-trans* isomerization and/or N–Ti bond dissociation. Although different sets of signals should be present in the ^{13}C NMR spectra of the *trans* and *cis* isomers for compound **20**–**28**, it is very difficult to determine unambiguously the type of isomer in this case because of the presence of several diastereomers of these compounds in solution resulting from the asymmetric carbon atoms. However, the importance of the synthesis of compounds with asymmetric car-

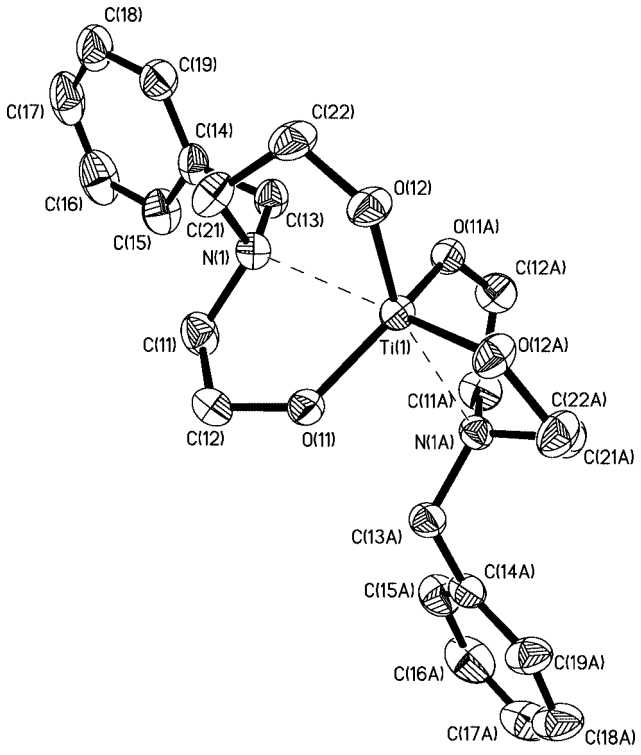


Figure 2. Molecular structure of **19** (one independent molecule). Hydrogen atoms are omitted for clarity.

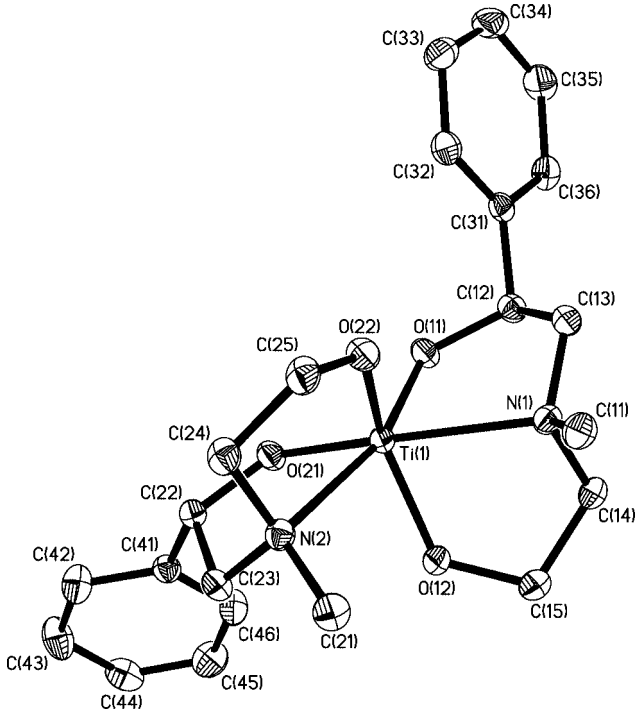


Figure 3. Molecular structure of **20**. Hydrogen atoms and solvate toluene molecules are omitted for clarity.

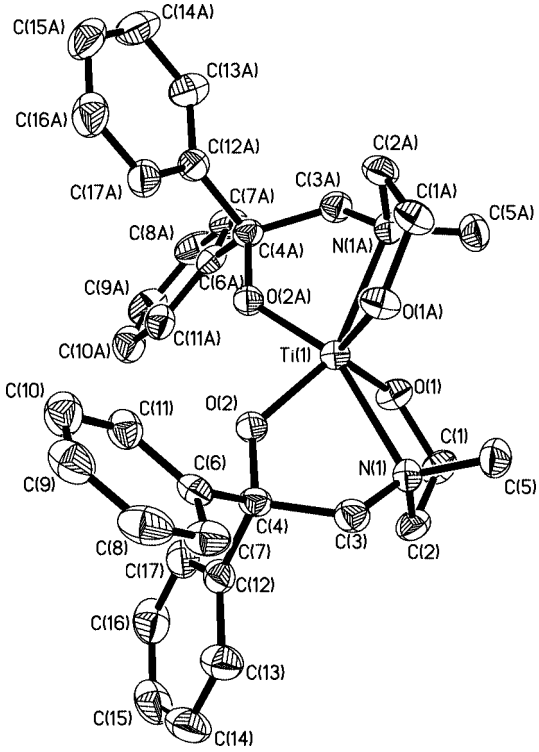


Figure 4. Molecular structure of **23**. Hydrogen atoms and solvate dichloromethane molecules are omitted for clarity.

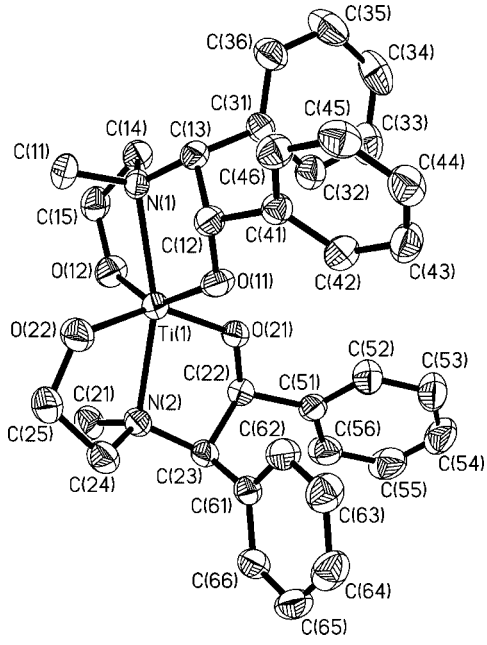


Figure 5. Molecular structure of **24**. Hydrogen atoms and solvate toluene molecules are omitted for clarity.

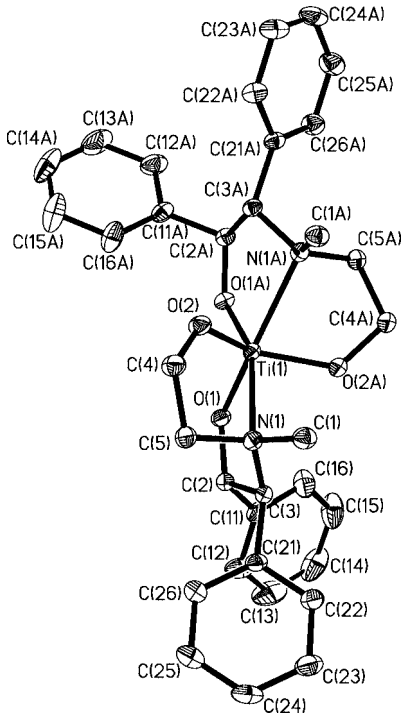


Figure 6. Molecular structure of **25**. Hydrogen atoms and solvate dichloromethane molecules are omitted for clarity.

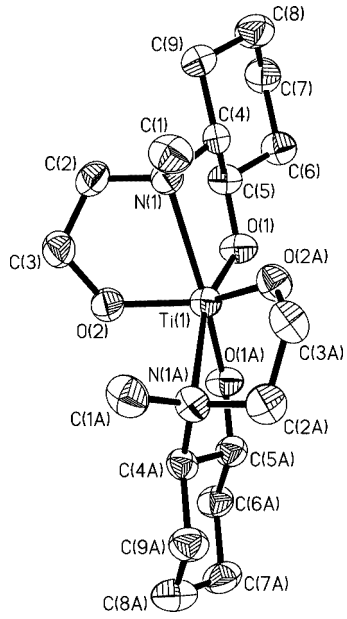


Figure 7. Molecular structure of **27**. Hydrogen atoms are omitted for clarity.

bon atoms is connected with the usefulness of these derivatives in catalytic processes.

The structures of six spirobititanocanes **19**, **20**, **23**, **24**, **25**, **27** were studied by X-ray diffraction. The monomeric nature of all the studied species with a hexacoordinate titanium center was confirmed. The coordination polyhedron of the titanium atom in these compounds represents a distorted octahedron. The molecular structures of **19** (one independent molecule), **20**, **23**, **24**, **25**, and **27** are shown in Figure 2, Figure 3, Figure 4, Figure 5, Figure 6, and Figure 7, respectively. Table 2 and Table 3 list selected geometrical parameters for these compounds.

Table 3. Selected bond lengths [Å] and angles [°] for **24**.

Ti(1)–N(1)	2.339(2)	O(12)–Ti(1)–O(21)	95.6(1)
Ti(1)–N(2)	2.310(2)	O(22)–Ti(1)–O(21)	146.1(1)
Ti(1)–O(11)	1.878(2)	O(11)–Ti(1)–O(21)	86.41(9)
Ti(1)–O(12)	1.864(2)	O(12)–Ti(1)–N(1)	74.34(9)
Ti(1)–O(21)	1.883(2)	O(22)–Ti(1)–N(1)	93.17(9)
Ti(1)–O(22)	1.873(2)	O(11)–Ti(1)–N(1)	74.39(8)
O(12)–Ti(1)–O(22)	102.1(1)	O(21)–Ti(1)–N(1)	119.57(8)
O(12)–Ti(1)–O(11)	145.0(1)	N(2)–Ti(1)–N(1)	162.91(8)
O(22)–Ti(1)–O(11)	95.0(1)		

The compounds **19**, **20**, **23**, **25**, and **27** exhibit a *cis* disposition of the two nitrogen atoms at the Ti atom. An analogous structure was previously found in **29**.[20] On the contrary, the nitrogen atoms in **24** occupy the *trans* positions in an octahedral environment of the Ti atom. This type of

Table 2. Selected bond lengths [Å] and angles [°] for **19**, **20**, **23**, **25**, **27**.

	19		**20**	**23**	**25**	**27**
Ti–N	2.451(2)	2.467(2)	2.352(2) 2.367(2)	2.357(2)	2.363(2)	2.471(3)
Ti–$O_{trans\ to\ N}$	1.839(2)	1.830(2)	1.855(2) 1.862(2)	1.865(1)	1.872(2)	1.849(2)
Ti–$O_{trans\ to\ O}$	1.852(2)	1.844(2)	1.875(2) 1.885(2)	1.859(1)	1.867(2)	1.845(3)
N(1)–Ti–O	73.40(7) 75.87(7) 83.15(7) 163.61(7)	74.55(9) 75.52(8) 81.94(8) 164.91(8)	75.66(7) 75.88(7) 82.31(7) 163.95(7)	73.68(5) 75.46(6) 82.34(6) 154.98(5)	74.55(6) 75.12(7) 82.15(7) 158.18(7)	74.1(1) 75.2(1) 81.7(1) 161.9(1)
N–Ti–N	118.1(1)	117.8(1)	117.58(7)	129.69(8)	125.37(9)	120.5(1)
O–Ti–O	91.9(1) 101.50(8) 110.35(8) 133.7(1)	92.4(1) 101.9(1) 109.8(1) 133.7(1)	92.38(7) 98.95(7) 99.17(7) 110.72(7) 111.40(7) 136.17(8)	85.33(8) 102.89(6) 116.23(6) 126.24(9)	87.68(9) 101.81(7) 114.44(7) 129.2(1)	91.2(2) 101.4(1) 113.3(1) 130.0(2)

structure is considered to be *trans*-isomer **B** (Scheme 3). To the best of our knowledge, compound **24** is the first example of such a structure; however, a similar *trans* disposition of the nitrogen atoms in TiO_4N_2 was previously found.[48]

The Ti–N distances in **19**, **20**, **23**, **24**, **25**, and **27** vary over the range 2.310(2)–2.471(3) Å, the shortest distance being found in compound **24** (*trans* disposition of N atoms). These values are close to that previously found for **29** [2.422(2) Å].[20] The substitution of hydrogen atoms (**19**, **29**) of the ocane skeleton for phenyl groups (**20**, **23**, **24**, **25**) shortens the Ti–N bond, while the substitution with alkyl groups (**27**) slightly elongates this distance. In general, the Ti–N distances in phenolic compounds [*n*PrN(CH_2-*o*-ArO)$_2$]-Ti[(O-*o*-Ar′CH_2)$_2$NR] [2.248(2)–2.308(4) Å][27] are shorter than those in **19**, **20**, **23**, **24**, **25**, **27**, and **29** based on dialkanolamine-type ligands. This difference is probably explained by the higher polarity of the Ti–O bonds in phenolic species, which leads to depletion of electron density at the titanium center. A similar tendency was found for Ti–O bonds in hexacoordinate compounds discussed above. In general, the shorter Ti–N bonds in the molecules correspond to longer Ti–O bonds. This tendency is also supported by the fact that Ti–O bonds in the only X-ray studied monomeric tetraalkoxy titanium derivative with a tetracoordinate Ti atom [1.752(2)–1.825(2) Å][49] are considerably shorter than those in the hexacoordinate compounds.

All five-membered unsubstituted rings of the ocane skeletons in **19**, **20**, **23**, **24**, **25**, and **27** adopt an "envelope"-like conformation, all carbon atoms in the α positions to the N atom occupy "flap" sites. In the case of substituted rings their conformation may be treated as an "envelope" with α-C atoms in "flap" sites (**20**, **23**, and **25**) or a "twist" (**24** and **27**).

Conclusion

We have found that tetraisopropoxytitanium or cyclopentadienyltrimethoxytitanium react with one equivalent of dialkanolamines **1**–**3** leading to the formation of the corresponding dialkoxytitanocanes **13**–**16**. The substitution reaction of diisopropoxy derivative **15** with L-(–)-menthol easily occurs to give dimenthoxytitanocane **17**. The nature of the alkoxy substituent at the Ti atom strongly affects the structure and dynamic behavior of **13**–**17** in solution. The reaction of Ti(O*i*Pr)$_4$ with two equivalents of dialkanolamines **1**, **3**–**12** led to the corresponding spirobititanocanes **18**–**28** with a hexacoordinate Ti atom. The structure of latter compounds is governed by the nature of the ligands: depending on the substituents in the ocane skeleton the nitrogen atoms occupy *cis* or *trans* positions around the Ti atom. Spirobititanocane **18** is easily converted into the corresponding titanocane **13** by its reaction with one equivalent of Ti(O*i*Pr)$_4$. The reaction of titanocanes **14** and **15** with the different dialkanolamines (**1**, **3** and **2**, **8**, respectively) did not give the expected bisheteroleptic compounds but resulted in a mixture of bishomoleptic titanocanes **18** and **29**, **19** and **29** and **19** and **29**, **19** and **24**, respectively.

Experimental Section

General Remarks: All manipulations were performed under a dry, oxygen-free argon atmosphere using standard Schlenk techniques. Solvents were dried by standard methods and distilled prior to use. PhN(CH_2CH_2OH)$_2$ (**1**), MeNHCH_2CH_2OH (Aldrich) and (1*R*,2*S*,5*R*)-menthol (Acros) were used as supplied. HN($SiMe_3$)$_2$ (Aldrich), Ti(O*i*Pr)$_4$ (Aldrich), and $TiCl_4$ (Aldrich) were distilled before use. CpTi(OMe)$_3$,[50] $TiCl_4$(THF)$_2$,[51] Ti(CH_2Ph)$_4$,[52] MeN(CH_2CH_2OH)$_2$ (**2**),[53] PhCH_2N(CH_2CH_2OH)$_2$ (**3**),[54] MeN(CH_2CH_2OH)CH_2CH(Ph)OH (**4a**) and MeN(CH_2CH_2OH)-CH(Ph)CH_2OH (**4b**) as a mixture 9:1,[34] MeN(CH_2CH_2OH)-CH_2CH(Me)OH (**5**),[55] and MeN(CH_2CH_2OH)CH_2CH(Et)OH (**6**)[55] were prepared according to the literature. $^{13}C\{^1H\}$ NMR spectrum for **5**: δ = 20.17 (Me), 42.42 (MeN), 59.21, 59.73 (2 NCH_2 groups), 63.65, 65.52 (OCH_2 and OCH groups) ppm. $^{13}C\{^1H\}$ NMR spectrum for **6**: δ = 9.86 (CH_2CH_3), 27.71 (CH_2CH_3), 42.48 (NCH_3), 59.30, 59.75 (NCH_2), 63.77, 68.91 (OCH and OCH_2) ppm. PhCH_2N($CH_2CH_2OSiMe_3$)$_2$[43] and MeN(CH_2-CH_2OSn-*n*Bu$_3$)$_2$[38] were prepared according to the method reported previously. PhCH_2N($CH_2CH_2OSiMe_3$)$_2$: B.p. = 126–129 °C (0.7 Torr). NMR spectra: ^1H NMR: δ = 0.07 (s, 18 H, $SiMe_3$), 2.67 (t, 4 H, NCH_2), 3.61 (t, 4 H, OCH_2), 3.69 (s, 4 H, PhCH_2N), 7.18–7.32 (m, 5 H, C_6H_5) ppm. $^{13}C\{^1H\}$ NMR: δ = –0.54 ($SiMe_3$), 56.66 (NCH_2), 60.07 (OCH_2), 61.17 (PhCH_2), 126.83, 128.13, 128.78, 139.83 (aromatic carbons) ppm. MeN(CH_2CH_2OSn-*n*Bu$_3$)$_2$: NMR spectra: ^1H NMR: δ = 0.95–0.82 (m, 18 H, CH_2CH_3), 1.14–0.98 (m, 12 H, CH_2CH_3), 1.33–1.26 (m, 12 H, $SnCH_2CH_2$), 1.57–1.49 (m, 12 H, $SnCH_2$), 2.24 (s, 3 H, NCH_3), 2.47 (t, 4 H, NCH_2), 3.74 (t, 4 H, OCH_2) ppm. $^{13}C\{^1H\}$ NMR: δ = 13.61 (CH_2CH_3), 14.55 (CH_2CH_3), 27.16 ($SnCH_2CH_2$), 27.95 ($SnCH_2$), 43.83 (NCH_3), 62.65 (NCH_2), 64.04 (OCH_2) ppm.

A solution of *n*-butyllithium in hexane was obtained and analyzed by the Gilman double-titration method.[56] $CDCl_3$ was obtained from Deutero GmbH and dried with P_4O_{10}. ^1H NMR (300 MHz) and ^{13}C NMR (75 MHz) spectra were recorded with a Bruker–Evance spectrometer (in $CDCl_3$ at 295 K unless otherwise stated). Chemical shifts in the ^1H and ^{13}C NMR spectra are given in ppm relative to internal Me_4Si. Elemental analyses were carried out by the Microanalytical Laboratory of the Chemistry Department of the Moscow State University.

MeN(CH_2CH_2OH)CH_2C(Ph)$_2$OH (7): A mixture of *N*-methylethanolamine (1.15 g, 15 mmol) and 2,2-diphenyloxyrane (3.00 g, 15 mmol) was heated at 90 °C for 35 h. The resulting dense yellow oil was crystallized from the mixture diethyl ether/hexane (1:1) at –20 °C to give **7** as a white crystalline solid [3.14 g, 77%; 109–110 °C (110–111 °C[46])]. NMR spectra: ^1H NMR: δ = 2.12 (s, 3 H, NCH_3), 2.61 (t, 2 H, NCH_2), 3.36 (s, 2 H, NCH_2), 3.56 (t, 2 H, OCH_2), 7.16–7.20, 7.26–7.31, 7.46–7.49 (3 m, 10 H, 2 C_6H_5) ppm, the signal from the OH groups was not observed. $^{13}C\{^1H\}$ NMR: δ = 44.15 (NCH_3), 59.86, 61.27, 67.76 (2 NCH_2 and OCH_2 groups), 75.60 [C(C_6H_5)$_2$], 125.79, 126.73, 128.15, 146.55 (C_6H_5) ppm.

***erythro*-MeN(CH_2CH_2OH)CH(Ph)CH(Ph)OH (8):** A mixture of *N*-methylethanolamine (2.0 mL, 25 mmol) and *trans*-stilbene oxide (4.91 g, 25 mmol) was heated at 130 °C for 22 h. The resulting dense orange oil was crystallized from the mixture of diethyl ether/hexane (1:1) at –20 °C to give **8** as a light yellow crystalline solid (6.20 g, 91%; 90–91 °C). NMR spectra: ^1H NMR: δ = 1.98 (br. s, 2 H, 2 OH), 2.13 (s, 3 H, NCH_3), 2.38–2.51 (m, 2 H, NCH_2), 3.30–3.40 (m, 2 H, OCH_2), 3.71 (d, 1 H, NCH), 5.22 (d, 1 H, OCH), 7.23–7.37 (m, 10 H, 2 C_6H_5) ppm. $^{13}C\{^1H\}$ NMR: δ = 37.36 (NCH_3), 56.78 (NCH_2), 57.97 (OCH_2), 72.98 (NCH), 74.63 (OCH), 126.58, 127.89, 127.92, 128.30, 129.51, 134.85, 142.19 (C_6H_5).

$C_{17}H_{21}NO_2$ (271.35): calcd. C 75.25, H 7.80, N 5.16; found C 75.33, H 7.82, N 5.32 ppm.

***threo*-MeN(CH$_2$CH$_2$OH)CH(Ph)CH(Ph)OH (9):** Analogously to **8**, dialkanolamine **9** was obtained from *N*-methylethanolamine (0.82 mL, 10 mmol) and *cis*-stilbene oxide (1.96 g, 10 mmol) as a light yellow crystalline solid (2.26 g, 83%; 88–89 °C). NMR spectra: ^{1}H NMR: δ = 2.27 (s, 3 H, NCH_3), 2.42–2.49 (m, 1 H), 2.69–2.76 (m, 1 H) (NCH_2), 3.65–3.78 (m, 2 H, OCH_2), 3.69 (d, 1 H, NCH), 5.05 (d, 1 H, OCH), 7.05–7.15, 7.18–7.23 (2 m, 10 H, 2 C_6H_5) ppm, the signal of OH groups was not observed. ^{13}C{^{1}H} NMR: δ = 37.37 (NCH_3), 55.39 (NCH_2), 59.51 (OCH_2), 71.49 (NCH), 75.24 (OCH), 127.33, 127.39, 127.68, 127.89, 127.92, 129.77, 133.36, 141.10 (C_6H_5) ppm. $C_{17}H_{21}NO_2$ (271.35): calcd. C 75.25, H 7.80, N 5.16; found C 75.39, H 7.86, N 5.25.

MeN(CH$_2$CH$_2$OH)CH(C$_3$H$_6$)CHOH (10): A mixture of *N*-methylethanolamine (2.95 g, 40 mmol) and cyclopentene oxide (3.36 g, 40 mmol) was stirred at 85 °C for 20 h. The distillation of the reaction mixture gave **10** as a viscous light-yellow liquid [5.29 g, 91%; 105–106 °C (0.2 Torr)]. NMR spectra: ^{1}H NMR: δ = 1.93–1.35 (m, 6 H, cyclopentane 3CH_2), 2.25 (s, 3 H, NCH_3), 2.59 (m, 2 H, NCH_2), 2.74–2.81 (m, 1 H, NCH), 3.52–3.65 (m, 2 H, OCH_2), 3.76 (br. s, 2 H, OH), 3.99–4.06 (m, 1 H, OCH) ppm. ^{13}C{^{1}H} NMR: δ = 20.72, 24.39, 33.15 (cyclopentane carbons CH_2), 38.64 (NCH_3), 56.20 (NCH_2), 58.57 (OCH_2), 73.34 (NCH), 74.41 (OCH) ppm. $C_8H_{17}NO_2$ (159.23): calcd. C 60.35, H 10.76, N 8.80; found C 59.98, H 10.63, N 9.20.

MeN(CH$_2$CH$_2$OH)CH(C$_4$H$_8$)CHOH (11): A mixture of *N*-methylethanolamine (13.2 mL, 0.165 mol) and cyclohexene oxide (15.2 mL, 0.15 mol) was heated at 100 °C for 48 h. The distillation of the reaction mixture gave **11** as a viscous colorless liquid [22.89 g, 88%; 105–107 °C (0.2 Torr)]. NMR spectra: ^{1}H NMR: δ = 0.99–1.24, 1.59–1.69, 1.96–2.03 (3 m, 8 H, cyclohexane, 4 CH_2), 2.19 (s, 3 H, NCH_3), 2.14–2.22, 2.36–2.44, 2.58–2.67, 3.27–3.35, 3.48–3.59 (5 m, 6 H, NCH_2, OCH_2, NCH, OCH), 3.75 (br. s, 2 H, 2 OH) ppm. ^{13}C{^{1}H} NMR: δ = 21.82, 24.12, 25.20, 33.38 (cyclohexane carbons CH_2), 36.68 (NCH_3), 54.98 (NCH_2), 59.42 (OCH_2), 69.25, 69.42 (NCH, OCH) ppm. $C_9H_{19}NO_2$ (173.25): calcd. C 62.39, H 11.05, N 8.08; found C 61.99, H 11.07, N 8.42.

MeN(CH$_2$CH$_2$OH)CH(C$_6$H$_4$CH$_2$)CHOH (12): Analogously to **8** (except only diethyl ether was used for recrystallization), dialkanolamine **12** was obtained from *N*-methylethanolamine (2.30 g, 30 mmol) and indene oxide (3.96 g, 30 mmol) as a light-yellow crystalline solid (5.82 g, 94%; 75–76 °C). NMR spectra: ^{1}H NMR: δ = 2.44 (s, 3 H, NCH_3), 2.82–2.95, 3.26–3.34 [2 m, 2 H, CH_2C(OH) H], 2.88–2.95 (m, 2 H, NCH_2), 3.19 (br. s, 2 H, 2 OH), 3.66–3.79 (m, 2 H, OCH_2), 4.29 (d, 1 H, NCH), 4.66 (q, 1 H, OCH), 7.23–7.35 (m, 4 H, aromatic protons) ppm. ^{13}C{^{1}H} NMR: δ = 37.34 ($CHCH_2$), 39.68 (NCH_3), 55.87 (NCH_2), 58.44 (NCH), 73.75 (OCH_2), 113.46 (OCH), 125.06, 125.08, 126.79, 127.94, 140.00, 140.10 (aromatic carbons) ppm.

PhN(CH$_2$CH$_2$O)$_2$Ti(O*i*Pr)$_2$ (13): A mixture of alkanolamine **1** (2.00 g, 11.0 mmol), Ti(O*i*Pr)$_4$ (3.14 g, 11.0 mmol), and chloroform (20 mL) was refluxed for 8 h, and all volatiles were removed under reduced pressure. Hexane (20 mL) was added to a yellow, waxy solid. The solution was filtered and the solvent removed under reduced pressure to give **13** as a yellow solid (3.05 g, 80%). NMR spectra: ^{1}H NMR: δ = 1.19 (br. s, 12 H, CH_3), 3.47 (br. s, 4 H, NCH_2), 4.30–4.90 (br. m, 6 H, OCH_2, OCH), 6.53–6.70, 7.07–7.19 (2 m, 5 H, C_6H_5) ppm. ^{13}C{^{1}H} NMR (323 K): δ = 26.24 (CH_3), 55.21 (broad, NCH_2), 73.22 (broad, OCH_2), 77.44 (OCH), 113.38, 116.58, 130.05, 149.41 (broad, C_6H_5) ppm. Satisfactory results for the elemental analyses were unobtainable because of the presence of traces of **18**.

MeN(CH$_2$CH$_2$O)$_2$Ti(O*i*Pr)$_2$ (14): A mixture of alkanolamine **2** (2.14 g, 18.0 mmol), Ti(O*i*Pr)$_4$ (5.11 g, 18.0 mmol), and chloroform (20 mL) was refluxed for 7 h, all volatiles were removed under reduced pressure. The residue was dissolved in hexane (20 mL), the solution was filtered and stored at –30 °C for 18 h to give an oil under a supernatant solution. The solvent was removed through a cannula and **14** was obtained as a colorless oil (4.53 g, 89%). NMR spectra: ^{1}H NMR: δ = 1.07 (d, 12 H, CHCH_3), 2.48 (s, 3 H, NCH_3), 2.80 (br. s, 4 H, NCH_2), 4.20 (br. s, 4 H, OCH_2), 4.48 (br. s, 2 H, OCH) ppm. ^{13}C{^{1}H} NMR: δ = 25.70 (CHCH_3), 44.38 (NCH_3), 59.50 (NCH_2), 69.20 (OCH_2), 76.30 (OCH) ppm. Satisfactory results for the elemental analyses were unobtainable because of the presence of traces of **29**.

PhCH$_2$N(CH$_2$CH$_2$O)$_2$Ti(O*i*Pr)$_2$ (15): The procedure was the same as for **14** except that Ti(O*i*Pr)$_4$ (3.70 g, 13.0 mmol) was treated with alkanolamine **3** (2.50 g, 13.0 mmol) in toluene. The compound **15** was obtained as a white oil (4.30 g, 92%). NMR spectra: ^{1}H NMR: δ = 1.26 (d, 12 H, CHCH_3), 2.93 (br. s, 4 H, NCH_2), 4.19 (s, 2 H, $PhCH_2$), 4.39 (br. s, 4 H, OCH_2), 4.66 (br. s, 2 H, OCH), 7.23–7.34 (m, 5 H, C_6H_5) ppm. ^{13}C{^{1}H} NMR: δ = 26.11 (CHCH_3), 54.21 (NCH_2), 58.01 ($PhCH_2$), 69.43 (OCH_2), 76.53 (OCH), 128.01, 128.30, 131.01, 133.74 (C_6H_5) ppm. $C_{17}H_{29}NO_4Ti$ (359.28): calcd. C 56.51, H 7.98, N 3.72; found C 56.83, H 8.14, N, 3.90.

Reaction of PhCH$_2$N(CH$_2$CH$_2$OSiMe$_3$)$_2$ with TiCl$_4$(THF)$_2$: $PhCH_2N(CH_2CH_2OSiMe_3)_2$ (0.95 g, 2.8 mmol) was added dropwise to a suspension of $TiCl_4(THF)_2$ (0.94 g, 2.8 mmol) in toluene (15 mL). The reaction mixture was refluxed for 14 h, and then filtered off to give a yellow solid, which was insoluble in the usual organic solvents. According to NMR spectroscopic data in $(CD_3)_2$-SO, a mixture of unidentified compounds formed.

Reaction of MeN(CH$_2$CH$_2$OSn-*n*Bu$_3$)$_2$ with Cp$_2$TiCl$_2$: $MeN(CH_2CH_2OSn\text{-}nBu_3)_2$ (2.35 g, 3.4 mmol) was added dropwise to a solution of Cp_2TiCl_2 (0.60 g, 2.4 mmol) in $CHCl_3$ (65 mL). The reaction mixture was stirred for 10 h, then all volatiles were removed under reduced pressure. According to NMR spectroscopic data of the residue a mixture of CpSn-*n*Bu$_3$ with unidentified compounds formed.

[PhCH$_2$N(CH$_2$CH$_2$O)$_2$Ti(OMe)$_2$]$_2$ (16): A solution of alkanolamine **3** (0.71 g, 3.6 mmol) in THF (10 mL) was added dropwise at –50 °C to a solution of $CpTi(OMe)_3$ (0.75 g, 3.6 mmol) in THF (20 mL). The mixture was warmed to room temperature and stirred overnight. The solid that formed was filtered off and recrystallized from the mixture of dichloromethane/heptane (1:1) to give **16** as white microcrystals (0.84 g, 77%). NMR spectra: ^{1}H NMR: δ = 2.85–2.90, 3.05–3.10 (2 br. m, 4 H, NCH_2), 4.17, 4.22 (2 s, 6 H, OCH_3), 4.43 (br. s, 2 H, $PhCH_2$), 4.28–4.36, 4.57–4.63 (2 br. m, 4 H, OCH_2), 7.25–7.36 (m, 5 H, C_6H_5) ppm. ^{13}C{^{1}H} NMR: δ = 54.22 (NCH_2), 55.70 ($PhCH_2$), 60.46, 64.74 (OCH_3), 68.82 (OCH_2), 127.88, 128.22, 131.47, 134.01 (C_6H_5) ppm. Satisfactory results for the elemental analyses were unobtainable because of the presence of traces of **19**.

PhCH$_2$N(CH$_2$CH$_2$O)$_2$Ti(OMenth)$_2$ (17): L-(–)-Menthol (1.56 g, 10 mmol) was added to a stirred solution of the compound **15** (1.80 g, 5.0 mmol) in chloroform (30 mL) at room temperature. The reaction mixture was refluxed for 6 h, all volatiles were removed under reduced pressure. Hexane (20 mL) was added to the white oil. The mixture was stored at –30 °C for several days. The solid that formed was filtered off to give **17** as a white powder (2.64 g, 96%). NMR spectra: ^{1}H NMR: δ = 0.76 (d, 3 H, CH_3), 0.82 (br.

d, 6 H, CH_3), 0.85–0.95 (m, 13 H, CH_3, CH_2), 1.01–1.18 (m, 4 H, CH_2), 1.38 (br. s, 2 H, CH), 1.50–1.62 (br. m, 4 H, CH_2), 2.07–2.12, 2.17–2.22 (2 br. m, 2 H, CH), 2.33–2.48 (br. m, 2 H, CH), 2.84, 3.00 (2 br. s, 4 H, NCH_2), 3.83–3.90, 4.05–4.14 (2 m, 2 H, OCH), 4.16 (br. s, 2 H, $PhCH_2$), 4.33, 4.46 (2 br. s, 4 H, OCH_2), 7.26–7.37 (m, 5 H, C_6H_5) ppm. $^{13}C\{^1H\}$ NMR: δ = 15.78, 21.20, 22.25 (CH_3), 22.70 (CH_2), 25.45, 31.65 (CH), 34.63, 46.51 (CH_2), 50.98 (CH), 54.22 (broad, NCH_2), 57.84 ($PhCH_2$), 69.37 (OCH_2), 84.14, 85.01 (OCH), 128.05, 128.36, 131.10, 133.89 (C_6H_5) ppm. Satisfactory results for the elemental analyses were unobtainable because of the presence of traces of **19**.

[PhN(CH$_2$CH$_2$O)$_2$]$_2$Ti (18): A mixture of alkanolamine **1** (0.83 g, 4.6 mmol), Ti(O*i*Pr)$_4$ (0.65 g, 2.3 mmol), and toluene (15 mL) was refluxed for 13 h, and all volatiles were removed under reduced pressure. The residue was recrystallized from toluene to give **18** as a yellow solid (0.77 g, 82%). NMR spectra: ^1H NMR: δ = 3.41 (br. s, 8 H, NCH_2), 4.17 (br. s, 8 H, OCH_2), 6.58–6.70, 7.13–7.26 (m, 10 H, C_6H_5) ppm $^{13}C\{^1H\}$ NMR: δ = 56.71 (broad, NCH_2), 73.52 (broad, OCH_2), 112.01, 116.02, 130.46, 148.16 (C_6H_5) ppm. $C_{20}H_{26}N_2O_4Ti$ (406.30): calcd. C 59.12, H 6.45, Ti 11.79; found C 59.46, H 6.44, Ti 11.51.

[PhCH$_2$N(CH$_2$CH$_2$O)$_2$]$_2$Ti (19). Method 1: The procedure was the same as that for **18** except that Ti(O*i*Pr)$_4$ (0.94 g, 3.3 mmol) was treated with alkanolamine **3** (1.29 g, 6.6 mmol). The compound was obtained as white microcrystals (1.22 g, 85%). NMR spectra: ^1H NMR: δ = 3.00 (t, 8 H, NCH_2), 4.11 (s, 4 H, $PhCH_2$), 4.49 (t, 8 H, OCH_2), 7.27–7.38 (m, 10 H, C_6H_5) ppm. $^{13}C\{^1H\}$ NMR: δ = 53.48 (broad, NCH_2), 56.73 ($PhCH_2$), 70.22 (OCH_2), 127.92, 128.29, 130.99, 133.90 (C_6H_5) ppm. $C_{22}H_{30}N_2O_4Ti$ (434.38): calcd. C 60.83, H 6.96, N 6.45; found C 61.01, H 7.10, N 6.59.

Method 2: A solution of alkanolamine **3** (1.10 g, 5.6 mmol) and triethylamine (1.15 g, 11.4 mmol) in THF (30 mL) was added dropwise at –50 °C to a suspension of $TiCl_4(THF)_2$ (0.94 g, 2.8 mmol) in THF (20 mL). The mixture was stirred for 1 h at the same temperature, and was then warmed to room temperature overnight. All volatiles were evaporated under reduced pressure. A white solid was extracted with hot benzene (3 × 20 mL). The solvent was removed under reduced pressure, and the residue was recrystallized from toluene to give **19** as white microcrystals (0.4 g, 33%).

Method 3: A solution of alkanolamine **3** (0.70 g, 3.6 mmol) in toluene (5 mL) was added dropwise to a solution of Ti(CH_2Ph)$_4$ (0.75 g, 1.8 mmol) in toluene (40 mL) at (–40 °C). The reaction mixture was slowly warmed to room temperature and then refluxed for 1 h. The resulting solution was concentrated under vacuum, to give **20** as a white solid (0.78 g, 100%).

[MeN(CH$_2$CH$_2$O)(CH$_2$CHPhO)]$_2$Ti (20): The procedure was the same as that for **18** except that Ti(O*i*Pr)$_4$ (0.77 g, 2.7 mmol) was treated with a mixture of (**4a** and **4b**) (9:1) (1.05 g, 5.4 mmol). The compound **20** was obtained as colorless microcrystals, a mixture of diastereomers. NMR spectra: ^1H NMR: δ = 2.61, 2.64, 2.66 (3 s, 6 H, NCH_3), 2.72–2.85, 2.98–3.25, 3.37–3.54 (3 m, 8 H, NCH_2), 4.26–4.31, 4.57–4.66 (2 m, 4 H, OCH_2), 5.63–5.70, 5.75–5.81 (2 m, 2 H, OCH), 7.13–7.47 (m, 10 H, C_6H_5) ppm. $^{13}C\{^1H\}$ NMR: δ = 42.15, 42.72, 44.18 (NCH_3), 56.23, 59.49 (NCH_2), 69.43 (broad, OCH_2), 80.67, 80.78 (OCH), 124.33, 124.86, 125.55, 126.18, 126.35, 126.93, 127.32, 128.04, 128.24, 143.73, 143.85, 144.18 (C_6H_5) ppm, the signals of several carbons were not found, the signals of solvated toluene are not described. $C_{22}H_{30}N_2O_4Ti$*$PhCH_3$ (526.51): calcd. C 66.16, H 7.27, N 5.32; found C 66.06, H 7.01, N 4.89.

[MeN(CH$_2$CH$_2$O)(CH$_2$CHMeO)]$_2$Ti (21): The procedure was the same as for **18** except that the mixture of alkanolamine **5** (2.40 g, 18.0 mmol) and Ti(O*i*Pr)$_4$ (2.56 g, 9.0 mmol) was refluxed for 15 h in toluene (15 mL). The compound **21** was obtained as a colorless oil (2.67 g, 96%), a mixture of diastereomers. NMR spectra: ^1H NMR: δ = 1.00, 1.02, 1.11 (3 d, 6 H, CH*C*H$_3$), 2.41, 2.43, 2.45 (3 s, 6 H, NCH_3), 2.48–2.53, 2.60–2.81, 3.00–3.24 (3 br. m, 8 H, NCH_2), 4.00–4.09, 4.46–4.51 (2 m, 4 H, OCH_2), 4.70 (br. s, 2 H, OCH) ppm. $^{13}C\{^1H\}$ NMR (323 K): δ = 20.90, 21.05, 21.22 (CH*C*H$_3$), 43.42, 44.27, 44.51 (NCH_3), 58.92, 59.70, 59.91 (NCH_2), 69.57, 69.51 (OCH_2), 74.89, 75.04 (OCH) ppm, the signals of several carbons were not found. $C_{12}H_{26}N_2O_4Ti$ (310.21): calcd. C 46.46, H 8.45, N 9.03; found C 46.20, H 8.56, N 8.94.

[MeN(CH$_2$CH$_2$O)(CH$_2$CHEtO)]$_2$Ti (22): The procedure was the same as for **18** except that alkanolamine **6** (2.97 g, 20 mmol) was treated with Ti(O*i*Pr)$_4$ (2.87 g, 10 mmol) in toluene (15 mL). Compound **22** was obtained as a colorless oil (3.18 g, 94%), a mixture of diastereomers. NMR spectra: ^1H, δ = 0.78–0.81 (m, 6 H, CH_2CH_3), 1.30 (br. s, 4 H, CH_2CH_3), 2.42 (br. s, 6 H, NCH_3), 2.45–2.55, 2.76–2.85, 3.15–3.39 (3 br. m, 8 H, NCH_2), 4.07, 4.48 (2 br. s, 6 H, OCH_2, OCH); $^{13}C\{^1H\}$, δ = 9.08 (broad, CH_2CH_3), 27.67 (broad, CH_2CH_3), 41.93, 43.71 (NCH_3), 59.22, 60.35 (NCH_2), 68.25 (broad, OCH_2), 79.64 (broad, OCH), the signals of several carbons were not found. $C_{14}H_{30}N_2O_4Ti$ (338.27): calcd. C 49.71, H 8.94, N 8.28; found C 49.29, H 8.73, N 8.09.

[MeN(CH$_2$CH$_2$O)(CH$_2$CPh$_2$O)]$_2$Ti (23). Method 1: The procedure was the same as for **18** except that alkanolamine **7** (0.97 g, 3.6 mmol) was treated with Ti(O*i*Pr)$_4$ (0.51 g, 1.8 mmol) in chloroform (10 mL). Compound **23** was obtained as white microcrystals (0.70 g, 90%). NMR spectra: ^1H NMR: δ = 2.42 (br. s, 6 H, NCH_3), 2.84, 2.97 (2 br. s, 4 H, N*C*H$_2$), 3.85, 3.98 (2 d, 4 H, N*C*H$_2$CPh$_2$), 4.35 (br. s, 4 H, OCH_2), 7.10–7.30, 7.50–7.56 (2 m, 20 H, C_6H_5) ppm. $^{13}C\{^1H\}$ NMR: δ = 44.79 (NCH_3), 61.45 (NCH_2), 70.41 (OCH_2), 88.75 (O*C*Ph$_2$), 125.46, 125.51, 126.08, 126.14, 127.98, 128.01, 149.68 (C_6H_5) ppm, the signals of several carbons were not found. $C_{34}H_{38}N_2O_4Ti$ (586.54): calcd. C 69.62, H 6.53, Ti 8.16; found C 69.86, H 6.64, Ti 8.17.

Method 2: Alkanolamine **7** (1.14 g,4.2 mmol) was added to a solution of titanium tetrabenzyl (0.87 g, 2.1 mmol) in toluene (50 mL) at (–40 °C). The reaction mixture was slowly warmed to room temperature and then refluxed for 1 h. The resulting colorless solution was concentrated under vacuum, to give **23** as a white solid (1.23 g, 100%). Crystals, suitable for X-ray analysis, were obtained by recrystallization from the mixture of dichloromethane/*n*-hexane.

***erythro*-[MeN(CH$_2$CH$_2$O)(CHPhCHPhO)]$_2$Ti (24):** The procedure was the same as that for **13** except that alkanolamine **8** (2.17 g, 8.0 mmol) was treated with Ti(O*i*Pr)$_4$ (1.14 g, 4.0 mmol) in chloroform (20 mL). Compound **24** was obtained as colorless microcrystals (1.97 g, 84%), a mixture of diastereomers. NMR spectra: ^1H NMR: δ = 2.57 (br. s, 6 H, NCH_3), 2.96–3.38 (br. m, 4 H, NCH_2), 4.15–4.32 (br. m, 4 H, OCH_2), 4.50–4.59 (br. m, 2 H, NCH), 6.10–6.15, 6.26–6.45 (br. m, 2 H, OCH), 7.05–7.34 (m, 20 H, C_6H_5) ppm. $^{13}C\{^1H\}$ NMR: δ = 42.29, 42.36, 45.82 (NCH_3), 60.63 (broad, NCH_2), 69.72, 70.46 71.48, 71.52 (OCH_2, NCHPh), 86.51 (broad, OCHPh), 125.90, 126.22, 126.43, 126.90, 127.11, 127.27, 127.45, 127.68, 127.84, 131.21, 142.11, 142.77 (C_6H_5) ppm, the signals of several carbons were not found. $C_{34}H_{38}N_2O_4Ti$ (586.54): calcd. C 69.62, H 6.53, Ti 8.16; found C 70.55, H 6.83, N 4.55.

***threo*-[MeN(CH$_2$CH$_2$O)(CHPhCHPhO)]$_2$Ti (25):** The procedure was the same as that for **13** except that the mixture of alkanolamine **9** (2.00 g, 7.4 mmol),Ti(O*i*Pr)$_4$ (1.05 g, 3.7 mmol) and chloroform (20 mL) was refluxed for 16 h. The compound **25** was recrystallized from the mixture of dichloromethane/heptane (4:1) and isolated as colorless microcrystals (1.52 g, 96%), a mixture of diastereomers.

NMR spectra: ^{1}H NMR: δ = 2.42, 2.47, 2.55 (s, 6 H, NCH_3), 2.68–2.79, 3.35–3.48, 3.93–4.05 (m, 4 H, NCH_2), 4.26–4.32, 4.41–4.48 (m, 2 H, NCH), 4.50–4.58, 4.92–4.97 (m, 4 H, OCH_2), 5.94–6.02 (m, 2 H, OCH), 7.00–7.42 (m, 20 H, C_6H_5) ppm. $^{13}C\{^1H\}$ NMR: δ = 38.40, 39.87, 40.20 (NCH_3), 54.10, 56.84 (NCH_2), 69.80, 70.00, 73.09 (NCHPh), 78.84, 79.36 (OCH_2), 84.93, 86.01 (OCH), 126.86, 127.08, 127.37, 127.54, 127.84, 128.14, 128.38, 130.15, 131.01, 131.75, 133.36, 143.45 (C_6H_5) ppm, the signals of several carbons were not found, the signals of solvated dichloromethane are not described. $C_{34}H_{38}N_2O_4Ti{\cdot}CH_2Cl_2$ (671.49): calcd. C 62.60, H 6.00, N 4.17; found C 62.08, H 5.84, N 3.85.

{MeN(CH$_2$CH$_2$O)[CH(CH$_2$)$_3$CHO]}$_2$Ti (26): The procedure was the same as that for **18** except that the mixture of alkanolamine **10** (1.08 g, 6.8 mmol), Ti(O*i*Pr)$_4$ (0.97 g, 3.4 mmol) and toluene (7 mL) was refluxed for 15 h. The compound **26** was obtained as a yellow solid (1.10 g, 89%), a mixture of diastereomers. NMR spectra: ^{1}H NMR: δ = 1.21–1.36, 1.55–1.79 (br. m, 12 H, cyclopentane 6 CH_2), 2.46, 2.49, 2.50 (c, 6 H, NCH_3), 2.41–2.46, 3.01–3.15 (br. s, 6 H, NCH_2, NCH), 4.04–4.08, 4.65–4.72 (m, 4 H, OCH_2), 4.73–4.81 (m, 2 H, OCH) ppm $^{13}C\{^1H\}$ NMR: δ = 16.20, 18.56, 27.34 (broad, CH_2 groups of cyclopentane rings), 40.61, 41.20, 41.53 (NCH_3), 53.59, 53.88 (NCH_2), 71.02, 71.17, 71.38 (OCH_2), 73.50 (broad, NCH), 84.28 (broad, OCH) ppm, the signals of several carbons were not found. $C_{16}H_{30}N_2O_4Ti$ (362.29): calcd. C 53.04, H 8.35, N 7.73; found C 52.12, H 8.11, N 7.53.

{MeN(CH$_2$CH$_2$O)[CH(CH$_2$)$_4$CHO]}$_2$Ti (27): The procedure was the same as that for **18** except that alkanolamine **11** (1.49 g, 8.6 mmol) was treated with Ti(O*i*Pr)$_4$ (1.22 g, 4.3 mmol) in toluene (15 mL). Compound **27** was obtained as colorless microcrystals (1.54 g, 92%), a mixture of diastereomers. NMR spectra: ^{1}H, δ = 1.07–1.15, 1.61–1.68, 1.85–1.91 (br. m, 16 H, cyclopentane 8 CH_2), 2.41 (br. s, 6 H, NCH_3), 2.25–2.37, 2.60–2.90, 3.10–3.14, 3.29–3.36 (br. m, 6 H, NCH, NCH_2), 3.91–4.13, 4.29–4.37 (br. m, 4 H, OCH_2), 4.41–4.63 (br. m, 2 H, OCH); $^{13}C\{^1H\}$, δ = 23.14, 24.57, 24.88, 34.95 (broad, CH_2 groups of cyclohexane ring), 39.61 (NCH_3), 52.38 (NCH_2), 70.34, 73.00 (NCH, OCH_2), 82.90 (broad, OCH), the signals of several carbons were not found. $C_{18}H_{34}N_2O_4Ti$ (390.37): calcd. C 55.39, H 8.78, N 7.19; found C 55.65, H 8.76, N 7.21.

{MeN(CH$_2$CH$_2$O)[CH(C$_6$H$_4$CH$_2$)CHO]}$_2$Ti (28): The procedure was the same as that for **18** except that alkanolamine **12** (1.00 g, 4.8 mmol) was treated with Ti(O*i*Pr)$_4$ (0.69 g, 2.4 mmol) in toluene (15 mL). The compound **28** was recrystallized from the mixture of toluene/heptane (2:1) and isolated as a yellow solid (0.91 g, 83%), a mixture of diastereomers. NMR spectra: ^{1}H (323 K), δ = 2.71 (br. s, 6 H, NCH_3), 2.60–2.66, 2.92–3.04 (m, CH_2), 3.15, 3.28 (br. s, 4 H, NCH_2), 4.25–4.34 (m, 4 H, OCH_2), 4.64 (br. s, 2 H, NCH), 5.13 (br. s, 2 H, OCH), 7.09–7.28 (m, 8 H, C_6H_4); $^{13}C\{^1H\}$ (323 K), δ = 37.85 (broad, NCH_3, CH_2), 57.88 (broad, NCH_2), 69.09 (broad, OCH_2), 76.31 (broad, NCH), 83.62 (broad, OCH) 123.82, 125.44, 126.22, 127.20, 139.37, 140.39 (C_6H_4). $C_{24}H_{30}N_2O_4Ti$ (458.37): calcd. C 62.89, H 6.60, N 6.11; found C 62.43, H 6.32, N 5.94.

Reaction of 14 with Alkanolamine 1: Alkanolamine **1** (0.83 g, 4.6 mmol) was added to a solution of **14** (1.30 g, 4.6 mmol) in toluene (10 mL). The mixture was refluxed for 2 h, and all volatiles were removed under reduced pressure. According to NMR spectroscopic data a mixture of **18** and **29**[20] was formed.

Reaction of 14 with Alkanolamine 3: Alkanolamine **3** (0.90 g, 4.6 mmol) was added to a solution of **14** (1.30 g, 4.6 mmol) in tolu-

Table 4. Crystal data, data collection, structure solution, and refinement parameters for **16**, **19**, **20**, **23**, **24**, **25**, and **27**.

	16	**19**	**20**	**23**	**24**	**25**	**27**
Formula	$C_{26}H_{38}N_2O_8Ti_2{\cdot}2CH_2Cl_2$	$C_{22}H_{30}N_2O_4Ti$	$C_{22}H_{30}N_2O_4Ti{\cdot}C_7H_8$	$C_{34}H_{38}N_2O_4Ti{\cdot}2CH_2Cl_2$	$C_{34}H_{38}N_2O_4Ti{\cdot}0.5C_7H_8$	$C_{34}H_{38}N_2O_4Ti{\cdot}CH_2Cl_2$	$C_{18}H_{34}N_2O_4Ti$
M_r [g·mol^{-1}]	772.24	434.38	526.51	756.42	632.63	671.49	390.37
Crystal system	orthorhombic	monoclinic	monoclinic	monoclinic	monoclinic	orthorhombic	monoclinic
Space group	*Pbcn*	*P*2/*n*	*P*2$_1$/*c*	*C*2/*c*	*P*2$_1$/*c*	*Pbcn*	*C*2/*c*
a [Å]	15.9481(9)	9.443(4)	12.8626(12)	21.447(3)	13.401(1)	6.9964(4)	21.545(5)
b [Å]	9.8954(5)	12.749(3)	16.5027(16)	8.223(1)	12.780(2)	20.5113(11)	8.943(4)
c [Å]	22.2450(12)	18.207(3)	12.5842(13)	21.056(3)	19.660(3)	23.6918(14)	10.435(6)
β [°]		93.17(2)	90.558(2)	98.54(1)	91.28(1)		93.79(4)
V [Å^3]	3510.5(3)	2188.6(11)	2671.1(5)	3672.2(9)	3366.2(8)	3399.9(3)	2006.2(15)
Z	4	4	4	4	4	4	4
d_{calcd} [g·cm^{-3}]	1.461	1.318	1.309	1.368	1.248	1.312	1.292
Abs. coeff. [mm^{-1}]	0.807	0.421	1.357	0.564	0.295	0.449	0.450
F(000)	1600	920	1120	1576	1340	1408	840
Diffractometer	Bruker SMART	Nonius CAD4	Bruker SMART	Stoe IPDS II	Nonius CAD4	Bruker SMART	Nonius CAD4
Temperature [K]	120	293	120	173	293	120	293
θ range [°]	3.04–28.00	2.24–25.48	1.23–28.00	1.92–25.98	2.07–25.47	1.72–28.00	2.47–25.97
Index ranges	$-15 \le h \le 21$ $-13 \le k \le 8$ $-29 \le l \le 29$	$-11 \le h \le 11$ $-3 \le k \le 15$ $-4 \le l \le 22$	$-14 \le h \le 16$ $-21 \le k \le 21$ $-15 \le l \le 16$	$-26 \le h \le 26$ $-10 \le k \le 9$ $-25 \le l \le 25$	$-16 \le h \le 16$ $-2 \le k \le 15$ $-3 \le l \le 23$	$-9 \le h \le 9$ $-27 \le k \le 15$ $-31 \le l \le 29$	$-26 \le h \le 26$ $-4 \le k \le 11$ $-4 \le l \le 12$
Reflections collected	16611	6766	17996	24987	9029	21508	4419
Independent reflections	4205	4071	6400	3570	6247	4120	1969
R_{int}	0.03332	0.0283	0.0401	0.0746	0.0306	0.0394	0.1158
Data/param.	4205/283	4071/281	6400/478	3570/215	6247/390	4120/281	1969/115
GOF on F^2	1.051	1.008	1.027	0.787	1.007	1.090	0.991
R_1 [$I > 2\sigma(I)$]	0.0399	0.0372	0.0507	0.0323	0.0446	0.0536	0.0637
wR_2 (all data)	0.1088	0.1094	0.1352	0.0619	0.1498	0.1315	0.1788
Largest diff. peak/hole [e·Å^{-3}]	0.875/–0.312	0.226/–0.238	0.403/–0.476	0.265/–0.379	0.691/–0.399	1.318/–1.085	1.059/–0.589

ene (10 mL). The mixture was refluxed for 2 h, and all volatiles were removed under reduced pressure. According to NMR spectroscopic data, a mixture of **19** and **29**[20] was formed.

Reaction of 15 with Alkanolamine 2: Alkanolamine **2** (0.46 g, 2.5 mmol) was added to a solution of **15** (0.91 g, 2.5 mmol) in chloroform (15 mL). The mixture was refluxed for 3 h, and all volatiles were removed under reduced pressure. According to NMR spectroscopic data, a mixture of **19** and **29**[20] was formed.

Reaction of 15 with Alkanolamine 8: Alkanolamine **8** (1.32 g, 4.9 mmol) was added to a solution of compound **15** (1.75 g, 4.9 mmol) in toluene (10 mL). The mixture was refluxed for 2 h, and all volatiles were removed under reduced pressure. Ether (20 mL) was added to the residue, the precipitate was filtered off to give **19** as a white powder (1.02 g). According to NMR spectroscopic data, the mother liquor contained a mixture of **19** and **24**.

Reaction of 18 with Ti(O*i*Pr)$_4$: Ti(O*i*Pr)$_4$ (0.52 g, 1.8 mmol) was added dropwise to a solution of compound **18** (0.74 g, 1.8 mmol) in chloroform (20 mL), and the reaction mixture was refluxed for 5 h. After cooling to room temperature, all volatiles were removed under reduced pressure. Hexane (10 mL) was added to the yellow oil. The solution was filtered, and the solvent was removed under reduced pressure to give **13** as a yellow solid (1.22 g, 97%).

Reaction of 19 with TiCl$_4$: TiCl$_4$ (0.44 g, 2.3 mmol) was added at –78 °C to a suspension of **19** (1.00 g, 2.3 mmol) in toluene (15 mL) and the mixture was stirred for 2 h at the same temperature. A yellow solid formed. The reaction mixture was warmed to room temperature, and all volatiles were removed under reduced pressure. The formed yellow solid was insoluble in the usual organic solvents. According to NMR spectroscopic data in $(CD_3)_2SO$, a mixture of unidentified compounds formed.

X-ray Crystallographic Study: Crystal data, data collection, structure solution, and refinement parameters for compounds **16**, **19**, **20**, **23**, **24**, **25**, and **27** are given in Table 4. Experimental data were collected using Mo-K_α radiation (λ = 0.71073 Å). The structures were solved by direct methods[57] and refined by full-matrix least-squares based on F^2 with anisotropic thermal parameters for all non-hydrogen atoms.[58] In the structures **16**, **20**, and **25**, all hydrogen atoms were found from diff. Fourier syntheses and refined isotropically. As for **19**, **23**, **24**, and **27** all hydrogen atoms were placed in calculated positions and refined using a riding model. The structure **25** contains disordered CH_2Cl_2 molecules lying on a crystallographic twofold axis; **24** contains disordered toluene molecules lying on a crystallographic inversion center. In **19**, one of the two independent molecules possesses disordered -CH_2CH_2- skeleton fragments with an occupancy ratio of 0.71/0.29.

CCDC-292591 to -292597 contain 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.

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