Synthesis of new titanatranes containing organic substituents in the atrane fragment

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Titanatrane $CpTi(OCH(CH_3)CH_2)_3N$ (**3**) was prepared by the reaction of $CpTiCl_3$ with $N(CH_2CH(CH_3)OH)_3$ in the presence of triethylamine. The reaction of $CpTi(OMe)_3$ (**8**) with $N(CH_2CH_2OH)_2(CH_2CHPhOH)$, *erythro*-$N(CH_2CH_2OH)_2(CHPhCHPhOH)$, and $N(CH_2CH_2OH)_2(CH_2CPh_2OH)$ gave cyclopentadienyltitanatranes **12**—**14**. Compound **8** reacts with *threo*-$N(CH_2CH_2OH)_2(CHPhCHPhOH)$ to give a mixture of *threo*-$CpTi(OCH_2CH_2)_2(OCHPhCHPh)N$ and *threo*-$MeOTi(OCH_2CH_2)_2(OCHPhCHPh)N$. Slow hydrolysis of the latter product gave *threo*-$[Ti_3O(OMe)\{(OCH_2CH_2)_2(OCHPhCHPh)N\}_3]_2$, which was studied by X-ray diffraction analysis. The crystal structures of **3** and **12** were also determined by X-ray diffraction analysis. The titanium coordination polyhedron in these complexes is a distorted trigonal bipyramid in which the equatorial positions are occupied by three oxygen atoms and the axial positions contain the N atom and the Cp group. The titanium—nitrogen distances (2.313(2), 2.291(2) Å in two independent molecules of **3** and 2.271(2) Å in compound **12**) confirm the presence of Ti←N transannular interaction.

Key words: titanatranes, trialkanolamines, transalkoxylation, transannular interaction, X-ray diffraction analysis.

The chemistry of metallatranes, cyclic ethers of trialkanolamines, has been vigorously developing during the last fifty years. Derivatives of most of chemical elements have now been synthesized. The interest in these unusual compounds is due to the possible formation of an intramolecular coordination bond, which changes substantially the structure and properties of metallatranes compared to the structures and properties of their close analogs, tris-alkoxides in which this type of intramolecular interaction is missing. In particular, well known is a higher stability of metallatranes against hydrolysis. Therefore, metallatranes may prove more promising from the applied standpoint[1] compared to other metal compounds.

The compounds of main group elements, especially silatranes and germatranes, possessing a broad spectrum of biological activities, have been studied in most detail.[2,3] Transition metal compounds have been much less studied,[4—6] although they could find a broad application, for example, as catalysts for various organic reactions. It is of interest to compare the structures and properties of transition metal atranes with those of the related compounds formed by nontransition elements; this may provide additional information on the nature of the element—nitrogen transannular bond in this type of compound.

In this paper we consider titanatranes, which are structural analogs of well-studied silatranes and germatranes. Although the first representatives of titanatranes were synthesized back in the 1960s,[7—9] and in recent decade, the interest in these derivatives has increased,[10—14] at most 20 publications on this topic are known. The attention was focused on the specific features of the structure[15—17] and catalytic properties of chiral trialkanolamine complexes in the polymerization of olefins and lactide[18—20] and oxidation of sulfides.[21—25] A broad range of titanatranes containing various cyclopentadienyl substituents (Cp*, C_5Me_4H, C_5Me_4Et, C_5Me_4Ph и C_5Me_4Tol) at the titanium atom and the Ph and Me groups at the carbon atoms of the atrane skeleton have been reported.[26—28] The atranes were synthesized by the reaction of the corresponding trichloro(η^5-2,4-cyclopentadien-1-yl)titanium with trialkanolamine in the presence of Et_3N. The catalytic properties of the obtained compounds were studied in styrene polymerization; the structures of six cyclo-

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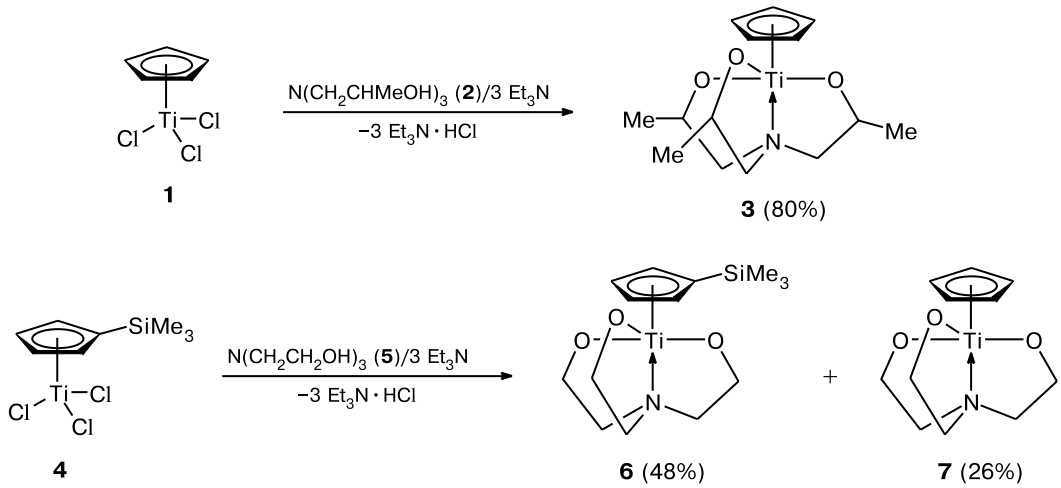
pentadienyl derivatives were determined by X-ray diffraction. By the beginning of our study, only one titanatrane containing the unsubstituted cyclopentadienyl ring, $N(CH_2CH_2O)_3TiCp$, has been described in the literature. This compound was prepared both by the reaction of CpNa with $N(CH_2CH_2O)_3TiCl$[10] and by transalkoxylation with $CpTi(OMe)_3$ and triethanolamine.[11]

This paper reports the synthesis and studies of the structure of cyclopentadienyltitanatranes containing different substituents at the carbon atoms of the atrane skeleton. The structures of two compounds were established by X-ray diffraction. The nature of the Ti←N bond in titanatranes was investigated by quantum chemical methods. Of particular interest for estimation of the effect of substituents in the Cp ring on the titanium—nitrogen transannular interaction was to compare the structures of compounds we synthesized with the data[26—28] obtained previously for related compounds.

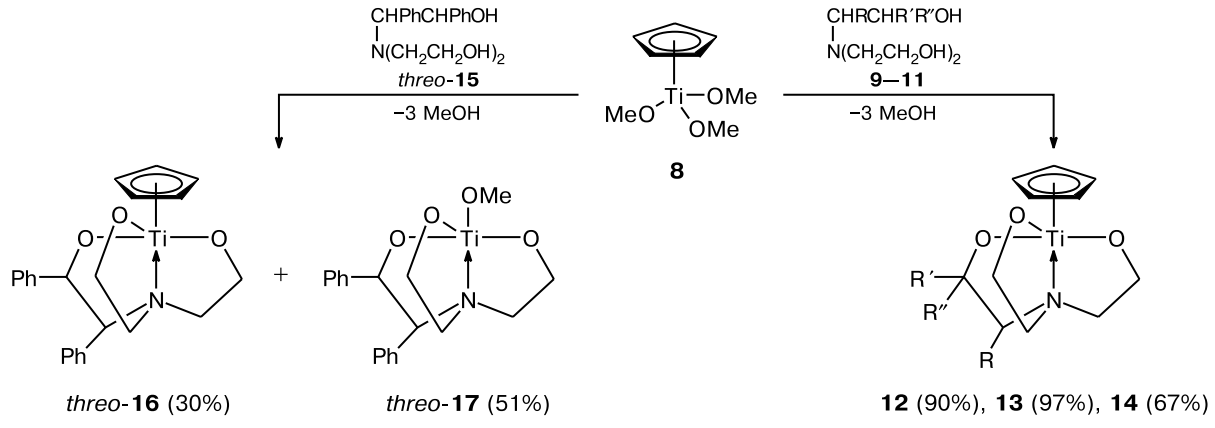
Results and Discussion

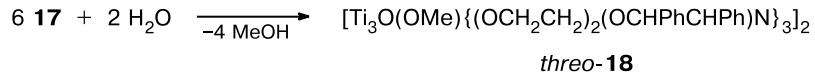
For the synthesis of titanatranes, we tested several methods for the formation of the atrane skeleton (Schemes 1—4). The reaction of trichloride **1** with

Scheme 1



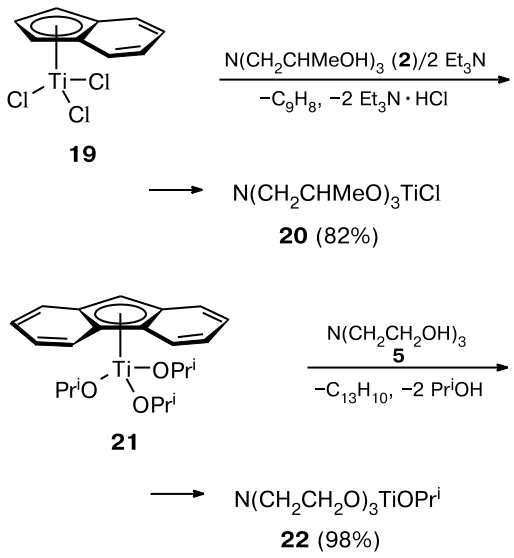
Scheme 2



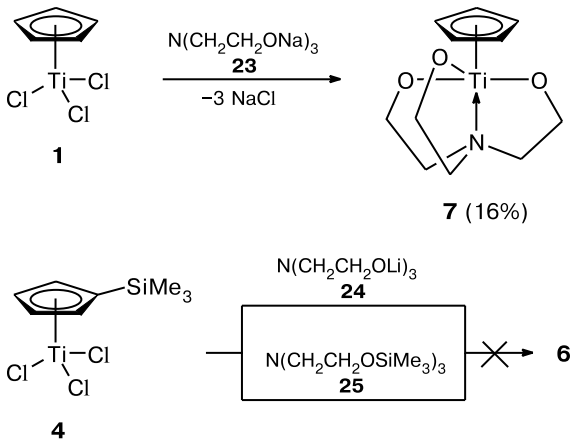


9, 12: R = H, R′ = Ph
10, 13: R = Ph, R′ = Ph (*erythro*)
11, 14: R = H, R′ = R″ = Ph

Scheme 3



Scheme 4



triisoropanolamine (**2**) in the presence of Et_3N gave titanatrane **3** in a high yield (see Scheme 1). Quite an unexpected result was obtained on an attempt to extend the scope of this reaction. Treatment of trichloride **4**, containing a Me_3Si group in the Cp ring, with triethanolamine (**5**) gave not only the expected atrane **6** but also desilylated complex **7** (the ratio **6** : **7** = 7 : 3). In this case, desilylation can be induced by either triethanolamine (**5**), which is converted into monotrimethylsilyl ether, or by HCl (from $Et_3N \cdot HCl$).

Transalkoxylation (see Scheme 2) of trimethoxy(η^5-2,4-cyclopentadien-1-yl)titanium (**8**) with trialkanolamines **9**—**11** afforded titanatranes **12**—**14** in high yields. However, the reaction of alkoxide **8** with trialkanolamine **15** (*threo*-configuration of the phenyl groups) affords not only the expected complex **16**, but also compound **17**, resulting from cleavage of the Ti—Cp bond by methanol evolved during the reaction. This outcome is apparently due to the low solubility of initial trialkanolamine **15**. On long-term keeping of a solution of compound **17** (dichloromethane—*n*-heptane) in air, hydrolysis takes place, giving rise to the Ti—O bonds in titanatrane **18**, which crystallizes as a hexanuclear structure. The structures of two closely related titanatranes, which also contain six titanium atoms in the molecule, have been studied previously[17] by X-ray diffraction analysis. Apparently, the formation of hexameric titanatranes in hydrolysis under mild conditions is a general feature of titanium compounds with trialkanolamines.

The attempts to extend these two methods for generation of the titanatrane moiety to the synthesis of indenyl- and fluorenyltitanatranes failed; however, we were able to isolate known compounds **20** [23] and **22** [12] in high yields (see Scheme 3). The results of these reactions are consistent with the known data[29] indicating a higher lability of the Ti—C bond in the indenyl- and fluorenyltrialkoxytitanium derivatives compared to the cyclopentadienyl derivatives.

We also studied other approaches to the synthesis of titanatranes based on the reactions of titanium trichlorides **1** and **4** with Na, Li, and Me_3Si trialkanolamine derivatives (see Scheme 4). The reaction of trichloride **1** with triethanolamine trisodium salt (**23**) furnished atrane **7** described previously[12] in a moderate yield. However, the reaction of the trilithium salt **24** with trichloride **4** resulted in a mixture of poorly identifiable products. Treatment of complex **4** with ether **25** did not give compound **6** either; according to ^1H NMR data, refluxing of the reactant mixture in xylene yields the compound [$(Me_3Si\text{-}\eta^5\text{-}C_5H_4)TiCl_3 \cdot N(CH_2CH_2OSiMe_3)_3$]. Previously, the formation of a similar donor-acceptor complex [$BHal_3 \cdot MeN(CH_2CH_2OSiMe_3)_2$] was detected in the reactions of boron compounds.[30]

Thus, the procedure of choice for the synthesis of a particular cyclopentadienyltitanatrane depends on both the substituents in the Cp ring and the trialkanolamine structure.

The structures of the previously unknown cyclopentadienyltitanatranes **3**, **6**, **12**—**14**, and **16** and compound **17** were confirmed by ^1H and ^{13}C NMR spectroscopy and, in some cases, by mass spectrometry. Titanatranes bearing substituents in the atrane fragment have one or several chiral centers, which accounts for the formation of the corresponding isomers. Atrane **3** is formed as a mixture of two diastereomers differing in the arrangement of three Me groups relative to the titanium—nitrogen bond axis.[2] Compounds **13**, **16**, and **17** were obtained as one diastereomer pair.

The structures of compounds **3**, **12**, and **18** were established by X-ray diffraction (Fig. 1—3, Tables 1 and 2). The quality of crystals **18** proved unsatisfactory for

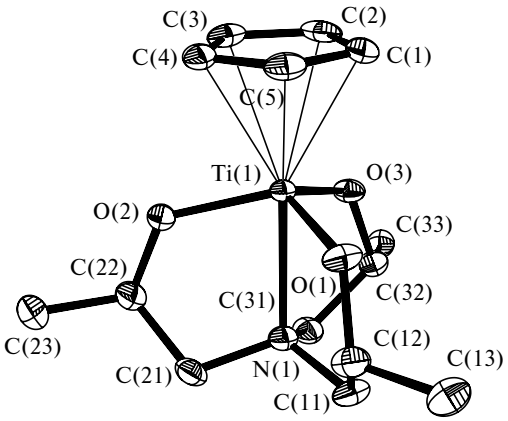


Fig. 1. Molecular structure of complex **3** (one crystallographically independent molecule).

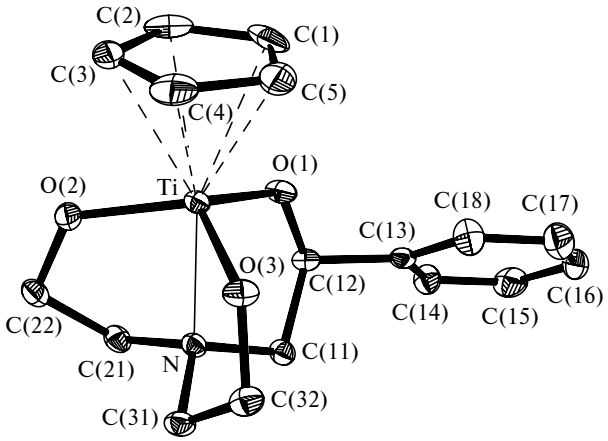


Fig. 2. Molecular structure of complex **12**.

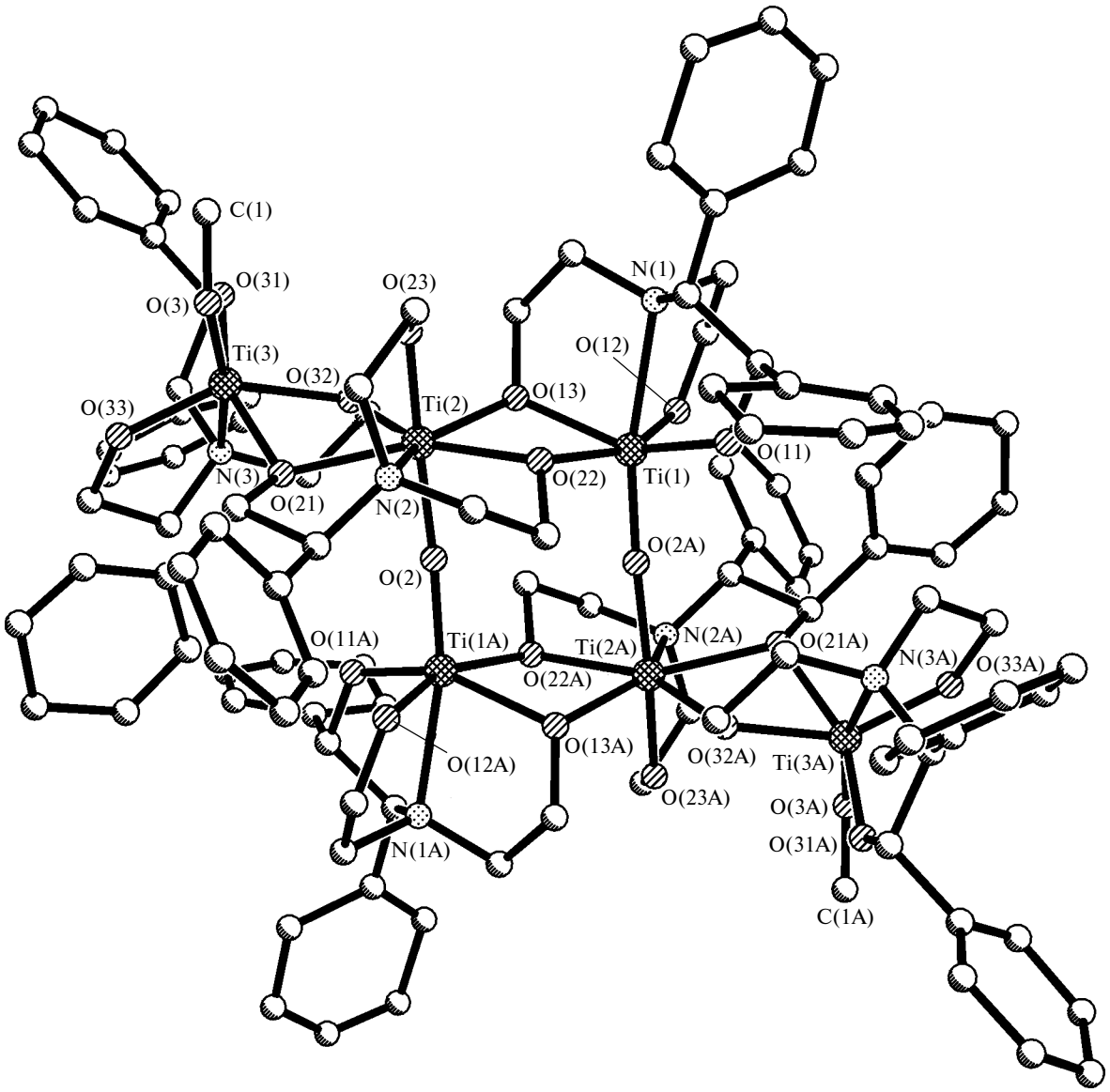


Fig. 3. Molecular structure of complex **18**.

Table 1. Selected interatomic distances (*d*) in structures **3** and **12**

Bond	*d*/Å	Bond	*d*/Å
Compound **3***		Compound **3***	
Ti(1)—O(1)	1.8816(14)	Ti(2)—C(7)	2.3894(18)
Ti(1)—O(2)	1.8804(13)	Ti(2)—C(8)	2.3824(17)
Ti(1)—O(3)	1.8983(13)	Ti(2)—C(9)	2.4277(17)
Ti(2)—O(4)	1.8905(14)	Ti(2)—C(10)	2.4513(18)
Ti(2)—O(5)	1.8816(14)	Compound **12**	
Ti(2)—O(6)	1.8931(13)	Ti—O(1)	1.883(2)
Ti(1)—N(1)	2.3129(15)	Ti—O(2)	1.880(2)
Ti(2)—N(2)	2.2910(15)	Ti—O(3)	1.886(2)
Ti(1)—C(1)	2.4299(18)	Ti—N	2.271(2)
Ti(1)—C(2)	2.4385(19)	Ti—C(1)	2.431(3)
Ti(1)—C(3)	2.4428(19)	Ti—C(2)	2.433(3)
Ti(1)—C(4)	2.4455(18)	Ti—C(3)	2.454(3)
Ti(1)—C(5)	2.4480(18)	Ti—C(4)	2.436(3)
Ti(2)—C(6)	2.4454(19)	Ti—C(5)	2.418(3)

* Two independent molecules.

discussing structural details; however, the mutual positions of the atoms were determined unambiguously.

By the beginning of this work, the structures of 18 titanatranes have been studied by X-ray diffraction analysis. Of these, fifteen contain $N(CH_2CH_2O)_3Ti$ group, while the other ones, *viz.*, *S*,*S*,*S*-$N(CH_2CHMeO)_3TiCl$, *S*,*S*,*S*-$N(CH_2CHMeO)_3TiCp^*$, and *S*-$N(CH_2CHMeO)$-$(CH_2CH_2O)_2TiCp^*$ (Cp* is pentamethylcyclopentadienyl), contain substituents in the atrane core. The compounds $N(CH_2CH_2O)_3TiX$ (X = OPr^i, OAc, NMe_2, SPr^i, OBu^t) crystallize as dimers in which the Ti atom has a coordination number equal to six due to the additional bridging type bond with the oxygen atom of the atrane core of a second molecule. All titanatranes with substituents in the atrane core are monomeric in the crystal. The titanium—nitrogen distances in titanatranes (monomers and dimers) occur in the range of 2.255(3)—2.427(8) Å,[18,23] this bond length being independent of the coordination number of the titanium atom. Comparison of the titanatrane and silatrane structures indicates that the length of the titanium—nitrogen bond depends on the nature of the substituent at the titanium atom to a lesser extent than the silicon—nitrogen bond length.[31] Conversely, the Ti—O_{eq} bonds in monomeric titanatranes are more susceptible to the influence of the axial substituent (*S*,*S*,*S*-$N(CH_2CHMeO)_3TiCl$, 1.800(2)—1.813(2) Å;[23] *S*-$N(CH_2CHMeO)$-$(CH_2CH_2O)_2TiCp^*$, 1.873(5)—1.888(5) Å (see Ref. 27)) than the Si—O_{eq} bonds in silatranes.[31] These facts can be attributed to different ways of formation of the additional bond in the atranes. Indeed, complexes of d-elements tend to experience strong donor—acceptor interaction, whereas in the case of p-elements, the transannular bond can be considered as a hypervalent bond, its length varying over a broad range depending on the nature of the substituent at the element atom.

The titanium coordination polyhedron in atranes **3** and **12** is a distorted trigonal bipyramid in which the equatorial positions are occupied by three oxygen atoms, and the axial positions, by the nitrogen atom and the Cp group. The titanium—nitrogen distances (2.313(2), 2.291(2) Å in two independent molecules of complex **3**; 2.271(2) Å in complex **12**) attest unambiguously to the presence of Ti←N interaction in these compounds. The Ti—C bond lengths are in the 2.430(2)—2.448(2) and 2.382(2)—2.451(2) Å ranges (for the two independent molecules in the crystal of **3**) and in the 2.418(3)—2.454(3) Å range (in complex **12**). Titanatranes

Table 2. Selected bond angles (ω) in structures **3** and **12**

3*				**12**	
Angle	ω/deg	Angle	ω/deg	Angle	ω/deg
O(2)—Ti(1)—O(1)	116.69(6)	O(5)—Ti(2)—O(4)	113.98(6)	O(2)—Ti—O(1)	114.03(9)
O(2)—Ti(1)—O(3)	111.86(6)	O(5)—Ti(2)—O(6)	114.45(6)	O(2)—Ti—O(3)	115.18(9)
O(1)—Ti(1)—O(3)	113.75(6)	O(4)—Ti(2)—O(6)	114.45(7)	O(1)—Ti—O(3)	113.92(10)
O(2)—Ti(1)—N(1)	75.56(5)	O(5)—Ti(2)—N(2)	76.41(6)	O(2)—Ti—N	76.09(9)
O(1)—Ti(1)—N(1)	75.34(6)	O(4)—Ti(2)—N(2)	75.61(6)	O(1)—Ti—N	75.78(8)
O(3)—Ti(1)—N(1)	76.21(6)	O(6)—Ti(2)—N(2)	75.79(6)	O(3)—Ti—N	76.25(9)
C(21)—N(1)—C(11)	112.86(16)	C(61)—N(2)—C(41)	112.67(16)	C(11)—N—C(31)	112.0(2)
C(21)—N(1)—C(31)	111.79(15)	C(61)—N(2)—C(51)	112.62(16)	C(11)—N—C(21)	112.4(2)
C(11)—N(1)—C(31)	111.67(15)	C(41)—N(2)—C(51)	110.87(16)	C(31)—N—C(21)	112.5(2)
C(21)—N(1)—Ti(1)	106.31(11)	C(61)—N(2)—Ti(2)	107.11(11)	C(11)—N—Ti	106.71(17)
C(11)—N(1)—Ti(1)	107.35(11)	C(41)—N(2)—Ti(2)	107.19(11)	C(31)—N—Ti	106.15(17)
C(31)—N(1)—Ti(1)	106.39(11)	C(51)—N(2)—Ti(2)	105.92(11)	C(21)—N—Ti	106.51(18)
C(12)—O(1)—Ti(1)	126.68(12)	C(42)—O(4)—Ti(2)	126.15(12)	C(12)—O(1)—Ti	126.98(17)
C(22)—O(2)—Ti(1)	126.30(11)	C(52)—O(5)—Ti(2)	125.98(12)	C(22)—O(2)—Ti	125.60(19)
C(32)—O(3)—Ti(1)	124.71(11)	C(62)—O(6)—Ti(2)	125.78(12)	C(32)—O(3)—Ti	125.18(18)

* Two independent molecules.

containing an unsubstituted Cp group at the titanium atom have not been studied previously by X-ray diffraction; however, according to known data,[26–28] the Ti—C bond lengths in related titanatranes containing a Cp* group are similar to the values we found: 2.40(1)—2.46(1) (*S,S,S*-$N(CH_2CHMeO)_3TiCp^*$) and 2.416(6)—2.461(8) Å (*S*-$N(CH_2CHMeO)$-$(CH_2CH_2O)_2TiCp^*$). It was of interest to estimate the influence of the additional Ti←N interaction in titanatranes on the Ti—Cp bond parameters. Three compounds of tetracoordinated titanium that contain a Cp group and three Ti—O bonds have now been studied by X-ray diffraction, namely, $CpTi[O(2,6\text{-}Pr^i_2C_6H_3)]_3$ (d_{Ti-C} = 2.373—2.421 Å),[32] $CpTi(p\text{-}Bu^t\text{-calix[6]arene}-3H)$ (d_{Ti-C} = 2.355—2.378 Å), and $(CpTi)_2(p\text{-}Bu^t$-calix[6]arene−6H) (d_{Ti-C} = 2.340—2.382 and 2.362—2.380 Å).[33] Thus, an increase in the coordination number of titanium results in a regular elongation of the Ti—Cp bond located in the *trans*-position with respect to nitrogen as an additional electron donor.

The Ti—O bond lengths in the studied compounds (1.880(1)—1.898(1) and 1.881(1)—1.893(1) Å for the two independent molecules in the crystal of **3** and 1.880(2)—1.886(2) Å for compound **12**) are closely similar to those found previously[26,27] for various cyclopentadienyltitanatranes (Cp*, C_5Me_4H, C_5Me_4Ph, C_5Me_4Tol), namely, 1.856(7)—1.888(5) Å. Meanwhile, the Ti—O bond lengths in molecules **3** and **12** markedly exceed the values (1.824(2)—1.832(2) Å) found[34] for a single monomeric titanium trialkoxide with a Cp ring that was studied by X-ray diffraction, namely, $[\eta^5\text{-}C_5H_3(SiMe_3)_2]Ti(C_6H_9O_3)$ ($C_6H_9O_3H_3$ is 1,3,5-*cis*-hexanetriol).

In compounds **3** and **12**, all the five-membered rings of the atrane skeleton incorporating the Ti←N bond have an envelope conformation, the envelope "flaps" being formed by the carbon atoms located in the α-positions to the N atom of the atrane moiety. Note that in the conformation found previously for nontransition metal atranes with substituents in the β-positions to nitrogen, the envelope "flaps" are formed by the methyl-substituted ring carbon atoms. The crystal of compound **3** contains only the symmetrical diastereomer.

To elucidate the structural features of titanatranes, we performed a quantum chemical (DFT/PBE) study of three compounds, namely, cyclopentadienyltitanatranes **3** and **7** and 1-chlorotitanatrane $N(CH_2CH_2O)_3TiCl$ (**26**). The main calculated bond lengths and bond angles are summarized in Table 3. These values for compound **3** are consistent with the values determined by X-ray crystallography. Comparison of the calculated bond lengths for compounds **3** and **7** with the corresponding values for compound **26** confirms the conclusion based on analysis of X-ray diffraction data: the presence of an additional titanium—nitrogen interaction markedly affects parameters of the Ti—O equatorial bonds but has little influence on the Ti—X (axial substituent) bond length.

Table 3. Selected calculated bond lengths (*d*) and bond angles (ω) in structures **3**, **7**, and **26**

Parameter	**3**	**7**	**26**
Bond		*d*/Å	
Ti—N	2.486	2.416	2.430
Ti—O(1)	1.895	1.905	1.847
Ti—O(2)	1.897	1.905	1.847
Ti—O(3)	1.895	1.906	1.847
Ti—Cl	—	—	2.270
Ti—C(1)	2.453	2.450	—
Ti—C(2)	2.456	2.447	—
Ti—C(3)	2.447	2.452	—
Ti—C(4)	2.462	2.440	—
Ti—C(5)	2.454	2.451	—
Angle		ω/deg	
N—Ti—O(1)	73.9	74.8	75.4
N—Ti—O(2)	74.0	74.8	75.4
N—Ti—O(3)	74.0	74.8	75.4
N—Ti—Cl	—	—	180.0

We studied the topological properties of the bonds formed by titanium using the approach proposed by Bader.[35] The calculated electron densities ($\rho(\boldsymbol{r}_b)$), electron density Laplacians ($\nabla^2\rho(\boldsymbol{r}_b)$), and bond ellipticities (ε) and the eigen values of the Hesse matrix of the electron density function $|\lambda 1|/\lambda 3$ in the critical points of the Ti—N, Ti—O, and Ti—Cl bonds (CP(3, −1) type of critical points) are summarized in Table 4. The results obtained imply an ionic character of the bonds studied ("closed shell" interaction). Comparison of the resulting values with the known values for silicon and germanium compounds attests to similarity of the topological properties

Table 4. Calculated values of the electron density ($\rho(\boldsymbol{r}_b)$), electron density Laplacian ($\nabla^2\rho(\boldsymbol{r}_b)$), bond ellipticity (ε), and $|\lambda 1|/\lambda 3$ in the critical points of the Ti←X bonds (X = N, O, Cl, type of critical points CP(3, −1)) for compounds **3**, **7**, and **26**

Compound	X	$\rho(\boldsymbol{r}_b)$	$\nabla^2\rho(\boldsymbol{r}_b)$	ε	$\lvert\lambda 1\rvert/\lambda 3$
3	N	0.036	0.115	0.003	0.187
	O(1)	0.122	0.482	0.132	0.248
	O(2)	0.122	0.482	0.131	0.248
	O(3)	0.121	0.481	0.131	0.248
7	N	0.041	0.135	0.004	0.201
	O(1)	0.118	0.471	0.142	0.247
	O(2)	0.119	0.472	0.143	0.248
	O(3)	0.119	0.472	0.140	0.248
26	N	0.041	0.133	0.000	0.202
	O(1)	0.137	0.541	0.132	0.254
	O(2)	0.138	0.541	0.131	0.254
	O(3)	0.138	0.541	0.134	0.255
	Cl	0.083	0.195	0.000	0.256

of bonds (including transannular bonds) in titanatranes and in silatranes or germatranes,[36—38] despite the obvious difference in the modes of formation of the transannular bond in silatranes and titanatranes, which follows from comparison of the geometric parameters of the molecules (see above).

Experimental

All operations with organotitanium compounds were carried out using standard Schlenk technique under argon. The solvents were purified by known procedures immediately prior to use. Tetrahydrofuran, dimethoxyethane (DME), and triethylamine were kept over potassium hydroxide and then distilled over Na benzophenone ketyl; toluene, benzene, *m*-xylene, *n*-hexane, *n*-heptane, and *n*-octane were kept over and then distilled from sodium metal; chloroform and dichloromethane were treated with concentrated sulfuric acid, washed with an aqueous solution of potassium carbonate and water, dried by anhydrous calcium chloride, and distilled from CaH_2.

^1H and ^{13}C NMR spectra were recorded in $CDCl_3$ on a Varian VXR-400 spectrometer (400 and 100 MHz, respectively). The residual protons of the deuterated solvents were used as the internal standard; the chemical shifts are referred to Me_4Si. The mass spectra were recorded with direct sample injection and at an ionizing voltage of 70 eV on a Varian CH-7a mass spectrometer (Phillips University, Magburg, Germany); the signals were assigned using masses of the most abundant isotopes.

Commercial triethanolamine (**5**) and triisopropanolamine (**2**) (Merck) were used.

Trichloro(η^5-2,4-cyclopentadien-1-yl)titanium (**1**), trichloro[(1,2,3,4,5-η)-1-(trimethylsilyl)-2,4-cyclopentadien-1-yl]titanium (**4**),[39] trimethoxy(η^5-2,4-cyclopentadien-1-yl)titanium (**8**),[40] indenyltrichlorotitanium[41] (**19**), fluorenyltriisopropoxytitanium (**20**),[29] 2-[bis(2-hydroxyethyl)amino]-1-phenyl-1-ethanol (**9**),[42] 2-[bis(2-hydroxyethyl)amino]-1,2-*erythro*-diphenyl-1-ethanol (**10**), 2-[bis(2-hydroxyethyl)amino]-1,1-diphenyl-1-ethanol (**11**), and 2-[bis(2-hydroxyethyl)amino]-1,2-*threo*-diphenyl-1-ethanol (**15**)* were prepared by known procedures.

{[(1,1′,1′′-Nitrilotris[2-propanolato])-(3)-*N*,*O*,*O*′,*O*′′]-[1,2,3,4,5-η]cyclopenta-2,4-dien-1-yl}titanium (3). Triethylamine (0.66 g, 6.57 mmol) was added to a solution of compound **2** (0.42 g, 2.19 mmol) in dichloromethane (15 mL). The reaction mixture was cooled to −78 °C and then a solution of complex **1** in dichloromethane (20 mL) was added dropwise with stirring. After 12 h, the solvent was removed under reduced pressure, anhydrous benzene (20 mL) was added, and the solution was filtered. The precipitate was washed with benzene (2×20 mL) on the filter and the solvent was evaporated. The residue was recrystallized from toluene to give titanatrane **3** as a white powder (0.53 g 80%), which represented a mixture of two diastereomers in 4 : 1 ratio (symmetrical : asymmetrical).

Symmetrical titanatrane **3**. ^1H NMR, δ: 6.27 (s, 5 H, Cp); 4.68—4.61 (m, 3 H, OCH); 2.78—2.68 (m, 6 H, NCH_2); 1.02 (d, 9 H, Me, J = 6.4 Hz). ^{13}C NMR, δ: 116.43 (Cp); 76.21 (OCH); 62.68 (NCH_2); 41.62 (Me).

Asymmetrical titanatrane **3**. ^1H NMR, δ: 6.29 (s, 5 H, Cp); 4.54—4.50 (m, 3 H, OCH); 2.67—2.57 (m, 6 H, NCH_2); 1.21, 1.01, 0.99 (all d, 3 H each, Me, J = 6.3 Hz). No signals were detected in the ^{13}C NMR spectrum due to low concentration of the sample.

MS, m/z (I_{rel} (%)): 301 $[M]^+$ (6), 257 $[M - MeCHO]^+$ (84), 236 $[M - Cp]^+$ (18), 213 $[M - 2\ MeCHO]^+$ (100), 192 $[M - Cp - MeCHO]^+$ (29), 158 $[M - 2\ MeCHO - C_2H_4 - HCN]^+$ (23), 129 $[M - 2\ MeCHO - C_2H_4 - HCN - CH_2Me]^+$ (14), 113 $[CpTi]^+$ (5).

Reaction of complex 4 with triethanolamine (5). The synthesis was carried out similarly to the previous experiment starting from complex **4** (1.05 g, 3.60 mmol), triethanolamine (**5**) (0.54 g, 3.60 mmol), and triethylamine (1.10 g, 10.80 mmol). The removal of the solvent gave a white powder (0.82 g); according to ^1H NMR, this was a mixture of (Me_3Si-η^5-C_5H_4)$Ti(OCH_2CH_2)_3N$ (**6**) and $CpTi(OCH_2CH_2)_3N$ (**7**) in 7 : 3 ratio. Complex **6**. ^1H NMR, δ: 6.50 and 6.39 (both t, 2 H each, Cp, J = 3.2 Hz); 4.27 (t, 6 H, OCH_2, J = 4.8 Hz); 2.94 (t, 6 H, NCH_2, J = 4.8 Hz); 0.19 (s, 27 H, $SiMe_3$). The ^1H NMR signals of compound **7** correspond to published data.[12]

Reaction of complex 19 with triisopropanolamine (2). The synthesis was carried out similarly to the previous experiment starting from complex **19** (0.73 g, 2.71 mmol), compound **2** (0.52 g, 2.71 mmol), and triethylamine 0.82 g (8.13 mmol). After removal of the solvent, the residue was washed with *n*-hexane and filtered to give a white powder (0.60 g); according to ^1H NMR, this was chloro{[(1,1′,1″-nitrilotris[2-propanolato])-(3)-*N*,*O*,*O*′,*O*″]}titanium (**20**)[23].

{[1-(2-Phenylethanolato)-(1′,1′′-nitrilobis[ethanolato])-(3)-*N*,*O*,*O*′,*O*′′]-[1,2,3,4,5-η]cyclopenta-2,4-dien-1-yl}titanium (12). A solution of trialkanolamine **9** (1.23 g, 5.49 mmol) in THF (15 mL) was added dropwise with stirring to a solution of complex **8** (1.13 g, 5.49 mmol) in THF (20 mL). After 10 h, the solvent was evaporated under reduced pressure and the residue was recrystallized from a dichloromethane—*n*-octane mixture to give titanatrane **12** as a white powder (1.65 g, 90%). ^1H NMR, δ: 7.36—7.21 (m, 5 H, Ph); 6.40 (s, 5 H, Cp); 5.61 (dd, 1 H, OCHPh, J = 10.4 Hz, J = 4.4 Hz); 4.54 and 4.43 (both td, 1 H each, OCH_2, J = 11.8 Hz, J = 3.9 Hz); 4.20 and 4.13 (both dd, 1 H each, OCH_2, J = 11.8 Hz, J = 6.1 Hz); 3.36 and 3.17 (both td, 1 H Hz, NCH_2, J = 11.4 Hz, J = 6.2 Hz); 3.08 (dd, 1 H, NCH_2, J = 12.2 Hz, J = 4.4 Hz); 2.91—2.85 (m, 2 H, NCH_2); 2.73 (dd, 1 H, NCH_2, J = 12.2 Hz, J = 3.7 Hz). ^{13}C NMR, δ: 143.91, 128.33, 127.42, 125.16 (Ph); 116.92 (Cp); 82.36 (OCH); 70.79 (OCH_2); 62.74, 56.34, 55.49 (all NCH_2). MS, m/z (I_{rel} (%)): 335 $[M]^+$ (3), 305 $[M - CH_2O]^+$ (2), 270 $[M - Cp]^+$ (4), 229 $[M - PhCHO]^+$ (100), 199 $[M - PhCHO - CH_2O]^+$ (62), 164 $[M - Cp - PhCHO]^+$ (12), 144 $[M - PhCHO - CH_2O - C_2H_4 - HCN]^+$ (16), 129 $[M - PhCHO - CH_2O - C_2H_4 - HCN - CH_3]^+$ (15), 106 $[M - Cp - PhCHO - CH_2O - C_2H_4]^+$ (7).

{[(1*R*,2*S*/1*S*,2*R*)-[1,2-Diphenylethanolato]-(1′,1′′-nitrilobis[ethanolato])-(3)-*N*,*O*,*O*′,*O*′′]-[1,2,3,4,5-η]cyclopenta-2,4-dien-1-yl}titanium (13). The synthesis was carried out similarly to the previous experiment starting from complex **8** (1.2 g, 5.83 mmol) and ligand **10** (1.76 g, 5.83 mmol) to give titanatrane **13** as a white powder (2.32 g, 97%). ^1H NMR, δ: 7.30—7.16, 6.98—6.90 (both m, 5 H each, Ph); 6.49 (s, 5 H, Cp); 5.66 (d, 1 H, OCHPh, J = 8.4 Hz); 4.75—4.68 (m, 2 H, NCHPh, OCH(H)); 4.37—4.34 (m, 1 H, OCH(H)); 4.24—4.20,

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4.03—3.99 (both m, 1 H each, OCH_2); 3.49—3.43, 3.02—2.96, 2.82—2.78, 2.54—2.50 (all m, 1 H each, NCH_2). ^{13}C NMR, δ: 142.16, 133.13, 131.74, 128.62, 127.91, 127.30, 126.98 (Ph); 117.01 (Cp); 88.28 (OCH); 71.65, 71.20 (OCH_2); 71.45 (NCH), 55.40, 54.35 (all NCH_2).

{[(1,1-Diphenylethanolato)-(1′,1″-nitrilobis[ethanolato])-(3)-*N*,*O*,*O*′,*O*″]-[1,2,3,4,5-η]cyclopenta-2,4-dien-1-yl}titanium (14). The synthesis was carried out similarly to the previous experiment starting from complex **8** (0.66 g, 3.19 mmol) and ligand **11** (0.96 g, 3.19 mmol). Recrystallization from a dichloromethane—*n*-heptane mixture gave titanatrane **14** as a white powder (0.87 g, 67%). ^1H NMR, δ: 7.41—7.11 (m, 10 H, Ph); 6.51 (s, 5 H, Cp); 4.24—4.19, 4.16—4.10 (both m, 2 H each, OCH_2); 3.80 (s, 2 H, NCH_2CPh_2); 2.84—2.72 (m, 4 H, NCH_2). ^{13}C NMR, δ: 148.04, 133.32, 128.30, 128.25, 126.48, 125.36, 124.96, 124.46 (Ph); 116.81 (Cp); 76.32 (CPh_2); 70.76 (NCH_2CPh_2); 65.78 (OCH_2); 57.34, 56.72 (both NCH_2).

Reaction of complex 21 with triethanolamine (5). A solution of triethanolamine (**5**) (0.19 g, 1.28 mmol) in THF (10 mL) was added dropwise with stirring and cooling (−78 °C) to a solution of complex **21** (0.50 g (1.28 mmol) in THF (10 mL). After 12 h, the solvent was removed under reduced pressure, the residue was washed with *n*-hexane and filtered to give a white powder (0.32 g); according to ^1H NMR, this was (2-propanolato)-{[(2,2′,2″-nitrilotris[ethanolato])-(3)-*N*,*O*,*O*′,*O*″]}titanium (**22**)[12].

Reaction of complex 8 with trialkanolamine 15. Ligand **15** (1.99 g, 6.60 mmol) was added in small portions, as the material dissolved, over a period of 2 h to a stirred solution of complex **8** (1.36 g, 6.60 mmol) in THF (20 mL). After 4 days, the precipitated white solid was filtered off and recrystallized from a dichloromethane—*n*-hexane mixture to give methoxy-{[(1*R*,2*S*/1*S*,2*R*)-[1,2-diphenylethanolato]-(1′,1″-nitrilobis[ethanolato])-(3)-*N*,*O*,*O*′,*O*″]}titanium (**17**) as a white powder (1.26 g, 51%). The mother liquor was concentrated and the residue was recrystallized from a dichloromethane—*n*-octane mixture to give {[(1*R*,2*R*/1*S*,2*S*)-(1,2-diphenylethanolato)-(1′,1″-nitrilobis[ethanolato])-(3)-*N*,*O*,*O*′,*O*″]-[1,2,3,4,5-η]cyclopenta-2,4-dien-1-yl}titanium (**16**) as a white powder (0.82 g, 32%).

Complex **17**. Found (%): C, 60.63; H, 6.36; N, 3.98; Ti, 12.62. $C_{19}H_{23}NO_4Ti$. Calculated (%): C, 60.49; H, 6.14; N, 3.71; Ti, 12.69. ^1H NMR, δ: 7.29—7.09 (m, 10 H, Ph); 6.12 (d, 1 H, OCHPh, J = 11.8 Hz); 5.02—4.95, 4.77—4.73 (both m, 1 H each, OCH(H)); 4.42—4.35 (m, 2 H, OCH_2); 4.26 (s, 3 H, OMe); 3.88—3.84 (m, 1 H, NCHPh); 3.45—3.43 (m, 1 H, NCH(H)); 3.19—3.16 (m, 2 H, NCH_2); 2.55—2.50 (m, 1 H, NCH(H)). MS, m/z (I_{rel} (%)): 377 $[M]^+$ (10), 271 $[M - PhCHO]^+$ (100), 241 $[M - PhCHO - CH_2O]^+$ (32), 227 $[M - PhCHO - CH_2CH_2O]^+$ (40), 180 $[M - PhCHO - PhCH_2]^+$ (14), 64 $[TiO]^+$ (17).

Complex **16**. ^1H NMR, δ: 7.30—7.00 (m, 10 H, Ph); 6.44 (s, 5 H, Cp); 5.94 (d, 1 H, OCHPh, J = 9.9 Hz); 4.77, 4.50 (both td,

Table 5. Crystal data and X-ray experiment and structure refinement details for compounds **3** and **12**

Parameter	**3**	**12**
Molecular formula	$C_{15.75}H_{25}N_1O_3Ti_1$	$C_{18}H_{23}Cl_2N_1O_3Ti_1$
Molecular mass	324.27	420.17
Crystal size/mm	0.15×0.10×0.05	0.10×0.05×0.05
System	Triclinic	Monoclinic
Space group	$P\bar{1}$	$P2_1/n$
a/Å	8.7434(4)	12.533(1)
b/Å	8.7864(4)	9.5498(9)
c/Å	23.4031(11)	16.819(2)
α/deg	95.737(1)	90
β/deg	96.388(1)	109.956(2)
γ/deg	113.946(1)	90
V/Å^3	1611.97(13)	1892.2(3)
Z	4	4
d_{calc}/g cm^{-3}	1.336	1.475
μ/mm^{-1}	0.539	0.751
F(000)	690	872
Scan range over θ/deg	2.58—28.00	2.49—25.99
Ranges of reflection indexes	$-11 \le h \le 11$	$-14 \le h \le 15$
	$-11 \le k \le 10$	$-11 \le k \le 11$
	$-30 \le l \le 30$	$-20 \le l \le 20$
The number of measured reflections	12414	11303
The number of independent reflections (R_{int})	7436 (0.0184)	3706 (0.0448)
The number of refinement parameters	581	317
R_1 ($I \le 2\sigma(I)$)	0.0402	0.0491
wR_2 (for all reflections)	0.1091	0.1297
Quality for F^2	1.044	1.029
Residual electron density (max/min)/e Å^{-3}	0.876/−0.348	1.665/−0.857

1 H each, OCH_2, J = 11.7 Hz, J = 3.7 Hz); 4.27—4.23 (m, 2 H, OCH_2); 3.96 (d, 1 H, NCHPh, J = 11.1 Hz); 3.66—3.59, 3.11—3.03 (both m, 1 H each, NCH_2); 2.74, 2.43 (both dd, 1 H each, NCH_2, J = 11.8 Hz, J = 3.5 Hz).

On long-term keeping of a solution of compound **17** (dichloromethane—*n*-heptane) in air, compound **18** precipitated as a finely crystalline white solid poorly soluble in organic solvents. The structure of compound **18** was determined by X-ray diffraction analysis.

Reaction of complex 1 with compound 23. A solution of ligand **5** (0.51 g, 3.42 mmol) in DME (15 mL) was added dropwise to sodium hydride (0.40 g, 10.61 mmol) in DME (20 mL). The reaction mixture was refluxed for 6 h and then, with cooling to −50 °C, a solution of compound **1** (0.75 g, 3.42 mmol) in DME (20 mL) was added. After 15 h, the NaCl precipitate was filtered off and washed with hot chloroform (3×30 mL). The solvent was removed *in vacuo* and the residue was recrystallized from benzene to give titanatrane **7** as a white powder (0.14 g, 16%). The ^{1}H NMR signals of compound **7** agree with published data.[12]

Reaction of complex 4 with compound 24. A solution of Bu^nLi (5.30 mL) in *n*-hexane (1.98 mol L^{-1}) was added to a solution of compound **5** (0.50 g, 3.36 mmol) in DME (10 mL). The reaction mixture was stirred for 10 h and cooled to −50 °C, and a solution of complex **4** (0.98 g, 3.36 mmol) in DME (10 mL) was added dropwise. After 12 h, the precipitate was filtered off, and the solvent was evaporated *in vacuo*. According to ^{1}H NMR, the reaction gave a product mixture difficult to identify.

Reaction of complex 4 with compound 25. Compound **25** (1.31 g, 3.60 mmol) was added to a solution of complex **4** (1.05 g, 3.60 mmol) in *m*-xylene (20 mL). The reaction mixture was refluxed for 20 h, and the solvent was evaporated *in vacuo* to give the product $(Me_3Si\text{-}\eta^5\text{-}C_5H_4)TiCl_3 \cdot N(CH_2CH_2OSiMe_3)_3$ as a poorly soluble red powder (2.32 g). ^{1}H NMR, δ: 6.88 and 6.57 (both t, 2 H each, Cp, J = 3.4 Hz); 4.05 (t, 6 H, OCH_2, J = 5.1 Hz); 3.25 (t, 6 H, NCH_2, J = 5.1 Hz); 0.09 (s, 27 H, Me).

X-ray diffraction study. The atrane crystals suitable for X-ray crystallography were obtained on cooling to −30 °C of a solution in toluene (for compound **3**), a dichloromethane—*n*-octane mixture (for compound **12**), and a dichloromethane—*n*-heptane mixture (for compound **18**). The experimental reflection intensities were collected on a Bruker SMART automated diffractometer at 120.0(2) K using Mo-Kα-radiation (λ = 0.71073 Å, graphite monochromator). The adsorption corrections were applied by measuring the intensities of equivalent reflections.[43] The structures were solved by the direct method (SHELX-86[44]). All the nonhydrogen atoms were refined in the full-matrix anisotropic least-squares calculations for F^2 (SHELXL-97[45]). The H atoms (except for the solvation toluene molecule in compound **3**) were identified from the difference synthesis and refined isotropically. The H atoms in the solvation C_7H_8 molecule disordered at the inversion center (compound **3**) were placed into calculated positions and refined using the riding model. The crystal parameters, X-ray experiment and structure refinement details for compounds **3** and **12** are summarized in Table 5. The atom coordinates are deposited with the Cambridge Structural Database.

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