A Calix[4]arene Monoalkyl Ether as a Model of a Tris(phenolate) Ligand with a Hemilabile Anisole Moiety: Syntheses, Molecular Structures and Bonding of Calix[4]arene Ether Supported Titanium Complexes and Their Catalytic Activity in Epoxidation Reactions

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New mononuclear titanium complexes [TiCl(Rcalix)] [R = Me (**1**), Bz (**2**), $SiMe_3$ (**3**)] supported by *p-tert*-butylcalix[4]arene mono(organyl)ethers (Rcalix) were prepared in good yield from H_2R_2calix and [$TiCl_4(THF)_2$]. The crystallographically characterized complex [TiCl(Mecalix)] (**1**) reacts readily with NaCp and $LiNR_2$ to afford the complexes [TiCp(Mecalix)] (**4**) and [$Ti(NR_2)$(Mecalix)] [R = Me (**5**), Et (**6**), *i*Pr (**7**), Ph (**8**)], respectively. Reactions of [$Ti(NR_2)$(Mecalix)] (**5**) with alcohols, phenols and thiols proceed cleanly with amide exchange, as exemplified by the synthesis of [Ti(OR)(Mecalix)] [R = Me (**10**), *i*Pr (**11**), *t*Bu (**12**), 4-$tBuC_6H_4$ (**13**), 2,6-$iPr_2C_6H_3$ (**14**)], and [Ti(S*t*Bu)(Mecalix)] (**15**). Depending on the steric demand of the ligand coordinated to the [Ti(Mecalix)] complex fragment these compounds are monomeric or dimeric in the solid state, as demonstrated by the molecular structures of monomeric [$Ti(OC_6H_3$-2,6-iPr_2)(Mecalix)] (**14**) and [Ti(S*t*Bu)(Mecalix)] (**15**), or dimeric [$\{Ti(OMe)(Mecalix)\}_2$] (**10**). In all complexes the calix[4]arene ligand adopts an elliptically distorted cone conformation in which the distance of the titanium atom from the anisole oxygen atom varies between 2.342 Å and 2.438 Å for the structurally characterized complexes, with the exception of the Cp complex **4**. MP2 calculations on model complexes demonstrate that the titanium–anisole oxygen bond is weak, with a particularly shallow potential energy surface in the region between 2.30 Å and 2.80 Å. The Mecalix ligand system therefore might be described as a tris(phenolate) ligand with a hemilabile anisole group in the titanium compounds reported. Despite the labile anisole ether titanium bond, isomerization of the calix[4]arene ligand to a *paco* coordination mode, as described earlier for the Me_2calix complexes [$Ti(OC_6H_4$-4-R$)_2$(Me_2calix)], has not been observed in these complexes. Preliminary results on the catalytic epoxidation of cyclooctene with TBHP using calix[4]arene-stabilized titanium(IV) complexes are also briefly presented.

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Introduction

Calix[*n*]arenes are macrocyclic molecules consisting of *n* phenol units connected by *ortho*-methylene groups.[1,2] Calix[4]arenes, with four phenolic residues in the macrocyclic ring, are the simplest and most common compounds of this family. These molecules and their derivatives have been extensively studied for their interesting properties, for example as hosts for cations, anions and neutral molecules, and for the formation of supramolecular assemblies.[3]

Because of the four phenoxy groups in the calix[4]arenes (*p-tert*-butylcalix[4]arene = H_4calix), reactions with transition metal complexes can produce metal phenolate compounds with substitution of up to four hydrogen atoms.[4] Calix[4]arenes have some unique geometrical peculiarities when acting as poly(phenolate) ligands. The fully deprotonated form of the parent calix[4]arene acts as a tetraanionic ligand and usually assumes a cone conformation, which keeps the set of oxygen donor atoms quasi-planar. Depending on the exact geometry adopted in the complex and on the presence of additional metal centers in the complex, this cone conformation readily distorts towards an elliptical cone conformation.[5]

The charge of the O_4 set can be tuned by etherification or esterification of the lower rim of the calix[4]arene, and the degree of functionalization of the metal atom can be controlled by alkylating or silylating the oxygen atom(s), which also offers steric protection. The [Me_2calix] homologues, in particular have received much attention in organotransition metal chemistry over the last 10 years, and a rich chemistry has emerged comprising mainly mononuclear group 4 and 5 metals. In these complexes, the [R_2calix]$^{2-}$ ligands usually provide two negatively charged phenolate oxygen donor atoms and two neutral anisole oxygen donors to a transition metal atom. If the calix[4]arene ethers coordinate in their elliptically distorted cone conformations, these ligands provide a robust and well-defined O_4 coordination environment, similar to other widely used sup-

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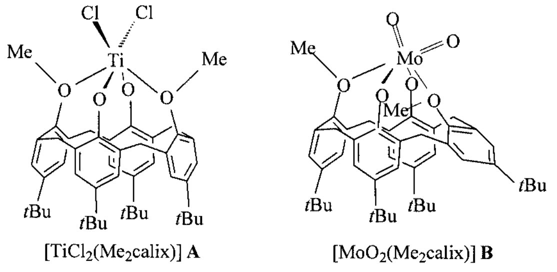
porting dianionic ligands such as the O_2N_2 donor ligands of salen-type Schiff bases or N_4 donor ligands such as porphyrins and dibenzotetraaza[14]annulenes.[6–8]

In contrast to these nitrogen-containing ligand systems, the calix[4]arene dialkyl ethers are conformationally much more flexible. The coordination mode of calix[4]arene dialkyl ethers is largely determined by the nature of the ether group, the coordination number of the metal atom, and the nature of the co-ligands. The cavity of the macrocyclic ligand can therefore be influenced by other ligands in transition metal calix[4]arene complexes if strongly directing co-ligands such as oxo groups are used. We have shown that in the d^0-transition metal complex [$TiCl_2(Me_2calix)$] (**A**) the calix[4]arene ligand adopts an elliptically distorted cone conformation, whereas in the related d^0-transition metal complex [MoO_2(*paco*-Me_2calix)] (**B**) the metalated calix[4]arene ligand is coordinated in the solid state as well as in solution in a form which is reminiscent of the partial cone (*paco*) conformation of calix[4]arene (see Scheme 1).[9] In these complexes, one of the methoxy groups of the ligand is located inside the cavity of the calix[4]arene complex.



Scheme 1. Coordination modes of the calix[4]arene dimethyl ether ligand in [$TiCl_2(Me_2calix)$] (**A**) and [MoO_2(*paco*-Me_2calix)] (**B**)

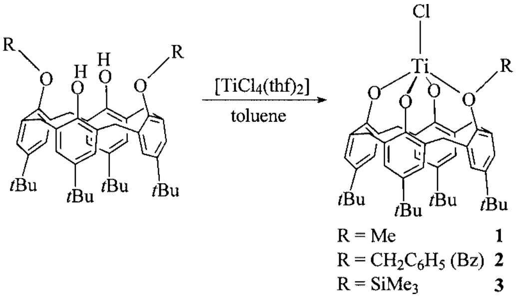
In compound **B** the [$Mo(Me_2calix)$] complex fragment is further stabilized by two additional O^{2-} ligands, which exhibit a strong *trans* influence; density functional calculations on models of different isomers of **A** and **B** indicate that this phenomenon is mainly driven by the co-ligands employed in these complexes.

Furthermore, in compounds of the type [$Ti(OC_6H_4\text{-}4\text{-}R)_2(Me_2calix)$] (R = Me or *t*Bu; **C**), both types of coordination mode have been observed.[10] These bis(phenolate) complexes have been isolated in good to excellent yields from the reaction of the imidotitanium complex [Ti(N*t*Bu)(Me_2calix)] and 2 equiv. of the corresponding *para*-substituted phenol to afford complexes in which the calix[4]arene is coordinated in an elliptically distorted cone conformation. These complexes undergo elimination and/or rearrangement reactions in nonpolar solvents such as pentane and hexane. The metal-containing products of the elimination reactions are the dinuclear compounds [{$Ti(OC_6H_4\text{-}4\text{-}R)$(Mecalix)}$_2$] and the products of the rearrangement reaction are [$Ti(OC_6H_4\text{-}4\text{-}R)_2$(*paco*-$Me_2$calix)] (**C**). Density functional calculations on model compounds of [$Ti(OC_6H_5)_2$(*cone*-Me_2calix)] and [$Ti(OC_6H_5)_2$(*paco*-Me_2calix)] reveal a slight thermodynamic preference for the *paco* isomer, but the pathway of this isomerization process is not yet clear. The rearrangement reaction is sensitive to changes of the sterics of the [$M(OAr)_2$] fragment; complexes [$Ti(OC_6H_3\text{-}2,6\text{-}R_2)_2(Me_2calix)$] with *ortho*-substituted phenolate ligands do not rearrange. We have also prepared the analogous zirconium complexes [$Zr(OC_6H_4\text{-}4\text{-}Me)_2(Me_2calix)$] and [$Zr(OC_6H_3\text{-}2,6\text{-}Me_2)_2(Me_2calix)$] from [$Zr(NC_6H_3\text{-}2,6\text{-}$*i*$Pr_2)(Me_2calix)$] and the corresponding phenol; they also do not undergo rearrangement or elimination reactions.[10] Furthermore, *paco* coordination was only observed for complexes of the calix[4]arene dimethyl ether in distorted octahedrally coordinated compounds of the type [$MX_2(Me_2calix)$]. At this point we became interested in investigating the coordination behavior of calix[4]arene monomethyl ether complexes of the type [MX(Mecalix)]. In this contribution we report our results on titanium complexes of the type [TiX(Rcalix)], which are stabilized with the trianion of the calix[4]arene alkyl ether H_3Rcalix and different donor ligands X (Cl, NR_2, OR, SR).

Results and Discussion

Calix[4]arene Chlorotitanium Complexes

The preparation of [TiCl(Mecalix)] starting from H_2Me_2calix and [$TiCl_4(THF)_2$] has already been published by Floriani and co-workers.[11] The outcome of this reaction depends critically upon the reaction conditions. The reaction of H_2Me_2calix and [$TiCl_4(THF)_2$] in toluene at 60 °C for 1 d affords the titanacalix[4]arene dimethyl ether [$TiCl_2(Me_2calix)$],[9,10] whereas a prolonged reaction time in refluxing toluene leads to elimination of MeCl to give [TiCl(Mecalix)] [**1**; see Equation (1)]. Similarly, the reaction of H_2Bz_2calix[12] with [$TiCl_4(THF)_2$] in toluene at 80 °C for 1 h affords [TiCl(Bzcalix)] (**2**) in good yield. The elimination of BzCl seems to be more favorable than MeCl cleavage in [$TiCl_2(Me_2calix)$].

 (1)

The bis(trimethylsilyl)ether $H_2(Me_3Si)_2$calix[13] also reacts readily with [$TiCl_4(THF)_2$] at room temperature to afford the titanacalix[4]arene [TiCl{(Me_3Si)calix}] (**3**). The thermal stability of the calixarene ether dichloro complexes [$TiCl_2(R_2calix)$] with respect to RCl elimination is $SiMe_3 <$ Bz << Me, which reflects the stability of the radical species R — possible intermediates during the cleavage reaction — as well as the steric demand of the R group. On the other hand, formation of the dichloro complex

$[TiCl_2\{(Me_3Si)_2calix\}]$ as a possible intermediate was not observed during the reaction of the silyl ether; NMR investigations of reaction mixtures of $H_2(SiMe_3)_2calix$ and $[TiCl_4(THF)_2]$ have shown that **3** is formed within a few minutes. Therefore, it is likely that HCl as well as TMSCl elimination are involved in the first Ti−bond formation step. Raising the reaction temperature leads to further Me_3SiCl cleavage from **3** and formation of polynuclear calix[4]arene complexes.[14]

Compounds **1**−**3**, which were obtained as their toluene solvates, were characterized by elemental analysis, NMR spectroscopy and mass spectrometry. The ^1H NMR spectra of these compounds show signals typically found for calix[4]arene complexes with local C_s symmetry of the macrocyclic ligand. Three resonances were detected for the *t*Bu groups of the calix[4]arene ligand and four doublets for the methylene protons. The protons of the R substituents of [TiCl(Rcalix)] appear at δ = 3.84 (R = CH_3), 5.38 (R = CH_2Ph) and 0.49 (R = $SiMe_3$) ppm. Accurate integration of the signals confirms the cleavage of one ether group from the starting material. Furthermore, the signals are not significantly shifted to higher field, as observed previously for endohedrally located anisole ether groups, which suggests a distorted cone coordination mode of the calix[4]arene ligand. This was confirmed for **1** by X-ray analysis (Figure 1).

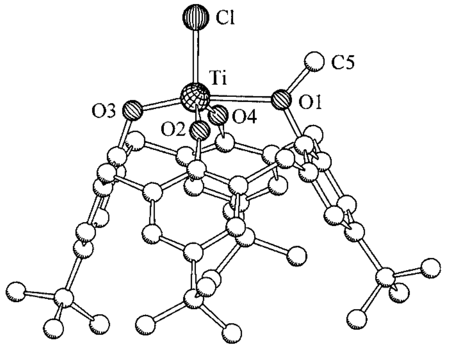


Figure 1. SCHAKAL plot of the molecular structure of [TiCl(Mecalix)] in $1\cdot1.5C_7H_8$; H atoms and solvent molecules have been omitted for clarity; selected bond lengths [Å] and angles [°]: Ti−Cl 2.258(1), Ti−O(1) 2.424(2), Ti−O(2) 1.796(2), Ti−O(3) 1.813(2), Ti−O(4) 1.784(2); Cl−Ti−O(1) 90.1(1), Cl−Ti−O(2) 112.9(1), Cl−Ti−O(3) 103.4(1), Cl−Ti−O(4) 113.7(1), O(1)−Ti−O(2) 78.1(1), O(1)−Ti−O(3) 166.5(1), O(1)−Ti−O(4) 76.7(1), O(2)−Ti−O(3) 96.5(1), O(2)−Ti−O(4) 126.3(1), O(3)−Ti−O(4) 97.3(1), C(5)−O(1)−C(10) 112.8(2), Ti−O(1)−C(5) 129.7(2), Ti−O(1)−C(10) 117.4(2), Ti−O(2)−C(20) 156.5(2), Ti−O(3)−C(30) 121.9(2), Ti−O(4)−C(40) 159.4(2)

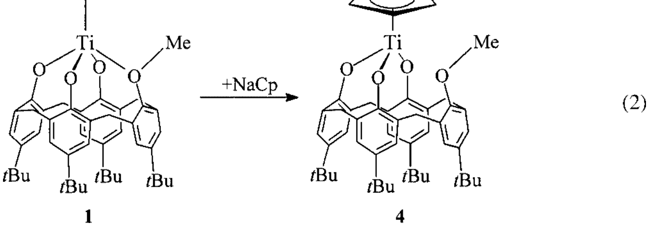
Single crystals of **1** were grown from saturated toluene solutions of the compound. This structure is identical, within experimental errors, with that published previously by Floriani and co-workers,[11] but it is nevertheless important to describe briefly its main features in the context of this paper for comparison with other structurally characterized complexes of the type [TiX(Mecalix)] reported here and the results of theoretical calculations described below.

Complex **1** crystallizes with an additional toluene molecule that is hosted inside the calixarene cavity and half of a toluene molecule in the asymmetric unit, which occupies a general position in the lattice. The X-ray crystal structure of **1** confirms the mononuclear character of the compound in the solid state, in which the calixarene is coordinated in an elliptically distorted cone conformation. The coordination polyhedron at the titanium atom can be described as a distorted trigonal bipyramid, in which the oxygen atoms O(1) and O(3) occupy the axial positions and Cl, O(2), and O(3) the equatorial sites. The angles Cl−Ti−O(3) [103.4(1)°] and O(2)−Ti−O(4) [126.3(1)°] reflect the significant distortions of the ideal polyhedron. The angle O(1)−Ti−O(3) between the mutually *trans*-oxygen atoms O(1) and O(3) [166.5(1)°] also reveals a deviation from a linear alignment of these atoms.

The Ti−Cl distance of 2.258(1) Å is approximately 0.10 Å shorter than that found in the distorted octahedral complex $[TiCl_2(Me_2calix)]$,[9] but it is similar to those observed in other pentacoordinated titanium complexes such as $[TiCl_2(mbmp)(THF)]$ ($[H_2mbmp = 2,2'\text{-}CH_2\{6\text{-}t\text{Bu-}4\text{-}MeC_6H_2(OH)\}_2]$).[15] The Ti−O distances to the oxygen atoms O(2), O(3) and O(4) of the phenolate units [1.796(2) Å, 1.813(2) Å and 1.784(2) Å, respectively] are similar to those found in $[TiCl_2(Me_2calix)]$. The Ti−O(1) bond to the oxygen atom of the anisole unit [2.424(2) Å] is significantly longer (approximately 0.30 Å) than in $[TiCl_2(Me_2calix)]$. However, the sum of the Ti−O(1) and Ti−O(3) distances is almost identical to the sum of the corresponding Ti−O distances in $[TiCl_2(Me_2calix)]$ (4.234 Å vs. 4.237 Å), which reflects the geometrical constraint of the calix[4]arene ligand. In other words, the titanium atom moves from an ideal, central position between the anisole oxygen atoms in $[TiCl_2(Me_2calix)]$ towards the stronger phenolate oxygen donor atom O(3) in [TiCl(Mecalix)].

A Calix[4]arene Cyclopentadienyltitanium Complex

In the series [TiX(Mecalix)], Floriani et al. have already reported alkyl complexes of the type [TiR(Mecalix)] (R = Me, $CH_2C_6H_5$, 4-MeC_6H_4). In these compounds, the calix[4]arene binds in a distorted cone conformation to the [Ti−R] complex fragment, as was shown by NMR spectroscopy and a structural analysis of $[Ti(C_6H_4\text{-}4\text{-}Me)(Mecalix)]$.[11] We were interested in coordinating the excellent σ,π-donor ligand $C_5H_5^-$ to the calix[4]arene titanium fragment. According to Equation (2), [TiCp(Mecalix)] (**4**) can be prepared in good yields from the reaction of **1** with NaCp.



(2)

Compound **4** was characterized by elemental analysis, mass spectrometry, and NMR spectroscopy. The NMR spectra are in accordance with a pseudo-C_s-symmetric structure of the complex in solution, as shown in Equation (2). The signals of the protons of the anisole methyl groups at δ = 3.89 ppm and of the Cp ligand at δ = 6.80 ppm, in the integration ratio 3:5, are sharp singlets at room temperature and do not change on cooling to −60 °C, which confirms the η^5-coordination mode of the Cp ligand. It is interesting to note that the chemical shifts of the protons of the anisole methyl groups at δ = 3.44 ppm in C_6D_6 and δ = 3.89 ppm in $CDCl_3$ are similar to the NMR shifts obtained for the uncomplexed ligand at δ = 3.49 ppm (C_6D_6) and δ = 3.93 ppm ($CDCl_3$). The resonances observed for **1** are significantly shifted to higher field compared to those of the uncomplexed ligand at δ = 3.84 ppm (C_6D_6) and δ = 4.26 ppm ($CDCl_3$). Similar observations have been made in the $^{13}C\{^1H\}$ NMR spectra of **4**, which points to an uncoordinated anisole group in solution. This probably reflects better electronic as well as steric shielding of the metal atom in **4** compared to the chloro complex **1**.

The molecular structure of **4** is shown in Figure 2. Complex **4** crystallizes in the space group $P2_1/c$ with one formula unit and two additional solvent molecules in the unit cell, which occupy general positions in the lattice. The titanium atom in **4** is tetrahedrally coordinated to the Cp ligand and three phenolate oxygen atoms of the calixarene. The Ti−O distances of 1.807(4) Å, 1.864(4) Å, and 1.809(4) Å are slightly longer than those observed in **1**, but similar to Ti−O bond lengths found in other stable complexes of the type $[TiCp(OR)_3]$, such as $[TiCp(OC_6H_3\text{-}2,6\text{-}i\text{Pr}_2)_3]$ [average 1.80(2) Å] and $[TiCp(OC_6F_4H)_3]$ [1.826(3) Å, 1.830(3) Å and 1.867(3) Å].[16] In comparison with the chloro complex **1**, the titanium atom is displaced further from the center of the calix[4]arene ligand; the Ti−O(1) distance of 3.498(6) Å can be regarded as nonbonding. Whereas the size of the C(50)−O(1)−C(10) angle [113.4(5)°] is similar to the corresponding angle C(5)−O(1)−C(10) [112.8(2)°] in **1**, a significant difference in the bonding of the fragments $[TiCl]^{3+}$ and $[Ti(\eta^5\text{-}C_5H_5)]^{3+}$ to the $[\text{Mecalix}]^{3-}$ ligand is also reflected in the Ti−O(1)−C(10) angles of 87.1(4)° in **4** and 117.4(1)° in **1**. As a consequence, the calixarene cavity is significantly influenced by the metal complex fragment bound at the lower rim of the ligand. The distance to the phenolate carbon atoms C(15) and C(35) in the *para* positions is 5.463 Å in the Cp complex, which is much smaller than the corresponding distance in the chloro compound **1** (7.685 Å); this distortion of the calix[4]arene ligand prevents inclusion of a solvent molecule inside the calixarene cavity.

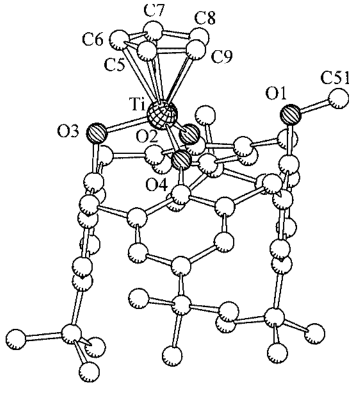


Figure 2. SCHAKAL plot of the molecular structure of [TiCp(Mecalix)] in $\mathbf{4}\cdot 2C_7H_8$; H atoms and solvent molecules have been omitted for clarity; selected bond lengths [Å] and angles [°]: Ti−O(1) 3.498(6), Ti−O(2) 1.807(4), Ti−O(3) 1.864(4), Ti−O(4) 1.809(4), Ti−Cp_{centr} 2.039(7), Ti−C(5) 2.365(7), Ti−C(6) 2.373(6), Ti−C(7) 2.359(7), Ti−C(8) 2.319(7), Ti−C(9) 2.327(7); Cp_{centr}−Ti−O(1) 88.5(2), Cp_{centr}−Ti−O(2) 119.6(2), Cp_{centr}−Ti−O(3) 108.1(2), Cp_{centr}−Ti−O(4) 119.5(2), O(1)−Ti−O(2) 69.4(4), O(1)−Ti−O(3) 163.4(4), O(1)−Ti−O(4) 70.2(4), O(2)−Ti−O(3) 100.98(17), O(2)−Ti−O(4) 104.84(17), O(3)−Ti−O(4) 100.68(17), Ti−O(1)−C(10) 87.1(4), Ti−O(1)−C(50) 158.4(3), C(50)−O(1)−C(10) 113.4(5), Ti−O(2)−C(20) 161.3(4), Ti−O(3)−C(30) 111.0(3), Ti−O(4)−C(40) 162.4(4)

Calix[4]arene Amidotitanium Complexes

Calix[4]arene-stabilized amidotitanium complexes of the type $[Ti(NR_2)(\text{Mecalix})]$ with different substituents R = Me (**5**), Et (**6**), *i*Pr (**7**), Ph (**8**) are readily available by metathetical exchange of the chloro ligand in **1** with an equimolar amount of the corresponding lithium amide in toluene (see Scheme 2). These complexes can be isolated in good to reasonable yields as yellow to red powders. The mass spectra of these substances show peaks for the molecular ions as the base peaks at *m*/*z* = 751 (**5**), 779 (**6**), 807 (**7**), and 875 (**8**), which are in accordance with their formulation as mononuclear species. However, based on NMR spectroscopic data it is impossible to distinguish a monomeric complex from a possible dinuclear, amido-bridged complex of the composition $[\{Ti(\mu\text{-}NR_2)(\text{Mecalix})\}_2]$.

The compounds $[Ti(NMe_2)(\text{Mecalix})]$ (**5**) and $[Ti(NPh_2)(\text{Mecalix})]$ (**8**) were structurally characterized. The molecular structures of these complexes are shown in Figures 3 and 4. All attempts to crystallize **5** from various solvents led to crystals unsuitable for X-ray diffraction. However, after prolonged storage as a THF solution, we obtained suitable crystals of complex **5** cocrystallized with its product of hydrolysis, $[\{Ti(\text{Mecalix})\}_2(\mu\text{-}O)]$ (**9**). Complex **8** crystallizes with two independent molecules $[Ti(NPh_2)(\text{Mecalix})]$ in the space group $P2_1/c$, which differ only slightly in their molecular structures. Since there are no significant differences between the two sets of bond lengths and angles we will refer specifically only to those from one of the molecules [at Ti(1)]; the parameters of the other molecule are given in the caption to Figure 4.

The results of the X-ray analyses confirm the mononuclear nature of **5** and **8** in the solid state, as postulated in Scheme 2. Typically, all calixarene ligands host a solvent molecule in their cavities. The coordination sphere at the metal atom in **5** and **8** is best described as distorted trigonal-bipyramidal, in which the oxygen atoms O(1) and O(3) occupy axial positions and the oxygen atoms O(2) and O(4), as well as the nitrogen atom of the amide ligand, span the equatorial plane. The oxygen atoms in the axial positions

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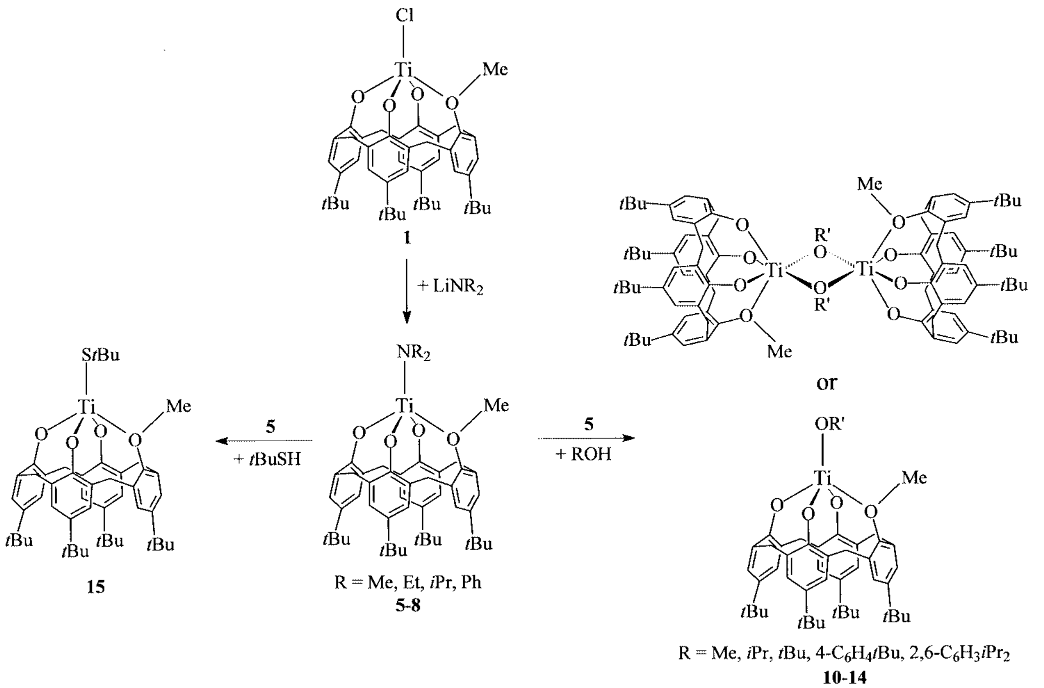

Scheme 2. Synthesis of Mecalix-stabilized amidotitanium alkoxide, phenolate, and thiolate complexes

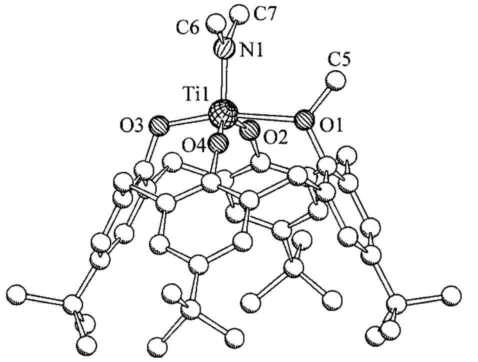

Figure 3. SCHAKAL plot of the molecular structure of [Ti(NMe$_2$)(Mecalix)] (**5**) in **5**·9·5C$_4$H$_8$O; H atoms and solvent molecules have been omitted for clarity; selected bond lengths [Å] and angles [°]: Ti(1)−N(1) 1.846(5), Ti(1)−O(1) 2.342(4), Ti(1)−O(2) 1.818(4), Ti(1)−O(3), 1.874(4), Ti(1)−O(4) 1.814(5); Ti(1)−N(1)−C(6) 123.8(5), Ti(1)−N(1)−C(7) 123.3(5), C(6)−N(1)−C(7) 112.6(6), N(1)−Ti(1)−O(1) 90.6(2), N(1)−Ti(1)−O(2) 109.3(2), N(1)−Ti(1)−O(3) 103.3(2), N(1)−Ti(1)−O(4) 109.6(2), O(1)−Ti(1)−O(2) 79.5(2), O(1)−Ti(1)−O(3) 166.1(2), O(1)−Ti(1)−O(4) 79.5(2), O(2)−Ti(1)−O(3) 95.7(2), O(2)−Ti(1)−O(4) 135.6(2), O(3)−Ti(1)−O(4) 95.4(2), Ti(1)−O(1)−C(5) 125.9(4), Ti(1)−O(1)−C(10) 119.2(3), Ti(1)−O(2)−C(20) 150.9(4), Ti(1)−O(3)−C(30) 121.0(4), Ti(1)−O(4)−C(40) 151.7(4)

are almost linearly aligned, with O(1)−Ti−O(3) angles of 166.1(2)° (**5**) and 166.5(1)° (**8**). The N(1)−Ti−O(3) angles of 103.3(2)° (**5**) and 104.5(1)° (**8**), as well as the other bond angles in the equatorial plane, reflect a significant distortion from an ideal polyhedron. The metal atoms in **5** and **8** are dislocated from a central position in the trigonal bipyramid towards the phenolate oxygen donor atom O(3), as described above for the chloro complex **1**, but this distortion is not as pronounced as observed in the solid-state structure

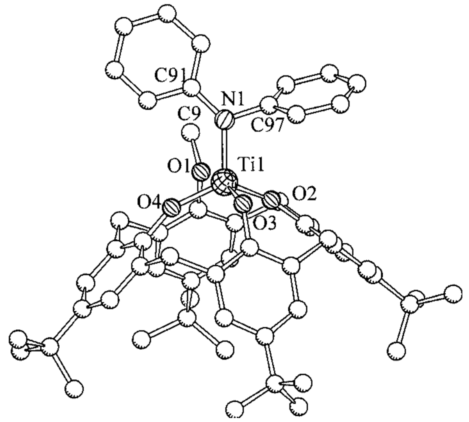

Figure 4. SCHAKAL plot of the molecular structure of [Ti(NPh$_2$)(Mecalix)]·(**8**) in **8**·8C$_4$H$_8$O·0.5C$_6$H$_6$; H atoms and solvent molecules have been omitted for clarity; selected bond lengths [Å] and angles [°]: Molecule 1: Ti(1)−N(1) 1.920(3), Ti(1)−O(1) 2.385(3), Ti(1)−O(2) 1.783(3), Ti(1)−O(3) 1.857(3), Ti(1)−O(4) 1.799(3); Ti(1)−N(1)−C(91) 1.338(3), Ti(1)−N(1)−C(97) 107.7(3), C(91)−N(1)−C(97) 118.0(3), N(1)−Ti(1)−O(1) 89.1(1), N(1)−Ti(1)−O(2) 111.4(1), N(1)−Ti(1)−O(3) 104.5(1), N(1)−Ti(1)−O(4) 115.5(1), O(1)−Ti(1)−O(2) 78.3(1), O(1)−Ti(1)−O(3) 166.5(1), O(1)−Ti(1)−O(4) 78.1(1), O(2)−Ti(1)−O(3) 95.6(1), O(2)−Ti(1)−O(4) 126.5(1), O(3)−Ti(1)−O(4) 96.4(1), Ti(1)−O(1)−C(9) 130.1(3), Ti(1)−O(1)−C(10) 116.8(2), Ti(1)−O(2)−C(20) 163.2(3), Ti(1)−O(3)−C(30) 120.2(2), Ti(1)−O(4)−C(40) 155.8(3), C(9)−O(1)−C(10) 113.0(3); Molecule 2: Ti(2)−N(2) 1.930(3), Ti(2)−O(5) 2.378(3), Ti(2)−O(6) 1.792(3), Ti(2)−O(7) 1.853(3), Ti(2)−O(8) 1.789(3); N(2)−Ti(2)−O(5) 89.88(12), N(2)−Ti(2)−O(6) 113.65(14), N(2)−Ti(2)−O(7) 103.96(13), N(2)−Ti(2)−O(8) 112.85(14), O(5)−Ti(2)−O(6) 78.48(11), O(5)−Ti(2)−O(7) 166.13(11), O(5)−Ti(2)−O(8) 77.65(11), O(6)−Ti(2)−O(8) 127.03(13), O(6)−Ti(2)−O(7) 96.43(13), O(7)−Ti(2)−O(8) 95.77(12), Ti(2)−O(5)−C(50) 117.1(2), Ti(2)−O(6)−C(60) 158.8(3), Ti(2)−O(7)−C(70) 121.1(2), Ti(2)−O(8)−C(80) 159.3(3), Ti(2)−O(5)−C(90) 129.0(3), Ti(2)−N(2)−C(103) 133.0(3), Ti(2)−N(2)−C(109) 108.6(2)

of the Cp complex **4**. The sum of the X−Ti−Y angles of all atoms that are aligned in the equatorial plane [O(2), O(4), N/Cl/Cp_{centr}] is 352.9° in **1**, 354.5° in **5**, 353.4° in **8** and only 343.9° in **4**. They follow a similar trend as the Ti−O(1) bond lengths [2.424(2) Å (**1**), 2.342(4) Å (**5**), 2.38.5(3) Å (**8**), and 3.498(6) Å (**4**)], which indicates that the Ti−O(1) bond lengths do not follow only simple trends such as different steric hindrance or different electronic properties of the chloro, amido, and Cp ligands in this series.

The Ti−N distances [1.846(5) Å (**5**) and 1.920(3) Å (**8**)] are shorter than expected from the ionic radii (approximately 2.07 Å),[17] but are similar to the Ti−N bond lengths found in bis(amido)titanium complexes such as [$Ti(NMe_2)_2(OC_6H_3$-2,6-$tBu_2)_2$] and [$Ti(NMe_2)_2(OC_6H_2$-2,4,6-$tBu_3)_2$], with values between 1.864 Å and 1.897 Å.[18] This can be attributed to π-donation of the amide ligand to the titanium atom, in which the nitrogen lone pair is involved in Ti−N bonding. Furthermore, the amido [NC_2] entity is almost planar, as revealed by the sum of the angles at the nitrogen atoms [359.7° (**5**) and 359.5° (**8**)]. The diorganylamido ligand in both complexes is oriented in such a way that the plane through the amido nitrogen atom and the N−C carbon atom is almost perpendicular to the plane through the atoms Ti, O(1) and O(3). These planes intersect each other with an angle of 89.9(10)° (**5**) and 74.8(6)° (**8**).

As mentioned above, the air- and moisture-sensitive amido complex **5** was cocrystallized with [{Ti(Mecalix)}$_2$(μ-O)] (**9**). Since the anisole methyl ether groups of **9** in **5**·**9**·5C_4H_8O are disordered over two sites, the formation of complex **9** starting from the amido complex **5** was verified and its molecular structure was determined separately. Complex **9** crystallizes from saturated benzene solutions at room temperature in the form of thin plates in the space group $P2_1/n$ with two formula units and eight solvent molecules in the unit cell. The molecular structure of **9**, as found in **9**·4C_6H_6, is shown in Figure 5; selected bond lengths and angles are given in the figure caption.

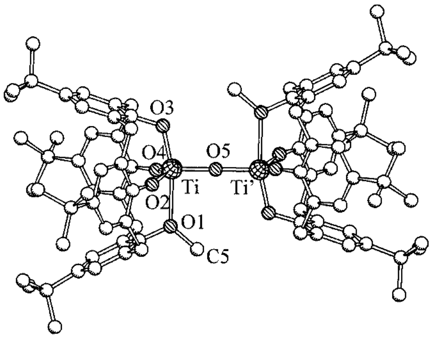

Figure 5. SCHAKAL plot of the molecular structure of [{Ti(Mecalix)}$_2$(μ-O)] in **9**·4C_6H_6; H atoms and solvent molecules have been omitted for clarity; selected bond lengths [Å] and angles [°]: Ti−O(1) 2.389(4), Ti−O(2) 1.784(4), Ti−O(3) 1.841(4), Ti−O(5) 1.798(1), Ti−O(4) 1.798(4); Ti−O(5)−Ti′ 180.0(1), O(1)−Ti−O(2) 77.2(2), O(1)−Ti−O(3) 166.7(1), O(1)−Ti−O(4) 79.1(2), O(1)−Ti−O(5) 91.2(1), O(2)−Ti−O(3) 95.2(2), O(2)−Ti−O(4) 126.0(2), O(2)−Ti−O(5) 115.5(1), O(3)−Ti−O(4) 97.2(2), O(3)−Ti−O(5) 102.0(1), O(4)−Ti−O(5) 112.8(1), Ti−O(1)−C(5) 129.9(3), Ti−O(1)−C(10) 115.9(3), Ti−O(2)−C(20) 167.3(4), Ti−O(3)−C(30) 119.0(3), Ti−O(4)−C(40) 151.2(3), C(5)−O(1)−C(10) 114.1(4)

The coordination sphere at the titanium atoms in **9** is also distorted trigonal-bipyramidal. The molecular unit of **9** as found in **5**·**9**·5C_4H_8O has similar geometrical data. In this compound two [Ti(Mecalix)]$^+$ units are linked by a linear μ-O^{2-} ligand. The Ti−O−Ti′ angle (180.0°) in both molecular structures of **9** is superimposed by crystallographic symmetry, since the oxygen atoms are aligned in both cases on an inversion center. The Ti−O distances in the bridge are 1.798(1) Å in **9**·4C_6H_6 and 1.791(1) Å in **5**·**9**·5C_4H_8O; the Ti−O(1) bond length is 2.389(4) Å.

Calix[4]arene Titanium Alkoxide, Phenoxide, and Thiolate Complexes

There are several ways to synthesize complexes of the type [Ti(OR)(Mecalix)]. The basic strategies are: (i) salt metathesis using [TiCl(Mecalix)] and an alkali metal alkoxide or phenolate; (ii) to introduce the calix[4]arene ligand into titanium alkoxide or phenolate complexes; and (iii) to introduce the alkoxide or phenolate by metathesis of more basic alkyl, aryl or amide ligands. The general route we chose for the preparation of such compounds is the reaction of equimolar amounts of alcohols or phenols with [$Ti(NMe_2)$(Mecalix)] (**5**). These reactions afford the complexes [Ti(OR)(Mecalix)] (**10**; R = Me), (**11**; R = *i*Pr), (**12**; R = *t*Bu), (**13**; R = 4-$tBuC_6H_4$), and (**14**; R = 2,6-$iPr_2C_6H_3$) in good yield (Scheme 2). Similarly, thiolate ligands can be introduced into the calixarene titanium system, as exemplified by the synthesis of [Ti(S*t*Bu)(Mecalix)] (**15**). Other routes are also viable, as was shown for the synthesis of compound **12** from the reaction of [TiCl(Mecalix)] with KO*t*Bu, or the synthesis of **11** starting from [$Ti(OiPr)_4$] and 1 equiv. of H_3Mecalix. Whereas the latter approach is advantageous for the isopropoxide system, salt metathesis generally leads to lower yields and purities.

The composition of the resulting bright yellow metal complexes was verified by elemental analysis. In the mass spectra of these compounds, the molecular peaks for the mononuclear ions at m/z = 738 (**10**), 766 (**11**), 780 (**12**), 856 (**13**), 885 (**14**), and 796 (**15**) were found as base peaks. The ^1H and ^{13}C NMR spectra reveal signals typically found for pseudo-C_s-symmetrical calix[4]arene complexes. However, on the basis of NMR spectroscopic data a differentiation between monomeric and dimeric alkoxide-bridged species is not possible. The molecular structures of [$Ti(OC_6H_4$-4-*t*Bu)(Mecalix)] (**13**) and [$Ti(OC_6H_4$-4-Me)(Mecalix)] (**C**), synthesized previously from the reaction of [Ti(N*t*Bu)(Me_2calix)] and the corresponding phenol, show that these complexes are dimers in the solid state.

In addition, X-ray analyses of the methoxide and diisopropylphenolate complexes **10** and **14** were performed. Crystals suitable for X-ray diffraction studies were grown from saturated toluene solutions. The molecular structures of these complexes are shown in Figures 6 and 7.

The methoxide complex **10** is a methoxy-bridged dimer in the solid state, in which two methoxide ligands bridge

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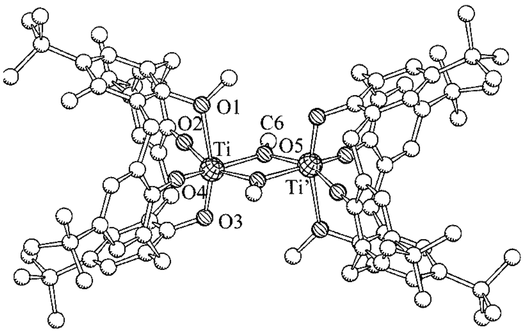

Figure 6. SCHAKAL plot of the molecular structure of [{Ti(OMe)(Mecalix)}$_2$] in **10**·6C_7H_8; H atoms and solvent molecules have been omitted for clarity; selected bond lengths [Å] and angles [°]: Ti−O(1) 2.438(2), Ti−O(2) 1.808(2), Ti−O(3) 1.847(2), Ti−O(4) 1.800(2), Ti−O(5) 2.032(2), Ti−O(5)′ 2.026(2); O(1)−Ti−O(2) 76.0(1), O(1)−Ti−O(3) 164.2(1), O(1)−Ti−O(4) 76.9(1), O(1)−Ti−O(5) 94.6(1), O(1)−Ti−O(5)′ 90.0(1), O(2)−Ti−O(3) 94.4(1), O(2)−Ti−O(4) 104.2(1), O(2)−Ti−O(5) 158.8(1), O(2)−Ti−O(5)′ 91.0(1), O(3)−Ti−O(4) 93.8(1), O(3)−Ti−O(5) 98.5(1), O(3)−Ti−O(5)′ 103.0(1), O(3)−Ti−O(4) 76.9(1), O(4)−Ti−O(5) 91.8(1), O(4)−Ti−O(5)′ 156.5(1), O(5)−Ti−O(5)′ 69.8(1), O(1)−Ti−Ti′ 92.7(1), O(2)−Ti−Ti′ 125.4(1), O(3)−Ti−Ti′ 103.1(1), O(4)−Ti−Ti′ 125.2(1), O(5)−Ti−Ti′ 34.8(1), O(5)′−Ti−Ti′ 35.0(1), Ti′−O(5)−Ti 110.2(1), Ti−O(1)−C(5) 131.5(2), Ti−O(1)−C(10) 115.4(2), Ti−O(2)−C(20) 167.7(2), Ti−O(3)−C(30) 120.2(2), Ti−O(4)−C(40) 167.2(2), Ti−O(5)−C(6) 124.2(2), Ti′−O(5)−C(6) 125.3(2)

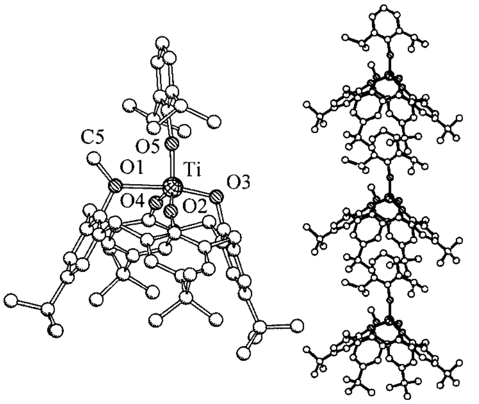

Figure 7. SCHAKAL plot of the molecular structure of [Ti(OC_6H_3-2,6-*i*Pr_2)(Mecalix)] in **14**·C_6H_3*i*Pr_2OH; H atoms and solvent molecules have been omitted for clarity; (left) molecular unit; (right) plot of the columnar stacking of these molecular units to give a chain along the crystallographic *b* axis; selected bond lengths [Å] and angles [°]: Ti−O(1) 2.384(3), Ti−O(2) 1.768(3), Ti−O(3) 1.864(3), Ti−O(4) 1.785(3), Ti−O(5) 1.792(3); O(1)−Ti−O(2) 78.2(1), O(1)−Ti−O(3) 169.3(1), O(1)−Ti−O(4) 79.2(1), O(1)−Ti−O(5) 86.5(1), O(2)−Ti−O(3) 96.4(1), O(2)−Ti−O(4) 119.7(1), O(2)−Ti−O(5) 117.9(1), O(3)−Ti−O(4) 95.9(1), O(3)−Ti−O(5) 104.2(1), O(4)−Ti−O(5) 115.5(1), Ti−O(1)−C(10) 114.9(2), Ti−O(1)−C(5) 130.0(2), Ti−O(2)−C(20) 168.0(2), Ti−O(3)−C(30) 116.0(2), Ti−O(4)−C(40) 166.8(3), Ti−O(5)−C(50) 168.7(3)

two [Ti(Mecalix)] fragments. This complex has a crystallographically imposed inversion center at the center of the planar [Ti_2O_2] four-membered ring. The coordination sphere at the titanium atom is distorted octahedral, and these two octahedra are connected by an common edge. The O−Ti−O and Ti−O−Ti′ angles within the four-membered ring are 69.8(1)° and 110.2(1)°, respectively. The Ti−Ti distance of 3.32.9(1) Å is nonbonding. The Ti−O(1) bond length to the oxygen atom of the anisole group of the calix[4]arene [2.438(2) Å] is similar to the distances found in the chloro and amido complexes. The distances of the bridging oxygen atoms from the titanium atoms are 2.032(2) Å and 2.026(2) Å, similar to other alkoxide-bridged compounds such as [{Ti(ONp)$_4$}$_2$].[19]

In contrast to the dinuclear phenolate complexes [Ti(OC_6H_4-4-*t*Bu)(Mecalix)] (**13**) and [Ti(OC_6H_4-4-Me)-(Mecalix)] (**C**), the calixarene-stabilized diisopropylphenolate compound **14** is a monomer in the solid state, which is mainly due to the enhanced steric demand of the *ortho*-substituted phenolate ligand. The molecular structure of **14** is depicted on the left-hand side of Figure 7, with the stacking along the crystallographic *b* axis shown on the right. The coordination sphere around the titanium atom in this monomeric complex is best described as a distorted trigonal bipyramid, in which the oxygen atoms O(2), O(4) and O(5) occupy the equatorial positions. The O(2)−Ti−O(4), O(2)−Ti−O(5) and O(4)−Ti−O(5) angles [115.5(1)°−119.7(1)°] differ only slightly from their ideal value of 120°.

The distances between the titanium atom and the oxygen atoms O(2), O(4) and O(5) are in the narrow range of 1.768(3)−1.792(3) Å, whereas the Ti−O(3) distance of 1.864(3) Å is significantly longer. The Ti−O(1) distance of 2.384(3) Å, as well as the sum of the Ti−O distances to the oxygen atoms O(1) and O(3) (4.248 Å), are similar to the other calix[4]arene monomethyl ether complexes described in this paper.

Additional stabilization of the compound is provided by stacking of the molecular units. The right-hand side of Figure 7 shows the linear polymeric structure of **14** in the solid state. The aryl unit of the diisopropylphenolate ligand is oriented in the cavity of a neighboring calix[4]arene ligand with the plane defined by the aryl carbon atoms almost ideally aligned with the plane through the oxygen atoms O(2) and O(4) and the corresponding *ipso*-carbon atoms of the macrocyclic ligand [angle of intersection 8.9(4)°]. The closest distance between the carbon atoms of the diisopropylphenolate ligand and the carbon atoms of the calix[4]arene is 3.660(3) Å.

The thiolate complex **15** is also a monomer in the solid state, as can be seen from the molecular structure of **15** depicted in Figure 8. Crystals of this compound were obtained from saturated hexane solutions, from which the compound crystallizes in the monoclinic space group $P2_1/c$ with four molecular units and four solvent molecules in the unit cell. The titanium atom is in a distorted trigonal-bipyramidal coordination mode with the four oxygen atoms of the calix[4]arene ligand and the sulfur atom of the thiolate ligand. The oxygen atoms O(1) and O(3) occupy the axial positions. The Ti−O(1) bond length (to the oxygen atom of the anisole group) is 2.389(3) Å. The thiolate ligand in **15** is not linearly coordinated, with the Ti−S−C(6) angle of 110.8(2)° being close to the tetrahedral angle, which indicates that the sulfur lone pairs in **15** are not involved in Ti−S bonding. However, the Ti−S bond of 2.314(2) Å is significantly shorter than those in [$TiCp_2(StBu)_2$] [2.416(1) Å].[20a] In more Lewis-acidic titanium thiolate complexes or in complexes with sterically less demanding ligands such as [$TiCp_2(SEt)_2$] and [$Ti(diars)Cl_2(StBu)_2$] [diars = 1,2-($Me_2As)_2C_6H_4$], the Ti−S bond lengths are 2.387(3) Å and 2.398(3) Å (in the metallocene),[20b] and 2.332(3) Å (in the complex).[20c]

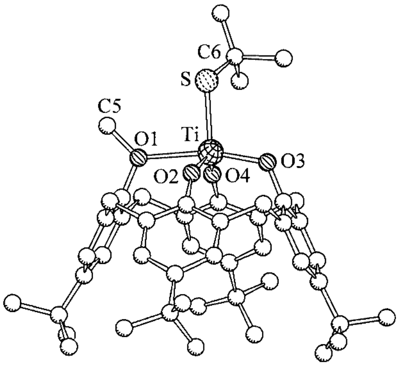

Figure 8. SCHAKAL plot of the molecular structure of [Ti(S*t*Bu)(Mecalix)] in **15**·C_6H_{14}; H atoms and solvent molecules have been omitted for clarity; selected bond lengths [Å] and angles [°]: Ti−S 2.314(2), Ti−O(1) 2.389(4), Ti−O(2) 1.793(4), Ti−O(3) 1.880(4), Ti−O(4) 1.787(3); S−Ti−O(1) 91.5(1), S−Ti−O(2) 108.1(1), S−Ti−O(3) 102.4(1), S−Ti−O(4) 115.9(1), O(1)−Ti−O(2) 79.2(2), O(1)−Ti−O(3) 166.1(2), O(1)−Ti−O(4), 79.2(1), O(2)−Ti−O(3) 96.9(2), O(2)−Ti−O(4) 131.1(2), O(3)−Ti−O(4) 93.8(2), Ti−S−C(6) 110.8(2), Ti−O(1)−C(5) 130.1(4), Ti−O(1)−C(10) 117.5(3), Ti−O(2)−C(20) 151.9(3), Ti−O(3)−C(30) 122.1(3), Ti−O(4)−C(40) 159.4(4)

Ab initio Calculations on Model Complexes

Ab initio and DFT calculations[21−24] were performed on model compounds to gain a better understanding of the main electronic and structural properties of the titanium complexes supported by the calix[4]arene methyl ether ligand. The aim of these calculations was to study the main features of the ligand in the titanium complexes described above as well as the frontier orbitals of the calix[4]arene titanium complex fragment, and their structural consequences.

Two models were considered in the calculations: A detailed model, [$TiX(Mecalix^H)$], in which the ligand has been slightly modified by a replacement of the *t*Bu groups with hydrogen atoms. In the second, more simplified model, [$TiX(OMe)_3(OMe_2)$], the coordination environment at the titanium atom was maintained to resemble the main features of the ligand, but the aryl groups were replaced by methyl groups. Calculations on different detailed model complexes showed that DFT methods describe the geometry of the complexes rather poorly, especially the Ti−O(1) distance (anisole oxygen atom), which was overestimated (approximately 2.50 Å for different complexes [$TiX(Mecalix^H)$] and different functionals employed). Ab initio methods performed much better here, and all the results reported below are from MP2 calculations.

With the exception of [$Ti(OC_6H_3$-2,6-$i$$Pr_2$)(Mecalix)] (**14**), all the structures given above can be described in terms of the isolated molecular units present in the crystal, or their solvates, in which one of the additional solvent molecules is located inside the calix[4]arene cavity. The calculated geometries of [$TiCl(Mecalix^H)$] and its benzene solvate [$TiCl(Mecalix^H)$](C_6H_6) converge with almost identical geometries of the complex, the maximal deviation in the Ti−O distance and Ti−O−C angles are 0.006 Å and 1.23°, respectively, which are in good agreement with the experimentally observed geometry. The main structural features of the complex are therefore determined by coordination of the metal complex fragment [$TiX]^{3+}$ to the [$Mecalix]^{3-}$ ligand and are not significantly affected by lattice interactions or guest molecules in the calix[4]arene cages.

We were interested in learning more about the labile anisole ether coordination in the titanium complexes. The energy calculated for the removal of the OMe_2 group from the simplified model [$TiCl(OMe)_3(OMe_2)$] is 45.2 kJ/mol, which indicates only weak bonding of the ether group to the titanium complex fragment. Moreover, the energy potential calculated for the elongation or compression of the Ti−O(ether) bond, which is shown in Figure 9, is very flat. The region between 2.30 Å and 2.80 Å lies within a narrow range of 5−6 kJ/mol, which indicates that the Ti−O(1) bond lengths are mainly determined by steric factors, that is, either interactions resulting from the ligand L with the anisole ether group or from an internal reorganization energy of the calix[4]arene ligand.

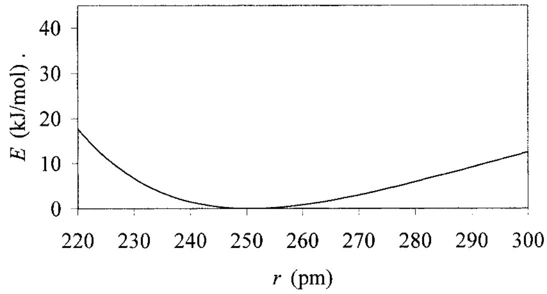

Figure 9. Potential energy curve calculated for the Ti−OMe_2 bond in [$TiCl(OMe)_3(OMe_2)$]

Geometry optimizations of the detailed model of the amido complex **5** confirmed the planar arrangement of the dimethylamido group and its perpendicular alignment with respect to the Ti−O(1) vector. A schematic FMO diagram of the interactions of an amido ligand [$NMe_2]^-$ with a calixarene metal fragment [$Ti(Mecalix)]^+$ is depicted on the right-hand side of Figure 10. The lowest metal-centered, unoccupied orbitals of the [$Ti(Mecalix)]^+$ fragment are shown on the left-hand side of the FMO scheme, while orbital plots of these relevant fragment orbitals drawn for the simplified model are given on the left-hand side of Figure 10.

The [$Ti(Mecalix)]^+$ orbitals responsible for binding of the calixarene-stabilized metal atom to a σ,π-donor ligand are three metal-centered, unoccupied orbitals. The lowest or-

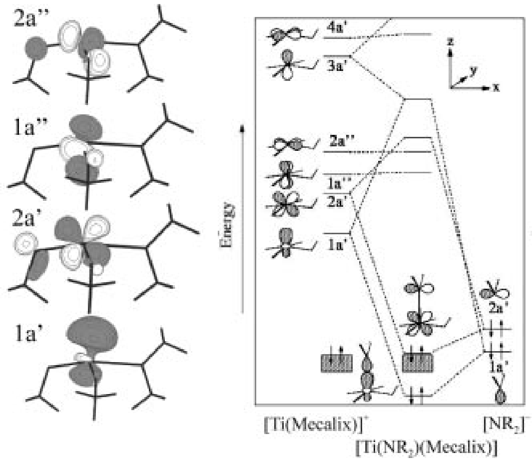

Figure 10. Schematic FMO diagram of the interaction of an amido ligand $[NMe_2]^-$ with the calixarene metal fragment $[Ti(Mecalix)]^+$ (right) and orbital plots of the relevant metal fragment orbitals of the simplified model $[Ti(OMe)_3(OMe_2)]^+$ (left)

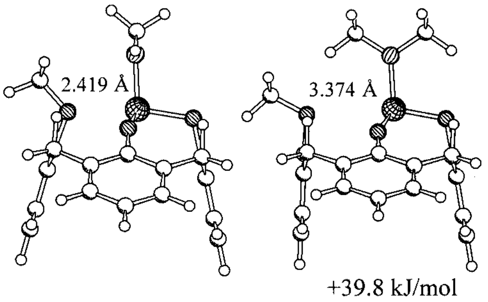

Figure 11. Geometry-optimized isomers of $[Ti(NMe_2)(Mecalix^H)]$ in which the amido ligand is oriented parallel (right) and perpendicular (left) to the Ti−O(1) vector

bital in energy, 1a′, is mainly d_{z^2} in character and can be involved in Ti−L σ bonding. The 2a′ orbitals, which are mainly d_{xz}, and 1a′′, which has predominant contributions from Ti d_{yz}, are responsible for π interactions with the ligand. Dependent on the orientation of the amide ligand, 2a′ or 1a′′ are involved in Ti−N bonding, as shown schematically for the experimentally verified orientation of the amido ligand in the FMO diagram. However, a detailed analysis of the possible interactions of the nitrogen p orbital with either 2a′ or 1a′′ reveals only minor differences. This might be supported by the calculations using the simpler model and an NH_2 amido ligand. The experimentally observed geometry in this case is only 6.9 kJ/mol lower in energy than the model complex in which the NH_2 group is aligned along the Ti−O(1) vector. For the detailed models $[Ti(NMe_2)(Mecalix^H)]$ these two orientations optimize with a much larger difference in energy, as shown in Figure 11. The model that resembles the experimentally observed structure is 26.8 kJ/mol lower in energy than the other isomer, which also indicates that steric factors strongly influence the orientation of the amido ligand. This can be substantiated by a significant elongation calculated for the Ti−O(1) bond of the energetically disfavored molecule from 2.419 Å to 3.374 Å. Models in which the calixarene binds in a *paco* coordination mode are at least 75.4 kJ/mol higher in energy and should be experimentally unavailable by isomerization reactions.

Catalytic Epoxidation of Cyclooctene with TBHP

Titanium-containing synthetic zeolites such as titanium silicalite-1 (TS-1)[25] have received considerable attention in recent years because of their excellent catalytic properties.[26] TS-1 acts as a catalyst in a number of oxygen-transfer reactions utilizing hydrogen peroxide, including the epoxidation of alkenes, the oxidation of alcohols to aldehydes or ketones, the hydroxylation of aromatic compounds, and the oxidation of alkanes to alcohol/ketone mixtures. The application of these remarkable catalytic properties is limited by the pore size of the zeolite used, which was the basic motivation for research on titanium-silica mixed oxides[27] and amorphous forms of titania supported on silica.[28] These investigations led to the synthesis of zeolites with large[29] and "ultralarge"[30] pore sizes, in which titanium atoms can be located.

To gain a better understanding of the factors that determine the unique catalytic properties of these materials, special care was taken to clarify the nature of the catalytically active species.[31,32] An isolated tetrahedrally coordinated titanium complex was initially assumed to be the active species,[25,31] although further studies indicated the involvement of tripodally coordinated titanium sites. According to DFT calculations published by Rösch et al.,[33] both the reaction energy and the activation energy for the transition-metal-catalyzed epoxidation of ethene are identical, or more favorable, for the model complexes $[(HO)_3Ti(OOR)]$, $[(HO)_3Ti(OOR)(L)]$ or $[(HO)_3Ti(OOR)(L)_2]$ than models for the active species of methyltrioxorhenium (MTO)[34] or the Mimoun catalyst.[35] According to these calculations, titanium catalysts in which the $[(HO)_3Ti(OOR)]$ unit is stabilized by a further neutral ligand L (e.g. NH_3) are most favorable for epoxidation reactions using alkyl hydroperoxides.

One approach to model oxo surfaces that bind metal atoms on a molecular level is to employ ligands with a preorganized set of oxygen donor atoms in a quasiplanar arrangement, as provided, for example, by calixarenes. The titanium-containing calix[4]arene compounds [TiX(Mecalix)] exactly meet the requirements proposed by Rösch and co-workers.[33] The metal atom is threefold-coordinated by phenolate ligands and stabilized by an additional ether moiety. A fifth coordination site, occupied by a ligand X, may be used for the coordination of alkyl peroxides. Calix[4]arene complexes of the type [TiX(Rcalix)] (L = Cl, OR′, NR'_2) therefore might be able to transform the catalytic properties of titanasilicates to homogeneous catalytic systems.

We chose the titanium-catalyzed epoxidation of cyclooctene as a model reaction to test the catalytic properties of our calix[4]arene-stabilized titanium(IV) complexes in epoxidation reactions of olefins with TBHP. In a first experiment, the complexes were applied to a reaction using 5 mol % of the pre-catalyst and equimolar amounts of TBHP (see Figure 12).

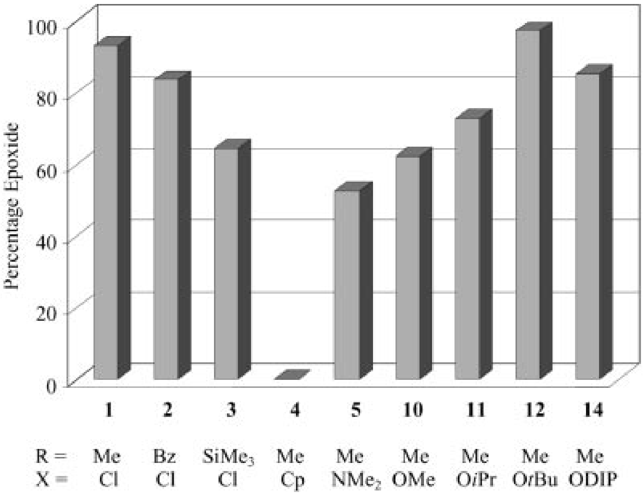

Figure 12. Conversion rate depending on the catalyst for the catalytic epoxidation of cyclooctene using 5 mol % pre-catalyst after a reaction time of 4 h; the formation of other oxidation products of cyclooctene were not observed

Whereas the Cp complex **4** is not an active catalyst, all other nine pre-catalysts tested show catalytic behavior. The best conversion rates were obtained for the complexes [TiCl(Mecalix)] (**1**; 93% conversion) and [Ti(O*t*Bu)(Mecalix)] (**12**; 97%), while the activity of the compounds [TiCl{(SiMe$_3$)calix}] (**3**; 65%) and [Ti(NMe$_2$)(Mecalix)] (**5**; 53%) is significantly lower. The reason for the low catalytic activity of complex **3** is presumably due to silyl ether cleavage, which leads to the formation of catalytically ineffective calix[4]arene titanium complexes of higher nuclearity. Compound **11** is almost as active as **12** when it is used in its isolated form as a precatalyst. For the runs shown in Figure 12, **11** was generated in situ starting from [Ti(O*i*Pr)$_4$] and H$_3$Mecalix. The lower activity in this case reflects the autoretarding mechanism observed for the catalytic process (see below). Complex **5** also reveals an unexpectedly low catalytic activity compared to the other Mecalix complexes. In this case the formation of the catalytically active peroxide complex is suppressed by oxidation of the ligand and formation of a catalytically ineffective dimethylhydroxylaminato complex [Ti(ONMe$_2$)(Mecalix)] (**16**).

Complex **16** was prepared independently from the reaction of the amide complex **5** and 1.1 equiv. of TBHP. The ^{1}H and ^{13}C{^{1}H} NMR spectra of **16** reveal local C_s symmetry of the calix[4]arene ligand. Compared with the amido complex **5**, the signals of the *N*-methyl protons are significantly shifted at δ = 2.92 ppm (δ = 3.59 ppm in **5**). The mass spectrum of **16** shows the molecular ion peak at m/z = 767 as the base peak of the spectrum.

According to kinetic measurements of the epoxidation reaction using [Ti(O*t*Bu)(Mecalix)] (**12**) as a catalyst, the process is neither of first nor of second order, in contrast to the findings of Abbenhuis and co-workers for the epoxidation of cyclooctene with TBHP using [{(*c*-C$_6$H$_{11}$Si)$_7$O$_{12}$}Ti(η^5-C$_5$H$_5$)].[36] For the calix[4]arene system the kinetics reveal an autoretarding mechanism. This autoretarding effect of the co-product *t*BuOH has been observed previously in a variety of homogeneous and heterogeneous titanium and vanadium catalysts.[37]

In the reaction mixtures of precatalyst, peroxide and substrate, we detected a new complex by NMR spectroscopy, which might be the catalytically active species [Ti(OO*t*Bu)(Mecalix)]. The resonances observed in the ^{1}H NMR spectra are four doublets for the methylene protons of the calix[4]arene ligand at δ = 4.43 and 3.37 ppm with a coupling constant of 13.7 Hz and at δ = 4.38 and 3.35 ppm with a coupling constant of 12.8 Hz, as well as a signal for the methoxy group at δ = 3.73 ppm. The resonances in the range of the *t*Bu groups could not be assigned unambiguously because this region also contains various other signals under the conditions of the catalysis. However, the calixarene signals do not belong to other possible species such as [Ti(O*t*Bu)(Mecalix)] or [{(Mecalix)Ti}$_2$O] or the Mecalix ligand. We have been unable so far to isolate this compound, but are currently exploring calixarene−titanium-catalyzed epoxidation and oxidation reactions further.

Conclusions

The complexes [TiCl(Rcalix)] **1**−**3** are easily accessible starting materials for studying the chemistry of calix[4]arene monoalkyl or silyl ether titanium complexes. For methyl ether stabilized calix[4]arene−titanium species, the dimethylamido complex **5** proved to be a convenient entry point. The results reported above show that the trianion [Mecalix]$^{3-}$ is a suitable ancillary ligand to stabilize titanium(IV) chloride, cyclopentadienyl amide, alkoxide, phenolate and thiolate functionalities. In all the complexes reported here the calix[4]arene ligand adopts an elliptically distorted cone conformation in which the anisole oxygen−titanium distance Ti−O(1) varies between 2.342 Å and 2.438 Å, with the exception of the Cp complex, for which a distance of almost 3.50 Å was observed. MP2 calculations reveal that the anisole oxygen−titanium bond is weak, particularly in the region between 2.30 Å and 2.80 Å, where the potential energy surface is very shallow. Thus, the Mecalix ligand system might be described as a tris(phenolate) ligand with a hemilabile anisole group. Despite the labile anisole oxygen−titanium bond, isomerization reactions of the calix[4]arene ligand to a *paco* coordination mode are not observed, and MP2 calculations reveal a considerable thermodynamic preference for the cone isomers. Most of the compounds are active catalysts in epoxidation reactions of cyclooctene using TBHP as an oxidant, the best results being observed for the complexes [Ti(O*t*Bu)(Mecalix)], [Ti(O*i*Pr)(Mecalix)], and [TiCl (Mecalix)].

Experimental Section

General Remarks: All air/moisture-sensitive manipulations were performed using standard Schlenk-line (N_2) and dry-box (Ar) techniques. Solvents were pre-dried and refluxed in the presence of sodium, potassium or sodium/potassium alloy (1:3, w/w) (benzene, toluene, pentane, hexane, diethyl ether, THF), or P_2O_5 (acetonitrile, dichloromethane) under N_2. Solvents were distilled at atmospheric pressure prior to use. Deuterated solvents were dried with sodium (C_6D_6) or calcium hydride ($CDCl_3$, CD_2Cl_2) under N_2. ^{1}H and ^{13}C{^{1}H} NMR spectra were recorded with a Bruker AC 250 spectrometer at 298 K. Spectra are referenced internally to residual protonated-solvent resonances (^{1}H: $CDCl_3$: δ = 7.24 ppm; C_6D_6: δ = 7.15 ppm) or solvent resonances (^{13}C: $CDCl_3$: δ = 77.0 ppm; C_6D_6: δ = 128.0 ppm) and are reported relative to tetramethylsilane (δ = 0.00 ppm). Chemical shifts are quoted in δ (ppm) and coupling constants in Hz. Standard DEPT-135 experiments were recorded to distinguish CH_3 and CH carbon atoms from C and CH_2 carbon atoms in the ^{13}C NMR spectra. IR spectra were recorded with a Bruker IFS28 spectrometer as KBr pellets. All data are quoted in wavenumbers [cm^{-1}]. Mass spectra were recorded with a Finnigan MAT 900 XLT. All data are quoted as their mass/charge (*m*/*z*) ratios. Elemental analyses were carried out by the analytical laboratory of the Institute of Inorganic Chemistry of the University Karlsruhe (TH). The complexes isolated from toluene are usually solvate adducts, in which a toluene molecule is hosted inside the calix[4]arene cavity. The compound/solvent ratio was determined by integration of the appropriate peaks in the ^{1}H NMR spectra. This endohedrally hosted solvent molecule is usually displaced in the solvation process with the deuterated solvent (C_6D_6, $CDCl_3$) and is subtracted in the NMR spectra reported here. The mass spectra of these solvates show the peaks expected for the unsolvated species. CHN analyses were either performed on the solvates or on the unsolvated complexes as stated below. To obtain compounds free from additional solvent molecules, the complexes have to be dried vigorously or have to be recrystallized or suspended in non-polar solvents such as pentane and hexane, filtered and dried in vacuo. No satisfactory elemental analysis was obtained for complexes **2** and **3** due to their ease of decomposition, or for **6** due to the compound's sensitivity. The composition of these complexes was verified by their mass spectra. H_4calix,[37] H_2Me_2calix,[12] H_2Bz_2calix[12] and $H_2(SiMe_3)_2$calix[38] were synthesized according to literature procedures. The synthesis of [TiCl(Mecalix)] has been reported previously,[13] but here we briefly report a modified version of this method for completeness.

[TiCl(Mecalix)]·C_7H_8 (1·C_7H_8): Toluene (180 mL) was added to a mixture of H_2Me_2calix (12.9 g, 19.1 mmol) and [$TiCl_4$(THF)$_2$] (6.37 g, 19.1 mmol) at room temperature. The resulting red suspension was refluxed for 48 h and the solution was concentrated to approximately 50 mL after cooling to room temperature. Hexane (130 mL) was added and, after stirring for 30 min, product **1**·C_7H_8 was isolated by filtration as a red solid, which was washed with two 15-mL portions of hexane and dried in vacuo (13.6 g, 81%). Crystals suitable for X-ray diffraction were grown from hot saturated toluene solutions of **1** $C_{45}H_{55}ClO_4Ti·C_7H_8$ (835.4): calcd. C 74.76, H 7.60; found C 74.92, H 7.60. MS: *m*/*z* (%) = 742 (100) [M$^+$], 727 (57) [M − CH_3]. IR: $\tilde{\nu}$ = 3055 m, 3024 m, 2962 vs br, 1603 m br, 1479 vs br, 1415 m, 1393 m, 1362 s, 1303 s br, 1254 vs, 1205 vs br, 1122 m, 1111 s, 1093 m, 1003 s br, 943 vs, 923 m, 876 vs, 831 s, 814 w, 797 vs, 763 m, 729 s, 695 w, 677 w, 647 w, 603 m, 585 vs, 568 m, 461 s, 446 s, 431 s, 401 m, 297 w cm^{-1}. ^{1}H NMR (C_6D_6): δ = 0.68 [s, 9 H, $\mathrm{C(C}H_3)_3$], 0.77 [s, 9 H, $\mathrm{C(C}H_3)_3$], 1.37 [s, 18 H, $\mathrm{C(C}H_3)_3$], 3.13 (d, $^{2}J_{H,H}$ = 12.5 Hz, 2 H, $\mathrm{C}H_2$), 3.22 (d, $^{2}J_{H,H}$ = 13.0 Hz, 2 H, $\mathrm{C}H_2$), 3.84 (s, 3 H, $\mathrm{OC}H_3$), 4.31 (d, $^{2}J_{H,H}$ = 12.5 Hz, 2 H, $\mathrm{C}H_2$), 4.97 (d, $^{2}J_{H,H}$ = 13.0 Hz, 2 H, $\mathrm{C}H_2$), 6.78 (s, 2 H, Aryl-H_m), 6.82 (s, 2 H, Aryl-H_m), 7.14 (s, 4 H, Aryl-H_m) ppm. ^{13}C NMR (C_6D_6): δ = 30.56, 30.88, 31.86 [$\mathrm{C(}C\mathrm{H_3)_3}$], 33.49, 33.65 ($C\mathrm{H_2}$), 33.88, 34.30, 34.50 [$C\mathrm{(CH_3)_3}$], 65.67 ($\mathrm{O}C\mathrm{H_3}$), 123.94, 125.29, 125.65, 127.22 (Aryl-C_m), 129.22, 131.47, 132.10, 132.23 (Aryl-C_o), 146.26, 146.38, 148.39 (Aryl-C_p), 151.82, 160.48, 162.97 (Aryl-C_i) ppm.

[TiCl(Bzcalix)]·C_7H_8·(2·C_7H_8): Toluene (20 mL) was added to a mixture of H_2Bz_2calix (1.00 g, 1.21 mmol) and [$TiCl_4$(THF)$_2$] (402 mg, 1.21 mmol). The reaction mixture immediately turned dark red and was stirred at 80 °C for 1 h. All volatiles were removed under reduced pressure and the dark red residue was suspended in 5 mL of hexane. The product was filtered off and [TiCl(Bzcalix)]·C_7H_8 (**2**·C_7H_8) was dried in vacuo (876 mg, 77%). MS: *m*/*z* (%) = 819 (26) [M$^+$], 818 (42) [M − H], 762 (12) [M − $C(CH_3)_3$] 728 (3) [M − Bz], 692 (8) [M − Bz − Cl]. ^{1}H NMR (C_6D_6): δ = 0.68 [s, 9 H, $\mathrm{C(C}H_3)_3$], 0.76 [s, 9 H, $\mathrm{C(C}H_3)_3$], 1.35 [s, 18 H, $\mathrm{C(C}H_3)_3$], 2.92 (d, $^{2}J_{H,H}$ = 12.6 Hz, 2 H, $\mathrm{C}H_2$), 3.22 (d, $^{2}J_{H,H}$ = 12.9 Hz, 2 H, $\mathrm{C}H_2$), 4.08 (d, $^{2}J_{H,H}$ = 12.6 Hz, 2 H, $\mathrm{C}H_2$), 4.96 (d, $^{2}J_{H,H}$ = 12.9 Hz, 2 H, $\mathrm{C}H_2$), 5.38 (s, 2 H, Bz-$\mathrm{C}H_2$), 6.77 (s, 2 H, Aryl-H_m), 6.81 (s, 2 H, Aryl-H_m), 7.11−7.05 (m, 7 H, Aryl-H_m), 7.37 (m, 2 H, Bz-Aryl-*H*) ppm. ^{13}C NMR (C_6D_6): δ = 30.57 [$\mathrm{C(}C\mathrm{H_3)_3}$], 30.88 [$\mathrm{C(}C\mathrm{H_3)_3}$], 31.84 [$\mathrm{C(}C\mathrm{H_3)_3}$], 33.60 ($C\mathrm{H_2}$), 33.88 ($C\mathrm{H_2}$), 34.46 [$C\mathrm{(CH_3)_3}$], 81.13 (Bz-$C\mathrm{H_2}$), 123.87, 125.18, 125.59, 127.06 (s, Aryl-C_m), 128.66, 129.21, 131.17 (Bz-*C*), 128.73, 131.86, 132.09, 132.87 (Aryl-C_o), 135.74 (Bz-C_i) 146.26, 146.46, 148.26 (Aryl-C_p), 149.85, 160.46, 163.04 (Aryl-C_i) ppm.

[TiCl{(Me_3Si)calix}]·3C_7H_8 (3·3C_7H_8): Toluene (15 mL) was added to a mixture of $H_2(SiMe_3)_2$calix (1.00 g, 1.26 mmol) and [$TiCl_4$(THF)$_2$] (421 mg, 1.26 mmol). The reaction mixture was stirred at room temperature for 2 h and its color changed from yellow to red. The red, cloudy solution was filtered through a pad of Celite and the filtrate concentrated to dryness to afford [TiCl{(Me_3Si)calix}]·3C_7H_8 as a red powder (990 mg, 72.9%). MS: *m*/*z* (%) = 801 (100) [M$^+$], 786 (23) [M − CH_3], 693 (6) [M − CH_3 − $Si(CH_3)_3$]. ^{1}H NMR (C_6D_6): δ = 0.49 [s, 9 H, $\mathrm{Si(C}H_3)_3$], 0.70 [s, 9 H, $\mathrm{C(C}H_3)_3$], 0.80 [s, 9 H, $\mathrm{C(C}H_3)_3$], 1.40 [s, 18 H, $\mathrm{C(C}H_3)_3$], 3.10 (d, $^{2}J_{H,H}$ = 12.4 Hz, 2 H, $\mathrm{C}H_2$), 3.31 (d, $^{2}J_{H,H}$ = 13.0 Hz, 2 H, $\mathrm{C}H_2$), 4.56 (d, $^{2}J_{H,H}$ = 12.4 Hz, 2 H, $\mathrm{C}H_2$), 4.92 (d, $^{2}J_{H,H}$ = 13.0 Hz, 2 H, $\mathrm{C}H_2$), 6.78 (s, 4 H, Aryl-H_m), 7.17 (s, 4 H, Aryl-H_m) ppm. ^{13}C NMR (C_6D_6): δ = 1.78 [$\mathrm{Si(}C\mathrm{H_3)_3}$], 30.59 [$\mathrm{C(}C\mathrm{H_3)_3}$], 30.91 [$\mathrm{C(}C\mathrm{H_3)_3}$], 31.84 [$\mathrm{C(}C\mathrm{H_3)_3}$], 33.51 ($C\mathrm{H_2}$), 33.73 [$C\mathrm{(CH_3)_3}$], 33.79 ($C\mathrm{H_2}$), 34.48 [$C\mathrm{(CH_3)_3}$], 123.94, 125.41, 126.48 (Aryl-C_m), 131.12, 131.77, 132.34 (Aryl-C_o), 146.12, 146.31, 146.77 (Aryl-C_p), 148.03, 159.80, 162.82 (Aryl-C_i) ppm.

[Ti(η^5-C_5H_5)(Mecalix)]·C_7H_8 (4·C_7H_8): A mixture of **1**·C_7H_8 (500 mg, 0.60 mmol) and [NaCp(THF)] (96.0 mg, 0.60 mmol) was suspended in 10 mL of toluene. The resulting suspension became orange after a few minutes and was stirred at room temperature for 12 h, filtered through a pad of Celite and the filtrate was concentrated to dryness. The orange product [Ti(η^5-C_5H_5)(Mecalix)]·C_7H_8 (**4**·C_7H_8) was dried in vacuo (342 mg, 66%). Crystals suitable for X-ray diffraction were grown from a saturated toluene solution at −30 °C. $C_{50}H_{60}O_4Ti·C_7H_8$ (865.0): calcd. C 79.14, H 7.92; found C 79.27, H 7.77. MS: *m*/*z* (%) = 772 (100) [M$^+$] 757 (22) [M − CH_3], 707 (14) [M − Cp]. IR: $\tilde{\nu}$ = 2962 vs br, 1603 w, 1580 w, 1467 vs br, 1392 w, 1362 m, 1301 s br, 1254 vs br, 1205 vs br, 1170 m, 1105 s br, 1019 vs br, 938 s, 922 m, 872 s, 861 vs, 822 s, 804 vs br, 752 s, 714 w, 676 m, 647 w, 603 m, 580 m, 562 s, 510 w br, 481 w, 455 m, 431 m cm^{-1}. ^{1}H NMR (C_6D_6): δ = 0.85 [s, 9 H, $\mathrm{C(C}H_3)_3$], 1.07 [s, 9 H, $\mathrm{C(C}H_3)_3$], 1.39 [s, 18 H, $\mathrm{C(C}H_3)_3$], 3.21 (d, $^2J_{\mathrm{H,H}}$ = 12.9 Hz, 2 H, CH_2), 3.25 (d, $^2J_{\mathrm{H,H}}$ = 12.9 Hz, 2 H, CH_2), 3.44 (s, 3 H, OCH_3), 4.46 (d, $^2J_{\mathrm{H,H}}$ = 12.9 Hz, 4 H, CH_2), 6.57 (s, 5 H, C_5H_5), 6.70 (s, 2 H, Aryl-H_m), 6.88 (s, 2 H, Aryl-H_m), 7.18 (s, 2 H, Aryl-H_m), 7.21 (s, 2 H, Aryl-H_m) ppm. ^{13}C NMR (C_6D_6): δ = 31.17, 31.47, 31.88 [C(CH_3)$_3$], 32.06, 33.61 (CH_2), 33.86, 33.93, 34.22 [C(CH_3)$_3$], 61.78 (OCH_3), 117.28 (C_5H_5), 124.32, 125.02, 125.14, 125.46 (Aryl-C_m), 126.05, 131.49, 132.22, 133.09 (Aryl-C_o), 143.17, 144.32, 146.06 (Aryl-C_p), 153.70, 158.85, 162.00 (Aryl-C_i) ppm.

[Ti(NMe$_2$)(Mecalix)]·(5): A solution of **1**·C_7H_8 (2.00 g, 2.40 mmol) and LiNMe$_2$ (135 mg, 1.15 equiv., 2.64 mmol) in toluene (50 mL) was stirred for 12 h. During this time the red solution became orange and cloudy. It was then filtered through a pad of Celite and all volatiles of the filtrate were removed in vacuo. The residue was suspended in hexane (15 mL), and yellow [Ti(NMe$_2$)(Mecalix)] (**5**) was collected and dried in vacuo. A second fraction was obtained after concentrating the mother liquor to approximately 5 mL and cooling to −30 °C for 5 d (combined yield: 1.71 g, 95%). Crystals of **5** were grown from a saturated solution of **5** in THF after prolonged storage at room temperature. $C_{47}H_{61}NO_4Ti$ (751.9): calcd. C 75.08, H 8.18, N 1.24; found C 74.79, H 8.26, N 1.53. MS: *m*/*z* (%) = 751 (100) [M$^+$], 736 (30) [M − CH$_3$]. ^{1}H NMR (C_6D_6): δ = 0.74 [s, 9 H, C(CH_3)$_3$], 0.83 [s, 9 H, C(CH_3)$_3$], 1.44 [s, 18 H, C(CH_3)$_3$], 3.29 (d, $^2J_{\mathrm{H,H}}$ = 12.1 Hz, 2 H, CH_2), 3.40 (d, $^2J_{\mathrm{H,H}}$ = 12.3 Hz, 2 H, CH_2), 3.59 [s, 6 H, N(CH_3)$_2$], 3.48 (s, 3 H, OCH_3), 4.39 (d, $^2J_{\mathrm{H,H}}$ = 12.1 Hz, 2 H, CH_2), 5.21 (d, $^2J_{\mathrm{H,H}}$ = 12.3 Hz, 2 H, CH_2), 6.90 (s, 4 H, Aryl-H_m), 7.25 (d, $^4J_{\mathrm{H,H}}$ = 2.4 Hz, 2 H, Aryl-H_m), 7.31 (d, $^4J_{\mathrm{H,H}}$ = 2.4 Hz, 2 H, Aryl-H_m) ppm. ^{13}C NMR (C_6D_6): δ = 30.66 [s, C(CH_3)$_3$], 31.08 [s, C(CH_3)$_3$], 32.06 [s, C(CH_3)$_3$], 33.77 (s, CH_2), 33.88 (s, CH_2), 34.06 [s, C(CH_3)$_3$], 34.40 [s, C(CH_3)$_3$], 47.95 [s, N(CH_3)$_2$], 65.17 (s, OCH_3), 123.73, 125.39, 125.76, 127.02 (s, Aryl-C_m), 129.28, 129.94, 132.31, 132.58 (s, Aryl-C_o), 143.24, 144.05, 148.64 (s, Aryl-C_p), 150.40, 154.78, 159.62 (s, Aryl-C_i) ppm.

[Ti(NEt$_2$)(Mecalix)]·C_7H_8 (6·C_7H_8): A solution of **1**·C_7H_8 (1.00 g, 1.20 mmol) in 40 mL of toluene was added at room temperature to a solution of LiNEt$_2$ (100 mg, 1.27 mmol) in 25 mL of toluene. After 8 h of stirring at room temperature, all undissolved components of the cloudy, orange reaction mixture were filtered off through a pad of Celite and the filtrate was concentrated to dryness. The resulting greenish yellow powder of [Ti(NEt$_2$)(Mecalix)]·C_7H_8 (**6**·C_7H_8) was dried in vacuo (0.91 g, 87%). MS: *m*/*z* (%) = 779 (100) [M$^+$], 764 (50) [M − CH$_3$], 707 (62) [M − NEt$_2$], 677 (13) [M − 2 CH$_3$ − NEt$_2$]. IR: $\tilde{\nu}$ = 2963 vs br, 1603 w br, 1480 vs br, 1393 m, 1362 m, 1308 s br, 1261 m, 1208 vs br, 1095 s br, 1013 s br, 939 m, 920 m, 872 vs br, 798 vs, 756 m, 727 s, 694 w, 676 w, 584 s, 567 s, 552 s, 465 m, 428 m cm^{-1}. ^{1}H NMR (C_6D_6): δ = 0.74 [s, 9 H, C(CH_3)$_3$], 0.83 [s, 9 H, C(CH_3)$_3$], 1.44 [s, 18 H, C(CH_3)$_3$], 1.46 (t, $^3J_{\mathrm{H,H}}$ = 7.1 Hz, 6 H, NCH$_2$CH_3), 3.31 (d, $^2J_{\mathrm{H,H}}$ = 12.1 Hz, 2 H, CH_2), 3.40 (d, $^2J_{\mathrm{H,H}}$ = 12.3 Hz, 2 H, CH_2), 3.56 (s, 3 H, OCH_3), 3.92 (q, $^3J_{\mathrm{H,H}}$ = 7.1 Hz, 4 H, NCH_2CH$_3$), 4.42 (d, $^2J_{\mathrm{H,H}}$ = 12.1 Hz, 2 H, CH_2), 5.16 (d, $^2J_{\mathrm{H,H}}$ = 12.3 Hz, 2 H, CH_2), 6.90 (s, 2 H, Aryl-H_m), 6.91 (s, 2 H, Aryl-H_m), 7.25 (d, $^4J_{\mathrm{H,H}}$ = 2.4 Hz, 2 H, Aryl-H_m), 7.30 (d, $^4J_{\mathrm{H,H}}$ = 2.4 Hz, 2 H, Aryl-H_m) ppm. ^{13}C NMR (C_6D_6): δ = 15.77 (NCH$_2$$CH_3$), 30.67, 31.09, 32.06 [C(CH_3)$_3$], 33.53, 33.73 [C(CH$_3$)$_3$], 33.80, 33.99 (CH_2), 34.39 [C(CH$_3$)$_3$], 51.35 (NCH_2CH$_3$), 65.54 (OCH_3), 123.76, 125.42, 125.65, 127.00 (Aryl-C_m), 129.28, 130.03, 132.24, 132.47 (Aryl-C_o), 143.20, 143.93, 148.52 (Aryl-C_p), 150.66, 155.04, 159.75 (Aryl-C_i) ppm.

[Ti(N*i*Pr$_2$)(Mecalix)] (7): A solution of LiN*i*Pr$_2$ (69.0 mg, 0.64 mmol) in 10 mL of THF was slowly added at −30 °C to a solution of **1**·C_7H_8 (500 mg, 0.60 mmol) in 10 mL of THF. The initially red solution rapidly became orange, and the reaction mixture was allowed to reach room temperature during 8 h. At approximately +5 °C the orange solution turned brownish. Volatile components were evaporated in vacuo and the residue was extracted into 10 mL of toluene and filtered through a pad of Celite. The filtrate was concentrated to dryness and the remaining solid was suspended in 2 mL of hexane and filtered off to afford [Ti(N*i*Pr$_2$)(Mecalix)] (**7**) as a yellow powder (145 mg, 30%). $C_{51}H_{69}NO_4Ti$ (808.0): calcd. C 75.81 H 8.61 N 1.73; found C 75.86, H 9.01, N 1.56. MS: *m*/*z* (%) = 807 (29) [M$^+$], 792 (100) [M − CH$_3$], 707 (32) [M − N*i*Pr$_2$]. IR: $\tilde{\nu}$ = 2962 vs br, 1603 w br, 1480 vs br, 1393 w, 1362 m, 1308 s br, 1276 m sh, 1260 s, 1207 vs br, 1169 w br, 1123 m, 1113 m, 1104 m, 1014 m br, 941 m, 922 w, 873 s br, 815 m, 798 vs, 755 s, 730 s br, 646 w, 586 m, 567 m, 557 m cm^{-1}. ^{1}H NMR (C_6D_6): δ = 0.72 [s, 9 H, C(CH_3)$_3$], 0.80 [s, 9 H, C(CH_3)$_3$], 0.96 (d, $^3J_{\mathrm{H,H}}$ = 6.2 Hz, 6 H, NCH(CH_3)$_2$], 1.43 [s, 18 H, C(CH_3)$_3$], 2.79 (sept, $^3J_{\mathrm{H,H}}$ = 6.2 Hz, 1 H, NCH(CH$_3$)$_2$], 3.25 (d, $^2J_{\mathrm{H,H}}$ = 12.8 Hz, 2 H, CH_2), 3.32 (d, $^2J_{\mathrm{H,H}}$ = 12.6 Hz, 2 H, CH_2), 4.55 (s, 3 H, OCH_3), 4.71 (d, $^2J_{\mathrm{H,H}}$ = 12.8 Hz, 2 H, CH_2), 5.04 (d, $^2J_{\mathrm{H,H}}$ = 12.6 Hz, 2 H, CH_2), 6.86 (s, 2 H, Aryl-H_m), 6.92 (s, 2 H, Aryl-H_m), 7.20 (s, 2 H, Aryl-H_m), 7.23 (s, 2 H, Aryl-H_m) ppm. ^{13}C NMR (C_6D_6): δ = 23.64 [NCH(CH_3)$_2$], 30.66, 30.98, 32.04 [C(CH_3)$_3$], 33.61 [C(CH$_3$)$_3$], 33.72, 33.90 (CH_2), 34.21, 34.45 [C(CH$_3$)$_3$], 45.36 [NCH(CH$_3$)$_2$], 66.03 (OCH_3), 123.94, 125.11, 125.85, 127.84 (Aryl-C_m), 129.28, 130.96, 131.66, 132.65 (Aryl-C_o), 144.65, 144.95, 148.43 (Aryl-C_p), 151.88, 157.79, 161.24 (Aryl-C_i) ppm.

[Ti(NPh$_2$)(Mecalix)]·C_7H_8 (8·C_7H_8): A mixture of **1**·C_7H_8 (500 mg, 0.60 mmol) and LiNPh$_2$ (112 mg, 0.64 mmol) was suspended in 10 mL of toluene. After 8 h of stirring at room temperature, the resulting red suspension was filtered through a pad of Celite and the filtrate was concentrated to dryness to afford [Ti(NPh$_2$)(Mecalix)]·C_7H_8 (**8**·C_7H_8) as a dark-red powder (485 mg, 84%). Crystals suitable for X-ray analysis were obtained by diffusion of hexane into a saturated toluene solution of **8**. $C_{57}H_{65}NO_4Ti$·C_7H_8 (968.2): calcd. C 79.40, H 7.60, N 1.45; found C 78.97, H 7.51, N 1.54. MS: *m*/*z* (%) = 875 (100) [M$^+$], 860 (10) [M − CH$_3$], 707 (20) [M − NPh$_2$]. IR: $\tilde{\nu}$ = 2953 vs br, 1593 m br, 1478 vs br, 1415 w, 1392 w, 1361 m, 1306 s br, 1275 s, 1260 vs br, 1207 vs br, 1176 s, 1123 s, 1111 m, 1095 m, 1013 m br, 941 2, 932 s, 921 s, 873 vs br, 826 s, 797 vs, 748 s br, 695 s, 645 w, 634 w, 597 w, 585 m, 567 m, 556 m, 523 m, 503 w, 471 w, 445 w br cm^{-1}. ^{1}H NMR (C_6D_6): δ = 0.72 [s, 9 H, C(CH_3)$_3$], 0.80 [s, 9 H, C(CH_3)$_3$], 1.38 [s, 18 H, C(CH_3)$_3$], 3.27 (d, $^2J_{\mathrm{H,H}}$ = 12.6 Hz, 2 H, CH_2), 3.30 (d, $^2J_{\mathrm{H,H}}$ = 12.3 Hz, 2 H, CH_2), 3.68 (s, 3 H, OCH_3), 4.52 (d, $^2J_{\mathrm{H,H}}$ = 12.3 Hz, 2 H, CH_2), 4.95 (d, $^2J_{\mathrm{H,H}}$ = 12.6 Hz, 2 H, CH_2), 6.90−7.31 (Aryl-H of Mecalix and NPh) ppm. ^{13}C NMR (C_6D_6): δ = 30.63, 31.00, 31.96 [C(CH_3)$_3$], 33.58 [C(CH$_3$)$_3$], 33.71, 33.79 (CH_2), 34.14, 34.43 [C(CH$_3$)$_3$], 65.19 (OCH_3), 122.98 (Phenyl-C_m), 124.56 (Phenyl-C_p), 123.88, 125.47, 125.66, 127.13 (Aryl-C_m), 129.94 (Phenyl-C_o), 126.21, 130.54, 131.98, 132.21 (Aryl-C_o), 144.80 (Phenyl-C_i), 144.52, 148.39, 150.28 (Aryl-C_p), 151.51, 157.38, 161.26 (Aryl-C_i) ppm.

[{Ti(Mecalix)}$_2$(μ-O)] (9): Whilst stirring, 0.33 mL of a 1 M solution of H_2O in THF was added slowly to a solution of **5** (500 mg, 0.67 mmol) in toluene (10 mL). The initially yellow solution turned red for a moment and became orange after stirring at room temperature. After 30 min, the clear, orange solution was concentrated to dryness and the resulting orange powder was suspended in pentane (5 mL), filtered, and dried in vacuo to afford [{Ti(Mecalix)}$_2$(μ-O)] (**9**) as an orange powder (420 mg, 83%).

Crystals suitable for X-ray analysis were obtained from saturated benzene solutions. $C_{90}H_{110}O_9Ti_2\cdot 2C_7H_8$ (1615.9): calcd. C 75.51, H 7.74; found C 75.64, H 7.77. MS: *m*/*z* (%) = 1431 (98) [M$^+$], 1430 (100) [M − H], 1416 (18) [M − CH$_3$]. IR: $\tilde{\nu}$ = 2951 vs br, 1603 w br, 1582 w, 1482 vs br, 1393 w, 1362 m, 1301 s br, 1260 s, 1215 vs br, 1124 m, 1113 m, 1094 m, 1010 m br, 943 s, 921 s, 875 s, 815 s, 799 vs, 725 vs br, 676 m, 634 w, 601 s, 586 s, 567 s, 554 s, 508 w br, 449 m, 431 m cm^{-1}. ^{1}H NMR (C$_6$D$_6$): δ = 0.71 [s, 9 H, C(C*H*$_3$)$_3$], 0.79 [s, 9 H, C(C*H*$_3$)$_3$], 1.41 [s, 18 H, C(C*H*$_3$)$_3$], 3.25 (d, $^2J_{\mathrm{H,H}}$ = 12.6 Hz, 2 H, C*H*$_2$), 3.30 (d, $^2J_{\mathrm{H,H}}$ = 12.3 Hz, 2 H, C*H*$_2$), 4.48 (s, 3 H, OC*H*$_3$), 4.68 (d, $^2J_{\mathrm{H,H}}$ = 12.3 Hz, 2 H, C*H*$_2$), 5.01 (d, $^2J_{\mathrm{H,H}}$ = 12.6 Hz, 2 H, C*H*$_2$), 6.85 (s, 2 H, Aryl-H_m), 6.91 (s, 2 H, Aryl-H_m), 7.18 (d, $^4J_{\mathrm{H,H}}$ = 2.4 Hz, 2 H, Aryl-H_m), 7.21 (d, $^4J_{\mathrm{H,H}}$ = 2.4 Hz, 2 H, Aryl-H_m) ppm. ^{13}C NMR (C$_6$D$_6$): δ = 30.66 [s, C(*C*H$_3$)$_3$], 30.98 [s, C(*C*H$_3$)$_3$], 32.04 [s, C(*C*H$_3$)$_3$], 33.60 [s, *C*(CH$_3$)$_3$], 33.71 [s, *C*(CH$_3$)$_3$], 33.89 (s, *C*H$_2$), 33.94 (s, *C*H$_2$), 34.44 [s, *C*(CH$_3$)$_3$], 65.97 (s, O*C*H$_3$), 123.96, 125.12, 125.84, 127.23 (s, Aryl-C_m), 126.44, 130.96, 131.67, 132.66 (s, Aryl-C_o), 144.50, 144.88, 148.37 (s, Aryl-C_p), 152.04, 157.93, 161.30 (s, Aryl-C_i) ppm.

[Ti(OMe)(Mecalix)]·C$_7$H$_8$ (10·C$_7$H$_8$): Methanol (27.0 µL, 0.77 mmol) was added at room temperature to a solution of **5** (500 mg, 0.67 mmol) in toluene (10 mL). The initially yellow solution turned slightly orange and became cloudy. After 12 h of stirring at room temperature, the resulting yellow precipitate was isolated by filtration and dried in vacuo to afford [Ti(OMe)(Mecalix)]·C$_7$H$_8$ as a yellow solid. (357 mg, 64%). The product was recrystallized from refluxing toluene. $C_{46}H_{58}O_5Ti\cdot C_7H_8$ (831.0): calcd. C 76.79, H 7.78; found C 76.65, H 7.77. MS: *m*/*z* (%) = 738 (100) [M$^+$]; 723 (43) [M − CH$_3$]. IR: $\tilde{\nu}$ = 2952 vs br, 1602 w, 1580 w, 1480 vs br, 1393 w, 1362 m, 1315 s br, 1271 s br, 1238 w, 1209 vs br, 1170 w, 1122 m br, 1097 m, 1031 m br, 1004 s br, 939 s, 921 m, 874 vs, 865 s, 825 m, 795 s, 757 m, 731 s, 677 w, 646 w, 603 w, 586 s br, 537 vs br, 476 w, 457 m, 430 w cm^{-1}. ^{1}H NMR (CDCl$_3$): δ = 1.15 [s, 9 H, C(C*H*$_3$)$_3$], 1.16 [s, 9 H, C(C*H*$_3$)$_3$], 1.28 [s, 18 H, C(C*H*$_3$)$_3$], 3.28 (d, $^2J_{\mathrm{H,H}}$ = 13.0 Hz, 4 H, C*H*$_2$), 4.13 (d, $^2J_{\mathrm{H,H}}$ = 13.0 Hz, 2 H, C*H*$_2$), 4.39 (s, 3 H, Ti-OC*H*$_3$), 4.45 (s, 3 H, OC*H*$_3$), 4.73 (d, $^2J_{\mathrm{H,H}}$ = 13.0 Hz, 2 H, C*H*$_2$), 6.96 (s, 2 H, Aryl-H_m), 6.98 (s, 2 H, Aryl-H_m), 7.16 (s, 2 H, Aryl-H_m), 7.17 (s, 2 H, Aryl-H_m) ppm. ^{13}C NMR (CDCl$_3$): δ = 31.23, 31.45, 31.73 [C(*C*H$_3$)$_3$], 33.96 [*C*(CH$_3$)$_3$], 34.08 (*C*H$_2$), 34.19 [*C*(CH$_3$)$_3$], 34.38 (*C*H$_2$), 34.85 [*C*(CH$_3$)$_3$], 62.07 (TiO*C*H$_3$), 65.30 (O*C*H$_3$), 123.79, 124.74, 125.17, 126.86 (Aryl-C_m), 127.06, 131.17, 132.59, 132.73 (Aryl-C_o), 142.81, 143.32, 147.11 (Aryl-C_p), 154.49, 162.09, 163.13 (Aryl-C_i) ppm.

[Ti(O*i*Pr)(Mecalix)]·C$_7$H$_8$ (11·C$_7$H$_8$): A solution of [Ti(O*i*Pr)$_4$] (0.90 mL, 859 mg, 3.02 mmol) in toluene (10 mL) was added at room temperature to a solution of H$_3$Mecalix (2.00 g, 3.02 mmol) in toluene (20 mL). The initially colorless solution turned yellow immediately after addition of the metal complex. After 2 h of stirring at room temperature, all volatile components were removed in vacuo to afford analytically pure, pale-yellow **11**·C$_7$H$_8$ (2.32 g, 89%). $C_{48}H_{62}O_5Ti\cdot C_7H_8$ (859.0): calcd. C 76.90, H 8.21; found C 76.67, H 8.15. MS: *m*/*z* (%) = 766 (100) [M$^+$], 751 (20) [M − CH$_3$]. IR: $\tilde{\nu}$ = 2963 vs br, 1599 w, 1580 w, 1480 vs br, 1393 w, 1361 m, 1307 s br, 1262 s br, 1206 s br, 1167 m, 1104 vs br, 1013 s br, 988 vs br, 939 m, 922 m, 864 vs br, 827 m, 797 vs, 759 m, 675 w, 627 w br, 598 w, 582 s, 567 m, 554 m, 465 w, 449 w, 430 w cm^{-1}. ^{1}H NMR (C$_6$D$_6$): δ = 0.74 [s, 9 H, C(C*H*$_3$)$_3$], 0.82 [s, 9 H, C(C*H*$_3$)$_3$], 1.42 [s, 18 H, C(C*H*$_3$)$_3$], 1.50 (d, $^3J_{\mathrm{H,H}}$ = 6.1 Hz, 6 H, OCH(C*H*$_3$)$_2$], 3.27 (d, $^2J_{\mathrm{H,H}}$ = 12.3 Hz, 2 H, C*H*$_2$), 3.34 (d, $^2J_{\mathrm{H,H}}$ = 12.6 Hz, 2 H, C*H*$_2$), 3.76 (s, 3 H, OC*H*$_3$), 4.39 (d, $^2J_{\mathrm{H,H}}$ = 12.3 Hz, 2 H, C*H*$_2$), 4.89 (sept, $^3J_{\mathrm{H,H}}$ = 6.1 Hz, 1 H, OC*H*(CH$_3$)$_2$], 5.06 (d, $^2J_{\mathrm{H,H}}$ = 12.6 Hz, 2 H, C*H*$_2$), 6.89 (s, 2 H, Aryl-H_m), 6.91 (s, 2 H, Aryl-H_m), 7.23 (s, 2 H, Aryl-H_m), 7.24 (s, 2 H, Aryl-H_m) ppm. ^{13}C NMR (C$_6$D$_6$): δ = 26.35 [OCH(*C*H$_3$)$_2$], 30.67, 31.03, 32.04 [C(*C*H$_3$)$_3$], 33.58, 33.72 [*C*(CH$_3$)$_3$], 33.79, 33.90 (*C*H$_2$), 34.40 [*C*(CH$_3$)$_3$], 65.02 (O*C*H$_3$), 80.39 [O*C*H(CH$_3$)$_2$], 123.91, 125.32, 125.79, 126.75 (Aryl-C_m), 127.10, 130.39, 131.56, 132.52 (Aryl-C_o), 144.11, 144.42, 148.39 (Aryl-C_p), 151.36, 156.18, 160.27 (Aryl-C_i) ppm.

[Ti(O*t*Bu)(Mecalix)]·C$_7$H$_8$ (12·C$_7$H$_8$): *t*BuOH (125 µL, 1.33 mmol) was added to a yellow solution of **5** (1.00 g, 1.33 mmol) in toluene (20 mL), and the reaction mixture was stirred for 8 h. All volatiles were evaporated under reduced pressure to give **12**·C$_7$H$_8$ (890 mg, 77%) as a pale-yellow powder, which was dried in vacuo. $C_{49}H_{64}O_5Ti\cdot C_7H_8$ (873.1): calcd. C 77.04, N 8.31; found C 76.76, H 8.26. MS: *m*/*z* (%) = 780 (100) [M$^+$], 765 (6) [M − CH$_3$], 724 (14) [M − *t*Bu], 709 (37) [M − *t*Bu − CH$_3$], 707 (8) [M − O*t*Bu]. IR: $\tilde{\nu}$ = 2963 vs br, 1603 w br, 1580 w, 1480 vs br, 1393 w, 1362 s, 1310 s br, 1280 m, 1262 s br, 1208 vs br, 1169 s br, 1123 m, 1112 m, 1095 m, 1013 vs br, 940 s br, 921 s, 873 vs br, 825 m, 798 vs, 757 m, 727 s, 694 w, 676 w, 646 w, 632 w, 599 m, 584 s, 568 m, 554 m, 506 w br, 464 w, 446 w, 428 w cm^{-1}. ^{1}H NMR (C$_6$D$_6$): δ = 0.74 [s, 9 H, C(C*H*$_3$)$_3$], 0.83 [s, 9 H, C(C*H*$_3$)$_3$], 1.42 [s, 18 H, C(C*H*$_3$)$_3$], 1.61 [s, 9 H, OC(C*H*$_3$)$_3$], 3.27 (d, $^2J_{\mathrm{H,H}}$ = 12.3 Hz, 2 H, C*H*$_2$), 3.33 (d, $^2J_{\mathrm{H,H}}$ = 12.6 Hz, 2 H, C*H*$_2$), 3.82 (s, 3 H, OC*H*$_3$), 4.40 (d, $^2J_{\mathrm{H,H}}$ = 12.3 Hz, 2 H, C*H*$_2$), 5.04 (d, $^2J_{\mathrm{H,H}}$ = 12.6 Hz, 2 H, C*H*$_2$), 6.88 (s, 2 H, Aryl-H_m), 6.91 (s, 2 H, Aryl-H_m), 7.23 (s, 2 H, Aryl-H_m), 7.24 (s, 2 H, Aryl-H_m) ppm. ^{13}C NMR (C$_6$D$_6$): δ = 30.67 [C(*C*H$_3$)$_3$], 31.04 [C(*C*H$_3$)$_3$], 32.04 [C(*C*H$_3$)$_3$],32.06 [OC(*C*H$_3$)$_3$], 33.58 [*C*(CH$_3$)$_3$], 33.72 [*C*(CH$_3$)$_3$], 33.79 (*C*H$_2$), 33.95 (*C*H$_2$), 34.39 [*C*(CH$_3$)$_3$], 65.29 (O*C*H$_3$), 85.59 [O*C*(CH$_3$)$_3$], 123.92, 125.32, 125.72, 127.08 (Aryl-C_m), 129.28, 130.38, 131.54, 132.54 (Aryl-C_o), 144.01, 144.36, 148.38 (Aryl-C_p), 151.41, 156.20, 160.23 (Aryl-C_i) ppm.

[Ti(OC$_6$H$_4$-4-*t*Bu)(Mecalix)}]·C$_7$H$_8$ (13·C$_7$H$_8$): Toluene (10 mL) was added at room temperature to a mixture of **5** (500 mg, 0.67 mmol) and *p*-*tert*-butylphenol (100 mg, 0.67 mmol) to give an orange, slightly cloudy solution. This solution was stirred at 100 °C for 24 h with formation of an orange precipitate. After cooling to room temperature, the precipitate was filtered off and dried in vacuo to afford **13**·C$_7$H$_8$ as an orange-red solid (518 mg, 81%). $C_{55}H_{68}O_5Ti\cdot C_7H_8$ (949.2): calcd. C 78.46; H 8.07; found C 77.95, H 8.09. MS: *m*/*z* (%) = 856 (100) [M$^+$], 841 (60) [M − CH$_3$]. IR: $\tilde{\nu}$ = 2968 vs br, 1603 w, 1504 s, 1480 vs br, 1435 vs br, 1415 w, 1392 w, 1361 w, 1319 m, 1300 s br, 1266 vs br, 1221 vs br, 1206 vs br, 1122 m, 1096 m, 1010 s, 940 s, 921 m, 874 vs br, 842 s, 824 s, 795 vs, 756 m, 728 m, 678 w, 582 vs br, 535 s br cm^{-1}. ^{1}H NMR (CDCl$_3$): δ = 1.17 [s, 9 H, C(C*H*$_3$)$_3$], 1.18 [s, 9 H, C(C*H*$_3$)$_3$], 1.25 [s, 18 H, C(C*H*$_3$)$_3$], 1.31 [s, 9 H, C(C*H*$_3$)$_3$], 3.31 (d, $^2J_{\mathrm{H,H}}$ = 12.7 Hz, 4 H, C*H*$_2$), 3.32 (d, $^2J_{\mathrm{H,H}}$ = 12.4 Hz, 4 H, C*H*$_2$), 4.10 (s, 3 H, OC*H*$_3$), 4.34 (d, $^2J_{\mathrm{H,H}}$ = 12.4 Hz, 2 H, C*H*$_2$), 4.73 (d, $^2J_{\mathrm{H,H}}$ = 12.7 Hz, 2 H, C*H*$_2$), 7.29−6.75 (m, 10 H, Aryl- and Phenyl-*H*) ppm. ^{13}C NMR (CDCl$_3$): δ = 31.14 [C(*C*H$_3$)$_3$], 31.37 [C(*C*H$_3$)$_3$], 31.56 [C(*C*H$_3$)$_3$], 31.67 [C(*C*H$_3$)$_3$], 33.42 (*C*H$_2$), 33.59 (*C*H$_2$), 34.19 [*C*(CH$_3$)$_3$], 65.54 (O*C*H$_3$), 123.66, 124.94, 126.25, 127.21 (Aryl-C_m), 126.89, 129.45, 130.13, 132.45 (Aryl-C_o), 144.46, 144.77, 148.59 (Aryl-C_p), 151.18, 158.73, 160.50 (Aryl-C_i) ppm.

[Ti(OC$_6$H$_3$-2,6-*i*Pr$_2$)(Mecalix)] (14): 2,6-Diisopropylphenol (123.2 µL, 0.67 mmol) was added to a solution of **5** (500 mg, 0.67 mmol) in toluene (10 mL). The resulting orange solution was stirred for 12 h and then concentrated to dryness. The viscous orange residue was suspended in hexane, and the precipitate was collected and dried in vacuo to give **14** as a yellow powder (269 mg, 45%). Crystals suitable for X-ray diffraction were obtained from a saturated toluene solution at room temperature. $C_{57}H_{72}O_5Ti$ (885.1): calcd. C 77.35; H 8.20; found C 77.19, H 8.32. MS: *m*/*z* (%) = 885 (100) [M$^+$], 870 (37) [M − CH$_3$]. IR: $\tilde{\nu}$ = 2975 vs br, 1601 w br, 1582 w br, 1483 vs br, 1430 s br, 1412 w, 1393 w, 1362 s, 1302 vs br, 1256 vs br, 1236 s, 1191 vs br, 1121 s br, 1096 m, 1048 w, 1017 m, 949 vs, 917 vs br, 881 vs br, 825 s, 798 vs, 757 s br, 716 m, 676 w, 605 m, 586 vs br, 551 s br, 505 w, 476 w, 445 m, 427 m cm^{-1}. ^{1}H NMR (C_6D_6): δ = 0.74 [s, 9 H, C(CH_3)$_3$], 0.83 [s, 9 H, C(CH_3)$_3$], 1.40 [s, 18 H, C(CH_3)$_3$], 1.46 [d, $^3J_{H,H}$ = 6.9 Hz, 12 H, OPh{CH(CH_3)$_2$}$_2$], 3.31 (d, $^2J_{H,H}$ = 12.3 Hz, 2 H, CH_2), 3.41 (d, $^2J_{H,H}$ = 12.7 Hz, 2 H, CH_2), 3.61 (s, 3 H, OCH_3), 4.18 [sept, $^3J_{H,H}$ = 6.9 Hz, 2 H, OPh{CH(CH$_3$)$_2$}$_2$], 4.49 (d, $^2J_{H,H}$ = 12.3 Hz, 2 H, CH_2), 5.12 (d, $^2J_{H,H}$ = 12.7 Hz, 2 H, CH_2), 6.91 (s, 2 H, Aryl-H_m), 6.92 (s, 2 H, Aryl-H_m), 7.02 (m, 1 H, DIP-H_p), 7.14 (m, 2 H, DIP-H_m), 7.25 (s, 2 H, Aryl-H_m), 7.26 (s, 2 H, Aryl-H_m) ppm. ^{13}C NMR (C_6D_6): δ = 23.16 [CH(CH$_3$)$_2$], 28.35 [CH(CH$_3$)$_2$], 30.65 [C(CH$_3$)$_3$], 31.00 [C(CH$_3$)$_3$], 31.99 [C(CH$_3$)$_3$], 33.65 [C(CH$_3$)$_3$], 33.74 (CH$_2$), 33.90 (CH$_2$), 34.46 [C(CH$_3$)$_3$], 64.57 (OCH$_3$), 123.01 (s, DIP-C_p), 124.01 (s, DIP-C_m), 123.78, 125.45, 125.93, 127.27 (s, Aryl-C_m), 126.19, 130.57, 131.58, 132.33 (s, Aryl-C_o), 138.12 (s, DIP-C_o), 144.74, 145.13, 148.49 (s, Aryl-C_p), 151.88 (s, DIP-C_i), 157.86, 161.21, 163.03 (s, Aryl-C_i) ppm.

[Ti(S*t*Bu)(Mecalix)] (15): *t*BuSH (75.5 µL, 0.67 mmol) was added to a solution of **5** (500 mg, 0.67 mmol) in toluene (10 mL) at −30 °C. The Schlenk flask was then removed from the cooling bath and the solution stirred at room temperature for 2 h until it turned orange. All volatiles were removed in vacuo and the orange residue was suspended in 3 mL of hexane, filtered off and dried in vacuo to afford **15** as an orange powder (272 mg, 58%). Crystals suitable for X-ray diffraction were obtained from a hexane solution saturated at 60 °C with **15**. $C_{49}H_{64}O_4STi$ (797.0): calcd. C 73.85; H 8.09; found C 73.58, H 8.21. MS: *m*/*z* (%) = 797 (58) [M$^+$], 796 (100) [M − H], 740 (53) [M − *t*Bu], 725 (14) [M − *t*Bu − CH$_3$], 707 (7) [M − S*t*Bu]. IR: $\tilde{\nu}$ = 2969 vs br, 1602 w br, 1580 w, 1481 vs br, 1393 w, 1362 s, 1301 s br, 1253 s br, 1208 vs br, 1157 s br, 1124 s, 1112 s, 1004 s, 942 s, 922 s, 874 vs br, 831 s, 798 vs, 760 s, 725 s, 676 w, 634 w, 585 s, 567 s, 554 m, 504 w br, 466 m, 445 m, 431 m cm^{-1}. ^{1}H NMR (C_6D_6): δ = 0.70 [s, 9 H, C(CH_3)$_3$], 0.80 [s, 9 H, C(CH_3)$_3$], 1.40 [s, 18 H, C(CH_3)$_3$], 2.03 [s, 9 H, SC(CH_3)$_3$], 3.24 (d, $^2J_{H,H}$ = 12.3 Hz, 2 H, CH_2), 3.34 (d, $^2J_{H,H}$ = 12.7 Hz, 2 H, CH_2), 3.95 (s, 3 H, OCH_3), 4.49 (d, $^2J_{H,H}$ = 12.3 Hz, 2 H, CH_2), 5.17 (d, $^2J_{H,H}$ = 12.7 Hz, 2 H, CH_2), 6.81 (s, 2 H, Aryl-H_m), 6.85 (s, 2 H, Aryl-H_m), 7.20 (s, 2 H, Aryl-H_m), 7.21 (s, 2 H, Aryl-H_m) ppm. ^{13}C NMR (C_6D_6): δ = 30.61, 30.97, 31.93 [C(CH$_3$)$_3$], 32.05, 32.22 [C(CH$_3$)$_3$], 33.58, 34.01 (CH$_2$), 34.47 [C(CH$_3$)$_3$], 36.48 [SC(CH$_3$)$_3$], 53.27 [SC(CH$_3$)$_3$], 66.99 (OCH$_3$), 124.00, 125.49, 125.56, 125.61 (Aryl-C_m), 127.03, 131.03, 132.12, 132.14 (Aryl-C_o), 145.20, 145.51, 148.30 (Aryl-C_p), 150.90, 157.54, 161.89 (Aryl-C_i) ppm.

[Ti(ONMe$_2$)(Mecalix)]·C$_7$H$_8$ (16·C$_7$H$_8$): A 5.5 M solution of *tert*-butyl hydroperoxide (1.1 equiv., 0.27 mL, 1.46 mmol) in decane was added to a yellow solution of **5** (1.00 g, 1.33 mmol) in toluene (20 mL). The solution turned red shortly after addition and became yellow while stirring at room temperature for 1 h. All volatiles were removed in vacuo to give **16**·C_7H_8 as a yellow powder (1.03 g, 90%). $C_{47}H_{61}NO_5Ti\cdot C_7H_8$ (860.0): calcd. C 73.52, H 8.01, N 1.82; found C 73.48, H 7.94, N 1.67. MS: *m*/*z* (%) = 767 (100) [M$^+$] 752 (9) [M − CH$_3$], 723 (13) [M − N(CH$_3$)$_2$], 707 (12) [M − ON(CH$_3$)$_2$], 693 (12) [M − ON(CH$_3$)$_2$ − CH$_3$], 677 (12) [M − ON(CH$_3$)$_2$ − 2 CH$_3$]. IR: $\tilde{\nu}$ = 2962 vs br, 1603 w, 1580 w, 1480 vs br, 1393 w, 1362 s, 1309 s br, 1260 vs br, 1207 vs br, 1170 w, 1114 s br, 1096 s br, 1017 s br, 939 m, 921 m, 873 s, 797 vs, 756 m, 728 w, 676 w, 632 w br, 599 m, 584 m, 566 m, 508 w br, 478 w br cm^{-1}. ^{1}H NMR (C_6D_6): δ = 0.77 [s, 9 H, C(CH_3)$_3$], 0.86 [s, 9 H, C(CH_3)$_3$], 1.45 [s, 18 H, C(CH_3)$_3$], 2.92 [s, 6 H, ON(CH_3)$_2$], 3.28 (d, $^2J_{H,H}$ = 12.2 Hz, 2 H, CH_2), 3.37 (d, $^2J_{H,H}$ = 12.5 Hz, 2 H, CH_2), 3.79 (s, 3 H, OCH_3), 4.46 (d, $^2J_{H,H}$ = 12.2 Hz, 2 H, CH_2), 4.88 (d, $^2J_{H,H}$ = 12.5 Hz, 2 H, CH_2), 6.92 (s, 2 H, Aryl-H_m), 6.93 (s, 2 H, Aryl-H_m), 7.25 (s, 2 H, Aryl-H_m), 7.28 (s, 2 H, Aryl-H_m) ppm. ^{13}C NMR (C_6D_6): δ = 31.61 [s, C(CH$_3$)$_3$], 31.96 [s, C(CH$_3$)$_3$], 32.90 [s, C(CH$_3$)$_3$], 34.44 [s, C(CH$_3$)$_3$], 34.55 [s, C(CH$_3$)$_3$], 34.65 (s, CH$_2$), 34.85 (s, CH$_2$), 35.21 [s, C(CH$_3$)$_3$], 50.31 [s, N(CH$_3$)$_2$], 64.02 (s, OCH$_3$), 124.89, 126.13, 126.21, 127.51 (s, Aryl-C_m), 127.10, 132.08, 132.71, 133.33 (s, Aryl-C_o), 144.53, 144.71, 148.39 (s, Aryl-C_p), 153.12, 159.21, 161.87 (s, Aryl-C_i) ppm.

Epoxidation Reactions: In an NMR tube 0.029 mmol (based on monomeric units) of the precatalyst was layered with C_6D_6/TMS (0.30 mL) and frozen in liquid nitrogen. Cyclooctene (74.3 µL, 0.573 mmol) and a 5.5 M solution of *tert*-butyl hydroperoxide in decane (104.6 µL, 0.573 mmol) were then added. To determine the kinetics the samples were thawed and mixed shortly before they were placed into the NMR spectrometer. The ratio between substrate, product and catalyst was determined by integration of the resonances of the olefinic protons of the cyclooctene, the protons of the epoxide ring and the protons of the methoxy groups of the calixarene complexes relative to TMS. The entries in Figure 12 are averages of three runs.

Computational Details: All density functional and MP2 calculations reported were carried out by using the TURBOMOLE set of programs, developed by Ahlrichs and co-workers, within the RI-J approximation.[21,22] Standard SV(P) basis sets and auxiliary basis sets as implemented in the TURBOMOL package were used for all atoms.[22,23] The acronym SV(P) (split valence plus polarization) refers to TURBOMOLE split-valence basis sets, augmented by a shell of polarization functions. DFT calculations were performed including gradient corrections, Becke's nonlocal correction for exchange and Perdew's nonlocal correction for correlation to the local density approximation part of the density functional.[24]

Crystal Structure Determination of [TiCl(Mecalix)]·1.5C$_7$H$_8$, [Ti(η^5-C$_5$H$_5$)(Mecalix)]·3C$_7$H$_8$, [Ti(NMe$_2$)(Mecalix)]·[{Ti(Mecalix)}$_2$-(µ-O)]·5C$_4$H$_8$O, 2·[Ti(NPh$_2$)(Mecalix)]·8C$_4$H$_8$O·0.5C$_6$H$_6$, [{Ti(OMe)(Mecalix)}$_2$]·6C$_7$H$_8$, [Ti(OC$_6$H$_3$-2,6-*i*Pr$_2$)(Mecalix)]·C$_6$H$_3$*i*Pr$_2$OH, and [Ti(S*t*Bu)(Mecalix)]·C$_6$H$_{14}$: Crystal data collection and processing parameters are given in Tables 1 and 2. Crystals were immersed in a film of perfluoropolyether oil on a glass fiber and transferred to a Stoe-STADI 4 (Mo-K_α radiation for **1**·1.5C$_7$H$_8$) or Stoe-IPDS diffractometer (Ag-K_α radiation for the rest) equipped with an FTS AirJet low-temperature device. Data were collected at 203 K. The IPDS images were processed with the Stoe IPDS software package and equivalent reflections were merged. Corrections for Lorentz polarization effects and absorption were performed where necessary and the structures were solved by direct methods. Subsequent difference-Fourier syntheses revealed the positions of all other non-hydrogen atoms, and hydrogen atoms were included in calculated positions. Extinction corrections were applied as required. Crystallographic calculations were performed using SHELXS-97 and SHELXL-97.[39] For compound **4** the methyl carbon atoms of two of the calixarene *tert*-butyl groups [C(17) to C(19) and C(47) to C(49)] were disordered over two sites. These carbon atoms were refined in an isotropic approximation with occupancy factors of 70%/30% and 50%/50%, respectively. For **5**·**9**·5C$_4$H$_8$O the following carbon atoms of the calixarene *tert*-butyl groups were disordered over two sites and refined in an isotropic approximation with occupancy factors of 50% each: C(17), C(18),

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Table 1. X-ray data collection and processing parameters for **1**·1.5C_7H_8, **4**·2C_7H_8, **5**·**9**·5C_4H_8O and **8**·8C_4H_8O·0.5C_6H_6

	1·1.5C_7H_8	**4**·2C_7H_8	**5**·**9**·5C_4H_8O	**8**·8C_4H_8O·0.5C_6H_6
Empirical formula	$C_{55.5}H_{67}ClO_4Ti$	$C_{64}H_{76}O_4Ti$	$C_{112}H_{156}O_{13.5}Ti_2$	$C_{149}H_{197}N_2O_{16}Ti_2$
Formula mass	881.4	957.2	1828.18	2367.88
Crystal system	monoclinic	monoclinic	triclinic	monoclinic
Space group	*I*2/*a*	*P*2$_1$/*c*	*P*$\bar{1}$	*P*2$_1$/*c*
a [Å]	24.944(5)	16.561(1)	13.317(1)	26.366(2)
b [Å]	13.359(3)	14.970(1)	21.304(2)	20.525(1)
c [Å]	30.121(6)	23.676(2)	21.319(2)	27.381(2)
α [°]	90	90	100.944(8)	90
β [°]	94.77(3)	108.479(9)	100.244(8)	114.791(6)
γ [°]	90	90	100.196(8)	90
V [Å^3]	10003(3)	5566.9(7)	5702.7(7)	13451.6(12)
Z	8	4	2	4
μ [mm^{-1}]	0.268	0.111	0.108	0.102
Tot./indep. reflns.	9836/9836	31081/7485	26742/13513	80108/19065
Observed reflns.[a]	7718	3845	8652	13675
Parameters	574	602	1090	1440
Final *R*,[b] *wR*$_2$ [c] [d]	0.0611, 0.1521	0.0777, 0.1805	0.0976, 0.2746	0.0802, 0.2233

[a] Reflections with $I > 2\sigma(I)$. [b] $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [c] $wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$. [d] For data with $I > 2\sigma(I)$.

Table 2. X-ray data collection and processing parameters for **9**·4C_6H_6, **10**·6C_7H_8, **14**·C_6H_3·*i*Pr_2OH and **15**·C_6H_{14}

	9·4C_6H_6	**10**·6C_7H_8	**14**·C_6H_3·*i*Pr_2OH	**15**·C_6H_{14}
Empirical formula	$C_{114}H_{134}O_9Ti_2$	$C_{134}H_{164}O_{10}Ti_2$	$C_{69}H_{90}O_6Ti$	$C_{55}H_{78}O_4Sti$
Formula mass	1744.0	2030.5	1063.3	813.1
Crystal system	monoclinic	monoclinic	monoclinic	monoclinic
Space group	*P*2$_1$/*n*	*C*2/*c*	*P*2$_1$/*c*	*P*2$_1$/*c*
a [Å]	1307.3(1)	28.472(6)	22.814(3)	1548.4(1)
b [Å]	17.612(1)	17.134(3)	10.570(3)	1666.4(1)
c [Å]	21.831(2)	2396.2(5)	24.710(4)	2167.1(1)
α [°]	90	90	90	90
β [°]	96.354(11)	91.11(3)	91.759(16)	106.676(6)
γ [°]	90	90	90	90
V [Å^3]	4995.6(7)	11687(4)	5956(2)	5356.5(5)
Z	2	4	4	4
μ [mm^{-1}]	0.120	0.109	0.109	0.130
Tot./indep. reflns.	15565/	45691/11128	23524/9321	29817/10096
Observed reflns.[a]	6003	7829	5962	5008
Parameters	536	605	702	538
Final *R*,[b] *wR*$_2$ [c] [d]	0.0609, 0.1082	0.0732, 0.2094	0.0692, 0.1843	0.0973, 0.2247

[a] Reflections with $I > 2\sigma(I)$. [b] $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [c] $wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$. [d] For data with $I > 2\sigma(I)$.

C(19), C(29), C(37), C(38), C(39), C(48), C(49), C(59), C(89). The anisole methyl group C(95) of the calixarene ligand of **9** was disordered in this structure over two sites at the oxygen atoms O(6) and O(8) and refined isotropically using equal occupancy. Furthermore, two methylene groups of one of the solvent molecules [C(109) and C(111)] were disordered and isotropically refined with occupancy factors of 50% each. For **8**·8C_4H_8O·0.5C_6H_6 the following carbon atoms of calixarene *tert*-butyl groups or THF molecules were disordered over two sites and refined in an isotropic approximation with occupancy factors of 50% each: C(19), C(49), C(122), C(129), C(130), C(131). The methylene carbon atoms C(132), C(133), C134), C(135), as well as C(137), C(138), C(144), C(145), C(147) of THF molecules were disordered over two sites. These carbon atoms were refined in an isotropic approximation with occupancy factors of 60%/40% and 70%/30%, respectively. The carbon atoms C(60) and C(61) of one of the isopropyl groups in **14**·C_6H_3 *i*Pr_2OH were disordered over two sites and refined in an isotropic approximation with occupancy factors of 45%/55%. For **15**·C_6H_{14} two of the *tert*-butyl groups of the calixarene ligand [C(27) to C(29) and C(37) to C(39)] and of the thiolate group [C(7) to C(9)] were disordered over two sites and refined in an isotropic approximation with occupancy factors of 65%/35%, 60%/40% and 50%/50%, respectively. CCDC-233967 to CCDC-233974 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: + 44-1223-336-033; E-mail: deposit@ccdc.cam.ac.uk].

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