Synthesis and Reactivity of Calix[4]arene-Supported Group 4 Imido Complexes

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Abstract: New mononuclear titanium and zirconium imido complexes [M(NR)(R'$_2$calix)] [M = Ti, R' = Me, R = *t*Bu (**1**), R = 2,6-$C_6H_3Me_2$ (**2**), R = 2,6-C_6H_3*i*Pr_2 (**3**), R = 2,4,6-$C_6H_2Me_3$ (**4**); M = Ti, R' = Bz, R = *t*Bu (**5**), R = 2,6-$C_6H_3Me_2$ (**6**), R = 2,6-C_6H_3*i*Pr_2 (**7**); M = Zr, R' = Me, R = 2,6-C_6H_3*i*Pr_2 (**8**)] supported by 1,3-diorganyl ether *p-tert*-butylcalix[4]arenes (R'$_2$calix) were prepared in good yield from the readily available complexes [MCl_2(Me$_2$calix)], [Ti(NR)Cl_2(py)$_3$], and [Ti(NR)Cl_2(NHMe$_2$)$_2$]. The crystallographically characterised complex [Ti(N*t*Bu)(Me$_2$calix)] (**1**) reacts readily with CO_2, CS_2, and *p*-tolyl-isocyanate to give the isolated complexes [Ti{N(*t*Bu)C(O)O}(Me$_2$calix)] (**10**), [{Ti(μ-O)(Me$_2$calix)}$_2$] (**11**), [{Ti(μ-S)(Me$_2$calix)}$_2$] (**12**), and [Ti{N(*t*Bu)C(O)N(-4-C_6H_4Me)}(Me$_2$calix)] (**13**). In the case of CO_2 and CS_2, the addition of the heterocumulene to the Ti–N multiple bond is followed by a cycloreversion reaction to give the dinuclear complexes **11** and **12**. The X-ray structure of **13·4(C_7H_8)** clearly establishes the N,N'-coordination mode of the ureate ligand in this compound. Complex **1** undergoes *tert*-butyl/arylamine exchange reactions to form **2**, **3**, [Ti(N-4-C_6H_4Me)(Me$_2$calix)] (**14**), [Ti(N-4-C_6H_4Fc)(Me$_2$calix)] (**15**) [Fc = Fe(η^5-C_5H_5)(η^5-C_5H_4)], and [{Ti(Me$_2$calix)}$_2${μ-(N-4-C_6H_4)$_2$CH$_2$}] (**16**). Reaction of **1** with H_2O, H_2S and HCl afforded the compounds [{Ti(μ-O)(Me$_2$calix)}$_2$] (**11**), [{Ti(μ-S)(Me$_2$calix)}$_2$] (**12**), and [TiCl_2(Me$_2$calix)] in excellent yields. Furthermore, treatment of **1** with two equivalents of phenols results in the formation of [Ti(O-4-C_6H_4R)$_2$(Me$_2$calix)] (R = Me **17** or *t*Bu **18**), [Ti(O-2,6-$C_6H_3Me_2$)$_2$(Me$_2$calix)] (**19**) and [Ti(mbmp)(Me$_2$calix)] (**20**; H$_2$mbmp = 2,2'-methylene-bis(4-methyl-6-*tert*-butylphenol) or CH$_2$({CH$_3$}{C$_4$H$_9$}C$_6$H$_2$-OH)$_2$). The bis(phenolate) compounds **17** and **18** with *para*-substituted phenolate ligands undergo elimination and/or rearrangement reactions in the nonpolar solvents pentane or hexane. The metal-containing products of the elimination reactions are dinuclear complexes [{Ti(O-4-C_6H_4R)(Mecalix)}$_2$] [R = Me (**23**) or *t*Bu (**24**)] where Mecalix = monomethyl ether of *p-tert*-butylcalix[4]arene. The products of the rearrangement reaction are [Ti(O-4-C_6H_4Me)$_2$(*paco*-Me$_2$calix)] (**25**) and [Ti(O-4-C_6H_4*t*Bu)$_2$(*paco*-Me$_2$calix)] (**26**), in which the metallated calix[4]arene ligand is coordinated in a form reminiscent of the *partial cone* (*paco*) conformation of calix[4]arene. In these compounds, one of the methoxy groups is located *inside* the cavity of the calix[4]arene ligand. The complexes **24**, **25** and **26** have been crystallographically characterised. Complexes with sterically more demanding phenolate ligands, namely **19** and **20** and the analogous zirconium complexes [Zr(O-4-C_6H_4Me)$_2$(Me$_2$calix)] (**21**) and [Zr(O-2,6-$C_6H_3Me_2$)$_2$(Me$_2$calix)] (**22**) do not rearrange. Density functional calculations for the model complexes [M(OC_6H_5)$_2$(Me$_2$calix)] with the calixarene possessing either *cone* or *partial cone* conformations are briefly presented.

Keywords: calixarenes · coordination modes · imido ligands · titanium · zirconium

Introduction

The synthesis and reactivity of transition metal imido complexes has been an area of considerable interest over the last twenty years.[1] Fully authenticated, highly reactive, terminal Group 4 imido complexes were first reported by Bergman and Wolczanski at the end of the 1980s,[2] and a number of research groups have been involved in the development of Group 4 imido chemistry since this time.[3] Work from the Mountford and other laboratories in this area has focussed mainly on titanium imido chemistry in a wide range of supporting ligand environments,[4] and one of the driving forces has been the discovery of new chemistry of the M=NR[5] linkage itself. In this latter regard, one of our approaches to developing complexes of the type [M(NR)(L$_n$)] (M = Group 4 metal, R = hydrocarbyl fragment) has been to make the supporting ligand set (L$_n$) a dianionic, chelating tri- or tetra-dentate system. We hoped that this would focus and channel reactivity

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DOI: 10.1002/chem.200204656

Abstract in German: *Ausgehend von den gut zugänglichen Verbindungen [MCl$_2$(Me$_2$calix)], [Ti(NR)Cl$_2$(py)$_3$] und [Ti(NR)Cl$_2$(NHMe$_2$)$_2$] wurden neue, mononukleare Imidokomplexe [M(NR)(R'$_2$calix)]]M = Ti, R' = Me, R = tBu (**1**), R = 2,6-C$_6$H$_3$Me$_2$ (**2**), R = 2,6-C$_6$H$_3$iPr$_2$ (**3**), R = 2,4,6-C$_6$H$_2$Me$_3$ (**4**); M = Ti, R' = Bz, R = tBu (**5**), R = 2,6-C$_6$H$_3$Me$_2$ (**6**), R = 2,6-C$_6$H$_3$iPr$_2$ (**7**); M = Zr, R' = Me, R = 2,6-C$_6$H$_3$iPr$_2$ (**8**)] des vierwertigen Titans und Zirkoniums dargestellt, welche durch 1,3-Diorganylether des p-tert-Butyl-Calix[4]arens (R'$_2$calix) stabilisiert werden. Der strukturell charakterisierte Komplex [Ti(NtBu)(Me$_2$calix)] (**1**) reagiert bereitwillig mit CO$_2$, CS$_2$, und p-Tolylisocyanat, wobei die Verbindungen [Ti{N(tBu)-C(O)O}(Me$_2$calix)] (**10**), [{Ti(μ-O)(Me$_2$calix)}$_2$] (**11**), [{Ti-(μ-S)(Me$_2$calix)}$_2$] (**12**) und [Ti{N(tBu)C(O)N(-4-C$_6$H$_4$Me)}-(Me$_2$calix)] (**13**) isoliert wurden. Im Falle der Addition der Heterokumulene CO$_2$ und CS$_2$ an die Ti–N-Mehrfachbindung erfolgt eine anschließende Cycloreversion, die zu den dinuklearen Verbindungen **11** und **12** führt. Die Molekülstruktur des Isocyanat-Additionsproduktes **13 · 4(C$_7$H$_8$)** belegt die N,N'-Koordination des aus der Reaktion hervorgehenden Ureatoliganden. Ferner wurden am tert-Butylimido-Komplex **1** Amin-Austauschreaktionen durchgeführt und so die verwandten Arylimidokomplexe **2**, **3**, [Ti(N-4-C$_6$H$_4$Me)(Me$_2$-calix)] (**14**), [Ti(N-4-C$_6$H$_4$Fc)(Me$_2$calix)] (**15**) [Fc = Fe(η^5-C$_5$H$_5$)(η^5-C$_5$H$_4$)] und [{Ti(Me$_2$calix)}$_2${μ-(N-4-C$_6$H$_4$)$_2$CH$_2$}] (**16**) dargestellt. Die Umsetzungen von **1** mit H$_2$O, H$_2$S und HCl führten zu den Verbindungen [{Ti(μ-O)(Me$_2$calix)}$_2$] (**11**), [{Ti(μ-S)(Me$_2$calix)}$_2$] (**12**) und [TiCl$_2$(Me$_2$calix)] in sehr guten Ausbeuten. Weiterhin lieferte die Reaktion von **1** mit zwei Äquivalenten des entsprechenden Phenols die Komplexe [Ti(O-4-C$_6$H$_4$R)$_2$(Me$_2$calix)] [R = Me (**17**) oder tBu (**18**)], [Ti(O-2,6-C$_6$H$_3$Me$_2$)$_2$(Me$_2$calix)] (**19**) und [Ti(mbmp)(Me$_2$-calix)] (**20**; H$_2$mbmp = 2,2'-Methylen-bis(4-methyl-6-tert-butylphenol); CH$_2$({CH$_3$}{C$_4$H$_9$}C$_6$H$_2$-OH)$_2$). In unpolaren Solvenzien gehen die Bis(phenolat)verbindungen mit para-substituierten Phenolatliganden **17** und **18** Eliminierungs- und Umlagerungsreaktionen ein. Die metallhaltigen Produkte der Eliminierungsreaktion sind dinukleare Verbindungen des Calix[4]aren-Monomethylethers [{Ti(O-4-C$_6$H$_4$R)(Mecalix)}$_2$] (**23**; R = Me) und (**24**; R = tBu); aus den Umlagerungsreaktionen gehen die Komplexe [Ti(O-4-C$_6$H$_4$Me)$_2$(paco-Me$_2$calix)] (**25**) und [Ti(O-4-C$_6$H$_4$tBu)$_2$(paco-Me$_2$calix)] (**26**) hervor, in denen der metallierte Calix[4]arenligand in einer Form koordiniert, die an die sogenannte partial cone (paco) Konformation des Calix[4]arens erinnert. In diesen Verbindungen ist eine der Methoxygruppen des Ligandensystems innerhalb der Kavität des Calix[4]arenliganden angeordnet. Die Verbindungen **24**, **25** und **26** wurden strukturanalytisch charakterisiert. Komplexe mit sterisch anspruchsvolleren Phenolatliganden wie **19** und **20** sowie analoge Verbindungen [Zr(O-4-C$_6$H$_4$Me)$_2$(Me$_2$calix)] **21** und [Zr(O-2,6-C$_6$H$_3$Me$_2$)$_2$(Me$_2$calix)] **22** des Zirkonium lagern nicht um. DFT-Berechnungen an Modellverbindungen [M(OC$_6$H$_5$)$_2$(Me$_2$calix)], in denen der Calix[4]arenligand in der cone oder paco Konformation vorliegt, weisen auf eine thermodynamische Präferenz des paco Isomeren hin.*

of these complexes towards the M=NR group. Supporting ligand systems so far studied in these contexts include: the carbon-donor cyclooctatetraenes;[6] N$_4$-donor dibenzotetraaza[14]annulenes (abbreviated as Me$_n$taa, $n = 4$ or 8) and porphyrins, "tren-like" and piperazine-derived diamide-diamines; N$_2$O$_2$-donor acen- and salen-type Schiff's bases; and N$_2$N-donor diamido-pyridine (abbreviated as N$_2$N$_{py}$) and some homologues.[7, 8] Among all these systems the diamido-pyridine **I** and dibenzotetraaza[14]annulene **II** complexes have shown the greatest diversity of reactivity at the Ti=NR bond.[7b, g, h]

I **II**

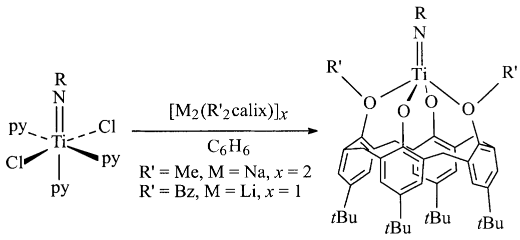
Scheme 1. Titanium imido diamido-pyridine **I** and dibenzotetraaza[14]annulene **II** complexes.

Like the widely successful N$_4$-donor Me$_n$taa systems[7h] the R$_2$calix ligands provide a robust and well-defined O$_4$-coordination environment. The Me$_2$calix homologues (where H$_2$Me$_2$calix = 1,3-dimethyl ether *p-tert*-butylcalix[4]arene) in particular have received much attention in organotransition metal chemistry over the last 10–15 years.[9] Gibson and Redshaw,[10] and also Radius and Attner,[11] have reported on aspects of Group 6 imido complexes supported by tetra-anionic calix[4]arenes. More recently Radius and Friedrich outlined the synthesis of new terminal imido titanium complexes, namely [Ti(N*t*Bu)(Me$_2$calix)] (**1**) and its crystallographically characterised homologue, [Ti(N-2,4,6-C$_6$H$_2$Me$_3$)-(Me$_2$calix)] (**4**), from [TiCl$_2$(Me$_2$calix)] and two equivalents of the appropriate lithiated primary amine, LiNHR.[12] As a part of a wider survey of zirconium chemistry with Me$_2$calix ligands Floriani showed that [Zr(η^4-C$_4$H$_6$)(Me$_2$calix)] reacts with PhN$_3$ to yield binuclear [{Zr(μ_2-NPh)(Me$_2$calix)}$_2$] which features μ_2-bridging phenyl imido ligands.[13]

In this contribution we report: i) a number of new and/or improved synthetic routes to a range of Group 4 calix[4]arene-supported imido complexes; ii) cycloaddition reactions of **1** with isocyanates, CO$_2$ and CS$_2$; iii) protonolysis reactions of **1** with O-H and S-H containing reagents, including some unusual rearrangement and some decomposition reactions of calix[4]arene-supported Group 4 bis(aryloxide) complexes, together with computational studies.

Results and Discussion

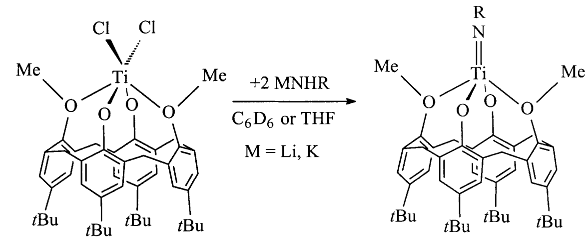
Syntheses of Group 4 imido complexes with Me$_2$calix ligands (Me$_2$calix = 1,3-dimethyl ether *p-tert*-butylcalix[4]arene): Although we previously briefly reported the syntheses of the calixarene-supported titanium imido compounds [Ti(NR)-(Me$_2$calix)] [R = *t*Bu (**1**) or R = 2,4,6-C$_6$H$_2$Me$_3$ (**4**)] from [TiCl$_2$(Me$_2$calix)] and two equivalents of the appropriate lithiated primary amine[12] we were interested to explore and develop different synthetic routes and also alternative imido N-substituents. To assess the generality of this first approach the NMR tube scale reactions of [TiCl$_2$(Me$_2$calix)] and two equivalents of LiNHAr (Ar = 2,6-C$_6$H$_3$Me$_2$ or 2,6-C$_6$H$_3$*i*Pr$_2$) were carried out according to Equation (1). These reactions proceeded cleanly and in >95% to form the arylimido complexes **2** and **3**, respectively (identical to samples prepared by alternative preparative scale methods, see below), and one equivalent of the corresponding ArNH$_2$ which is eliminated during the reaction. There is no evidence for interaction between the ArNH$_2$ and the complexes **2** or **3**, which, in principle, could form either an adduct with the free anilines or significant equilibrium concentrations of bis(anilide) species [Ti(NHAr)$_2$(Me$_2$calix)].



(2)

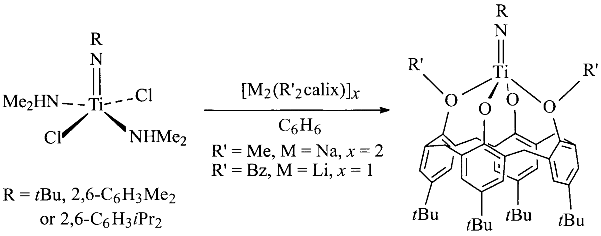
R = *t*Bu, 2,6-C$_6$H$_3$Me$_2$
or 2,6-C$_6$H$_3$*i*Pr$_2$

1: R' = Me, R = *t*Bu
2: R' = Me, R = 2,6-C$_6$H$_3$Me$_2$
3: R' = Me, R = 2,6-C$_6$H$_3$*i*Pr$_2$
5: R' = Bz, R = *t*Bu
6: R' = Bz, R = 2,6-C$_6$H$_3$Me$_2$
7: R' = Bz, R = 2,6-C$_6$H$_3$*i*Pr$_2$



(1)

1: R = *t*Bu
2: R = 2,6-C$_6$H$_3$Me$_2$
3: R = 2,6-C$_6$H$_3$*i*Pr$_2$
4: R = 2,4,6-C$_6$H$_2$Me$_3$



(3)

R = *t*Bu, 2,6-C$_6$H$_3$Me$_2$
or 2,6-C$_6$H$_3$*i*Pr$_2$

1: R' = Me, R = *t*Bu
2: R' = Me, R = 2,6-C$_6$H$_3$Me$_2$
3: R' = Me, R = 2,6-C$_6$H$_3$*i*Pr$_2$
5: R' = Bz, R = *t*Bu
6: R' = Bz, R = 2,6-C$_6$H$_3$Me$_2$
7: R' = Bz, R = 2,6-C$_6$H$_3$*i*Pr$_2$

In many previous studies[4, 6, 7] we found that the imidodichloride compounds [Ti(NR)Cl$_2$(py)$_3$] (R = *t*Bu or aryl)[14] are excellent entry points for new titanium imido complexes by substitution reactions of the chloride and/or pyridine ligands by the desired new ligands or their metallated derivatives. We have also recently reported the multi-gram synthesis and structure of [{Na$_2$(Me$_2$calix)}$_2$] from H$_2$Me$_2$calix and sodium hydride.[15] Very recently indeed we showed that reaction of [Ti(NMe$_2$)$_2$Cl$_2$] with a range of primary amines gave a new family of potential titanium imido synthons [Ti(NR)Cl$_2$(NHMe$_2$)$_2$] (R = alkyl or aryl).[16] These latter systems are apparently similar to the estabished [Ti(NR)Cl$_2$(py)$_3$] synthons mentioned above but allow for a much wider range of imido R-group incorporation.

Equation (2) summarises the preparative scale reactions of [{Na$_2$(Me$_2$calix)}$_2$] with compounds [Ti(NR)Cl$_2$(py)$_3$] in benzene at ambient temperatures to yield the yellow-orange compounds [Ti(NR)(Me$_2$calix)] [R = *t*Bu (**1**), R = 2,6-C$_6$H$_3$Me$_2$ (**2**) or R = 2,6-C$_6$H$_3$*i*Pr$_2$ (**3**)] in 90–92% isolated yields after minimal work-up.

The yield for **1** prepared this way is slightly superior to that previously reported. The successful salt-elimination route from [{Na$_2$(Me$_2$calix)}$_2$] was shown also to be viable with the bis(dimethylamine) synthons [Ti(NR)Cl$_2$(NHMe$_2$)$_2$] as depicted in Equation (3). These reactions were carried out on an NMR tube scale in deuterobenzene and proceeded in >95% yield to form **1**, **2** and **3**, the NMR spectra of which were identical to those obtained for isolated samples.

The NMR data for the new compounds [Ti(NAr)(Me$_2$calix)] [Ar = 2,6-C$_6$H$_3$Me$_2$ (**2**) or 2,6-C$_6$H$_3$*i*Pr$_2$ (**3**)] are analogous to those reported previously for [Ti(N*t*Bu)(Me$_2$calix)] (**1**) and [Ti(N-2,4,6-C$_6$H$_3$Me$_2$)(Me$_2$calix)] (**4**).[12] Thus, the NMR spectra are consistent with molecular C_{2v} symmetry with the molecular C_2 axis passing through the Ar–N=Ti bond vector.

We have also attempted to prepare titanium imido complexes of other 1,3-disubstituted ether *p-tert*-butylcalix[4]arene ligands, namely Bz$_2$calix (Bz = CH$_2$Ph) and (Me$_3$Si)$_2$calix, the metallated derivatives of which we have recently prepared. Thus reaction of one equivalent of Li$_2$(Bz$_2$calix) with [Ti(NR)Cl$_2$(py)$_3$] in benzene [Eq. (2)] gave [Ti(NR)(Bz$_2$calix)] [R = *t*Bu (**5**), R = 2,6-C$_6$H$_3$Me$_2$ (**6**) or R = 2,6-C$_6$H$_3$*i*Pr$_2$ (**7**)] in 86–92% isolated yields. The NMR data for these new compounds are analogous to those of the Me$_2$calix homologues **1**, **2** and **3** with the obvious difference that the ^{1}H and ^{13}C NMR resonance for the calixarene O-Me substituents are replaced by those attributable to O-Bz groups.

As for the homologous Me$_2$calix complexes **1**, **2** and **3** the corresponding NMR tube scale reactions of [Li$_2$(Bz$_2$calix)] with [Ti(NR)Cl$_2$(NHMe$_2$)$_2$] in deuterobenzene [Eq. (3)] also afforded [Ti(NR)(Bz$_2$calix)] (**5**)–(**7**). In contrast to the Me$_2$calix systems, synthesis of the compounds [Ti(NR)(Bz$_2$calix)] (**5**)–(**7**) from the corresponding LiNHR reagents and the dichloride complex [TiCl$_2$(Bz$_2$calix)] [see Eq. (1)] is not a feasible route since the dichloride itself is not stable and rapidly eliminates BzCl at room temperature to form [TiCl(Bzcalix)] (Bzcalix = monobenzyl ether of *p-tert*-butylcalix[4]arene).[17, 18] Disappointingly, the reaction of the disodium salt of the more sterically demanding bis(trimethylsilyl) substituted ligand $(Me_3Si)_2$calix with $[Ti(NR)Cl_2(py)_3]$ gave only a mixture of products and neither the target complexes $[Ti(NR)\{(Me_3Si)_2calix\}]$ nor any other could be isolated. As for the Bz_2systems, the dichloride $[TiCl_2\{(Me_3Si)_2calix\}]$ is not a viable starting material [compare Eq. (1) for the Me_2calix systems] since attempts to prepare it result in the monochloride $[TiCl(Me_3Sicalix)]$ (Me_3Sicalix = mono(trimethylsilyl) ether of *p-tert*-butylcalix[4]arene).[17, 18] $[TiCl_2(Me_2calix)]$ also decomposes through MeCl elimination to form the monochloride [TiCl(Mecalix)] (Mecalix = monomethyl ether of *p-tert*-butylcalix[4]arene),[19] but in this case heating at 80 °C for 20 hours is needed for complete conversion. The thermal stability of the calixarene ether dichloride complexes $[TiCl_2(R_2calix)]$ with respect to RCl elimination is $SiMe_3 <$ Bz $\ll$ Me to form the [TiCl(Rcalix)] compounds and so this possible side-reaction appears not to be detrimental to the syntheses of $[Ti(NR)(Me_2calix)]$ complexes as summarised in Equation (1).

To underpin our understanding of this family of alkyl- and aryl-imido complexes we have determined the X-ray crystal structure of $[Ti(NtBu)(Me_2calix)]$ (**1**). The compound **1** crystallises from either benzene or toluene to form diffraction quality crystals of either $[Ti(NtBu)(Me_2calix)]\cdot 2(C_6H_6)$ [**1·2(C$_6$H$_6$)**] or $[Ti(NtBu)(Me_2calix)]\cdot 2(C_7H_8)$ [**1·2(C$_7$H$_8$)**]. As observed in the X-ray crystal structure of **4·(C$_7$H$_8$)** reported previously,[12] in both cases one of the aromatic solvent molecules is included in the cavity of the calix[4]arene ligand. The other solvent molecule occupies a general position in the lattice and gives rise to no significant contacts with the molecules of **1**. The molecular structure of $[Ti(NtBu)(Me_2calix)]\cdot C_6H_6$ is shown in Figure 1 and selected bond lengths for molecules of **1** in both **1·2(C$_6$H$_6$)** and **1·2(C$_7$H$_8$)** are compared in Table 1.

There are no significant differences between the two sets of bond lengths and angles and so we will refer specifically only to those from the crystals of **1·2(C$_6$H$_6$)**. The five-coordinate metal centre in **1** possesses a trigonal bipyramidal geometry with the imido and aryloxide donors lying in the equatorial plane as is typically the case for Group 4 imido complexes of the type $[M(NR)X_2L_2]$ (X = amide or alkoxide/aryloxide; L = Lewis base donor).[20, 21] The Ti=N*t*Bu, $Ti{-}O_{aryloxide}$ and $Ti{-}O_{ether}$ distances are within the usual ranges for five-coordinate complexes,[4, 7, 20, 21] the $Ti{-}O_{aryloxide}$ bond lengths being shorter than those for $Ti{-}O_{ether}$ as expected. The Ti=N–*t*Bu bond angle of 175.7(2)° is consistent with the imido ligand acting as a 4-electron donor to titanium, while the $Ti\text{-}O_{aryloxide}\text{-}C$ angles of 149.8(2) and 177.6(2)° suggest that the aryloxide O-donors can act as at least three-electron donors potentially giving the titanium atom an 18 valence electron count. Although the structure of **1** is similar to that of the mesityl homologue **4**, the Ti=NR distance is slightly shorter and the Ti–OR slightly longer for the *tert*-butyl species. This is consistent with the general observation that Ti=NR bonds for arylimido complexes are typically longer than those in their *tert*-butyl homologues,[14, 22] and that *tert*-butylimido ligands are generally more labilising towards other ligands present than arylimido ligands in homologous complexes.

Table 1. Selected bond lengths [Å] and angles [°] for $[Ti(NtBu)(Me_2calix)]$ (**1**). The two sets of values correspond to those of the benzene solvate **1·2(C$_6$H$_6$)** followed by the corresponding ones of the toluene solvate **1·2(C$_7$H$_8$)**.

	1·2(C$_6$H$_6$)	**1·(2C$_7$H$_8$)**
Ti(1)–N(1)	1.709(2)	1.702(3)
Ti(1)–O(1)	2.180(2)	2.160(3)
Ti(1)–O(2)	1.894(2)	1.880(3)
Ti(1)–O(3)	2.172(2)	2.161(3)
Ti(1)–O(4)	1.865(2)	1.857(3)
N(1)–C(47)	1.447(3)	1.449(5)
N(1)-Ti(1)-O(1)	98.36(9)	99.4(2)
N(1)-Ti(1)-O(2)	113.9(1)	115.4(2)
N(1)-Ti(1)-O(3)	100.16(9)	98.7(2)
N(1)-Ti(1)-O(4)	119.0(1)	119.9(2)
C(47)-N(1)-Ti(1)	175.7(2)	174.9(4)
Ti(1)-O(1)-C(1)	117.9(1)	117.1(2)
Ti(1)-O(2)-C(13)	149.8(2)	151.5(3)
Ti(1)-O(3)-C(46)	117.6(1)	117.8(2)
Ti(1)-O(4)-C(27)	177.6(2)	175.4(3)

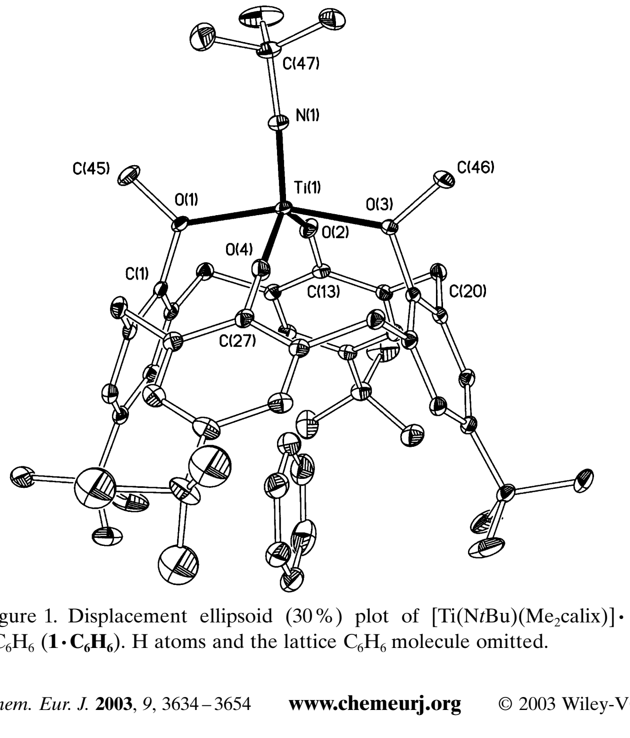
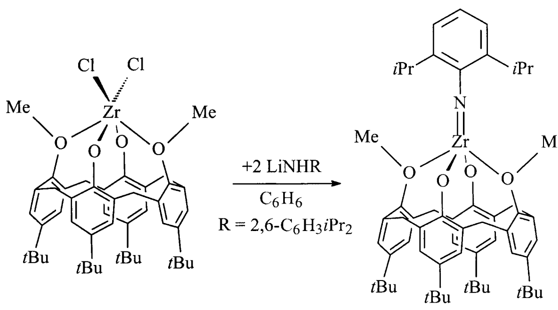


Figure 1. Displacement ellipsoid (30%) plot of $[Ti(NtBu)(Me_2calix)]\cdot 2C_6H_6$ (**1·C$_6$H$_6$**). H atoms and the lattice C_6H_6 molecule omitted.

As mentioned, Floriani has reported the synthesis of the structurally characterised, binuclear zirconium phenylimido complex $[\{Zr(\mu_2\text{-}NPh)(Me_2calix)\}_2]$ from PhN_3 and $[Zr(\eta^4\text{-}C_4H_6)(Me_2calix)]$.[13] We have explored non-azide routes to zirconium imido complexes based on those already discussed for the titanium systems above. Unlike the titanium set of synthons $[Ti(NR)Cl_2(L)_n]$ (L = py or $NHMe_2$, $n = 2$ or 3), no such convenient family of entry points to zirconium imido chemistry have yet been established, although Wigley has reported $[Zr(N\text{-}2,6\text{-}C_6H_3iPr_2)Cl_2(L)_n]$ $[(L)_n = (THF)_2$ or $(py)_3]$[23] which we and others have shown to be precursors to certain 2,6-diisopropyl-phenylimido complexes.[7, 23, 24] Unfortunately, while reaction of $[Na_2(Me_2calix)]_2$ with $[Zr(N\text{-}2,6\text{-}C_6H_3iPr_2)Cl_2(THF)_2]$ appeared to form the desired product $[Zr(N\text{-}2,6\text{-}C_6H_3iPr_2)(Me_2calix)]$ (**8**), the reaction was not at all clean and a better and potentially more general route was sought. In this case, the salt elimination starting from $[ZrCl_2(Me_2calix)]$[25] and two equivalents of LiNH-2,6-$C_6H_3iPr_2$ in benzene [Eq. (4)] is the superior route that gave the target imido complex as a white solid in 61% isolated yield.



(4)

8

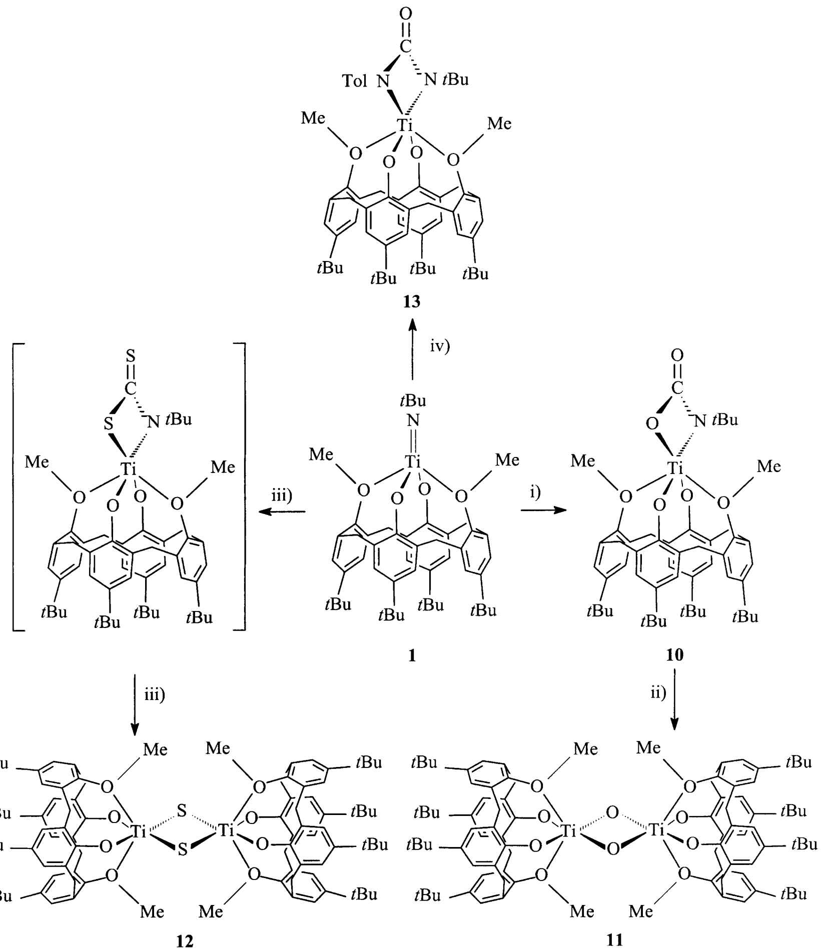
When the reaction was followed by ^1H NMR spectroscopy in deuterobenzene it was found to proceed quantitatively to **8** together with formation of the expected $ArNH_2$ (Ar = 2,6-$C_6H_3iPr_2$) aniline side-product. There was no evidence for any potential intermediates such as as the bis(anilide) [Zr(NH-2,6-$C_6H_3iPr_2)_2(Me_2calix)$], or of any interaction between $ArNH_2$ and molecules of **8**. An attempted NMR tube scale synthesis of **8** via the protonolysis (σ bond metathesis) reaction between one equivalent of $ArNH_2$ and the dialkyl complex $[Zr(CH_2SiMe_3)_2(Me_2calix)]$[26] gave only a 25% conversion to **8** and $SiMe_4$ after heating at 50 °C in deuterobenzene for two weeks. The sluggishness of this reaction is attributed to adverse steric factors.

Similar to its titanium congeners $[Ti(NR)(Me_2calix)]$ (**1**–**4**), compound [Zr(N-2,6-$C_6H_3iPr_2)(Me_2calix)$] (**8**) affords ^1H and $^{13}C\{^1H\}$ NMR spectra consistent with molecular C_{2v} symmetry. Typical resonances for 2,6-$C_6H_3iPr_2$ and Me_2calix are present in a 1:1 ratio by ^1H NMR integration. The EI-mass spectrum features a weak molecular ion corresponding to a monomeric structure with no fragments observed at higher *m*/*z* values (although the observed ion could in principle arise from fragmentation of a higher nuclearity species). While being mindful that Florani's bridging phenylimido complex possesses a binuclear, six-coordinate structure in the solid state,[13] we favour the formulation of **8** as a monomeric, five-coordinate species as drawn in Equation (4) although the NMR and other spectroscopic data are equally consistent with either formulation. Floriani's X-ray structure of $[\{Zr(\mu_2\text{-}NPh)(Me_2calix)\}_2]$ reveals an already crowded $Zr_2(\mu_2\text{-}NPh)_2$ core with molecular D_2 symmetry which is maintained in solution as shown by the presence of *two* pairs of diastereotopic methylene protons for the Me_2calix ligands. As mentioned above, the ^1H and $^{13}C\{^1H\}$ NMR spectra for **8** indicate molecular C_{2v} symmetry which is consistent with a monomeric structure, and indeed it is likely that the bulky *ortho* isopropyl ring substituents in **8** would very much favour a monomeric structure. Furthermore, all crystallographically characterised, 2nd and 3rd row calixarene-supported 2,6-disubstituted arylimido complexes have terminal imido ligands.[10c, 11, 12] Although we were not able to obtain diffraction-quality crystals of **8**, a monomeric structure is strongly supported by a cryoscopic solution molecular weight measurement (in benzene) which found a molecular weight of 965 $g\,mol^{-1}$ (calculated for monomeric $C_{58}H_{75}NO_4Zr$: 941.44 $g\,mol^{-1}$).

Encouraged by the successful synthesis of [Zr(N-2,6-$C_6H_3iPr_2)(Me_2calix)$] (**8**) we attempted the synthesis of other zirconium imides from $[ZrCl_2(Me_2calix)]$ and two equivalents of LiNHR (R = *t*Bu, Ph, 2,6-$C_6H_3Me_2$ or 2-C_6H_4tBu). In no case could zirconium imido products be isolated. When these reactions were followed by ^1H NMR spectroscopy the data suggested that in all cases (except where R = Ph) mixtures of imido and bis(amido) complexes, namely $[Zr(NR)(Me_2calix)]$ and $[Zr(NHR)_2(Me_2calix)]$, were formed in apparent equilibrium with each other, the relative amounts depending on the steric demands of the N-substituent. In the case for R = Ph, the only identifiable carbon-containing product of the NMR tube scale reaction between $[ZrCl_2(Me_2calix)]$ and two equivalents of LiNHPh appeared to be $[Zr(NHPh)_2(Me_2calix)]$ **9** with no evidence for Floriani's binuclear phenylimido complex $[\{Zr(\mu_2\text{-}NPh)(Me_2calix)\}_2]$. The ^1H and $^{13}C\{^1H\}$ NMR spectra of **9** feature C_{2v} symmetry with resonances for Ph and Me_2calix groups in a 2:1 ratio by ^1H NMR integration. An additional broad resonance in the ^1H spectrum at 6.37 ppm (integrating as 2H) is attributed to the N*H*Ph hydrogens. In the related dibenzotetraaza[14]annulene complexes $[Zr(NHAr)_2(Me_4taa)]$ (Ar = Ph, 2,6-$C_6H_3R_2$, R = Me or *i*Pr)[27] the N*H*Ar resonances appear in the range ≈5.3–5.8 ppm.

Although **9** defied isolation (solutions decompose to unidentified mixtures upon removal of volatiles) its likely formation and structure is strongly supported by the NMR data and our isolation and structural characterisation of the homologous bis(aryloxide) species [Zr(O-2,6-$C_6H_3Me_2)_2(Me_2calix)$] (**22**) obtained by reaction of **8** with HO-2,6-$C_6H_3Me_2$ (see below). Furthermore, addition of one equivalent of $PhNH_2$ to $[Zr(CH_2SiMe_3)_2(Me_2calix)]$ in deuterobenzene gave clean conversion to $[Zr(NHPh)_2(Me_2calix)]$ (**9**) and $SiMe_4$ (both in ca. 50% yield by integration) with consumption of all of the $PhNH_2$; the remaining $[Zr(CH_2SiMe_3)_2(Me_2calix)]$ (also ca. 50% by integration) did not react. Addition of a second equivalent of $PhNH_2$ gave complete conversion of the remaining dialkyl complex to **9** and $SiMe_4$.

The behaviour and ease of preparation (or otherwise) of the calixarene-supported titanium imido complexes parallel that of the previously described macrocyclic systems $[Ti(NR)(Me_4taa)]$ (**II** above where R = *t*Bu, aryl or NPh_2). These dibenzotetraaza[14]annulene-supported complexes are readily prepared by transmetallation reactions between Li_2Me_4taa and $[Ti(NR)Cl_2(py)_3]$.[7b] For the calixarene-supported zirconium congeners the situation is somewhat different. Macrocycle-supported [Zr(N-2,6-$C_6H_3iPr_2)(py)(Me_4taa)$] could only be prepared by a transmetallation reaction between Li_2Me_4taa and [Zr(N-2,6-$C_6H_3iPr_2)Cl_2(py)_3$].[7b] Reaction of LiNHAr (Ar = 2,6-$C_6H_3R_2$, R = Me or *i*Pr) with $[ZrCl_2(Me_4taa)]$, or of $ArNH_2$ (1 equiv) with the dialkyl analogue $[Zr(CH_2SiMe_3)_2(Me_4taa)]$,[26] gave only the bis(anilide) derivatives $[Zr(NHAr)_2(Me_4taa)]$, neither of which eliminated $ArNH_2$ to form corresponding imido complexes. It was also shown that addition of H_2N-2,6-C_6H_3*i*Pr_2 to the imido complex [Zr(N-2,6-C_6H_3*i*Pr_2)(py)(Me_4-taa)] quantitatively formed the corresponding bis(anilide). In this macrocyclic chemistry it was proposed that the poor size match between the macrocyle's cavity and the zirconium atom's radius leaves the metal atom sitting considerably out of the Me_4taa "N_4" plane, and is thus somewhat more exposed and reactive to incoming Lewis bases (namely the coordinated pyridine in [Zr(N-2,6-C_6H_3*i*Pr_2)(py)(Me_4taa)] itself) or anilines. Interestingly, Woo has reported that the monomeric five-coordinate imido complexes [M(N-2,6-C_6H_3*i*Pr_2)(TTP)] (M = Zr or Hf; TTP = *meso*-tetra-*p*-tolylporphyrinato dianion) can be prepared by reaction of LiNH-2,6-C_6H_3*i*Pr_2 (2 equiv) with [MCl_2(TTP)].[3i] This is consistent with TTP having an N_4 cavity some 0.1 Å larger in diameter than that for Me_4taa.[7h] However, reaction of [$HfCl_2$(TTP)] with LiNH-4-C_6H_4Me (two equivalents) gave only the bis(*p*-tolylamido) compound [Hf(NH-4-C_6H_4Me)$_2$(TTP)].[3i] In the compounds under consideration here, the Me_2calix ligand provides a satisfactory match with the zirconium atomic radius, but clearly the imido N-substituent still needs to provide adequate steric bulk to avoid reaction of [Zr(NR)(Me_2calix)] complexes with amines that may be present in the reaction mixture.



Scheme 2. Reactions of [Ti(N*t*Bu)(Me_2calix)] (**1**) with heterocumulenes. i) 1 atm CO_2, benzene, rt, 5 min, 93%; ii) 5 d, benzene; iii) CS_2, benzene, rt, 5 d, 79%; iv) OCN-4-C_6H_4Me, benzene, rt, 25 h, 94%.

Reactions of [Ti(N*t*Bu)(Me_2calix)] 1 with CO_2, CS_2 and RNCO: These reactions parallel to some extent those of the Me_ntaa-supported analogues. The compound **1** reacts swiftly and quantitatively with CO_2 in benzene at room temperature. The spectroscopic data are consistent with the formation of an orange, N,O-bound organocarbamate complex [Ti{N(*t*Bu)-C(O)O}(Me_2calix)] (**10**) as illustrated in Scheme 2. The NMR spectra for compound **10** suggest a C_s symmetrical species and feature equivalent anisole moieties and inequivalent phenoxide moieties. Thus the N(*t*Bu)C(O)O ligand has its N- and O-donors *trans* to the anionic phenoxide O-donors of Me_2calix with these four atoms (i.e., three O- and one N-donors) forming an equatorial plane. The coordination octahedron is completed by etheral O-donors in the mutually *trans* axial positions. This relative orientation of the carbamate and calix[4]arene ligands represents the most sterically favourable one.

The compound **10** is unstable at room temperature with respect to extrusion of *tert*-butylisocyanate and formation of the dimeric oxo complex [{Ti(μ-O)(Me_2calix)}$_2$] (**11**). This elimination reaction goes quite slowly in the dark (< 10% decomposition after ca. 5 h), but under ambient lighting is complete within one hour. Analogous behaviour was found in the Me_ntaa-supported systems, as mentioned, and also recently for some cyclopentadienyl-amidinate supported imidotitanium complexes,[28] although in these latter cases the *t*BuNCO reaction was entirely thermally activated. The reaction of **1** with CO_2 under ambient light is the most efficient and clean method for synthesising oxo compound **11**.

The corresponding reaction of [Ti(N*t*Bu)(Me_2calix)] (**1**) with CS_2 proceeds much more slowly, requiring five days at room temperature for complete consumption of **1**. The only observed products of this reaction (either in the dark or ambient light) are the bridging sulfido complex [{Ti(μ-S)(Me_2calix)}$_2$] (**12**) and *tert*-butyl isothiocyanate, *t*BuNCS (identified by comparison with an authentic sample). The reaction is assumed to proceed via an intermediate thiocarbamate complex [Ti{N(*t*Bu)C(S)S}(Me_2calix)] analogous to **10**; however, this intermediate is not observed when the reaction is monitored by ^{1}H NMR spectroscopy. The sluggish reaction of **1** with CS_2 compared to that with CO_2 is attributed to the lower electrophilicity of the carbon atom in the former, and the softer nature of sulfur which would disfavour any coordination to the hard titanium centre.

The dimeric nature of the μ-oxide and the μ-sulfide complexes **11** and **12** was established by the use of solution molecular weight measurements. In the case of the sulfide complex **12** the results unambiguously confirmed a dimeric structure in solution (calculated for dimeric **12**: 1509 $\mathrm{g\,mol^{-1}}$, found: 1616 $\mathrm{g\,mol^{-1}}$). However, the results obtained for the oxo complex **11** were more ambiguous (calculated for dimeric **11**: 1477 $\mathrm{g\,mol^{-1}}$, found: 915 $\mathrm{g\,mol^{-1}}$). We believe that the observed solution molecular weight determination of the oxo complex **11** possibly reflects a degree of dissociation of a dimeric complex in solution. Such a monomer–dimer equilibrium in solution would be entropically favourable. However, due to the lack of a terminal Ti=O stretch in the solid state IR spectrum of **11**, and the similarity to the related dimeric chromium μ-oxide complex $[\{\mathrm{Cr}(\mu\text{-O})(\mathrm{Me_2calix})\}_2]$ reported by Floriani[29] a dimeric structure is proposed in the solid state. By contrast, the tetraaza[14]annulene analogues $[\mathrm{Ti(O)(Me_ntaa)}]$ and $[\mathrm{Ti(S)(Me_ntaa)}]$ are monomeric, as are certain heavier chalcogen derivatives;[30] this suggests that the $\mathrm{Me_2calix}$ ligand provides a less sterically protecting environment for stablising sterically unprotected metal–ligand multiple bonds.

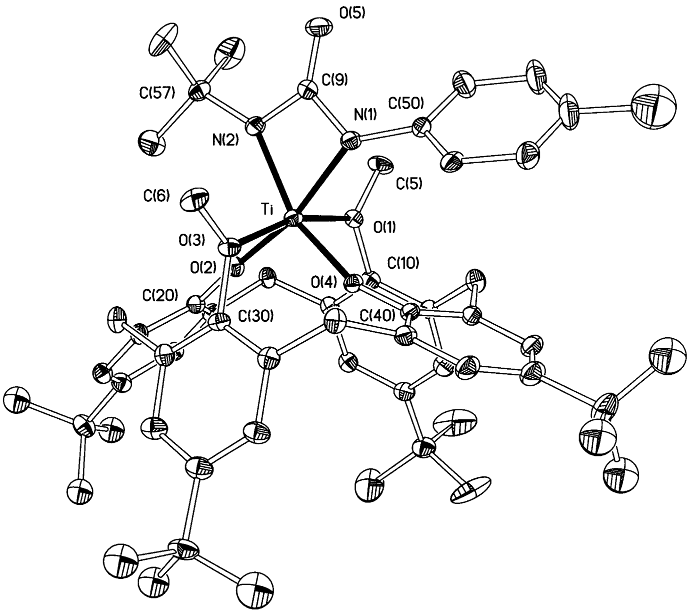


Figure 2. Displacement ellipsoid (25%) plot of $[\mathrm{Ti\{N(\mathit{t}Bu)C(O)N(4\text{-}C_6H_4Me)\}(Me_2calix)}]$ (**13**). H atoms and solvent molecules omitted. Selected bond lengths [Å] and angles [°]: Ti–N(1) 2.035(5), Ti–N(2) 2.002(5), Ti–O(1) 2.175(4), Ti–O(2) 1.838(4), Ti–O(3) 2.122(4), Ti–O(4) 1.832(4), N(1)–C(9) 1.400(8), N(1)–C(50) 1.407(8), N(2)–C(9) 1.371(8), N(2)–C(57) 1.488(8), C(9)–O(5) 1.237(8), N(1)-Ti-N(2) 65.6(2), N(1)-Ti-O(1) 91.61(18), N(1)-Ti-O(2) 164.57(19), N(1)-Ti-O(3) 100.94(18), N(1)-Ti-O(4) 92.11(19), N(2)-Ti-O(1) 95.45(18), N(2)-Ti-O(2) 99.8(2), N(2)-Ti-O(3) 98.23(19), N(2)-Ti-O(4) 157.7(2), N(2)-C(9)-N(1) 104.3(5), C(9)-N(1)-Ti 93.7(4), C(9)-N(2)-Ti 96.1(4), C(50)-N(1)-Ti 138.8(4), C(57)-N(2)-Ti 143.9(4), C(9)-N(1)-C(50) 122.5(5), C(9)-N(2)-C(57) 119.9(5), O(5)-C(9)-N(2) 130.2(6), O(5)-C(9)-N(1) 125.5(6), C(10)-O(1)-Ti 116.9(3), C(20)-O(2)-Ti 176.9(4), C(30)-O(3)-Ti 118.6(3), C(40)-O(4)-Ti 158.6(4).

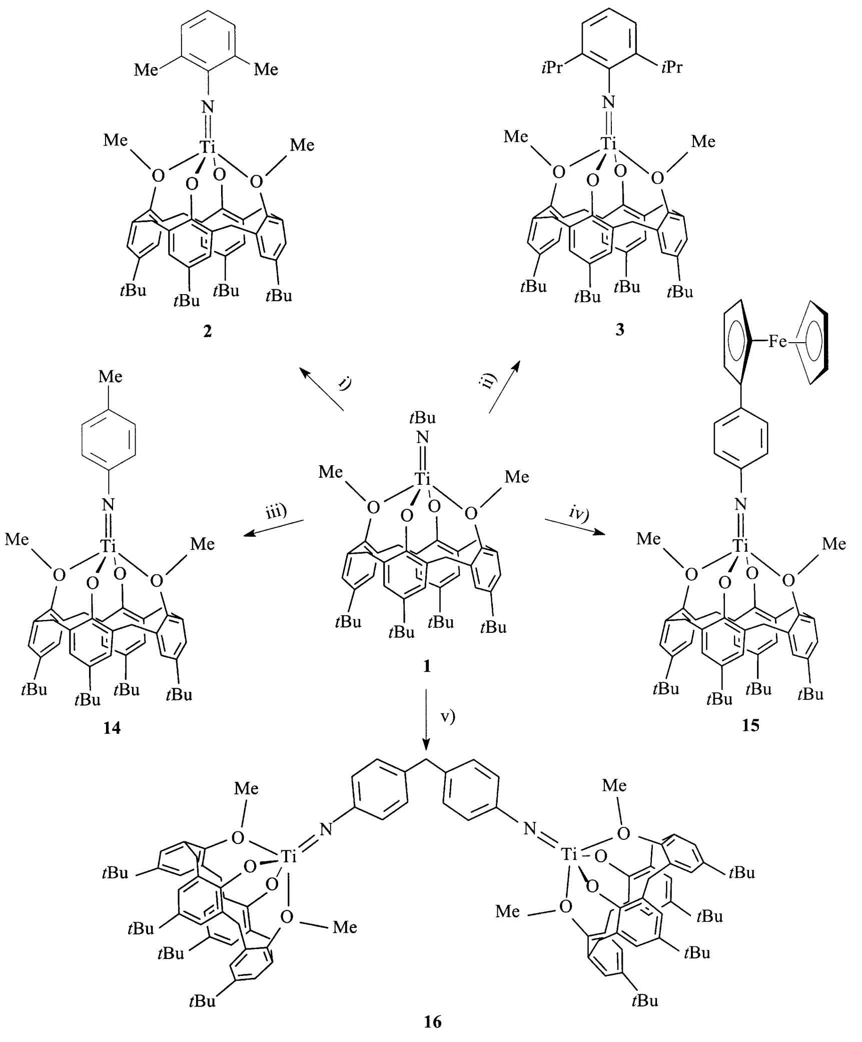
The reaction of $[\mathrm{Ti(N\mathit{t}Bu)(Me_2calix)}]$ (**1**) with *p*-tolyl isocyanate gave clean conversion in 94% yield to the *N,N′*-bound ureate complex $[\mathrm{Ti\{N(\mathit{t}Bu)C(O)N(\text{-}4\text{-}C_6H_4Me)\}(Me_2calix)}]$ (**13**) as shown in Scheme 2. Crystals of **13** grown from either toluene or THF solutions were generally of poor quality. The best results were obtained from saturated toluene solutions at −40 °C which gave crystals of $\mathbf{13\cdot 4(C_7H_8)}$ suitable for X-ray diffraction. The molecular structure is shown in Figure 2; selected bond lengths and angles are summarised in the legend. In $\mathbf{13\cdot 4(C_7H_8)}$, one of the four solvent molecules is included in the cavity of the calix[4]arene ligand (not shown in Figure 2), the others occupy general positions in the lattice. The NMR data for **13** are consistent with the solid state structure and indicate, as for the carbamate species **10** above, a C_s symmetrical compound with equivalent anisole moieties and inequivalent phenoxide groups of the calix[4]arene ligand. Unlike **10**, the ureate **13** is stable in solution in the absence of air and moisture with no evidence for decomposition/retrocyclisation.

The solid state structure of **13** is thus analogous to that proposed for the $\mathrm{CO_2}$ cycloadduct **10**. It clearly shows the *p*-tolylisocyanate moiety coupled across the former $\mathrm{Ti(1)–N(2)_{imide}}$ bond. The titanium atom has an approximately octahedral coordination geometry with the etheral O-donors of $\mathrm{Me_2calix}$ occupying mutually *trans* coordination sites, and with the four anionic donors [N(1), N(2), O(2) and O(4)] forming the equatorial plane of the octahedron. The distances and angles within the structure are as expected.[21] The slightly longer Ti(1)–N(1) distance of 2.035(5) Å compared to Ti(1)–N(2) of 2.002(5) Å is attributed to the relatively better electron-withdrawing effect of the aryl N-substituent. A similar feature was seen in the structure of $[\mathrm{Zr\{N(\mathit{t}Bu)C(O)N(\text{-}2,6\text{-}C_6H_3Me_2)\}(Me_4taa)}]$.[7b]

Although the NMR data for **13** are consistent with either an N,N′- or N,O-bound ureate ligand, the X-ray structure clearly establishes the former coordination mode. In the last three years the reaction chemistry of Group 4 imido complexes with $\mathrm{CO_2}$ and isocyanates has started to become better established and a diversity of behaviour is starting to emerge, which depends on the ancilliary ligand(s) and the imide and isocyanate N-substituents.[7b, 28] The reactions of *tert*-butyl- or aryl-isocyanates with certain arylimido compounds supported by the $\mathrm{Me_4taa}$ ligand give N,N′-bound ureate products which have been crystallographically characterised for the zirconium compound mentioned above (and partially characterised for $[\mathrm{Ti\{N(Ar)C(O)N(Ar)\}(Me_4taa)}]$ where $\mathrm{Ar = 4\text{-}C_6H_4Me}$).[7b] Reactions of $[\mathrm{Ti(N\mathit{t}Bu)(Me_4taa)}]$ with aryl isocyanates failed to give any tractable products. However, reaction of $[\mathrm{Ti(N\mathit{t}Bu)(Me_4taa)}]$ with *t*BuNCO gives an N,O-bound ureate product (observed by NMR spectroscopy but not isolable), as do $[\mathrm{Ti(N\mathit{t}Bu)(N_2N_{py})(py)}]$ **I** with ArNCO ($\mathrm{Ar = 2,6\text{-}C_6H_3\mathit{i}Pr_2}$)[30] and a number of cyclopentadienyl-amidinate supported *tert*-butylimido systems.[28a] In these latter cases the N,O-bound ureate intermediates are unstable with respect to cycloreversion to form cyclopentadienyl-amidinate titanium oxo complexes and the corresponding carbodiimides *t*BuNCNR (R = *t*Bu or aryl, i.e., the original R substituent of the isocyanate used in the reaction). The reaction of $[\mathrm{Ti(N\mathit{t}Bu)(Me_2calix)}]$ (**1**) with *p*-tolyl isocycanate to form the stable, *N,N′*-bound ureate **13** is therefore unusual in the still emerging field of Group 4 imide/heterocumulene reaction chemistry. Unfortunately, attempts to develop the analogous imide cycloaddition chemistry of the zirconium imido complex [Zr(N-2,6-C_6H_3*i*Pr_2)(Me_2calix)] (**8**) met with limited success. Although NMR scale reactions of **8** with CO_2 or ArNCO (Ar = 2,6-C_6H_3*i*Pr_2) afforded products tentatively assigned as [Zr{N(*t*Bu)C(O)O}(Me_2calix)] and [Zr{N(*t*Bu)-C(O)N(2,6-C_6H_3*i*Pr_2)}(Me_2calix)] all attempts to repeat these reactions on a preparative scale failed.

Reactions of [M(NR)(Me_2calix)] with R′NH_2, H_2O, H_2S, HCl and R′OH: In previous studies of the chemistry of the macrocyclic system [Ti(N*t*Bu)(Me_4taa)] it was found that reactions with a range of protic reagents would easily displace *t*BuNH_2 and introduce new N- and O-donor functional groups.[7a] We have carried out analogous reactions of [Ti(N*t*Bu)(Me_2calix)] **1** as summarised in Schemes 3 and 4.

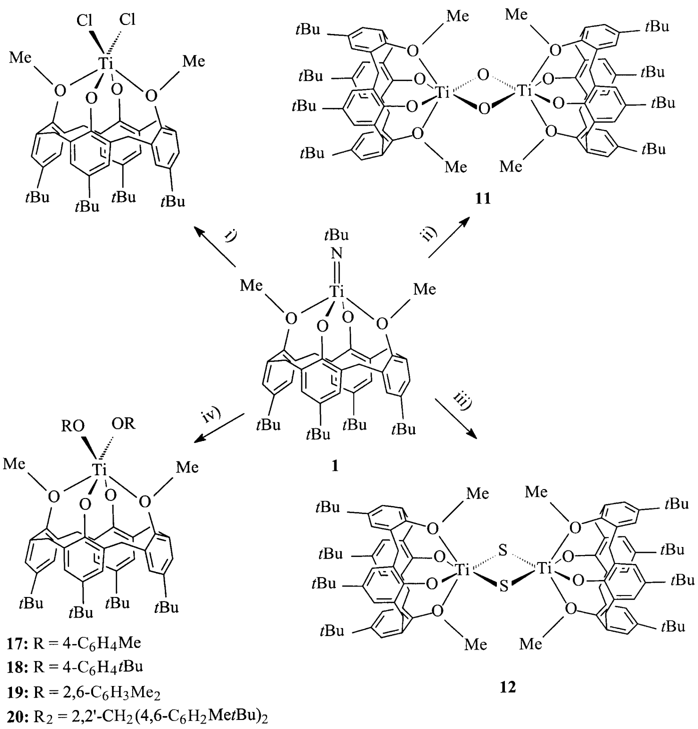
Scheme 3 summarises the *tert*-butylimide/arylamine exchange reactions of **1**. The reactions to form **2** and **3** (prepared above by halide metathesis reactions of [Ti(N*t*Bu)Cl_2(py)$_3$]) proceed quantitatively in C_6D_6 on an NMR tube scale. They are, however, rather slow requiring about 3 d at 65 °C to go to completion. The reaction with H_2N-4-C_6H_4Me to form [Ti(N-4-C_6H_4Me)(Me_2calix)] (**14**) (84 % isolated yield) is slightly faster (taking about 2 d at 50 °C, not optimised), presumably due to formation of a less sterically crowded six-coordinate bis(amide) likely intermediate [Ti(NH*t*Bu)(NH-4-C_6H_4Me)-(Me_2calix)] (not directly observed). Similar conditions and yields are associated with the reaction between H_2N-4-C_6H_4Fc [Fc = Fe(η^5-C_5H_4)(η^5-C_5H_5)] to form the heterobimetallic compound [Ti(N-4-C_6H_4Fc)(Me_2calix)] (**15**). No unusual features of the electrochemistry of **15** were found, with the oxidation of the ferrocene unit occurring at an identical potential (within experimental error) to ferrocenylaniline H_2N-4-C_6H_5Fc ($E_{1/2} = -0.067$ V). The homo-bimetallic analogue [{Ti(Me_2calix)}$_2${μ-(N-4-C_6H_4)$_2$$CH_2$}] (**16**) was also prepared. When the reaction that forms **16** was followed by ^{1}H NMR spectroscopy resonances attributable the expected intermediate [Ti(N-4-$C_6H_4$$CH_2$-4-$C_6H_4$$NH_2$)($Me_2$calix)] were observed but this compound was not isolated on a preparative scale. Homo- and heterobimetallic complexes involving bridging imido ligands have been described previously,[31] including a dinuclear molybdenum calix[4]arene imido compound.[10a]



Scheme 3. Protonolysis reactions of [Ti(N*t*Bu)(Me_2calix)] (**1**) with N-H bond substrates. i) H_2N-2,6-$C_6H_3Me_2$, C_6D_6, 65 °C, 70 h, 100 % by ^{1}H NMR; ii) H_2N-2,6-C_6H_3*i*Pr_2, C_6D_6, 65 °C, 70 h, 100 % by ^{1}H NMR; iii) H_2N-4-C_6H_4Me, benzene, 50 °C, 50 h, 84 %; iv) H_2N-4-C_6H_4Fc, benzene, 50 °C, 50 h, 81 %; v) CH_2(4-$C_6H_4NH_2$)$_2$, benzene, 50 °C, 50 h, 87 %.

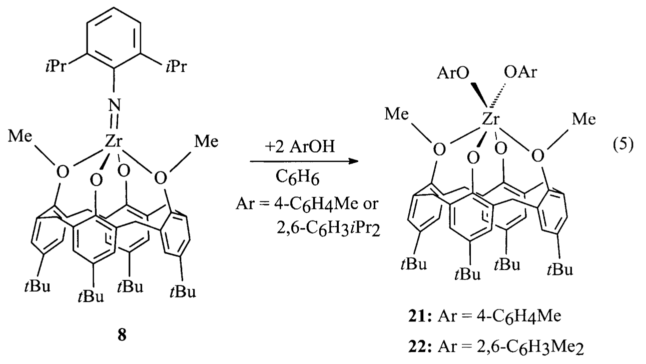
Scheme 4 summarises reactions of **1** with other protic reagents. For completeness and comparison with other macrocyclic systems we examined the reaction of **1** with H_2O, H_2S and HCl. These reactions afforded the expected products [{Ti(μ-O)(Me_2calix)}$_2$] (**11**), [{Ti(μ-S)(Me_2calix)}$_2$] (**12**), and [TiCl_2(Me_2calix)] in greater than 90 % yield. The reaction of **1** with H_2S to form **12** is clean and complete within 30 minutes and is therefore a more convenient synthesis of this compound than that from **1** and CS_2 (Scheme 2) which takes about 5 d.

Of particular interest are the aryloxide complexes [Ti(O-4-C_6H_4R)$_2$(Me_2calix)] [R = Me (**17**); R = *t*Bu (**18**)], [Ti(O-2,6-$C_6H_3Me_2$)$_2$(Me_2calix)] (**19**) and [Ti(mbmp)(Me_2calix)] (**20**; H_2mbmp = 2,2′-methylene-bis-(4-methyl-6-*tert*-butylphenol) or CH_2({CH_3}{C_4H_9}C_6H_2-OH)$_2$) the syntheses of which are summarised in Scheme 4. The first-formed products **17** and **18** undergo interesting further rearrangements (see below). We have also prepared for comparison the analogous zirconium complexes [Zr(O-4-C_6H_4Me)$_2$(Me_2calix)] (**21**) and [Zr(O-2,6-$C_6H_3Me_2$)$_2$(Me_2calix)] (**22**) from [Zr(N-2,6-C_6H_3*i*Pr_2)-(Me_2calix)] (**8**) and the corresponding phenol [Eq. (5)]. The



Scheme 4. Protonolysis reactions of [Ti(N*t*Bu)(Me$_2$calix)] (**1**) with O–H, S–H and Cl–H bond substrates. i) 2 M HCl (1 M solution in Et$_2$O), benzene, 5 °C → rt, 5 min, 97 %; ii) H$_2$O (1 M solution in Et$_2$O), C$_6$D$_6$, rt, 10 min, 90 % by ^{1}H NMR; iii) 1 atm H$_2$S, benzene, 5 °C → rt, 30 min, 89 %; iv) 2 equiv HO-4-C$_6$H$_4$Me, benzene, 5 °C → rt, 30 min, 68 %; 2 equiv HO-4-C$_6$H$_4$*t*Bu, toluene, −50 °C → rt, 30 min, 61 %; 2 equiv HO-2,6-C$_6$H$_3$Me$_2$, benzene, 5 °C → rt, 5 min, 37 %; 2 equiv 2,2′-(HO-4,6-C$_6$H$_2$Me*t*Bu)$_2$CH$_2$, toluene, −50 °C → rt, 30 min, 39 %.

zirconium congeners do not undergo further rearrangement and so as a kind of benchmark we discuss their spectra and structures first.



Samples of **21** prepared according to Equation (5) were always contaminated by traces of the arylamine side-product although the resonances attributed to **21** are fully consistent with the structure shown. Attempts to prepare aniline-free samples of **21** via other routes, namely by protonolysis of [Zr(CH$_2$SiMe$_3$)$_2$(Me$_2$calix)] with HO-4-C$_6$H$_4$Me or by chloride metathesis of [ZrCl$_2$(Me$_2$calix)] with LiO-4-C$_6$H$_4$Me afforded no tractable products. Fortunately, the homologous compound **22** was more readily isolated and its molecular structure (with a CH$_2$Cl$_2$ molecule of crystallisation entrapped in the calix[4]arene cavity) is shown in Figure 3; selected bond lengths and angles are presented in the legend. The solution NMR data are fully consistent with the solid state structure, which indicates C_{2v} symmetry with equivalent O-2,6-C$_6$H$_3$Me$_2$ ligands and calixarene anisole and phenoxide moieties. The

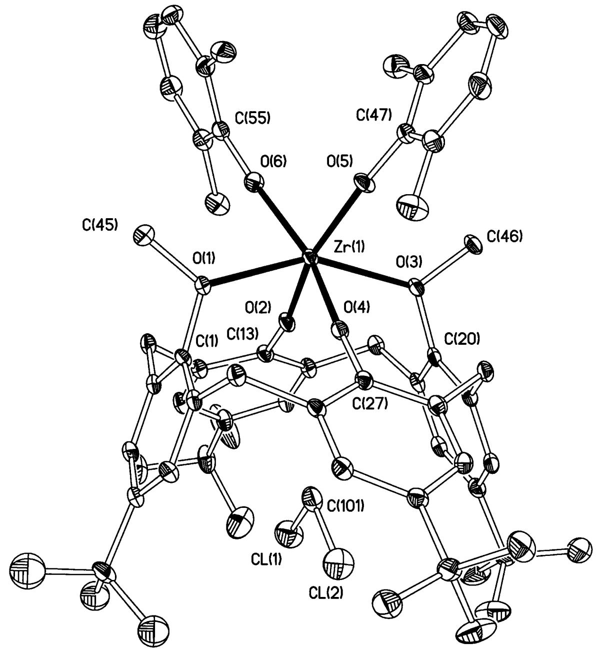


Figure 3. Displacement ellipsoid (30 %) plot of [Zr(O-2,6-C$_6$H$_3$Me$_2$)$_2$(-Me$_2$calix)] · CH$_2$Cl$_2$ (**22 · CH$_2$Cl$_2$**). H atoms and remaining (lattice) solvent molecules omitted. Selected bond lengths [Å] and angles [°]: Zr(1)–O(1) 2.312(2), Zr(1)–O(2) 1.947(2), Zr(1)–O(3) 2.393(3), Zr(1)–O(4) 1.976(2), Zr(1)–O(5) 1.949(2), Zr(1)–O(6) 2.028(3), O(1)-Zr(1)-O(2) 87.5(1), O(1)-Zr(1)-O(3) 152.72(9), O(1)-Zr(1)-O(4) 78.1(1), O(1)-Zr(1)-O(5) 114.76(11), O(1)-Zr(1)-O(6) 82.8(1), O(2)-Zr(1)-O(3) 74.46(9), O(2)-Zr(1)-O(4) 95.36(11), O(2)-Zr(1)-O(5) 157.49(11), O(2)-Zr(1)-O(6) 93.12(11), O(3)-Zr(1)-O(4) 83.3(1), O(3)-Zr(1)-O(5) 85.7(1), O(3)-Zr(1)-O(6) 117.8(1), O(4)-Zr(1)-O(5) 92.76(11), O(4)-Zr(1)-O(6) 158.75(11), O(5)-Zr(1)-O(6) 86.68(11), Zr(1)-O(1)-C(1) 117.7(2), Zr(1)-O(1)-C(45) 128.1(2), Zr(1)-O(2)-C(13) 168.5(2), Zr(1)-O(3)-C(20) 121.8(2), Zr(1)-O(3)-C(46) 127.7(2), Zr(1)-O(4)-C(27) 177.3(2), Zr(1)-O(5)-C(47) 175.7(3), Zr(1)-O(6)-C(55) 176.4(2).

methoxy donors of Me$_2$calix occupy the axial positions of the approximate octahedron formed at Zr(1) with the anionic O-donors forming the equatorial plane. The Zr–O distances lie in the ranges expected for such linkages.[21] The other features of **22** are analogous to previous zirconium calixarene compounds of the type reported by Floriani and co-workers.[13, 25] Neither compound **22** nor **23** show any evidence for rearrangement to other isomeric forms in solution.

In solution, the titanium bis(phenolate) complexes **17**–**20** (Scheme 4) also adopt a pseudo C_{2v} type structure as shown in Scheme 4. The ^{1}H NMR spectrum of **18**, by way of example, is depicted in the upper part of Figure 4. Three signals arise for the *tert*-butyl groups of the calix[4]arene and the *tert*-butylphenolate ligand, two doublets for the methylene protons of the calix[4]arene ligand and a singlet for the methyl groups of the anisole moiety. In the aryl region there are, in addition to the resonances of the protons of the calix[4]arene ligand, the

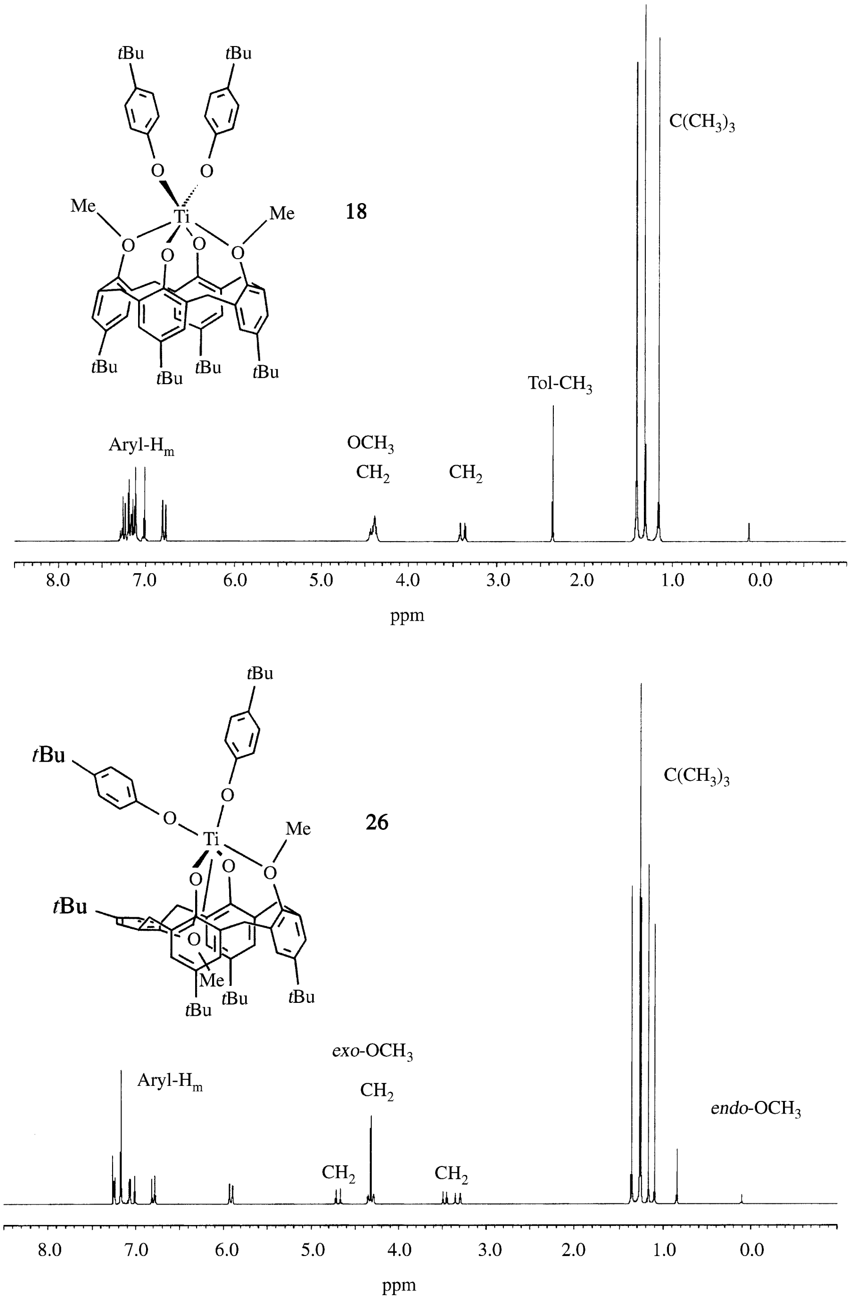


Figure 4. Proton NMR spectra of [Ti(O-4-C_6H_4*t*Bu)$_2$(Me$_2$calix)] (**18**) (upper part) and [Ti(O-4-C_6H_4*t*Bu)$_2$(*paco*-Me$_2$calix)] (**26**) (lower part) in $CDCl_3$.

signals of toluene, originally located in the cavity of the calix[4]arene ligand in the isolated compound **18**.

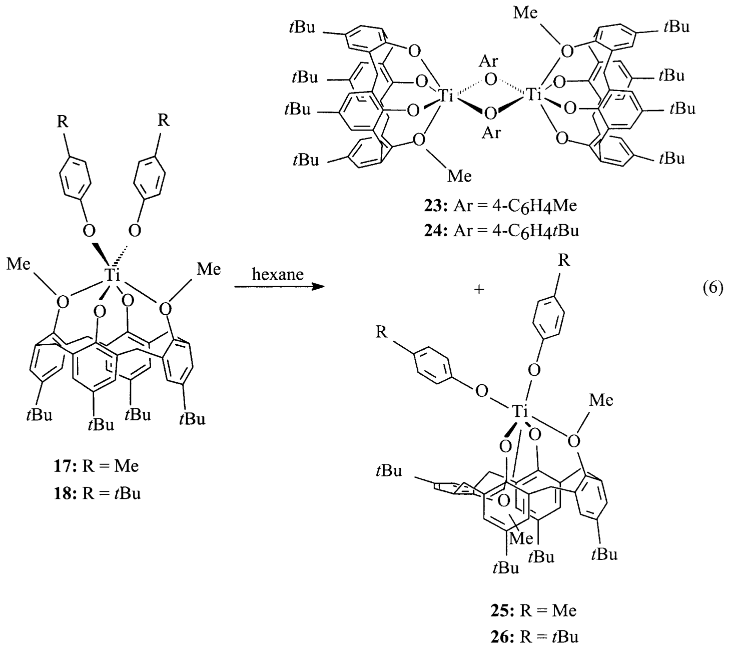
Rearrangement reactions of calix[4]arene-supported bis(aryloxide) complexes: During attempts to remove encapsulated toluene molecules by stirring the isolated compounds **17** and **18** in hexane, some interesting rearrangement and elimination reactions of the complexes were observed, as shown in Equation (6).

Stirring of the *para*-substituted bis(phenolate) compounds [Ti(O-4-C_6H_4Me)$_2$(Me$_2$calix)] (**17**) and [Ti(O-4-C_6H_4*t*Bu)$_2$(Me$_2$calix)] (**18**) in non-polar hydrocarbon solvents for a long period of time results in the formation of new complexes. Firstly, dinuclear compounds [{Ti(O-4-C_6H_4R)(Mecalix)}$_2$] (**23**; R = Me) and (**24**; R = *t*Bu) have been isolated, which are the products of the elimination of one equivalent of aryl methyl ether from **17** or **18**. Similar elimination reactions have been observed previously in metallacalix[4]arene chemistry. Especially for titanacalix[4]arenes, the elimination of an organyl chloride RCl from *di*organyl ether calix[4]arene complexes [TiCl$_2$(R$_2$calix)] to give compounds [TiCl(Rcalix)] containing a calix[4]arene *mono*-organyl ether is a very useful synthetic entry into the chemistry of monoorganyl ether calix[4]arene titanium complexes.[18]

Single crystals of **24·(C_7H_8)** were grown from hot, saturated toluene solutions of the compound. The X-ray crystal structure of **24·(C_7H_8)** confirms the dinuclear character of the compound in the solid state (see Figure 5). A crystallographically imposed center of inversion is located at the center of the four membered Ti_2O_2 ring. Two titanacalix[4]arene monomethyl ether complex fragments [Ti(Mecalix)] are bridged by the *para-tert*-butyl phenolate ligands. In contrast to the imido complexes [Ti(N*t*Bu)(Me$_2$calix)] (**1**) and [Ti(N-2,4,6-$C_6H_2Me_3$)(Me$_2$calix)] (**4**) the phenoxide complexes are not stable as five-coordinate monomeric compounds and dimerise to give complexes with distorted octahedrally coordinated titanium atoms. The resulting titanium titanium distance of 3.376(3) Å is—as expected—not within the bonding range.

The other isolated reaction products are isomers of **17** and **18**, namely the complexes [Ti(O-4-C_6H_4Me)$_2$(*paco*-Me$_2$calix)] (**25**) and [Ti(O-4-C_6H_4*t*Bu)$_2$(*paco*-Me$_2$calix)] (**26**), and are the result of an apparent rearrangement reaction of the coordinated calix[4]arene ligands in solution. Since these complexes are very soluble in hexane, they can be easily separated from the rather poorly soluble side-products **23** and **24**.

Whereas the calix[4]arene ligands in all complexes of the type [TiX$_2$(Me$_2$calix)] described so far adopt an *elliptical distorted cone* conformation in the solid state and in solution, the calix[4]arene ligands of **25** and **26** are coordinated in a form which is reminiscent of the *partial cone* (*paco*) con-



17: R = Me
18: R = *t*Bu

23: Ar = 4-C_6H_4Me
24: Ar = 4-C_6H_4tBu

25: R = Me
26: R = *t*Bu

(6)

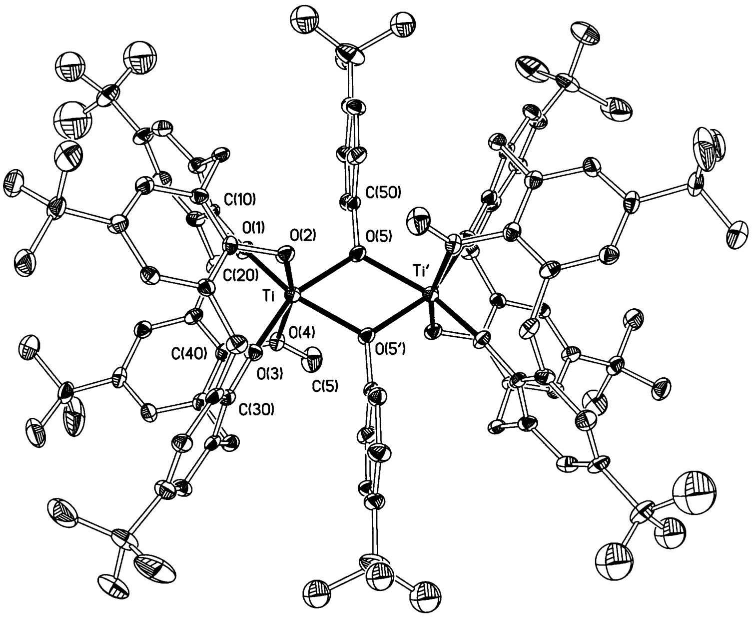


Figure 5. Displacement ellipsoid (25%) plot of [{Ti(O-4-C_6H_4tBu)(Mecalix)}$_2$] (**24**). H atoms and solvent molecule omitted. Selected bond lengths [Å] and angles [°]: Ti–O(1) 1.785(5), Ti–O(2) 1.921(6), Ti–O(3) 1.771(5), Ti–O(4) 2.367(6), Ti–O(5) 2.027(5), Ti–O(5)′ 2.066(5), Ti⋯Ti′ 3.376(3), O(1)-Ti-O(2) 91.5(2), O(1)-Ti-O(3) 106.3(3), O(1)-Ti-O(4) 79.7(2), O(1)-Ti-O(5) 92.5(2), O(1)-Ti-O(5)′ 159.9(2), O(2)-Ti-O(3) 92.5(2), O(2)-Ti-O(4) 165.3(2), O(2)-Ti-O(5) 98.9(2), O(2)-Ti-O(5)′ 98.7(2), O(3)-Ti-O(4) 78.9(2), O(3)-Ti-O(5) 157.8(2), O(3)-Ti-O(5)′ 90.7(2), O(4)-Ti-O(4) 93.3(2), O(4)-Ti-O(5)′ 93.4(2), O(5)-Ti-O(5)′ 68.9(2), Ti-O(5)-Ti′ 111.1(2), C(10)-O(1)-Ti 172.1(6), C(20)-O(2)-Ti 120.0(5), C(30)-O(3)-Ti 170.9(6), C(40)-O(4)-Ti 114.7(4), C(50)-O(5)-Ti 124.3(4), C(50)-O(5)-Ti′ 124.3(4), C(5)-O(4)-Ti 133.7(5).

formation of the calix[4]arene.[32] The ether groups of the calix[4]arene ligand are in *trans* positions with respect to the phenolate ligands. As a consequence, one of the methoxy groups is located *inside* the cavity of the calix[4]arene ligand leading to an "up, up, up, down" arrangement of the aryloxy units of the macrocycle. A powerful tool to investigate this behaviour in solution is ^{1}H NMR spectroscopy, where a signal pattern for the calix[4]arene ligand is found, which is typical for the macrocyclic ligand in a local C_s symmetry.

The proton NMR spectrum of compound **26**, by way of example, is shown in the lower part of Figure 4, beneath the NMR spectrum of its isomer [Ti(O-4-C_6H_4tBu)$_2$(*cone*-Me$_2$-calix)] (**18**). The *tert*-butyl groups of the calix[4]arene and phenolate ligands appear as signals at δ 1.33, 1.24, 1.23, 1.14, and 1.07 ppm in an integration ratio of 1:1:2:1:1 and four doublets can be found for the diastereotopic protons of the methylene bridges. Most significantly, we observe two signals for the methoxide groups of the anisole units, one of which appears at δ 4.30, while the other is shifted upfield to δ 0.82. Such shifts of *endohedrally* coordinated methyl groups due to ring current effects of the calix[4]arene phenyl rings have been recognized earlier.[32]

To confirm the coordination behaviour of the calix[4]arene ligand in the solid state, crystals of the compounds [Ti(O-4-C_6H_4Me)$_2$(*paco*-Me$_2$calix)] (**25**) and [Ti(O-4-C_6H_4tBu)$_2$(*paco*-Me$_2$calix)] (**26**) were grown from saturated hexane solutions at −30 °C. The molecular structure of the complexes is shown in Figures 6 and 7; selected bond lengths and angles are given in the legend.

The main feature of both molecular structures are the coordination modes of the calix[4]arene in the solid state. The calix[4]arene dimethyl ether ligand binds in both cases in a *paco*-like form to the Ti(OAr)$_2$ fragments, which confirms the results deduced by NMR spectroscopy for both compounds in solution. The calix[4]arene ligands are arranged in a way that the oxygen atoms O(2) and O(4) of the anisole moiety are in *trans* position of the monodendate phenoxide ligands. The methyl group at O(2) is located inside the cavity of the calix[4]arene. The titanium oxygen bond lengths to the phenoxide oxygen atoms, that is Ti–O(1), Ti–O(3), Ti–O(5), and Ti–O(6), fall between

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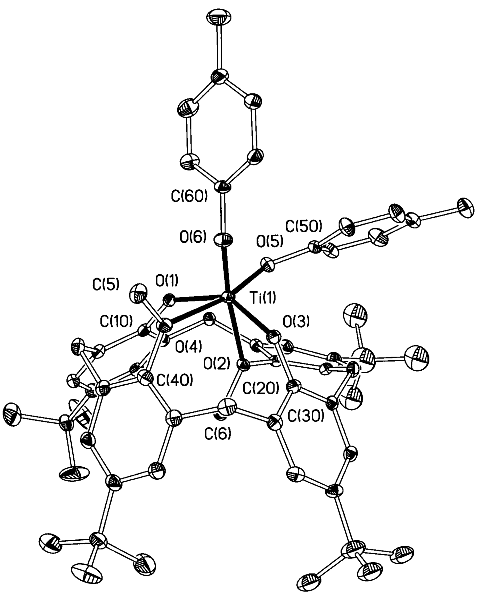

Figure 6. Displacement ellipsoid (30 %) plot of [Ti(O-4-$C_6H_4Me)_2$(*paco*-Me_2calix)] (**25**). H atoms and solvent molecule omitted. Selected bond lengths [Å] and angles [°]: Ti(1)–O(1) 1.861(3), Ti(1)–O(2) 2.282(3), Ti(1)–O(3) 1.866(3), Ti(1)–O(4) 2.444(3), Ti(1)–O(5) 1.821(3), Ti(1)–O(6) 1.849(3), O(1)-Ti(1)-O(2) 78.29(11), O(3)-Ti(1)-O(5) 106.76(13), O(1)-Ti(1)-O(3) 142.46(12), O(4)-Ti(1)-O(5) 168.64(12), O(2)-Ti(1)-O(3) 76.48(11), O(1)-Ti(1)-O(6) 108.47(13), O(1)-Ti(1)-O(4) 79.73(11), O(2)-Ti(1)-O(6) 173.23(13), O(2)-Ti(1)-O(4) 106.0(1), O(3)-Ti(1)-O(6) 97.45(13), O(3)-Ti(1)-O(4) 81.00(12), O(4)-Ti(1)-O(6) 75.67(12), O(1)-Ti(1)-O(5) 97.81(13), O(5)-Ti(1)-O(6) 94.82(13), O(2)-Ti(1)-O(5) 84.21(11), Ti(1)-O(1)-C(10) 142.5(2), Ti(1)-O(2)-C(6) 126.3(2), Ti(1)-O(4)-C(40) 118.8(2), Ti(1)-O(2)-C(20) 121.1(2), C(5)-O(4)-C(40) 113.5(3), C(6)-O(2)-C(20) 112.6(3), Ti(1)-O(5)-C(50) 143.5(3), Ti(1)-O(3)-C(30) 142.5(2), Ti(1)-O(6)-C(60) 142.5(3), Ti(1)-O(4)-C(5) 127.6(3).

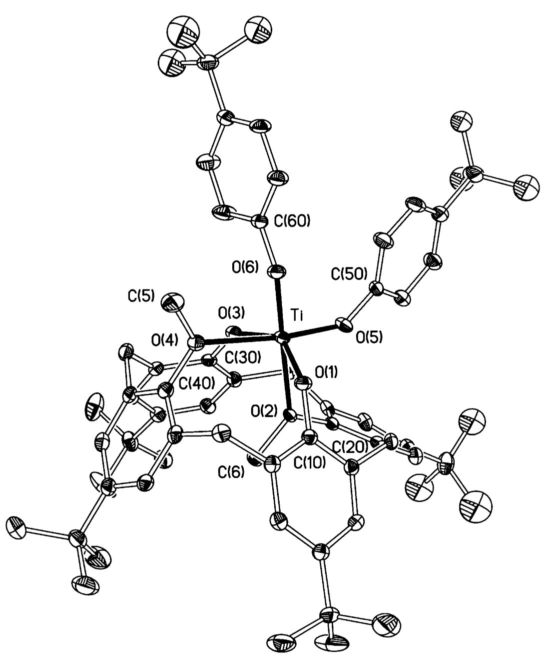

Figure 7. Displacement ellipsoid (30 %) plot of [Ti(O-4-C_6H_4*t*Bu$)_2$(*paco*-Me_2calix)] (**26**). H atoms and solvent molecule omitted. Selected bond lengths [Å] and angles [°]: Ti–O(1) 1.854(2), Ti–O(2) 2.276(2), Ti–O(3) 1.853(2), Ti–O(4) 2.474(2), Ti–O(5) 1.816(2), Ti–O(6) 1.823(2), O(1)-Ti-O(2) 77.81(9), O(1)-Ti-O(3) 140.89(10), O(1)-Ti-O(4) 79.11(9), O(1)-Ti-O(5) 102.19(11), O(1)-Ti-O(6) 103.96(11), O(2)-Ti-O(3) 77.03(9), O(2)-Ti-O(4) 105.95(8), O(2)-Ti-O(5) 81.93(9), O(2)-Ti-O(6) 177.74(10), O(3)-Ti-O(4) 79.63(9), O(3)-Ti-O(5) 103.36(11), O(3)-Ti-O(6) 102.13(11), O(4)-Ti-O(5) 172.07(9), O(4)-Ti-O(6) 75.86(9), O(5)-Ti-O(6) 96.27(11), C(10)-O(1)-Ti 141.6(2), C(20)-O(2)-Ti 120.50(17), C(30)-O(3)-Ti 143.7(2), C(40)-O(4)-Ti 118.18(17), C(50)-O(5)-Ti 145.1(2), C(60)-O(6)-Ti 142.6(2), C(6)-O(2)-Ti 127.79(17), C(5)-O(4)-Ti 127.5(2).

1.816(2) and 1.866(3) Å and are unexceptional and similar to the corresponding bond lengths of other titanacalix[4]arenes reported here and elsewhere.[12, 19, 32] The Ti–O distances to the anisole oxygen atoms O(2) of 2.282(3) (**25**) and 2.276(2) Å (**26**) and to O(4) of 2.444(3) (**25**) and 2.474(2) Å (**26**) are quite different, the shorter contacts are to the oxygen atoms located inside the calix[4]arene cavity. These distances as well as the angles O(1)-Ti-O(3) of 142.46(12) (**25**) and 140.89(10)° (**26**), respectively, indicate a significant distortion from an ideal octahedral coordination of the titanium atom. Another way of looking at this is consider that the metal atoms in the complexes are shifted away from the oxygen atoms O(2) and O(4) of the ether groups (in an ideal octahedral environment) to the oxygen atoms O(5) and O(6) of the *para*-substituted phenoxide ligands. A similar distortion has been observed in the complex [MoO_2(*paco*-Me_2calix)] before.[32]

DFT calculations on model compounds of the *cis,cone*, *trans,cone*, and *cis,paco* isomers of [$TiCl_2$(Me_2calix)] and [MoO_2(*paco*-Me_2calix)] have shown, that the coordination form of calix[4]arene ligands and therefore the cavity of the macrocyclic ligand can be controlled by other co-ligands in metallacalix[4]arenes.[32] According to these calculations, the energy difference of 72.9 kJ mol^{-1} between both *cis*-dioxo molybdenum compounds is quite pronounced in favour of the *cis,paco* isomer. For the titanium compounds an energy separation of 28.0 kJ mol^{-1} was calculated in favour of the *cis,cone* isomer. For the model complexes [Ti(O-$C_6H_5)_2$(*cone*-Me_2calix)] and [Ti(O-$C_6H_5)_2$(*paco*-Me_2calix)] we have calculated (at the same level of theory) a slight preference for the *paco* isomer, which is approximately 3.1 kJ mol^{-1} lower in energy as compared to the *cone* isomer. For the analogous zirconium system the situation is reversed, that is the cone isomer is 5.8 kJ mol^{-1} lower in energy with respect to its *paco* isomer. The calculations do not, however, give an indication of the magnitude of the barriers to interconversion between isomeric forms.

The parent *p*-*t*Bu-calix[4]arene exists both in solution and in the solid state in a *cone* conformation, which is stabilised by a circular array of hydrogen bonds. In solution, the *cone* conformation interconverts with its topomerized forms with a barrier of approximately 65.7 kJ mol^{-1}. This interconversion process involves the rotation of the four intraannular OH groups through the macrocyclic annulus. DFT calculations on different calix[4]arenes have shown, that the energy difference between the two most stable conformers of calix[4]arene, *cone* and *partial cone*, is approximately 42 kJ mol^{-1}.[33] Molecular modelling studies on partially methylated calix[4]arenes have demonstrated that the high barriers for a *cone* → *inverted cone* interconversion of these compounds are caused by the cooperative barriers of hydrogen bond rupture and the steric barrier of rotating a methoxy group through the annulus. The calculated barrier for the *cone* → *inverted cone* interconversion for the 1,3-dimethoxy calix[4]arene was calculated to be approximately 127 kJ mol^{-1},[34] mainly due to the rotation of the methoxy bearing ring (which is the rate limiting step). According to these calculations, the energy difference between *cone* and *paco* isomer (with an inverted anisole ring) is approximately 21.3 kJ mol^{-1} in favour of the *cone* conformation.

In the case of the bis(aryloxy) titanacalix[4]arenes reported here this energetic gap between *cone* and *paco* isomer is much lower, probably because of the lack of hydrogen bond stabilization of the former. Thermodynamically, this might be the reason that enables the formation of these isomers. However, the kinetic pathway of this isomerisation is far from obvious right now. Of the two possible unimolecular reaction mechanisms, namely rotating the anisole group of the ligand via the *t*Bu or the OMe group through the calixarene cavity, the latter has to be preferred for sterical reasons. A prerequisite that the methoxy bearing ring enters the annulus (and therefore for the interconversion of these isomers) is Ti–O bond breaking and Ti–O bond forming steps to the ether *and* to the phenoxide donors of the titanacalix[4]arene. This poses a fundamental question of the binding of the $Ti(OAr)_2$ fragment to the calixarene. It is interesting to recall that we observe these rearrangement reactions only in apolar solvents such as pentane or hexane. The cone isomers are indefinitely stable (with respect to isomerization) in solvents such as benzene, toluene, THF, which probably results from an extra stabilization of the *cone* isomer due to inclusion of the solvent molecule into the calix[4]arene cavity in solution. Experimental and theoretical investigations suggest a stabilization energy of approximately 10 kJ mol^{-1} for the inclusion of a toluene molecule into a calix[4]arene cavity,[35] which is actually greater than the energetic separation of the *cone* and *paco* isomers calculated by ourselves.

The rearrangement reaction described here implies a delicate steric balance. Whereas the complexes with *para* substituted phenoxide ligands [Ti(O-4-C_6H_4Me)$_2$(Me$_2$calix)] (**17**) and [Ti(O-4-C_6H_4*t*Bu)$_2$(Me$_2$calix)] (**18**) rearrange in apolar solvents, the complexes with the sterically more demanding phenoxides [Ti(O-2,6-$C_6H_3Me_2$)$_2$(Me$_2$calix)] (**19**) and [Ti(mbmp)(Me$_2$calix)] (**20**) do not undergo analogous rearrangements in benzene, pentane or hexane. Similarily, the two zirconium compounds [Zr(O-4-C_6H_4Me)$_2$(Me$_2$calix)] (**21**) and [Zr(O-2,6-$C_6H_3Me_2$)$_2$(Me$_2$calix)] (**22**) do not rearrange, which might be due to the stability of the *cone* isomer with respect to the *paco* isomer as calculated above, or due to the different ionic radii of the metal ions; this in turn might represent a kinetic as well as thermodynamic stabilisation of the *cone* isomer.

Conclusion

We have reported a number of new and/or improved synthetic routes to a range of Group 4 calix[4]arene-supported imido complexes. Feasible routes to the complexes [Ti(N*t*Bu)(Me$_2$calix)] and [Ti(NAr)(Me$_2$calix)] are the reactions of the dichloro compound [TiCl$_2$(Me$_2$calix)] with two equivalents of alkali metal amides MNH*t*Bu or MNHAr (Ar = 2,6-$C_6H_3Me_2$ or 2,6-C_6H_3*i*Pr$_2$), respectively, which proceed cleanly and usually in high yield. Alternative pathways are the reaction of imido complexes [Ti(NR)Cl$_2$(py)$_3$] or [Ti(NR)Cl$_2$(NHMe$_2$)$_2$] (R = *t*Bu or aryl) with metallated calix[4]arenes such as [Na$_2$(Me$_2$calix)]$_2$. For the synthesis of analogous titanium imido complexes of other 1,3-disubstituted ether *p-tert*-butylcalix[4]arene ligands, that is Bz$_2$calix (Bz = CH_2Ph) and (Me$_3$Si)$_2$calix, the synthesis via the dichloro compound [TiCl$_2$(R$_2$calix)] (R = Bz, SiMe$_3$) is not a feasible route since the dichlorides themself are not stable and rapidly eliminate RCl. For the Bz$_2$calix systems, reaction of one equivalent of Li$_2$(Bz$_2$calix) with [Ti(NR)Cl$_2$(py)$_3$] gave complexes [Ti(NR)(Bz$_2$calix)] (R = *t*Bu, 2,6-$C_6H_3Me_2$, C_6H_3*i*Pr$_2$) in good yield, whereas the reaction of the disodium salt of (Me$_3$Si)$_2$-calix with [Ti(NR)Cl$_2$(py)$_3$] gave only a mixture of products and neither the target complexes nor any other imido containing compound.

The molecular structures of [Ti(N*t*Bu)(Me$_2$calix)]$\cdot 2C_6H_6$, [Ti(N*t*Bu)(Me$_2$calix)]$\cdot 2C_7H_8$, and [Ti(N-2,4,6-$C_6H_2Me_3$)(Me$_2$-calix)] published earlier as well as NMR spectroscopy reveal the mononuclear character of these compounds, in contrast to the binuclear zirconium phenylimido complex [{Zr(μ_2-NPh)(Me$_2$calix)}$_2$] published earlier by Floriani et al.[13] An increase of the steric demand of the aryl imido ligand also leads to mononuclear zirconium compounds. This is demonstrated for [Zr(N-2,6-C_6H_3*i*Pr$_2$)(Me$_2$calix)] (**8**), a compound which is conveniently synthesised from [ZrCl$_2$(Me$_2$calix)] and and two equivalents of LiNH-2,6-C_6H_3*i*Pr$_2$. The use of other amides LiNHR (R = *t*Bu, Ph, 2,6-$C_6H_3Me_2$ or 2-C_6H_4*t*Bu) leads to no isolable zirconium imido products. ^{1}H NMR spectroscopic studies of the reaction mixtures suggest in all cases (except for R = Ph) mixtures of the corresponding imido and bis(amido) complexes. In the case of R = Ph, the only identifiable carbon-containing product of the NMR scale reaction between [ZrCl$_2$(Me$_2$calix)] and two equivalents of LiNHPh appeared to be [Zr(NHPh)$_2$(Me$_2$calix)] (**9**) with no evidence for Floriani's binuclear phenylimido complex.

The reactions of [Ti(N*t*Bu)(Me$_2$calix)] (**1**) with heterocumulenes such as *p*-tolyl-isocyanate, CO_2, and CS_2 lead to addition of the heterocumulene to the Ti=N multiple bond. In the case of CO_2 and CS_2, these complexes undergo further elimination reactions to afford binuclear compounds [{Ti(μ-E)(Me$_2$calix)}$_2$] (E = O, S). The addition reaction of CO_2 to form a carbamate complex is quantitative. The subsequent isocyanate elimination goes quite slowly in the dark, but is very clean and rapid under ambient lighting. The corresponding thiocarbamate complex was never observed in the reaction of [Ti(N*t*Bu)(Me$_2$calix)] (**1**) with CS_2. The only observed products in this case are the bridging sulfido complex [Ti(μ-S)(Me$_2$calix)]$_2$ (**12**) and *tert*-butyl isothiocyanate. The reaction of [Ti(N*t*Bu)(Me$_2$calix)] (**1**) with *p*-tolyl isocycanate gave clean conversion in 94% yield to the N,N′-bound ureate complex [Ti{N(*t*Bu)C(O)N(-4-C_6H_4Me)}(Me$_2$-calix)] (**13**). Unlike the carbamate and thiocarbamate complexes, the ureate **13** is very stable in solution with no evidence for decomposition or retrocyclisation. The X-ray structure of **13$\cdot$4(C_7H_8)** clearly establishes the N,N′-coordination mode of the ureate ligand. All attempts so far to develop the analogous imide cycloaddition chemistry of the zirconium imido complex [Zr(N-2,6-C_6H_3*i*Pr_2)(Me_2calix)] (**8**) met with limited success.

The reactions of [Ti(N*t*Bu)(Me_2calix)] (**1**) with $R'NH_2$, H_2O, H_2S, and HCl proceed smoothly with elimination of *t*BuNH_2. The *tert*-butyl imide/arylamine exchange reactions are rather slow requiring prolonged heating to ensure complete reaction. Other protic reagents as H_2O, H_2S and HCl require shorter reaction times to afford the corresponding compounds [{Ti(μ-O)(Me_2calix)}$_2$] (**11**), [{Ti(μ-S)(Me_2calix)}$_2$] (**12**), and [$TiCl_2$(Me_2calix)] in high yield.

Of particular interest are some of the aryloxide complexes [Ti(OAr)$_2$(Me_2calix)] synthesised from [Ti(N*t*Bu)(Me_2calix)] (**1**) and the corresponding phenols ArOH. In solution, these titanium bis(phenolate) complexes adopt a pseudo C_{2v} type structure according to NMR spectroscopy. The *para*-substituted bis(phenolate) compounds [Ti(O-4-C_6H_4Me)$_2$(Me_2calix)] (**17**) and [Ti(O-4-C_6H_4*t*Bu)$_2$(Me_2calix)] (**18**) decompose and rearrange in the non polar solvents pentane and hexane. The products of the elimination reactions are dinuclear compounds [{Ti(O-4-C_6H_4R)(Mecalix)}$_2$] (**23**; R = Me) and (**24**; R = *t*Bu), the products of the rearrangement reaction are [Ti(O-4-C_6H_4Me)$_2$(*paco*-Me_2calix (**25**) and [Ti(O-4-C_6H_4*t*Bu)$_2$(*paco*-Me_2calix)] (**26**). In the latter complexes, the calix[4]arene ligand is coordinated in a form reminiscent of a *partial cone* (*paco*) conformation of calix[4]arene. One of the methoxy groups is located *inside* the cavity of the calix[4]arene ligand, as was established by NMR spectroscopy and X-ray crystallography. DFT calculations on model compounds [Ti(O-C_6H_5)$_2$(*cone*-Me_2calix)] and [Ti(O-C_6H_5)$_2$(*paco*-Me_2calix)] reveal a slight thermodynamic preference for the *paco*-isomer, but the pathway of this isomerization process is not clear at this moment. The rearrangment reaction is sensitive to changes of the sterics of the M(OAr)$_2$ fragment. The complexes [Ti(O-2,6-$C_6H_3Me_2$)$_2$(Me_2calix)] (**19**) and [Ti(mbmp)(Me_2calix)] (**20**; H_2mbmp = 2,2′-methylene-bis(4-methyl-6-*tert*-butylphenol): CH_2({CH_3}{C_4H_9}C_6H_2-OH)$_2$) do not rearrange. We have also prepared for comparison the analogous zirconium complexes [Zr(O-4-C_6H_4Me)$_2$-(Me_2calix)] (**21**) and [Zr(O-2,6-$C_6H_3Me_2$)$_2$(Me_2calix)] (**22**) from [Zr(N-2,6-C_6H_3*i*Pr_2)(Me_2calix)] (**8**) and the corresponding phenol, which also do not undergo rearrangement or elimination reactions.

Experimental Section

General methods and instrumentation: All air/moisture sensitive manipulations were performed using standard Schlenk-line (Ar) and dry-box (Ar/N_2) techniques. Solvents were pre-dried over 4 Å molecular sieves and refluxed over sodium (toluene), potassium (benzene, hexane, THF), sodium/potassium alloy (1:3 *w*/*w*) (diethyl ether, pentane) and calcium hydride (acetonitrile, dichloromethane) under N_2. Solvents were distilled at atmospheric pressure and stored in Teflon valve ampoules. Deuterated solvents were dried over sodium (C_7D_8), potassium (C_6D_6) or calcium hydride ($CDCl_3$, CD_2Cl_2, C_5D_5N) under N_2. Deuterated solvents were distilled under reduced pressure and stored in Teflon valve ampoules. NMR samples were prepared in Wilmad 505-PS tubes fitted with J. Young NMR/5 valves.

^1H and $^{13}C\{^1H\}$ NMR spectra were recorded on a Varian Unity Plus 500, Varian Mercury 300, Bruker DPX 300, and Bruker AC 250 spectrometers. Spectra are referenced internally to residual protio-solvent (^1H) or solvent (^{13}C) resonances and are reported relative to tetramethylsilane (δ = 0 ppm). Chemical shifts are quoted in δ (ppm) and coupling constants in Hertz. Standard DEPT-135 experiments were recorded to distinguish -CH_3 and -CH type carbons from -C or -CH_2 type carbons in the ^{13}C NMR spectrum.

IR spectra were recorded on a Perkin–Elmer 1600, Perkin–Elmer 1710, and Bruker IFS28 spectrometers as Nujol mulls between KBr windows or as KBr pellets. All data are quoted in wavenumbers cm^{-1}.

Mass spectra were recorded on Micromass Autospec 500, AEI MS902, Finnigan MAT 900 XLT, and Varian MAT 3830 spectrometers. All data are quoted as their mass/charge (*m*/*z*) ratios.

Cyclic voltammograms were recorded using a glassy-carbon working electrode with platinum wire auxiliary and pseudo-reference electrodes. Measurements were made on deoxygenated solutions ca. 5×10^{-4} M in sample and 0.1 M in [*n*Bu_4N]$^+$[PF_6]$^-$ as supporting electrolyte. Solvents (CH_2Cl_2) were freshly distilled before use. Measurements on air-sensitive samples were made under a N_2 atmosphere in a specially constructed cell with a sidearm fitted with a Rotaflo tap; solutions of the sample and supporting electrolyte were transferred through a cannula into the cell. Potentials were referenced to the ferrocenium/ferrocene couple at 0 mV by addition of either Fe(η^5-Cp)$_2$ or 1,2,3,4,1′,2′,3′,4′-octamethylferrocene to the cell (−0.45 V in CH_2Cl_2 relative to [Fe(η^5-Cp)$_2$]$^+$/Fe(η^5-Cp)$_2$). The reversibility of the redox couple was judged by comparison with the behaviour of the ferrocenium/ferrocene couple under the same conditions.

Elemental analyses were carried out by the analytical laboratory of the Inorganic Chemistry Laboratory Oxford or the analytical laboratory of the Department of Inorganic Chemistry of the University Karlsruhe (TH).

Literature preparations: H_2Me_2calix,[36] H_2Bz_2calix,[36] [Na_2(Me_2calix)]$_2$,[15] [Li_2(Bz_2calix)],[17] [Ti(NR)Cl_2(py)$_3$],[14] [Ti(NR)Cl_2(NHMe_2)$_2$][16] (R = *t*Bu, 2,6-$C_6H_3Me_2$ or 2,6-C_6H_3*i*Pr_2) and [Zr(CH_2SiMe_3)$_2$(Me_2calix)][26] were prepared according to established methods. H_2N-4-C_6H_4Fc was provided by Prof. J. R. Dilworth. The syntheses of [$TiCl_2$(Me_2calix)], [Ti(N*t*Bu)-(Me_2calix)] **1** and [Ti(N-2,4,6-$C_6H_2Me_3$)(Me_2calix)] **4** have been reported previously,[12] but here we briefly report improved and modified versions of these methods for completeness.

[MCl_2(Me_2calix)] (M = Ti or Zr; alternative synthesis from [Na_2(Me_2-calix)]$_2$): A solution of [Na_2(Me_2calix)]$_2$ (2.000 g, 1.39 mmol) in benzene (50 mL) was added to a slurry of [$TiCl_4$(thf)$_2$] (0.926 g, 2.77 mmol) in benzene (25 mL) at 5 °C. The reaction mixture was stirred at rt for 10 h to give a dark red suspension. The suspension was filtered and washed with benzene (2 × 25 mL) to give a red solution. Removal of volatiles under reduced pressure afforded [$TiCl_2$(Me_2calix)] as a dark red solid (1.700 g, 84 %). The compound [$ZrCl_2$(Me_2calix)] was prepared in an analogous way starting from [$ZrCl_4$(thf)$_2$]; recrystallisation from CH_2Cl_2/pentane (1:1 *v*/*v*) gave the desired product (1.995 mg, 73 %). The compounds were characterised by comparison with previously reported data.[12, 19, 25, 32]

[Ti(N*t*Bu)(Me_2calix)] (1)

From [$TiCl_2$(Me_2calix)] (improved synthesis): A solution of LiNH*t*Bu (1.5 g, 19.0 mmol) in THF (30 mL) was added slowly to a solution of [$TiCl_2$(Me_2calix)] (7.2 g, 9.03 mmol) in THF (30 mL). The red reaction mixture was stirred for 2 h to become brown and cloudy. All volatiles were removed in vacuo, the residue was suspended in hot (80 °C) toluene (60 mL) and filtered through a pad of Celite. The brown solution was evaporated, the precipitate was suspended in hexane and filtered. The light yellow residue of [Ti(N*t*Bu)(Me_2calix)] (**1**) was dried in vacuo. Evaporation of the filtrate and suspension in pentane (40 mL) afforded a second crop of **1** (5.380 g, 75 %). Very pure [Ti(N*t*Bu)(Me_2calix)] is a light yellow compound, but with a few impurities it turns orange. The yield reported above is slightly lower than reported by us previously by this general route (83 %), but gives a very pure compound. Analytical and spectroscopic data of [Ti(N*t*Bu)(Me_2calix)] **1** have been reported previously.[12]

From [Ti(N*t*Bu)Cl_2(py)$_3$]: A solution of [Ti(N*t*Bu)Cl_2(py)$_3$] (2.963 g, 6.94 mmol) in benzene (50 mL) was added to a solution of [Na_2(Me_2calix)]$_2$ (5.00 g, 3.47 mmol) in benzene (50 mL) at 5 °C. The reaction mixture was stirred at rt and for 20 h to give an orange suspension. The reaction mixture was filtered and washed with benzene (2 × 25 mL) to give an orange solution. Removal of volatiles under reduced pressure afforded [Ti-(N*t*Bu)(Me_2calix)] (**1**) as an orange solid (5.066 g, 92 %). The compound was characterized by comparison with previously reported data.[12]

From [Ti(NtBu)Cl$_2$(NHMe$_2$)$_2$] (NMR tube scale): A solution of [Ti(NtBu)Cl$_2$(NHMe$_2$)$_2$] (0.004 g, 0.014 mmol) in C_6D_6 (0.5 mL) was added to [Na$_2$(Me$_2$calix)]$_2$ (0.010 g, 0.007 mmol) at rt. Reaction at rt for 15 h afforded an orange suspension. [Ti(NtBu)(Me$_2$calix)] (**1**) and NHMe$_2$ were formed in ca. 95 % yield by ^{1}H NMR spectroscopy. Analytical and spectroscopic data of [Ti(NtBu)(Me$_2$calix)] (**1**) have been reported previously.[12]

[Ti(N-2,6-C$_6$H$_3$Me$_2$)(Me$_2$calix)] (2)

From [TiCl$_2$(Me$_2$calix)] (NMR tube scale): A solution of [TiCl$_2$(Me$_2$calix)] (0.010 g, 0.014 mmol) in C_6D_6 (0.5 mL) was added to LiNH(2,6-C$_6$H$_3$Me$_2$) (0.004 g, 0.028 mmol). Reaction at rt for 30 min afforded an orange suspension. [Ti(N-2,6-C$_6$H$_3$Me$_2$)(Me$_2$calix)] (**2**) and H$_2$N-2,6-C$_6$H$_3$Me$_2$ were formed in quantitative yield by ^{1}H NMR spectroscopy.

From [Ti(N-2,6-C$_6$H$_3$Me$_2$)Cl$_2$(py)$_3$]: A solution of [Ti(N-2,6-C$_6$H$_3$Me$_2$)Cl$_2$(py)$_3$] (0.165 g, 0.35 mmol) in benzene (10 mL) was added to a solution of [Na$_2$(Me$_2$calix)]$_2$ (0.250 g, 0.17 mmol) in benzene (10 mL) at 5 °C. The reaction mixture was stirred at rt for 20 h to give an orange suspension. The reaction mixture was filtered and washed with benzene (2 × 5 mL) to give an orange solution. Removal of volatiles under reduced pressure afforded [Ti(N-2,6-C$_6$H$_3$Me$_2$)(Me$_2$calix)] (**2**) as an orange solid (0.264 g, 90 %).

From [Ti(N-2,6-C$_6$H$_3$Me$_2$)Cl$_2$(NHMe$_2$)$_2$] (NMR tube scale): A solution of [Ti(N-2,6-C$_6$H$_3$Me$_2$)Cl$_2$(NHMe$_2$)$_2$] (0.005 g, 0.014 mmol) in C_6D_6 (0.5 mL) was added to [Na$_2$(Me$_2$calix)]$_2$ (0.010 g, 0.007 mmol) at rt. Reaction at rt for 15 h afforded an orange suspension. [Ti(N-2,6-C$_6$H$_3$Me$_2$)(Me$_2$calix)] (**2**) and HNMe$_2$ were formed in ca. 95 % yield by ^{1}H NMR spectroscopy.

From [Ti(NtBu)(Me$_2$calix)] (NMR tube scale): H$_2$N-2,6-C$_6$H$_3$Me$_2$ (1.7 µL, 0.014 mmol) was added to a solution of [Ti(NtBu)(Me$_2$calix)] (**1**) (0.011 g, 0.014 mmol) in C_6D_6 (0.5 mL) and heated at 65 °C under reduced pressure for 70 h. [Ti(N-2,6-C$_6$H$_3$Me$_2$)(Me$_2$calix)] (**2**) and tBuNH$_2$ were formed in quantitative yield by ^{1}H NMR spectroscopy. ^{1}H NMR (C_6D_6, 300.1 MHz, 298 K): $\delta = 7.28$ (s, 4H, m-C$_6$H$_2$), 7.10 (d, ^3J(H,H) = 7.5 Hz, 2H, m-C$_6$H$_3$Me$_2$), 6.84 (s, 4H, m-C$_6$H$_2$), 6.80 (t, ^3J(H,H) = 7.5 Hz, 1H, p-C$_6$H$_3$Me$_2$), 4.66 (d, ^2J(H,H) = 12.0 Hz, 4H, CH$_2$), 4.02 (s, 6H, OMe), 3.31 (d, ^2J(H,H) = 12.0 Hz, 4H, CH$_2$), 3.00 (s, 6H, C$_6$H$_3$*Me*$_2$), 1.48 (s, 18H, CMe$_3$), 0.69 (s, 18H, CMe$_3$); ^{13}C{^{1}H} NMR (C_6D_6, 75.5 MHz, 298 K): $\delta =$ 160.2 (Cq-C$_6$H$_2$), 150.5 (Cq-C$_6$H$_2$), 149.3 (Cq-C$_6$H$_2$), 140.7 (Cq-C$_6$H$_2$), 133.3 (Cq-C$_6$H$_2$), 132.8 (o-2,6-C$_6$H$_3$Me$_2$), 129.0 (Cq-C$_6$H$_2$), 127.5 (m-2,6-C$_6$H$_3$Me$_2$), 127.1 (m-C$_6$H$_2$), 124.8 (m-C$_6$H$_2$), 121.5 (p-2,6-C$_6$H$_3$Me$_2$), 71.8 (OMe), 34.3 (*C*Me$_3$), 33.8 (*C*Me$_3$), 33.7 (CH$_2$), 32.2 (C*Me*$_3$), 30.6 (C*Me*$_3$), 19.7 (C$_6$H$_3$Me$_3$), (p-2,6-C$_6$H$_3$Me$_2$ resonance not observed); EI MS (70 eV): m/z (%): 841 [M]$^+$ (65); IR (KBr plates, Nujol): $\tilde{\nu} = 1734$ (w), 1599 (w), 1302 (m), 1260 (s), 1208 (m), 1164 (w), 1094 (s), 1019 (s), 936 (w), 872 (w), 802 (s), 755 (w), 570 (m), 427 cm^{-1} (w); elemental analysis calcd (%) for C$_{54}$H$_{67}$NO$_4$Ti: C 77.0, H 8.0, N 1.7; found: C 76.3, H 8.4, N 1.8.

[Ti(N-2,6-C$_6$H$_3$$iPr_2$)(Me$_2$calix)] (3)

From [TiCl$_2$(Me$_2$calix)] (NMR tube scale): A solution of [TiCl$_2$(Me$_2$calix)] (0.010 g, 0.014 mmol) in C_6D_6 (0.5 mL) was added to LiNH(2,6-C$_6$H$_3$$iPr_2$) (0.005 g, 0.028 mmol). Reaction at rt for 30 min afforded an orange suspension. [Ti(N-2,6-C$_6$H$_3$$iPr_2$)(Me$_2$calix)] (**3**) and H$_2$N-2,6-C$_6H_3$$iPr_2$ were formed in quantitative yield by ^{1}H NMR spectroscopy.

From [Ti(N-2,6-C$_6$H$_3$$iPr_2$)Cl$_2(py)_3$]: A solution of [Ti(N-2,6-C$_6$H$_3$$iPr_2$)Cl$_2(py)_3$] (0.185 g, 0.35 mmol) in benzene (10 mL) was added to a solution of [Na$_2$(Me$_2$calix)]$_2$ (0.250 g, 0.17 mmol) in benzene (10 mL) at 5 °C. The reaction mixture was stirred at rt for 20 h to give an orange suspension. The reaction mixture was filtered and washed with benzene (2 × 5 mL) to give an orange solution. Removal of volatiles under reduced pressure afforded [Ti(N-2,6-C$_6$H$_3$$iPr_2$)(Me$_2$calix)] (**3**) as an orange solid (0.287 g, 91 %).

From [Ti(N-2,6-C$_6$H$_3$$iPr_2$)Cl$_2$(NHMe$_2$)$_2$] (NMR tube scale): A solution of [Ti(N-2,6-C$_6$H$_3$$iPr_2$)Cl$_2$(NHMe$_2$)$_2$] (0.005 g, 0.014 mmol) in C_6D_6 (0.5 mL) was added to [Na$_2$(Me$_2$calix)]$_2$ (0.010 g, 0.007 mmol) at rt. Reaction at rt for 15 h afforded an orange suspension. [Ti(N-2,6-C$_6$H$_3$$iPr_2$)(Me$_2$calix)] (**3**) and NHMe$_2$ were formed in ca. 95 % yield by ^{1}H NMR spectroscopy.

From [Ti(NtBu)(Me$_2$calix)] (NMR tube scale): H$_2$N-2,6-C$_6$H$_3$$iPr_2$ (0.002 g, 2.1 µL, 0.014 mmol) was added to a solution of [Ti(NtBu)(Me$_2$calix)] (**1**; 0.010 g, 0.014 mmol) in C_6D_6 (0.5 mL) and heated at 65 °C under reduced pressure for 70 h. [Ti(N-2,6-C$_6$H$_3$$iPr_2$)(Me$_2$calix)] (**3**) and tBuNH$_2$ were formed in quantitative yield by ^{1}H NMR. ^{1}H NMR (C_6D_6, 300.1 MHz, 298 K): $\delta = 7.29$ (s, 4H, m-C$_6$H$_2$), 7.13 (d, ^3J(H,H) = 7.5 Hz, 2H, m-C$_6$H$_3$$iPr_2$), 6.92 (t, ^3J(H,H) = 7.5 Hz, 1H, p-C$_6$H$_3$$iPr_2$), 6.86 (s, 4H, m-C$_6H_2$), 4.80 (sept, ^3J(H,H) = 7.0 Hz, 2H, C*H*Me$_2$), 4.74 (d, ^2J(H,H) = 12.0 Hz, 4H, CH$_2$), 4.15 (s, 6H, OMe), 3.38 (d, ^2J(H,H) = 12.0 Hz, 4H, CH$_2$), 1.61 (d, ^3J(H,H) = 7.0 Hz, 12H, CH*Me*$_2$), 1.46 (s, 18H, CMe$_3$), 0.67 (s, 18H, CMe$_3$); ^{13}C{^{1}H} NMR (C_6D_6, 75.5 MHz, 298 K): $\delta = 160.1$ (Cq-C$_6$H$_2$), 157.5 (i-2,6-C$_6$H$_3$$iPr_2$), 150.4 (C$q$-C$_6H_2$), 149.4 (C$q$-C$_6H_2$), 144.2 ($o$-2,6-C$_6H_3$$iPr_2$), 140.6 (C$q$-C$_6H_2$), 132.8 (C$q$-C$_6H_2$), 128.9 (C$q$-C$_6H_2$), 127.1 ($m$-C$_6H_2$), 124.8 ($m$-C$_6H_2$), 122.6 ($p$-2,6-C$_6H_3$$iPr_2$), 122.5 ($m$-2,6-C$_6H_3$$iPr_2$), 71.4 (OMe), 34.2 (*C*Me$_3$), 33.7 (*C*Me$_3$), 33.7 (CH$_2$), 32.2 (C*Me*$_3$), 30.0 (C*Me*$_3$), 29.1 (*C*HMe$_2$), 23.8 (CH*Me*$_2$); EI MS (70 eV): m/z (%): 897 (5) [M]$^+$; IR (KBr plates, Nujol): $\tilde{\nu} = 1601$ (w), 1418 (w), 1319 (s), 1283 (m), 1212 (m), 1164 (w), 1121 (m), 1093 (w), 1001 (m), 976 (w), 940 (w), 914 (w), 871 (m), 856 (m), 847 (m), 795 (m), 754 (m), 678 (w), 638 (w), 566 (m), 552 (w), 530 (w), 445 cm^{-1} (w); elemental analysis calcd (%) for C$_{58}$H$_{75}$NO$_4$Ti: C 77.6, H 8.4, N 1.6; found: C 76.4, H 8.4, N 1.5.

[Ti(N-2,4,6-C$_6$H$_2$Me$_3$)(Me$_2$calix)] (4) from [TiCl$_2$(Me$_2$calix)] (improved synthesis): A solution of KH(N-2,4,6-C$_6$H$_2$Me$_3$) (1.17 g, 4.74 mmol) in THF (20 mL) was added at −30 °C to a solution of [TiCl$_2$(Me$_2$calix)] (1.80 g, 2.26 mmol) in THF (20 mL). After 1 h of stirring at rt the initially red reaction mixture had turned orange and viscous. All volatiles were removed in vacuo, the residue was suspended in chloroform (20 mL), filtered through a pad of Celite and washed with chloroform (5 mL). The solvent was removed under reduced pressure and the solid was recrystallised from toluene (40 mL). Filtration of the cooled (−40 °C) toluene solution afforded [Ti(N-2,6-C$_6$H$_2$Me$_3$)(Me$_2$calix)] (**4**) as a light-orange powder that was dried in vacuo (1.50 g, 70 %). Analytical and spectroscopic data of **4** have been reported previously.[12] The yield is slightly lower than reported previously (80 %) but is more convenient on a larger scale since no time-consuming extraction is required.

[Ti(NtBu)(Bz$_2$calix)] (5)

From [Ti(NtBu)Cl$_2$(py)$_3$]: A solution of [Ti(NtBu)Cl$_2$(py)$_3$] (0.128 g, 0.30 mmol) in benzene (10 mL) was added to a solution of [Li$_2$(Bz$_2$calix)] (0.250 g, 0.30 mmol) in benzene (10 mL) at 5 °C. The reaction mixture was stirred at rt for 20 h to give an orange suspension. The reaction mixture was filtered and washed with benzene (2 × 5 mL) to give an orange solution. Removal of volatiles under reduced pressure and trituration with pentane (5 mL) afforded [Ti(NtBu)(Bz$_2$calix)] (**5**) as an orange solid (0.246 g, 86 %).

From [Ti(NtBu)Cl$_2$(NHMe$_2$)$_2$] (NMR tube scale): A solution of [Ti(N-tBu)Cl$_2$(NHMe$_2$)$_2$] (0.003 g, 0.012 mmol) in C_6D_6 (0.5 mL) was added to [Li$_2$(Bz$_2$calix)] (0.010 g, 0.012 mmol) at rt. Reaction at rt for 15 h afforded an orange suspension. [Ti(NtBu)(Bz$_2$calix)] (**5**) and NHMe$_2$ were formed in ca. 90 % yield by ^{1}H NMR spectroscopy. ^{1}H NMR (C_6D_6, 300.1 MHz, 298 K): $\delta = 7.44$ (dd, ^3J(H,H) = 7.7, ^4J(H,H) = 1.5 Hz, 4H, o-C$_6$H$_5$), 7.16 (s, 4H, m-C$_6$H$_2$), 7.08–7.01 (m, 6H, m-C$_6$H$_5$ and p-C$_6$H$_5$), 6.69 (s, 4H, m-C$_6$H$_2$), 6.05 (s, 4H, OC*H*$_2$C$_6$H$_5$), 4.59 (d, ^2J(H,H) = 12.0 Hz, 4H, CH$_2$), 2.98 (d, ^2J(H,H) = 12.0 Hz, 4H, CH$_2$), 1.64 (s, 9H, NCMe$_3$), 1.43 (s, 18H, CMe$_3$), 0.65 (s, 18H, CMe$_3$); ^{13}C{^{1}H} NMR (C_6D_6, 75.5 MHz, 298 K): $\delta = 160.5$ (Cq-C$_6$H$_2$ or i-C$_6$H$_5$), 148.8 (Cq-C$_6$H$_2$ or i-C$_6$H$_5$), 147.5 (Cq-C$_6$H$_2$ or i-C$_6$H$_5$), 139.9 (Cq-C$_6$H$_2$ or i-C$_6$H$_5$), 134.4 (Cq-C$_6$H$_2$ or i-C$_6$H$_5$), 133.7 (Cq-C$_6$H$_2$ or i-C$_6$H$_5$), 131.8 (o-C$_6$H$_5$ or m-C$_6$H$_5$ or p-C$_6$H$_5$), 129.5 (o-C$_6$H$_5$ or m-C$_6$H$_5$ or p-C$_6$H$_5$), 129.4 (Cq-C$_6$H$_2$ or i-C$_6$H$_5$), 128.4 (o-C$_6$H$_5$ or m-C$_6$H$_5$ or p-C$_6$H$_5$), 126.4 (m-C$_6$H$_2$), 124.4 (m-C$_6$H$_2$), 87.5 (O*C*H$_2$C$_6$H$_5$), 70.7 (N*C*Me$_3$), 34.3 (CH$_2$), 34.1 (*C*Me$_3$), 34.0 (NC*Me*$_3$), 33.6 (*C*Me$_3$), 32.2 (C*Me*$_3$), 30.6 (C*Me*$_3$); EI MS (70 eV): m/z (%): 946 [M]$^+$ (10), 931 [M − Me]$^+$ (25); IR (KBr plates, Nujol): $\tilde{\nu} = 1601$ (w), 1304 (m), 1256 (w), 1208 (m), 1122 (w), 1021 (w), 935 (w), 927 (w), 871 (m), 847 (w), 793 (w), 751 (m), 698 (m), 556 cm^{-1} (w); elemental analysis calcd (%) for C$_{62}$H$_{75}$NO$_4$Ti: C 78.7, H 8.0, N 1.5; found: C 76.5, H 7.7, N 2.0.

[Ti(N-2,6-C$_6$H$_3$Me$_2$)(Bz$_2$calix)] (6)

From [Ti(N-2,6-C$_6$H$_3$Me$_2$)Cl$_2$(py)$_3$]: A solution of [Ti(N-2,6-C$_6$H$_3$Me$_2$)Cl$_2$(py)$_3$] (0.143 g, 0.30 mmol) in benzene (10 mL) was added to a solution of [Li$_2$(Bz$_2$calix)] (0.250 g, 0.30 mmol) in benzene (10 mL) at 5 °C. The reaction mixture was stirred at rt for 20 h to give an orange suspension. The reaction mixture was filtered and washed with benzene (2 × 5 mL) to give an orange solution. Removal of volatiles under reduced pressure and trituration with pentane (5 mL) afforded [Ti(N-2,6-C$_6$H$_3$Me$_2$)(Bz$_2$calix)] (**6**) as an orange solid (0.258 g, 86 %).

From [Ti(N-2,6-C$_6$H$_3$Me$_2$)Cl$_2$(NHMe$_2$)$_2$] (NMR tube scale): A solution of [Ti(N-2,6-C$_6$H$_3$Me$_2$)Cl$_2$(NHMe$_2$)$_2$] (0.004 g, 0.012 mmol) in C_6D_6 (0.5 mL) was added to [Li$_2$(Bz$_2$calix)] (0.010 g, 0.012 mmol) at rt. Reaction at rt for 15 h afforded an orange suspension. [Ti(N-2,6-C$_6$H$_3$Me$_2$)(Bz$_2$calix)] (**6**) and NHMe$_2$ were formed in ca. 90 % yield by ^{1}H NMR spectroscopy. ^{1}H NMR

(C_6D_6, 300.1 MHz, 298 K): $\delta = 7.22$ (dd, ^3J(H,H) = 7.7, ^4J(H,H) = 1.5 Hz, 4H, *o*-C_6H_5), 7.15 (s, 4H, *m*-C_6H_2), 7.10–6.85 (m, 9H, *m*-C_6H_5, *p*-C_6H_5, *m*-2,6-$C_6H_3Me_2$, *p*-2,6-$C_6H_3Me_2$), 6.80 (s, 4H, *m*-C_6H_2), 5.67 (s, 4H, OC*H*$_2$$C_6H_5$), 4.40 (d, ^2J(H,H) = 12.0 Hz, 4H, CH_2), 3.13 (s, 6H, 2,6-C_6H_3*Me*$_2$), 3.06 (d, ^2J(H,H) = 12.0 Hz, 4H, CH_2), 1.42 (s, 18H, CMe_3), 0.69 (s, 18H, CMe_3); $^{13}C\{^1H\}$ NMR (C_6D_6, 75.5 MHz, 298 K): $\delta = 160.1$ (C*q*-C_6H_2 or *i*-C_6H_5), 159.9 (*i*-2,6-$C_6H_3Me_2$), 149.1 (C*q*-C_6H_2 or *i*-C_6H_5), 148.5 (C*q*-C_6H_2 or *i*-C_6H_5), 140.5 (C*q*-C_6H_2 or *i*-C_6H_5), 134.2 (C*q*-C_6H_2 or *i*-C_6H_5), 133.9 (C*q*-C_6H_2 or *i*-C_6H_5), 133.6 (*o*-2,6-$C_6H_3Me_2$), 131.5 (*o*-C_6H_5 or *m*-C_6H_5 or *p*-C_6H_5), 129.6 (*o*-C_6H_5 or *m*-C_6H_5 or *p*-C_6H_5), 129.2 (C*q*-C_6H_2 or *i*-C_6H_5), 128.5 (*o*-C_6H_5 or *m*-C_6H_5 or *p*-C_6H_5), 127.8 (*m*-2,6-$C_6H_3Me_2$), 126.8 (*m*-C_6H_2), 124.5 (*m*-C_6H_2), 122.0 (*p*-2,6-$C_6H_3Me_2$), 87.9 (OC*H*$_2$$C_6H_5$), 34.3 ($CH_2$), 34.2 (*C*Me$_3$), 33.7 (*C*Me$_3$), 32.2 (C*Me*$_3$), 30.6 (C*Me*$_3$), 20.1 (2,6-$C_6H_3$*Me*$_2$); EI MS (70 eV): *m*/*z* (%): 993 [*M*]$^+$ (5); IR (KBr plates, Nujol): $\tilde{\nu} = 1601$ (w), 1314 (m), 1285 (w), 1261 (w), 1211 (m), 1178 (w), 1130 (m), 1092 (m), 1025 (m), 935 (m), 919 (m), 871 (m), 855 (m), 794 (m), 754 (s), 699 (m), 563 cm^{-1} (w). A satisfactory elemental analysis could not be obtained.

[Ti(N-2,6-C_6H_3*i*Pr_2)(Bz_2calix)] (7)

From [Ti(N-2,6-C_6H_3*i*Pr_2)Cl_2(py)$_3$]: A solution of [Ti(N-2,6-C_6H_3*i*Pr_2)Cl_2(py)$_3$] (0.159 g, 0.30 mmol) in benzene (10 mL) was added to a solution of [Li_2(Bz_2calix)] (0.250 g, 0.30 mmol) in benzene (10 mL) at 5 °C. The reaction mixture was stirred at rt for 20 h to give an orange suspension. The reaction mixture was filtered and washed with benzene (2 × 5 mL) to give an orange solution. Removal of volatiles under reduced pressure and trituration with pentane (5 mL) afforded [Ti(N-2,6-C_6H_3*i*Pr_2)(Bz_2calix)] (**7**) as an orange solid (0.290 g, 92 %).

From [Ti(N-2,6-C_6H_3*i*Pr_2)Cl_2($NHMe_2$)$_2$] (NMR tube scale): A solution of [Ti(N-2,6-C_6H_3*i*Pr_2)Cl_2($NHMe_2$)$_2$] (0.005 g, 0.012 mmol) in C_6D_6 (0.5 mL) was added to [Li_2(Bz_2calix)] (0.010 g, 0.012 mmol) at rt. Reaction at rt for 15 h afforded an orange suspension. [Ti(N-2,6-C_6H_3*i*Pr_2)(Bz_2calix)] (**7**) and $NHMe_2$ were formed in ca. 90 % yield by ^1H NMR spectroscopy. ^1H NMR (C_6D_6, 300.1 MHz, 298 K): $\delta = 7.25$ (dd, ^3J(H,H) = 7.7, ^4J(H,H) = 1.5 Hz, 4H, *o*-C_6H_5), 7.14 (s, 4H, *m*-C_6H_2), 7.10–6.80 (m, 9H, *m*-C_6H_5, *p*-C_6H_5, *m*-2,6-C_6H_3*i*Pr_2, *p*-2,6-C_6H_3*i*Pr_2), 6.77 (s, 4H, *m*-C_6H_2), 5.92 (s, 4H, OC*H*$_2$$C_6H_5$), 5.15 (sept, ^3J(H,H) = 6.8 Hz, 2H, C*H*Me$_2$), 4.54 (d, ^2J(H,H) = 12.3 Hz, 4H, CH_2), 3.07 (d, ^2J(H,H) = 12.3 Hz, 4H, CH_2), 1.64 (d, ^3J(H,H) = 6.8 Hz, 12H, CH*Me*$_2$), 1.40 (s, 18H, CMe_3), 0.68 (s, 18H, CMe_3); $^{13}C\{^1H\}$ NMR (C_6D_6, 75.5 MHz, 298 K): $\delta = 160.2$ (C*q*-C_6H_2 or *i*-C_6H_5), 157.6 (*i*-2,6-C_6H_3*i*Pr_2), 149.2 (C*q*-C_6H_2 or *i*-C_6H_5), 147.5 (C*q*-C_6H_2 or *i*-C_6H_5), 144.1 (*o*-2,6-C_6H_3*i*Pr_2), 140.5 (C*q*-C_6H_2 or *i*-C_6H_5), 133.8 (2 × overlapping C*q*-C_6H_2 or *i*-C_6H_5), 131.8 (*o*-C_6H_5 or *m*-C_6H_5 or *p*-C_6H_5), 129.6 (*o*-C_6H_5 or *m*-C_6H_5 or *p*-C_6H_5), 129.1 (C*q*-C_6H_2 or *i*-C_6H_5), 128.3 (*o*-C_6H_5 or *m*-C_6H_5 or *p*-C_6H_5), 126.7 (*m*-C_6H_2), 124.5 (*m*-C_6H_2), 123.1 (*p*-2,6-C_6H_3*i*Pr_2), 122.8 (*m*-2,6-C_6H_3*i*Pr_2), 87.0 (O*C*H$_2$$C_6H_5$), 34.2 ($CH_2$), 34.1 (*C*Me$_3$), 33.7 (*C*Me$_3$), 32.2 (C*Me*$_3$), 30.6 (C*Me*$_3$), 28.7 (*C*HMe$_2$), 24.3 (CH*Me*$_2$); EI MS (70 eV): *m*/*z* (%): 1049 [*M*]$^+$ (10); IR (KBr plates, Nujol): $\tilde{\nu} = 1600$ (w), 1558 (w), 1418 (w), 1319 (s), 1274 (s), 1262 (s), 1211 (s), 1166 (w), 1120 (m), 1094 (m), 1025 (m), 976 (w), 936 (m), 917 (m), 872 (s), 853 (w), 796 (s), 752 (s), 698 (m), 600 (w), 566 cm^{-1} (m). A satisfactory elemental analysis could not be obtained.

[Zr(N-2,6-C_6H_3*i*Pr_2)(Me_2calix)] (8): A solution of [$ZrCl_2$(Me_2calix)] (1.010 g, 1.21 mmol) in benzene (35 mL) was added at rt to a solution of LiNH(2,6-C_6H_3*i*Pr_2) (0.442 g, 2.41 mmol) in benzene (15 mL). The solution turned a pale yellow colour and the mixture was stirred for 48 h. After filtration through a 2.5 cm bed of Celite, volatiles were removed under reduced pressure to leave a yellow solid. This was washed with pentane (3 × 25 mL) and volatiles were removed under reduced pressure to afford [Zr(N-2,6-C_6H_3*i*Pr_2)(Me_2calix)] (**8**) as a white solid (0.691 g, 61 %). ^1H NMR (C_6D_6, 500.0 MHz, 298 K): $\delta = 7.32$ (d, ^3J(H,H) = 7.5 Hz, 2H, *m*-C_6*H*$_3$*i*Pr_2), 7.25 (s, 4H, *m*-C_6H_2), 7.02 (t, ^3J(H,H) = 7.5 Hz, 1H, *p*-C_6*H*$_3$*i*Pr_2), 6.83 (s, 4H, *m*-C_6H_2), 4.68 (sept, ^3J(H,H) = 7.0 Hz, 2H, C*H*Me$_2$), 4.50 (d, ^2J(H,H) = 13.0 Hz, 4H, CH_2), 3.98 (s, 6H, OMe), 3.25 (d, ^2J(H,H) = 13.0 Hz, 4H, CH_2), 1.65 (d, ^3J(H,H) = 7.0 Hz, 12H, CH*Me*$_2$), 1.40 (s, 18H, CMe_3), 0.63 (s, 18H, CMe_3);$^{13}C\{^1H\}$ NMR (C_6D_6, 125.7 MHz, 298 K): $\delta = 157.3$ (C*q*-C_6H_2 or *i*-*C*$_6$$H_3$*i*$Pr_2$), 153.7 (*i*-*C*$_6$$H_3$*i*$Pr_2$), 149.9 (C*q*-$C_6H_2$ or *i*-*C*$_6$$H_3$*i*$Pr_2$), 148.2 (C*q*-$C_6H_2$ or *i*-*C*$_6$$H_3$*i*$Pr_2$), 142.0 (C*q*-$C_6H_2$ or *i*-*C*$_6$$H_3$*i*$Pr_2$), 140.5 (C*q*-$C_6H_2$ or *i*-*C*$_6$$H_3$*i*$Pr_2$), 133.3 (C*q*-$C_6H_2$ or *i*-*C*$_6$$H_3$*i*$Pr_2$), 128.6 (C*q*-$C_6H_2$ or *i*-*C*$_6$$H_3$*i*$Pr_2$), 127.6 (*m*-$C_6H_2$), 124.9 (*m*-$C_6H_2$), 122.3 (*m*-*C*$_6$$H_3$*i*$Pr_2$), 119.1 (*p*-*C*$_6$$H_3$*i*$Pr_2$), 72.4 (OMe), 34.3 (*C*Me$_3$), 33.8 (*C*Me$_3$), 32.6 (CH_2), 32.2 (C*Me*$_3$), 30.4 (C*Me*$_3$), 29.5 (*C*HMe$_2$), 23.8 (CH*Me*$_2$);EI MS (70 eV): *m*/*z* (%): 941 [*M*]$^+$ (15), 161 [C_6H_3*i*Pr_2]$^+$ (100); IR (KBr plates, Nujol): $\tilde{\nu} = 1602$ (w), 1419 (m), 1363 (m), 1321 (s), 1286 (m), 1262 (m), 1213 (m), 1164 (w), 1120 (m), 1093 (s), 1020 (m), 986 (m), 940 (w), 872 (m), 848 (m), 795 (s), 753 (m), 638 (w), 549 cm^{-1} (m); elemental analysis calcd (%) for $C_{58}H_{75}NO_4Zr$: C 74.0, H 8.0, N 1.5; found: C 73.9, H 8.3, N 1.4.

NMR tube scale reaction of [Zr(CH_2SiMe_3)$_2$(Me_2calix)] with H_2N-2,6-C_6H_3*i*Pr_2: H_2N-2,6-C_6H_3*i*Pr_2 (2.2 µL, 0.012 mmol) was added to a solution of [Zr(CH_2SiMe_3)$_2$(Me_2calix)] (11.2 mg, 0.012 mmol) in C_6D_6 (0.75 mL). The mixture was heated at 50 °C for two weeks resulting in a ca. 25 % conversion of [Zr(CH_2SiMe_3)$_2$(Me_2calix)] to [Zr(N-2,6-C_6H_3*i*Pr_2)(Me_2calix)] (**8**) and $SiMe_4$.

NMR tube scale reaction of [$ZrCl_2$(Me_2calix)] with LiNHPh: A solution of LiNHPh (4.4 mg, 0.045 mmol) in C_6D_6 (0.3 mL) was added to [$ZrCl_2$(Me_2calix)] (18.7 mg, 0.022 mmol) in C_6D_6 (0.3 mL). The solution was transferred to a sealed NMR tube. After 1 h, the ^1H NMR spectrum suggested quantitative formation of a single product formulated as [Zr(NHPh)$_2$(Me_2calix)] (**9**). Removal of volatiles under reduced pressure resulted in the decomposition of the product. ^1H NMR (C_6D_6, 300.1 MHz, 298 K): $\delta = 7.33$ (s, 4H, *m*-C_6H_2), 7.24 (apparent d, ^3J(H,H) = 6.0 Hz, 4H, *o*-C_6H_5), 7.20 (apparent d, ^3J(H,H) = 6.9 Hz, 4H, *m*-C_6H_5), 6.82 (s, 4H, *m*-C_6H_2), 6.76 (tt, ^3J(H,H) = 6.9 Hz, 2H, *p*-C_6H_5), 6.37 (br s, 2H, NH), 4.44 (d, ^2J(H,H) = 12.6 Hz, 4H, CH_2), 3.64 (s, 6H, OMe), 3.27 (d, ^2J(H,H) = 12.6 Hz, 4H, CH_2), 1.48 (s, 18H, CMe_3), 0.69 (s, 18H, CMe_3).

[Ti{N(*t*Bu)C(O)O}(Me_2calix)] (10): CO_2 (1 atm) was added to a solution of [Ti(N*t*Bu)(Me_2calix)] (**1**) (0.200 g, 0.25 mmol) in benzene (20 mL) at rt. The reaction mixture was stirred at rt for 5 min to give an orange solution. Removal of volatiles under reduced pressure afforded [Ti{N(*t*Bu)C(O)O}(Me_2calix)] (**10**) as an orange solid (0.193 g, 93 %). ^1H NMR (C_6D_6, 500.1 MHz, 298 K): $\delta = 7.25$ (s, 2H, *m*-C_6H_2), 7.23 (s, 2H, *m*-C_6H_2), 6.81 (d, ^4J(H,H) = 2.5 Hz, 2H, *m*-C_6H_2), 6.78 (d, ^4J(H,H) = 2.5 Hz, 2H, *m*-C_6H_2), 4.41 (d, ^2J(H,H) = 12.6 Hz, 2H, CH_2), 4.40 (d, ^2J(H,H) = 13.5 Hz, 2H, CH_2), 3.70 (s, 6H, OMe), 3.25 (d, ^2J(H,H) = 12.6 Hz, 2H, CH_2), 3.14 (d, ^2J(H,H) = 13.5 Hz, 2H, CH_2), 1.72 (s, 9H, $NCMe_3$), 1.43 (s, 9H, CMe_3), 1.36 (s, 9H, CMe_3), 0.64 (s, 18H, CMe_3); $^{13}C\{^1H\}$ NMR (C_6D_6, 125.7 MHz, 298 K): $\delta = 167.3$ (CO), 162.6 (C*q*-C_6H_2), 161.0 (C*q*-C_6H_2), 155.1 (C*q*-C_6H_2), 149.2 (C*q*-C_6H_2), 143.6 (C*q*-C_6H_2), 142.7 (C*q*-C_6H_2), 132.4 (C*q*-C_6H_2), 131.3 (C*q*-C_6H_2), 131.0 (C*q*-C_6H_2), 130.1 (C*q*-C_6H_2), 127.7 (*m*-C_6H_2), 126.7 (*m*-C_6H_2), 124.8 (*m*-C_6H_2), 124.7 (*m*-C_6H_2), 69.9 (OMe), 59.3 (N*C*Me$_3$), 34.6 (CH_2), 34.5 (*C*Me$_3$), 34.4 (*C*Me$_3$), 34.0 (CH_2), 33.7 (*C*Me$_3$), 32.0 (NC*Me*$_3$), 31.9 (C*Me*$_3$), 31.6 (C*Me*$_3$), 30.5 (C*Me*$_3$); EI MS (70 eV): *m*/*z* (%): 738 [*M* – *t*BuNCO]$^+$ (100); IR (KBr plates, Nujol): $\tilde{\nu} = 1600$ (s), 1307 (s), 1277 (w), 1261 (w), 1209 (s), 1168 (w), 1123 (s), 1097 (w), 998 (m), 939 (m), 872 (s), 796 (m), 770 (w), 755 (w), 723 (w), 679 (w), 645 (w), 568 (s), 494 (w), 448 cm^{-1} (m); elemental analysis calcd (%) for $C_{51}H_{67}NO_6Ti$: C 73.1, H 8.1, N 1.7; found: C 71.6, H 7.8, N 1.8.

[{Ti(µ-O)(Me_2calix)}$_2$] (11): CO_2 (1 atm) was added to a solution of [Ti(N*t*Bu)(Me_2calix)] (**1**; 0.200 g, 0.25 mmol) in benzene (20 mL) at rt. The reaction mixture was stirred at rt for 125 h (in light) to give a red solution. Removal of volatiles under reduced pressure and washing with pentane (–50 °C) (2 × 5 mL) afforded [{Ti(µ-O)(Me_2calix)}$_2$] (**11**) as a red solid (0.146 g, 79 %). ^1H NMR (C_6D_6, 500.1 MHz, 298 K): $\delta = 7.25$ (s, 4H, *m*-C_6H_2), 6.77 (s, 4H, *m*-C_6H_2), 4.59 (d, ^2J(H,H) = 12.5 Hz, 4H, CH_2), 4.19 (s, 6H, OMe), 3.23 (d, ^2J(H,H) = 12.5 Hz, 4H, CH_2), 1.46 (s, 18H, CMe_3), 0.61 (s, 18H, CMe_3); EI MS (70 eV): *m*/*z* (%): 738 [½*M*]$^+$ (100); IR (KBr plates, Nujol): $\tilde{\nu} = 1305$ (s), 1258 (m), 1208 (s), 1168 (w), 1123 (m), 1097 (w), 1016 (m), 939 (m), 872 (s), 850 (m), 797 (m), 724 (m), 564 cm^{-1} (m); elemental analysis calcd (%) for $C_{92}H_{116}O_{10}Ti_2$: C 73.8, H 7.9; found: C 72.8, H 8.4.

[{Ti(µ-S)(Me_2calix)}$_2$] (12): CS_2 (0.023 g, 18.1 µL, 0.31 mmol) was added to a solution of [Ti(N*t*Bu)(Me_2calix)] (**1**; 0.250 g, 0.31 mmol) in benzene (25 mL) at rt. The mixture was stirred at rt for 5 d to give a red solution. Removal of volatiles and washing with pentane (–50 °C) (2 × 5 mL) afforded [{Ti(µ-S)(Me_2calix)}$_2$] (**12**) as a red solid (0.185 g, 79 %). ^1H NMR (C_6D_6, 500.1 MHz, 298 K): $\delta = 7.25$ (s, 4H, *m*-C_6H_2), 6.71 (s, 4H, *m*-C_6H_2), 4.70 (d, ^2J(H,H) = 12.5 Hz, 4H, CH_2), 4.31 (s, 6H, OMe), 3.20 (d, ^2J(H,H) = 12.5 Hz, 4H, CH_2), 1.41 (s, 18H, CMe_3), 0.58 (s, 18H, CMe_3); $^{13}C\{^1H\}$ NMR (C_6D_6, 125.7 MHz, 298 K): $\delta = 160.8$ (C*q*-C_6H_2), 149.9 (C*q*-C_6H_2), 149.3 (C*q*-C_6H_2), 142.6 (C*q*-C_6H_2), 132.1 (C*q*-C_6H_2), 129.4 (C*q*-C_6H_2), 127.0 (*m*-C_6H_2), 124.8 (*m*-C_6H_2), 77.3 (OMe), 34.3 (*C*Me$_3$), 33.6 (*C*Me$_3$), 33.5 (CH_2), 32.1 (C*Me*$_3$), 30.5 (C*Me*$_3$); EI MS (70 eV): *m*/*z* (%): 754 [½*M*]$^+$ (45), 739 [½*M* – Me]$^+$ (20); IR (KBr plates, Nujol): $\tilde{\nu} = 1311$ (s), 1262 (m), 1210 (s), 1169 (w), 1123 (m), 1114 (m), 1095 (w), 996 (m), 941 (m),

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924 (m), 875 (s), 816 (w), 797 (s), 730 (s), 638 (w), 572 (s), 528 cm^{-1} (w); elemental analysis calcd (%) for $C_{92}H_{116}O_8S_2Ti_2$: C 73.2, H 7.7; found: C 72.0, H 7.6.

[Ti{N(*t*Bu)C(O)N(-4-C_6H_4Me)}(Me_2calix)] (13): OCN-4-C_6H_4Me (0.043 g, 40.5 μL, 0.32 mmol) was added to a solution of [Ti(N*t*Bu)(Me_2calix)] (**1**; 0.250 g, 0.32 mmol) in benzene (20 mL) at rt. The reaction mixture was stirred at rt for 25 h to give a dark red solution. Removal of volatiles under reduced pressure afforded [Ti{N(*t*Bu)C(O)N(-4-C_6H_4Me)}(Me_2calix)] (**13**) as a dark red solid (0.279 g, 94 %). Crystals suitable for X-ray analysis were grown from saturated solutions of **13** in toluene. ^{1}H NMR (C_6D_6, 500.1 MHz, 298 K): $\delta = 7.70$ (d, ^3J(H,H) = 7.5 Hz, 2H, *m*-C_6H_4Me), 7.27 (s, 2H, *m*-C_6H_2), 7.20 (s, 2H, *m*-C_6H_2), 6.95 (d, ^3J(H,H) = 7.5 Hz, 2H, *o*-C_6H_4Me), 6.83 (d, ^4J(H,H) = 2.5 Hz, 2H, *m*-C_6H_2), 6.78 (d, ^4J(H,H) = 2.5 Hz, 2H, *m*-C_6H_2), 4.45 (d, ^2J(H,H) = 13.5 Hz, 2H, CH_2), 4.19 (d, ^2J(H,H) = 13.5 Hz, 2H, CH_2), 3.72 (s, 6H, OMe), 3.37 (d, ^2J(H,H) = 13.5 Hz, 2H, CH_2), 3.18 (d, ^2J(H,H) = 13.5 Hz, 2H, CH_2), 2.11 (s, 3H, N-4-C_6H_4*Me*), 1.90 (s, 9H, $NCMe_3$), 1.45 (s, 9H, CMe_3), 1.41 (s, 9H, CMe_3), 0.67 (s, 18H, CMe_3); ^{13}C{^{1}H} NMR (C_6D_6, 125.7 MHz, 298 K): $\delta = 168.7$ (CO), 162.5 (C*q*-C_6H_2), 161.9 (C*q*-C_6H_2), 155.1 (C*q*-C_6H_2), 148.9 (C*q*-C_6H_2), 147.2 (*i*-C_6H_4Me), 142.7 (C*q*-C_6H_2), 142.6 (C*q*-C_6H_2), 132.0 (C*q*-C_6H_2), 131.6 (C*q*-C_6H_2), 131.5 (C*q*-C_6H_2), 131.3 (C*q*-C_6H_2), 131.0 (*p*-C_6H_4Me), 128.6 (*o*-C_6H_4Me), 127.5 (*m*-C_6H_2), 126.9 (*m*-C_6H_2), 124.8 (*m*-C_6H_2), 124.5 (*m*-C_6H_2), 122.7 (*m*-4-C_6H_4Me), 69.4 (OMe), 59.9 (N*C*Me_3), 34.7 (CH_2), 34.5 (CH_2), 34.4 (2 × overlapping *C*Me_3), 33.6 (*C*Me_3), 32.2 (NC*Me*$_3$), 32.1 (C*Me*$_3$), 32.0 (C*Me*$_3$), 30.5 (C*Me*$_3$), 20.9 (N-4-C_6H_4*Me*); EI MS (70 eV): *m*/*z* (%): 926 [*M*]$^+$ (11), 827 [*M* – *t*BuNCO]$^+$ (100), 812 [*M* – *t*BuNCO – Me]$^+$ (14), 793 [*M* – OCN-4-C_6H_4Me]$^+$ (2), 778 [*M* – OCN-4-C_6H_4Me – Me]$^+$ (8), 738 [*M* – *t*BuNCN-4-C_6H_4Me]$^+$ (22), 723 [*M* – *t*BuNCN-4-C_6H_4Me – Me]$^+$ (11), 707 [*M* – *t*BuN(O)CN-4-C_6H_4Me – Me]$^+$ (17), 413 [*M* – *t*BuNCO]$^{2+}$); IR (KBr plates): $\tilde{\nu} = 2962$ (vs br), 1701 (w), 1654 (w br), 1602 (w), 1546 (w br), 1514 (m br), 1480 (vs br), 1393 (w), 1362 (m), 1311 (vs br), 1274 (s br), 1209 (vs br), 1164 (s), 1121 (m), 1091 (w), 999 (m br), 937 (s br), 923 (m), 873 (s), 856 (s br), 810 (w br), 795 (s br), 753 (w), 729 (w), 695 (w br), 638 (w br), 561 (m br), 508 (w br), 465 (w), 449 cm^{-1} (w); elemental analysis calcd (%) for $C_{58}H_{74}N_2O_5Ti$: C 75.2, H 8.1, N 3.0; found: C 75.0, H 8.0, N 2.6.

[Ti(N-4-C_6H_4Me)(Me_2calix)] (14): A solution of freshly sublimed H_2N-4-C_6H_4Me (0.053 g, 0.32 mmol) in benzene (10 mL) was added to a solution of [Ti(N*t*Bu)(Me_2calix)] (**1**; 0.250 g, 0.32 mmol) in benzene (25 mL) at rt. The reaction mixture was stirred at 50 °C for 50 h to give an orange solution. Removal of volatiles under reduced pressure and washing with cold (–50 °C) pentane (2 × 5 mL) afforded [Ti(N-4-C_6H_4Me)(Me_2calix)] (**14**) as an orange solid (0.222 g, 84 %). ^{1}H NMR (C_6D_6, 500.1 MHz, 298 K): $\delta = 7.30$ (s, 4H, *m*-C_6H_2), 7.21 (d, ^3J(H,H) = 8.5 Hz, 2H, *m*-4-C_6H_4Me), 7.04 (d, ^3J(H,H) = 8.5 Hz, 2H, *o*-4-C_6H_4Me), 6.83 (s, 4H, *m*-C_6H_2), 4.65 (d, ^2J(H,H) = 12.5 Hz, 4H, CH_2), 4.18 (s, 6H, OMe), 3.28 (d, ^2J(H,H) = 12.5 Hz, 4H, CH_2), 2.20 (s, 3H, C_6H_4*Me*), 1.46 (s, 18H, C*Me*$_3$), 0.65 (s, 18H, C*Me*$_3$); ^{13}C{^{1}H} NMR (C_6D_6, 125.7 MHz, 298 K): $\delta = 160.1$ (C*q*-C_6H_2), 159.9 (*i*-4-C_6H_4Me), 150.4 (C*q*-C_6H_2), 149.2 (C*q*-C_6H_2), 140.8 (C*q*-C_6H_2), 132.7 (C*q*-C_6H_2), 130.0 (C*q*-C_6H_2), 129.3 (*o*-4-C_6H_4Me), 129.1 (*p*-4-C_6H_4Me), 127.0 (*m*-C_6H_2), 124.8 (*m*-C_6H_2), 123.6 (*m*-4-C_6H_4Me), 71.7 (OMe), 34.3 (*C*Me_3), 33.7 (*C*Me_3), 33.6 (CH_2), 32.2 (C*Me*$_3$), 30.6 (C*Me*$_3$), 21.0 (C_6H_4*Me*); EI MS (70 eV): *m*/*z* (%): 827 [*M*]$^+$ (55); IR (KBr plates, Nujol): $\tilde{\nu} = 1300$ (s), 1261 (m), 1210 (s), 1167 (w), 1122 (m), 1095 (w), 1011 (m), 939 (m), 924 (m), 872 (m), 850 (w), 797 (m), 770 (w), 723 (m), 569 cm^{-1} (m); elemental analysis calcd (%) for $C_{53}H_{65}NO_4Ti$: C 76.9, H 7.9, N 1.7; found: C 74.1, H 7.4, N 1.7.

[Ti(N-4-C_6H_4Fc)(Me_2calix)] (15): A solution of H_2N-4-C_6H_4Fc (0.089 g, 0.32 mmol) in benzene (10 mL) was added to a solution of [Ti(N*t*Bu)-(Me_2calix)] (**1**; 0.250 g, 0.32 mmol) in benzene (25 mL) at rt. The reaction mixture was stirred at 50 °C for 50 h to give a dark red solution. Removal of volatiles under reduced pressure and washing with cold (–50 °C) pentane (2 × 5 mL) afforded [Ti(N-4-C_6H_4Fc)(Me_2calix)] (**15**) as a red solid (0.258 g, 81 %). ^{1}H NMR (C_6D_6, 500.1 MHz, 298 K): $\delta = 7.45$ (d, ^3J(H,H) = 8.5 Hz, 2H, *m*-4-C_6H_4Fc), 7.31 (s, 4H, *m*-C_6H_2), 7.24 (d, ^3J(H,H) = 8.5 Hz, 2H, *o*-4-C_6H_4Fc), 6.84 (s, 4H, *m*-C_6H_2), 4.67 (d, ^2J(H,H) = 12.5 Hz, 4H, CH_2), 4.53 (app t, app *J*(H,H) = 2.0 Hz, 2H, C_5H_4), 4.20 (s, 6H, OMe), 4.12 (app t, app *J*(H,H) = 2.0 Hz, 2H, C_5H_4), 3.97 (s, 5H, C_5H_5), 3.29 (d, ^2J(H,H) = 12.5 Hz, 4H, CH_2), 1.46 (s, 18H, CMe_3), 0.66 (s, 18H, CMe_3); ^{13}C{^{1}H} NMR (C_6D_6, 125.7 MHz, 298 K): $\delta =$ 160.5 (*i*-4-C_6H_4Fc), 160.2 (C*q*-C_6H_2), 150.4 (C*q*-C_6H_2), 149.3 (C*q*-C_6H_2), 140.9 (C*q*-C_6H_2), 132.7 (C*q*-C_6H_2), 131.6 (*p*-4-C_6H_4Fc), 129.1 (C*q*-C_6H_2), 127.0 (*m*-C_6H_2), 126.5 (*o*-4-C_6H_4Fc), 124.8 (*m*-C_6H_2), 123.7 (*m*-4-C_6H_4Fc), 71.8 (OMe), 69.8 (C_5H_5), 68.9 (C_5H_4), 66.4 (C_5H_4), 34.3 (2 × overlapping *C*Me_3), 33.7 (CH_2), 32.2 (C*Me*$_3$), 30.6 (C*Me*$_3$); EI MS (70 eV): *m*/*z* (%): 997 [*M*]$^+$ (100); IR (KBr plates, Nujol): $\tilde{\nu} = 1620$ (w), 1320 (s), 1211 (s), 1168 (w), 1122 (m), 1106 (w), 1096 (w), 1003 (m), 976 (m), 941 (m), 923 (w), 872 (w), 860 (w), 834 (m), 817 (m), 796 (m), 568 (m), 533 (w), 509 cm^{-1} (w); elemental analysis calcd (%) for $C_{62}H_{71}NFeO_4Ti$: C 74.6, H 7.2, N 1.4; found: C 73.0, H 7.7, N 1.5.

[{Ti(Me_2calix)}$_2${μ-(N-4-C_6H_4)$_2$$CH_2$}] (16): A solution of $CH_2(4\text{-}C_6H_4NH_2)_2$ (0.032 g, 0.16 mmol) in benzene (5 mL) was added to a solution of [Ti(N*t*Bu)(Me_2calix)] (**1**; 0.250 g, 0.32 mmol) in benzene (25 mL) at rt. The reaction mixture was stirred at 50 °C for 50 h to give a dark red solution. Removal of volatiles under reduced pressure and washing with cold (–50 °C) pentane (2 × 5 mL) afforded [{Ti(Me_2calix)}$_2${μ-(C_6H_4)$_2$$CH_2$}] (**16**) as a red solid (0.229 g, 87 %). ^{1}H NMR (C_6D_6, 300.1 MHz, 298 K): $\delta = 7.26$ (s, 8H, *m*-C_6H_2), 7.13 (2 × overlapping d, ^3J(H,H) = 6.0 Hz, 8H, *o*-C_6H_4 and *m*-C_6H_4), 6.79 (s, 8H, *m*-C_6H_2), 4.62 (d, ^2J(H,H) = 12.3 Hz, 8H, CH_2), 4.13 (s, 12H, OMe), 3.88 (s, 2H, CH_2), 3.26 (d, ^2J(H,H) = 12.3 Hz, 8H, CH_2), 1.45 (s, 36H, CMe_3), 0.65 (s, 36H, CMe_3); ^{13}C{^{1}H} NMR (C_6D_6, 75.5 MHz, 298 K): $\delta = 160.1$ (C*q*-C_6H_2), 150.4 (C*q*-C_6H_2), 149.2 (C*q*-C_6H_2), 140.8 (C*q*-C_6H_2), 134.7 (*p*-C_6H_4), 132.7 (C*q*-C_6H_2), 129.3 (*o*-C_6H_4), 129.1 (C*q*-C_6H_2), 126.9 (*m*-C_6H_2), 124.7 (*m*-C_6H_2), 123.5 (*m*-C_6H_4), 71.8 (OMe), 41.2 (CH_2), 34.3 (*C*Me_3), 33.7 (2 × overlapping CH_2 and *C*Me_3), 32.2 (C*Me*$_3$), 30.6 (C*Me*$_3$), *i*-C_6H_4 resonance not observed; IR (KBr plates, Nujol): $\tilde{\nu} = 1598$ (m), 1310 (s), 1262 (w), 1208 (s), 1168 (w), 1120 (m), 1094 (w), 1006 (s), 940 (m), 920 (w), 870 (m), 796 (m), 758 (w), 566 cm^{-1} (m); elemental analysis calcd (%) for $C_{105}H_{126}N_2O_8Ti_2$: C 76.9, H 7.7, N 1.7; found: C 74.3, H 7.9, N 1.6.

[$TiCl_2$(Me_2calix)] from [Ti(N*t*Bu)(Me_2calix)] and HCl: HCl (1 M solution in Et_2O) (26.0 μL, 0.26 mmol) was added to a solution of [Ti(N*t*Bu)(Me_2calix)] (**1**; 0.100 g, 0.13 mmol) in benzene (10 mL) at 5 °C. The reaction mixture was stirred at rt for 5 min to give a red solution. Removal of volatiles under reduced pressure afforded [$TiCl_2$(Me_2calix)] (0.097 g, 97 %) which was characterised by comparison with an authentic sample.

[{Ti(μ-O)(Me_2calix)}$_2$] (11) from [Ti(N*t*Bu)(Me_2calix)] and H_2O: H_2O (1 M solution in Et_2O) (14.0 μL, 0.014 mmol) was added to a solution of [Ti(N*t*Bu)(Me_2calix)] (**1**; 0.010 g, 0.013 mmol) in C_6D_6 (0.5 mL) at rt. Reaction at rt for 10 min afforded [{Ti(μ-O)(Me_2calix)}$_2$] (**11**) and H_2N*t*Bu in ca. 90 % yield by ^{1}H NMR.

[{Ti(μ-S)(Me_2calix)}$_2$] (12) from [Ti(N*t*Bu)(Me_2calix)] (1) and H_2S: H_2S (1 atm) was added to a solution of [Ti(N*t*Bu)(Me_2calix)] (**1**; 0.200 g, 0.25 mmol) in benzene (20 mL) at 5 °C. The reaction mixture was stirred at rt for 30 min to give a red solution. Removal of volatiles under reduced pressure afforded [{Ti(μ-S)(Me_2calix)}$_2$] (**12**) as a red solid (0.168 g, 89 %).

[Ti(O-4-C_6H_4Me)$_2$(Me_2calix)] (17): A solution of HO-4-C_6H_4Me (0.069g, 0.64 mmol) in benzene (10 mL) was added dropwise to a solution of [Ti(N*t*Bu)(Me_2calix)] (**1**; 0.250 g, 0.31 mmol) in benzene (25 mL) at 5 °C. The reaction mixture was stirred at rt for 30 min. Removal of volatiles under reduced pressure and washing with cold (–50 °C) pentane (2 × 5 mL) afforded [Ti(O-4-C_6H_4Me)$_2$(Me_2calix)] (**17**) as a dark orange solid (0.204 g, 68 %). ^{1}H NMR (C_6D_6, 500.1 MHz, 298 K): $\delta = 7.30$ (s, 4H, *m*-C_6H_2), 7.16 (d, ^3J(H,H) = 8.0 Hz, 4H, 4-C_6H_4Me), 7.01 (d, ^3J(H,H) = 8.0 Hz, 4H, 4-C_6H_4Me), 6.93 (s, 4H, *m*-C_6H_2), 4.55 (d, ^2J(H,H) = 13.0 Hz, 4H, CH_2), 3.91 (s, 6H, OMe), 3.34 (d, ^2J(H,H) = 13.0 Hz, 4H, CH_2), 2.12 (s, 6H, 4-C_6H_4*Me*), 1.43 (s, 18H, CMe_3), 0.68 (s, 18H, CMe_3); ^{13}C{^{1}H} NMR (C_6D_6, 125.7 MHz, 298 K): $\delta = 165.6$ (*i*-4-C_6H_4Me), 164.3 (C*q*-C_6H_2), 156.5 (C*q*-C_6H_2), 148.9 (C*q*-C_6H_2), 141.3 (C*q*-C_6H_2), 131.8 (C*q*-C_6H_2), 129.8 (4-C_6H_4Me), 128.9 (C*q*-C_6H_2), 128.2 (*p*-4-C_6H_4Me), 126.7 (*m*-C_6H_2), 124.7 (*m*-C_6H_2), 119.2 (4-C_6H_4Me), 67.8 (OMe), 34.9 (CH_2), 34.2 (*C*Me_3), 33.7 (*C*Me_3), 32.0 (C*Me*$_3$), 30.6 (C*Me*$_3$), 20.7 (4-C_6H_4*Me*); EI MS (70 eV): *m*/*z* (%): 829 [*M* – O-4-C_6H_4Me]$^+$ (15), 814 [*M* – OTol-Me]$^+$ (100), 799 [*M* – OTol – 2Me]$^+$ (50); IR (KBr plates, Nujol): $\tilde{\nu} = 1504$ (s), 1253 (s), 1209 (m), 1167 (w), 1124 (w), 1100 (w), 1017 (m), 874 (m), 840 (w), 820 (m), 800 (m), 785 (w), 723 (m), 581 cm^{-1} (m); elemental analysis calcd (%) for $C_{60}H_{72}O_6Ti$: C 76.9, H 7.7; found: C 75.5, H 9.4.

[Ti(O-4-C_6H_4*t*Bu)$_2$(Me_2calix)] (18): A solution of HO-4-C_6H_4*t*Bu (189 mg, 1.26 mmol) in toluene (5 mL) was added at –50 °C to a solution of [Ti(N*t*Bu)(Me_2calix)] (**1**; 500 mg, 0.63 mmol) in toluene (15 mL). The yellow solution turned immediately red and was stirred while it was allowed to reach rt. Removal of volatiles under reduced pressure afforded [Ti(O-4-C_6H_4*t*Bu)$_2$(Me$_2$calix)]·2C_7H_8 (**18·2C_7H_8**) as an orange solid (462 mg, 61%). ^{1}H NMR (C_6D_6, 250 MHz, 298 K): $\delta = 7.31$ (s, 4H, *m*-C_6H_2), 7.24 (d, ^3J(H,H) = 7.5 Hz, 4H, 4-C_6H_4*t*Bu), 7.11 (d, ^3J(H,H) = 7.5 Hz, 4H, 4-C_6H_4*t*Bu), 6.93 (s, 4H, *m*-C_6H_2), 4.58 (d, ^2J(H,H) = 13.0 Hz, 4H, CH_2), 3.94 (s, 6H, OMe), 3.37 (d, ^2J(H,H) = 13.0 Hz, 4H, CH_2), 1.47 (s, 18H, CMe$_3$), 1.26 (s, 18H, CMe$_3$), 0.73 (s, 18H, CMe$_3$); ^{13}C{^{1}H} NMR (C_6D_6, 62.9 MHz, 298 K): $\delta = 165.6$ (*i*-4-C_6H_4*t*Bu), 164.4 (C*q*-C_6H_2), 149.1 (C*q*-C_6H_2), 142.4 (C*q*-C_6H_2), 141.4 (C*q*-C_6H_2), 132.1 (C*q*-C_6H_2), 129.0 (C*q*-C_6H_2), 128.7 (*p*-4-C_6H_4*t*Bu), 126.8 (4-C_6H_4*t*Bu), 126.2 (C*m*-C_6H_2), 124.8 (C*m*-C_6H_2), 119.1 (4-C_6H_4*t*Bu), 67.9 (OMe), 35.1 (CH_2), 34.4 (*C*Me$_3$), 34.2 (4-C_6H_4*C*Me$_3$), 33.8 (*C*Me$_3$), 32.1 (C*Me*$_3$), 31.8 (C*Me*$_3$), 30.7 (4-C_6H_4C*Me*$_3$); ^{1}H NMR ($CDCl_3$, 250 MHz, 298 K): $\delta = 7.06$ (d, ^3J(H,H) = 8.7 Hz, 4H, 4-C_6H_4*t*Bu), 7.05 (s, 4H, *m*-C_6H_2), 6.94 (s, 4H, *m*-C_6H_2), 6.72 (d, ^3J(H,H) = 8.7 Hz, 4H, 4-C_6H_4*t*Bu), 4.34 (d, ^2J(H,H) = 13.4 Hz, 4H, CH_2), 4.31 (s, 6H, OMe), 3.32 (d, ^2J(H,H) = 13.4 Hz, 4H, CH_2), 1.33 (s, 18H, CMe$_3$), 1.24 (s, 18H, CMe$_3$), 1.09 (s, 18H, CMe$_3$); EI MS (70 eV): *m*/*z* (%): 1021 [*M*]$^+$ (2), 872 [*M* – O-4-C_6H_4*t*Bu]$^+$ (98), 871 [*M* – O-4-C_6H_4*t*Bu-H]$^+$ (98), 857 [*M* – O-4-C_6H_4*t*Bu-Me]$^+$ (15), 856 [*M* – O-4-C_6H_4*t*Bu-Me-H]$^+$ (23), 842 [*M* – O-4-C_6H_4*t*Bu-2Me]$^+$ (9), 841 [*M* – O-4-C_6H_4*t*Bu – 2Me – H]$^+$ (14), 428 [*M* – O-4-C_6H_4*t*Bu – Me – H]$^{2+}$ (7), 150 [*t*BuPhOH]$^+$ (42), 135 [*t*BuPhOH – Me]$^+$ (100); IR (KBr plates): $\tilde{\nu} = 3050$ (w), 2969 (vs br), 1601 (w), 1506 (vs), 1481 (vs br), 1413 (w), 1362 (m), 1318 (s br), 1249 (vs br), 1211 (vs br), 1174 (s), 1122 (m), 1091 (m), 994 (m br), 945 (w br), 873 (s br), 856 (s), 835 (s), 796 (s br), 752 (w), 730 (m), 707 (m br), 695 (w), 564 (s br), 465 (w), 436 cm^{-1} w (br); elemental analysis calcd (%) for $C_{80}H_{100}O_6Ti$: C 79.6, H 8.6; found: C 79.3, H 8.5.

[Ti(O-2,6-$C_6H_3Me_2$)$_2$(Me$_2$calix)] (19): A solution of HO-2,6-$C_6H_3Me_2$ (0.058 g, 0.478 mmol) in benzene (5 mL) was added dropwise to a benzene solution (10 mL) of [Ti(N*t*Bu)(Me$_2$calix)] (**1**; 0.200 g, 252 mmol) at 5°C. The reaction mixture was stirred for 5 min during which time the reaction mixture changed from orange to dark orange. Removal of volatiles under reduced pressure and washing with pentane (5 mL) afforded [Ti(O-2,6-$C_6H_3Me_2$)$_2$(Me$_2$Calix)] (**19**) as an orange solid (0.090 g, 37%). ^{1}H NMR (C_6D_6, 300.1 MHz, 298 K): $\delta = 7.19$ (s, 4H, *m*-C_6H_2), 6.80 (d, ^3J(H,H) = 7.5 Hz, 4H, *m*-2,6-$C_6H_3Me_2$), 6.70 (s, 4H, *m*-C_6H_2), 6.60 (t, ^3J(H,H) = 7.5 Hz, 2H, *p*-2,6-$C_6H_3Me_2$), 4.88 (d, ^2J(H,H) = 13.2 Hz, 4H, CH_2), 3.36 (s, 6H, OMe), 3.28 (d, ^2J(H,H) = 13.2 Hz, 4H, CH_2), 2.49 (s, 12H, 2,6-C_6H_3*Me*$_2$), 1.42 (s, 18H, CMe$_3$), 1.04 (s, 18H, CMe$_3$); ^{13}C{^{1}H} NMR (C_6D_6, 75.5 MHz, 298 K): $\delta = 165.6$ (*o*-2,6-$C_6H_3Me_2$), 162.7 (*i*-C_6H_2), 154.6 (*i*-C_6H_2), 146.4 (*p*-C_6H_2), 143.0 (*p*-C_6H_2), 133.1 (*o*-C_6H_2), 132.1 (*o*-C_6H_2), 128.0 (*m*-2,6-$C_6H_3Me_2$), 126.5 (*m*-C_6H_2), 126.2 (*i*-2,6-$C_6H_3Me_2$), 124.9 (*m*-C_6H_2), 120.7 (*p*-2,6-$C_6H_3Me_2$), 64.0 (OMe), 34.5 (*C*Me$_3$), 34.4 (*C*Me$_3$), 33.2 (CH_2), 32.2 (C*Me*$_3$), 31.8 (C*Me*$_3$), 18.1 (2,6-C_6H_3*Me*$_2$); EI MS (70 eV): *m*/*z* (%): 828 [*M* – {O-4-C_6H_4Me} – 2Me]$^+$ (100); IR (KBr plates, Nujol): $\tilde{\nu} = 1304$ (w), 1262 (s), 1232 (w), 1210 (s), 1122 (m), 1096 (m), 1020 (m), 994 (w), 940 (m), 920 (w), 898 (w), 878 (w), 858 (w), 796 (m), 760 (m), 730 (m), 570 cm^{-1} (m); elemental analysis calcd (%) for $C_{62}H_{76}O_6Ti$: C 76.9, H 7.7; found: C 74.8, H 7.7.

[Ti{2,2′-(O-4,6-C_6H_2Me*t*Bu)$_2$CH$_2$}(Me$_2$calix)] (20): To a cooled (–50°C) solution of [Ti(N*t*Bu)(Me$_2$calix)] (**1**; 500 mg, 0.63 mmol) in toluene (15 mL) an equally cooled solution of 2,2′-(HO-4,6-C_6H_2Me*t*Bu)$_2$CH$_2$ (214 mg, 0.63 mmol) was added. The yellow solution immediately turned dark brown and was stirred while it was allowed to reach rt. All volatiles were removed under reduced pressure, and the brown precipitate suspended in hexane (5 mL), filtered and washed with hexane (2 mL). Drying of the residue in vacuo afforded [Ti{2,2′-(O-4,6-C_6H_2Me*t*Bu)$_2$CH$_2$}(Me$_2$calix)] (**20**) as a brown powder (258 mg, 39%). ^{1}H NMR (C_6D_6, 250 MHz, 298 K): $\delta = 7.18$ (s, 4H, *m*-C_6H_2), 6.98 (d, ^4J(H,H) = 1.9 H, 2Hz, *m*-{2,2′-(O-4,6-C_6H_2Me*t*Bu)$_2$CH$_2$}), 6.73 (d, ^4J(H,H) = 1.9 Hz, 2H, *m*-{2,2′-(O-4,6-C_6H_2Me*t*Bu)$_2$CH$_2$}), 6.68 (s, 4H, *m*-C_6H_2), 5.32 (d, ^2J(H,H) = 13.9 Hz, 1H, {2,2′-(O-4,6-C_6H_2Me*t*Bu)$_2$C*H*$_2$}), 4.81 (d, ^2J(H,H) = 13.4 Hz, 4H, CH_2), 3.56 (s, 6H, OMe), 3.26 (d, ^2J(H,H) = 13.5 Hz, 4H, C*H*$_2$) underneath: (d, ^2J(H,H) = 13.9 Hz, 1H, {2,2′-(O-4,6-C_6H_2Me*t*Bu)$_2$C*H*$_2$}), 2.06 (s, 6H, {2,2′-(O-4,6-C_6H_2*Met*Bu)$_2$CH$_2$}), 1.64 (s, 18H, {2,2′-(O-4,6-C_6H_2Me*tBu*)$_2$CH$_2$}), 1.40 (s, 18H, CMe$_3$), 1.00 (s, 18H, CMe$_3$); ^{13}C{^{1}H} NMR (C_6D_6, 62.9 MHz, 298 K): $\delta = 163.6$ (C*q*-C_6H_2), 161.4 (C*q*-C_6H_2), 155.4 (C*q*-{2,2′-(O-4,6-C_6H_2Me*t*Bu)$_2$CH$_2$}), 146.5 (C*q*-C_6H_2), 143.1 (C*q*-C_6H_2), 138.8 (C*q*-{2,2′-(O-4,6-C_6H_2Me*t*Bu)$_2$CH$_2$}), 135.3 (C*q*-{2,2′-(O-4,6-C_6H_2Me*t*Bu)$_2$CH$_2$}), 132.9 (C*q*-C_6H_2), 131.8 (C_q-C_6H_2), 129.1 (C*q*-{2,2′-(O-4,6-C_6H_2Me*t*Bu)$_2$CH$_2$}), 128.1 (C*m*-{2,2′-(O-4,6-C_6H_2Me*t*Bu)$_2$CH$_2$}), 127.3 (C*m*-{2,2′-(O-4,6-C_6H_2Me*t*Bu)$_2$CH$_2$}), 126.3 (C*m*-C_6H_2), 125.1 (C*m*-C_6H_2), 65.4 (OMe), 37.6 ({2,2′-(O-4,6-C_6H_2Me*t*Bu)$_2$*C*H$_2$}), 36.1 ({2,2′-(O-4,6-C_6H_2Me*C*(CH$_3$)$_3$)$_2$CH$_2$}), 34.1 (*C*Me$_3$), 33.3 (CH_2), 32.7 (C*Me*$_3$), 31.8 ({2,2′-(O-4,6-C_6H_2MeC(*C*H$_3$)$_3$)$_2$CH$_2$}), 31.5 (C*Me*$_3$), 21.0 ({2,2′-(O-4,6-C_6H_2*Met*Bu)$_2$CH$_2$}); EI MS (70 eV): *m*/*z* (%): 1061 [*M*]$^+$ (9), 724 [*M* – {2,2′-(O-4,6-C_6H_2MetBu)$_2$CH$_2$}+H]$^+$ (100); IR (KBr plates): $\tilde{\nu} = 2956$ (vs br), 1759 (w br), 1600 (w br), 1482 (s), 1466 (s br), 1437 (s), 1392 (w), 1362 (w), 1300 (m), 1247 (vs), 1204 (vs br), 1144 (w), 1122 (s), 1014 (w), 990 (w), 939 (w), 873 (m), 857 (s), 836 (m br), 794 (m), 753 (w), 727 (w), 613 (w), 592 (w), 571 (m), 428 cm^{-1} (w br).

[Zr(O-4-C_6H_4Me)$_2$(Me$_2$calix)] (21): A solution of HO-4-C_6H_4Me (0.057 g, 0.53 mmol) in benzene (25 mL) was added at rt to a solution of [Zr(N-2,6-C_6H_3*i*Pr$_2$)(Me$_2$calix)] (**8**; 0.250 g, 0.27 mmol) in benzene (5 mL). The colourless solution was stirred at 25°C for 2 h. Volatiles were removed under reduced pressure to leave an oily solid, shown by ^{1}H NMR spectroscopy to be a mixture of [Zr(O-4-C_6H_4Me)$_2$(Me$_2$calix)] (**21**) and the side-product 2,6-diisopropylaniline. All attempts to separate the two products proved unsuccessful and so **21** was characterised by NMR spectroscopy only. ^{1}H NMR (C_6D_6, 300.1 MHz, 298 K): $\delta = 7.30$ (s, 4H, *m*-C_6H_2), 7.10 (d, ^3J(H,H) = 7.8 Hz, 4H, C_6*H*$_4$Me), 7.06 (d, ^3J(H,H) = 7.8 Hz, 4H, C_6*H*$_4$Me), 6.86 (s, 4H, *m*-C_6H_2), 4.47 (d, ^2J(H,H) = 12.6 Hz, 4H, CH_2), 3.76 (s, 6H, OMe), 3.29 (d, ^2J(H,H) = 12.6 Hz, 4H, CH_2), 2.16 (s, 6H, C_6H_4*Me*), 1.48 (s, 18H, CMe$_3$), 0.70 (s, 18H, CMe$_3$); ^{13}C{^{1}H} NMR (C_6D_6, 75.5 MHz, 298 K): $\delta = 161.8$ (C*q*$_)$, 159.0 (C*q*), 154.0 (C*q*), 148.9 (C*q*), 140.7 (C*q*), 131.7 (C*q*), 130.1 (C*q*), 129.4 (*o*/*m* C_6H_4Me), 127.1 (*m*-C_6H_2), 124.7 (*m*-C_6H_2), 119.7 (*o*/*m*-C_6H_4Me), 67.9 (OMe), 34.2 (*C*Me$_3$), 33.9 (*C*Me$_3$), 33.6 (CH_2), 32.1 (C*Me*$_3$), 30.5 (C*Me*$_3$), 20.7 (C_6H_4*Me*), one C*q* resonance is missing from the spectrum, due either to the resonance being hidden under the solvent peak or being be too weak to be observed.

[Zr(O-2,6-$C_6H_3Me_2$)$_2$(Me$_2$calix)] (22): A solution of HO-2,6-$C_6H_3Me_2$ (0.064 g, 0.52 mmol) in benzene (25 mL) was added at rt to a solution of [Zr(N-2,6-C_6H_3*i*Pr$_2$)(Me$_2$calix)] (**8**; 0.246 g, 0.26 mmol) in benzene (5 mL). After 5 min, **22** formed as a white precipitate and the reaction mixture was stirred at 25°C for 2 h. After filtration, the solid was washed with benzene (2 × 10 mL) and the volatiles were removed under reduced pressure (0.169 g, 64%). A crystalline sample could be obtained from a saturated CH_2Cl_2 solution. ^{1}H NMR (CD_2Cl_2, 500.0 MHz, 298 K): $\delta = 7.13$ (s, 4H, *m*-C_6H_2), 7.06 (s, 4H, *m*-C_6H_2), 6.89 (d, ^3J(H,H) = 7.5 Hz, 4H, *m*-C_6*H*$_3$Me$_2$), 6.59 (t, ^3J(H,H) = 7.5 Hz, 2H, *p*-C_6*H*$_3$Me$_2$), 4.40 (d, ^2J(H,H) = 12.5 Hz, 4H, CH_2), 4.21 (s, 6H, OMe), 3.35 (d, ^2J(H,H) = 12.5 Hz, 4H, CH_2), 2.10 (s, 12H, C_6H_3*Me*$_2$), 1.30 (s, 18H, CMe$_3$), 1.15 (s, 18H, CMe$_3$); ^{13}C{^{1}H} NMR (CD_2Cl_2, 75.5 MHz, 298 K): $\delta = 160.8$ (C*q*), 158.0 (C*q*), 154.0 (C*q*), 149.3 (C*q*), 142.0 (C*q*), 131.9 (C*q*), 129.6 (C*q*), 128.4 (*m*-*C*$_6$H$_3$Me$_2$), 127.3 (*m*-C_6H_2 of Me$_2$calix), 126.8 (C_q), 125.1 (*m*- C_6H_2), 118.3 (*p*-*C*$_6$H$_3$Me$_2$), 68.9 (OMe), 34.5 (*C*Me$_3$), 34.2 (*C*Me$_3$), 33.5 (CH_2), 31.8 (C*Me*$_3$), 31.2 (C*Me*$_3$), 17.2 (C_6H_3*Me*$_2$); EI MS (70 eV): *m*/*z* (%): 1008 [*M*]$^+$ (5), 885 [*M* – ($OC_6H_3Me_2$)]$^+$ (12), 122 [$OC_6H_3Me_2$]$^+$ (100); IR (KBr plates, Nujol): $\tilde{\nu} = 1592$ (m), 1462 (s), 1300 (m), 1272 (s), 1231 (m), 1214 (s), 1164 (w), 1124 (m), 1093 (m), 1052 (w), 1024 (w), 995 (m), 984 (w), 943 (w), 923 (w), 892 (m), 882 (m), 872 (m), 851 (s), 813 (w), 800 (w), 789 (m), 761 (m), 737 (w), 674 (w), 641 (w), 548 (m), 503 (w), 488 (w), 432 (w), 404 cm^{-1} (m); elemental analysis calcd (%) for $C_{62}H_{76}O_6Zr \times 0.25\,CH_2Cl_2$: C 72.8, H 7.4; found: C 72.6, H 7.1.

[{Ti(O-4-C_6H_4Me)(Mecalix)}$_2$] (23): A solution of HO-4-C_6H_4Me (0.136 g, 1.260 mmol) in benzene (10 mL) was added dropwise to a benzene solution (20 mL) of [Ti(N*t*Bu)(Me$_2$calix)] (**1**; 0.500 g, 0.630 mmol) at 5°C. The reaction mixture was warmed to room temperature and stirred for 30 min during which time the reaction mixture changed its colour from orange to dark orange. Removal of volatiles under reduced pressure afforded a dark orange solid. The solid was dissolved in hexane and stood at –30°C for 5 d. After 5 d a small amount of precipitate had formed and the reaction mixture was filtered to afforded [{Ti(O-4-C_6H_4Me)(Mecalix)}$_2$] (**23**) as a dark orange solid (0.050 g, 9%). As this complex could only be isolated in very small quantities it was characterised only by ^{1}H NMR spectroscopy. ^{1}H NMR (C_6D_6, 300.1 MHz, 298 K): $\delta = 7.50$–6.70 (overlapping multiplets, 24H, *m*-C_6H_2, *o*-4-C_6H_4Me and *m*-4-C_6H_4Me), 5.04 (d, ^2J(H,H) = 13.5 Hz, 4H, CH_2), 4.34 (d, ^2J(H,H) = 12.5 Hz, 4H, CH_2), 3.67 (s, 6H, OMe), 3.28 (d, ^2J(H,H) = 12.5 Hz, 4H, CH_2), 3.18 (d, ^2J(H,H) = 13.5 Hz, 4H, CH_2), 2.14 (s, 6H, 4-C_6H_4*Me*), 1.41 (s, 36H, CMe$_3$), 0.82 (s, 18H, CMe$_3$), 0.72 (s, 18H, CMe$_3$).

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[{Ti(O-4-C$_6$H$_4t$Bu)(Mecalix)}$_2$] (24): An orange solution of 462 mg (0.383 mmol) [Ti(O-4-C$_6$H$_4t$Bu)$_2$(Me$_2$calix)]·2(C$_7$H$_8$) (**18·2C$_7$H$_8$**) in hexane (15 mL) was stirred for 48 h at room temperature. During that time [{Ti(O-4-C$_6$H$_4t$Bu)(Mecalix)}$_2$] (**24**; 112 mg, 0.131 mmol, 34 %) forms as a dark orange precipitate which was filtered off and dried in vacuo. Crystals of **24**, suitable for X-ray analysis, were grown from saturated toluene solutions of the compound at rt. ^{1}H NMR (CDCl$_3$, 250 MHz, 298 K): δ = 7.29 – 6.75 (m, 12 H, aromatic H), 4.73 (d, ^2J(H,H) = 12.7 Hz, 2 H, CH$_2$), 4.34 (d, ^2J(H,H) = 12.4 Hz, 2 H, CH$_2$), 4.10 (s, 3 H, OMe), 3.32 (d, ^2J(H,H) = 12.4 Hz, 4 H, CH$_2$), 3.31 (d, ^2J(H,H) = 12.7 Hz, 4 H, CH$_2$), 1.31 (s, 9 H, CMe$_3$), 1.25 (s, 18 H, CMe$_3$), 1.18 (s, 9 H, CMe$_3$), 1.17 (s, 9 H, CMe$_3$); ^{13}C{^{1}H} NMR (C$_6$D$_6$, 62.9 MHz, 298 K): δ = 160.5 (C*q*), 158.7 (C*q*), 151.2 (C*q*), 148.6 (C*q*), 144.8 (C*q*), 144.5 (C*q*), 132.5 (C*q*), 130.1 (C*q*), 129.5 (C*o*), 126.9 (C*q*), 127.2 (C*m*), 126.3 (C*m*), 124.9 (C*m*), 123.7 (C*m*), 65.5 (OMe), 34.2 (*C*Me$_3$), 33.6 (*C*H$_2$), 33.4 (*C*H$_2$), 31.7 (C*Me*$_3$), 31.56 (C*Me*$_3$), 31.4 (C*Me*$_3$), 31.2 (C*Me*$_3$); EI MS (70 eV): *m*/*z* (%): 856 [*M*]$^+$ (100), 841 [*M* – Me]$^+$ (60), 428 [*M*]$^+$ (2), 421 [*M* – Me]$^+$ (5), 413 [*M* – 2 Me]$^+$ (37), 150 [HO-4-C$_6$H$_4t$Bu]$^+$ (2), 135 [HO-4-C$_6$H$_4t$Bu – Me]$^+$ (9); IR (KBr plates): $\tilde{\nu}$ = 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 cm^{-1} (s br); elemental analysis calcd (%) for C$_{110}$H$_{136}$O$_{10}$Ti$_2$: C 78.0, H 8.1; found: C 78.5, H 8.1.

[Ti(O-4-C$_6$H$_4$Me)$_2$(*paco*-Me$_2$calix)] (25): A solution of HO-4-C$_6$H$_4$Me (0.136 g, 1.260 mmol) in benzene (10 mL) was added dropwise to a benzene solution (20 mL) of [Ti(N*t*Bu)(Me$_2$calix)] (**1**; 0.500 g, 0.630 mmol) at 5 °C. The reaction mixture was warmed to room temperature and stirred for 30 min during which time the reaction mixture changed its colour from orange to dark orange. Removal of volatiles under reduced pressure afforded a dark orange solid. The solid was dissolved in pentane and stood at 5 °C for 12 h. After 12 h a precipitate had formed and the reaction mixture was filtered, the solid washed with cold pentane (5 mL, – 50 °C). Removal of volatiles under reduced pressure afforded [Ti(O-4-C$_6$H$_4$Me)$_2$-(*paco*-Me$_2$calix)] (**25**) as a dark orange solid (0.449 g, 76 %). Crystals suitable for X-ray diffraction were grown from a saturated pentane solution at 5 °C. ^{1}H NMR (C$_6$D$_6$, 500.1 MHz, 298 K): δ = 7.51 (d, ^3J(H,H) = 8.5 Hz, 2 H, *o*-4-C$_6$H$_4$Me), 7.24 (d, ^4J(H,H) = 3.0 Hz, 2 H, *m*-C$_6$H$_2$), 7.19 (d, ^4J(H,H) = 3.0 Hz, 2 H, *m*-C$_6$H$_2$), 7.18 (s, 2 H, *m*-C$_6$H$_2$), 7.06 (s, 2 H, *m*-C$_6$H$_2$), 6.97 (d, ^3J(H,H) = 8.5 Hz, 2 H, *m*-4-C$_6$H$_4$Me), 6.73 (d, ^3J(H,H) = 8.5 Hz, 2 H, *m*-4-C$_6$H$_4$Me), 6.40 (d, ^3J(H,H) = 8.5 Hz, 2 H, *o*-4-C$_6$H$_4$Me), 4.77 (d, ^2J(H,H) = 12.0 Hz, 2 H, CH$_2$), 4.71 (d, ^2J(H,H) = 14.5 Hz, 2 H, CH$_2$), 4.10 (s, 3 H, *exo*-OMe), 3.39 (d, ^2J(H,H) = 14.5 Hz, 2 H, CH$_2$), 3.30 (d, ^2J(H,H) = 12.0 Hz, 2 H, CH$_2$), 2.00 (s, 3 H, 4-C$_6$H$_4$*Me*), 1.90 (s, 3 H, 4-C$_6$H$_4$*Me*), 1.20 (s, 9 H, CMe$_3$), 1.19 (s, 18 H, CMe$_3$), 1.03 (s, 9 H, CMe$_3$), 0.92 (s, 3 H, *endo*-OMe); ^{13}C{^{1}H} NMR (C$_6$D$_6$, 75.5 MHz, 298 K): δ = 164.3 (*i*-4-C$_6$H$_4$Me), 163.4 (*i*-4-C$_6$H$_4$Me), 162.0 (C*q*-C$_6$H$_2$), 159.1 (C*q*-C$_6$H$_2$), 149.7 (C*q*-C$_6$H$_2$), 149.3 (C*q*-C$_6$H$_2$), 148.2 (C*q*-C$_6$H$_2$), 143.8 (C*q*-C$_6$H$_2$), 134.6 (C*q*-C$_6$H$_2$), 134.3 (C*q*-C$_6$H$_2$), 130.4 (*m*-4-C$_6$H$_4$Me), 129.9 (*m*-4-C$_6$H$_4$Me), 129.7 (C$_q$-C$_6$H$_2$), 129.2 (*p*-4-C$_6$H$_4$Me), 128.6 (*p*-4-C$_6$H$_4$Me), 127.0 (C$_6$H$_2$), 126.1 (C$_6$H$_2$), 125.8 (C$_6$H$_2$), 124.7 (C$_6$H$_2$), 118.8 (*o*-4-C$_6$H$_4$Me), 118.7 (*o*-4-C$_6$H$_4$Me), 66.4 (*exo*-OMe), 64.2 (*endo*-OMe), 37.5 (CH$_2$), 34.7 (*C*Me$_3$), 34.6 (*C*Me$_3$), 34.4 (*C*Me$_3$), 32.9 (CH$_2$), 32.1 (C*Me*$_3$), 32.0 (C*Me*$_3$), 31.6 (C*Me*$_3$), 21.1 (4-C$_6$H$_4$*Me*), 21.0 (4-C$_6$H$_4$*Me*); EI MS (70 eV): *m*/*z* (%): 830 [*M* – {O-4-C$_6$H$_4$Me}]$^+$ (50); IR (KBr plates, Nujol): $\tilde{\nu}$ = 1504 (m), 1278 (w), 1254 (s), 1206 (m), 1124 (w), 1114 (w), 1004 (w), 890 (m), 876 (m), 838 (m), 816 (w), 798 (m), 576 cm^{-1} (m); elemental analysis calcd (%) for C$_{60}$H$_{72}$O$_6$Ti: C 76.9, H 7.7; found: C 76.2, H 8.2.

[Ti(O-4-C$_6$H$_4t$Bu)$_2$(*paco*-Me$_2$calix)] (26): A solution of [Ti(O-4-C$_6$H$_4t$Bu)$_2$(Me$_2$calix)]·(2 C$_7$H$_8$) (**18·2 C$_7$H$_8$**) (462 mg, 0.383 mmol) in hexane (15 mL) was stirred for 48 h and all unsoluble material was filtered off. According to NMR spectroscopy, there is exclusively [Ti(O-4-C$_6$H$_4t$Bu)$_2$-(*paco*-Me$_2$calix)] (**26**) in solution. From this solution **26** can be precipitated after two days at – 40 °C as a yellow microcrystalline powder. The precipitate was isolated and dried in vacuo (130 mg, 0.127 mmol, 33 %). A crystalline sample was obtained from a saturated hexane solution at – 30 °C. ^{1}H NMR (CDCl$_3$, 250 MHz, 298 K): δ = 7.22 (d, ^3J(H,H) = 2.6 Hz, 2 H, 4-C$_6$H$_4t$Bu), 7.15 (s, 6 H, *m*-C$_6$H$_2$), 7.05 (d, ^3J(H,H) = 2.6 Hz, 2 H, 4-C$_6$H$_4t$Bu), 6.99 (s, 2 H, *m*-C$_6$H$_2$), 6.78 (d, ^3J(H,H) = 8.7 Hz, 2 H, 4-C$_6$H$_4t$Bu), 5.89 (d, ^3J(H,H) = 8.7 Hz, 2 H, 4-C$_6$H$_4t$Bu), 4.67 (d, ^2J(H,H) = 12.0 Hz, 2 H, CH$_2$), 4.30 (s, 3 H, *exo*-OMe), 4.30 (d, ^2J(H,H) = 14.6 Hz, 2 H, CH$_2$), 3.45 (d, ^2J(H,H) = 12.0 Hz, 2 H, CH$_2$), 3.30 (d, ^2J(H,H) = 14.6 Hz, 2 H, CH$_2$), 1.33 (s, 9 H, CMe$_3$), 1.24 (s, 9 H, CMe$_3$), 1.23 (s, 18 H, CMe$_3$), 1.14 (s, 9 H, CMe$_3$), 1.07 (s, 9 H, CMe$_3$), 0.82 (s, 3 H, *endo*-OMe); ^{13}C{^{1}H} NMR (C$_6$D$_6$, 62.9 MHz, 298 K): δ = 163.58, 162.96, 161.43, 158.44, 149.43, 149.33, 147.92, 143.79, 142.89, 142.57, 134.10, 133.82, 129.96, 128.02, 126.70, 125.84, 125.55, 124.63, 124.39, 117.76, 117.60 (all aryl-C), 66.31 (OMe), 63.61 (OMe), 36.60 (CH$_2$), 34.32 (*C*Me$_3$), 34.24 (*C*Me$_3$), 34.06 (*C*Me$_3$), 33.97 (*C*Me$_3$), 33.89 (C*Me*$_3$), 32.37 (CH$_2$), 31.62 (C*Me*$_3$), 31.47 (C*Me*$_3$), 31.13 (C*Me*$_3$); EI MS (70 eV): *m*/*z* (%): 1021 [*M*]$^+$ 1 %, 871 [*M* – (HO-4-C$_6$H$_4t$Bu)]$^+$ (100); IR (KBr plates): $\tilde{\nu}$ = 2966 (vs br), 2866 (m br), 1601 (w), 1505 (s), 1483 (s), 1455 (s), 1433 (w), 1393 (w), 1362 (m), 1282 (m), 1249 (vs br), 1217 (s), 1203 (s), 1176 (s), 1125 (m), 1110 (m), 992 (w br), 941 (w), 914 (w), 883 (m), 870 (s), 836 (vs), 798 (s), 770 (w), 707 (s), 684 (w), 641 (w), 597 (w), 565 (m br), 481 (w), 446 cm^{-1} (w br); elemental analysis calcd (%) for C$_{66}$H$_{84}$O$_{10}$Ti: C 77.6, H 8.3; found: C 77.2, H 8.5.

Crystal structure determination of [Ti(N*t*Bu)(Me$_2$calix)]·2(C$_6$H$_6$) [(1·2(C$_6$H$_6$)], [Ti(N*t*Bu)(Me$_2$calix)]·2(C$_7$H$_8$) [1·2(C$_7$H$_8$)], [Ti{N(*t*Bu)-C(O)N(-4-C$_6$H$_4$Me)}(Me$_2$calix)]·4(C$_7$H$_8$) [13·4(C$_7$H$_8$)], [Zr(O-2,6-C$_6$H$_3$Me$_2$)(Me$_2$calix)]·4(CH$_2$Cl$_2$) [22·4(CH$_2$Cl$_2$)], [{Ti(O-4-C$_6$H$_4t$Bu)(Mecalix)}$_2$]·C$_7$H$_8$ [24·C$_7$H$_8$], [Ti(O-4-C$_6$H$_4$Me)$_2$(*paco*-Me$_2$calix)] (25), and [Ti(O-4-C$_6$H$_4t$Bu)$_2$(*paco*-Me$_2$calix)]·0.5(C$_6$H$_{14}$) [26·0.5(C$_6$H$_{14}$)]: CCDC-199162 – 199168 contain the supplementary crystallographic data for this

Table 2. X-ray data collection and processing parameters.

	1·2(C$_6$H$_6$)	**1·2(C$_7$H$_8$)**	**13·4(C$_7$H$_8$)**	**22·4(CH$_2$Cl$_2$)**	**24·C$_7$H$_8$**	**25**	**26·0.5(C$_6$H$_{14}$)**
formula	C$_{50}$H$_{67}$NO$_4$Ti ·2(C$_6$H$_6$)	C$_{50}$H$_{67}$NO$_4$Ti ·2(C$_7$H$_8$)	C$_{58}$H$_{74}$N$_2$O$_5$Ti ·4(C$_7$H$_8$)	C$_{62}$H$_{76}$O$_6$Zr ·4(CH$_2$Cl$_2$)	C$_{55}$H$_{68}$O$_5$Ti ·C$_7$H$_8$	C$_{60}$H$_{72}$O$_6$Ti	C$_{66}$H$_{84}$O$_6$Ti ·0.5(C$_6$H$_{14}$)
formula weight	950.22	978.21	1298.65	1064.61	949.13	937.13	1064.32
crystal system	triclinic	triclinic	triclinic	triclinic	monoclinic	monoclinic	triclinic
space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P2_1/c$	$P2_1/c$	$P\bar{1}$
a/Å	12.8070(5)	12.909(3)	14.878(3)	12.8950(2)	13.007(3)	13.6988(2)	11.211(2)
b/Å	13.0250(5)	13.605(3)	14.985(3)	14.9659(3)	22.203(4)	24.5242(4)	16.824(3)
c/Å	19.6460(5)	19.051(4)	19.712(4)	17.5771(3)	19.062(4)	16.7938(4)	17.308(4)
α/°	76.092(2)	74.38(3)	101.14(3)	94.052(1)			104.57(3)
β/°	72.872(2)	78.41(3)	90.65(3)	94.440(1)	94.19(3)	113.6156(6)	100.83(3)
γ/°	63.787(2)	63.03(3)	115.96(2)	90.2792(9)			90.14(3)
V/Å^3	2786.4	2860.6	3854.2(14)	3373.3(1)	5520.0(19)	5131.7(2)	3099.0(11)
Z	2	2	2	2	4	4	2
μ/mm^{-1}	0.19	0.11	0.16	0.21	0.11	0.22	0.11
total refls.	10688	15792	21551	27511	17007	21126	22540
observed refls.	9485 [$I > 2\sigma(I)$]	5079 [$I > 2\sigma(I)$]	6276 [$I > 2\sigma(I)$]	10866 [$I > 3\sigma(I)$]	6200 [$I > 2\sigma(I)$]	6206 [$I > 3\sigma(I)$]	7057 [$I > 2\sigma(I)$]
final R,[a] and Rw[b] or wR_2[c]	0.0781,[d] 0.0731[b,d]	0.0698,[d] 0.1839[c,e]	0.1052,[d] 0.2831[c,e]	0.0780,[f] 0.0831[b,f]	0.0809,[d] 0.1866[c,e]	0.0662,[f] 0.1752[b,f]	0.0662,[d] 0.1752[c,e]

[a] $R = \Sigma ||F_o| - |F_c|| / \Sigma |F_o|$. [b] $R_w = \{\Sigma w(|F_o| - |F_c|)^2 / \Sigma w F_o^2\}^{1/2}$. [c] $wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2] / \Sigma[w(F_o^2)^2]\}^{1/2}$. [d] For data with $I > 2\sigma(I)$. [e] For all data. [f] For data with $I > 3\sigma(I)$.

paper. These data can be obtained free of charge via 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 or deposit@ccdc.cam.uk).

Crystal data collection and processing parameters are given in Table 2. Crystals were immersed in a film of perfluoropolyether oil on a glass fibre and transferred to an Enraf-Nonius DIP2000 or Kappa-CCD diffractometer ($Mo_{K\alpha}$ radiation) equipped with an Oxford Cryosystems low-temperature device[37] or a Stoe-IPDS image plate diffractometer ($Ag_{K\alpha}$ radiation) equipped with a FTS AirJet low temperature device. Data were collected at 150 or 200 K; equivalent reflections were merged and the images were processed with the DENZO and SCALEPACK programs (for **1·2(C_6H_6)**, **22·4(CH_2Cl_2)**), and **25**[38] or with the STOE IPDS software package. Corrections for Lorentz polarisation effects and absorption were performed 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 SIR92,[39] CRYSTALS-PC,[40] SHELXS-97 and SHELXL-97.[41]

For the compound **1·2(C_6H_6)** the methyl carbons for one calix[4]arene *tert*-butyl group [C(42) to C(44) and C(421) to C(441)] were disordered over two sites. Refinement of site occupancy factors with fixed *U*[iso] values showed the two orientations to be of equal occupancy. The two Me_3 groups were refined with in the isotropic approximation with similarity restraints applied to C(41)−C(Me) bond lengths and C(24)-C(41)-C(Me) angles. The largest peak in the final Fourier difference synthesis was located 0.89 Å from C(441) of the disordered *t*Bu group. The calix[4]arene *tert*-butyl groups containing C(27) to C(29), C(37) to C(39), and C(47) to C(49) were positionally disordered for compound **13·4(C_7H_8)**. These carbon atoms were refined in an isotropic approximation with occupancy factors of 70 and 30%. For the compound **22·4(CH_2Cl_2)** one of the calix[4]arene *tert*-butyl groups (containing C(30) to C(32)) was positionally disordered and these carbons were refined in an isotropic approximation. For compound **24**, the positionally disordered phenolate *tert*-butyl group containing C(57) to C(59) and the calix[4]arene *tert*-butyl group containing C(17) to C(18) were refined in an isotropic approximation as well as the positionaly disordered calix[4]arene *tert*-butyl group C(27) to C(29) and the positionally disordered phenolate *tert*-butyl groups C(27) to C(29), C(57) to C(59), and C(67) to C(69) of **26·0.5(C_6H_{14})**.

Acknowledgement

This work was supported by the EPSRC, Royal Society (London), Deutschen Forschungsgemeinschaft, Fonds der Chemischen Industrie. We acknowledge the use of the EPSRC Chemical Database Service at Daresbury Laboratory. We thank Dr. L. Doerer for collecting the X-ray data for **1·2(C_6H_6)** and Dr. S. C. Jones for his help with the cyclic voltammetry. U.R. and A.F. thank Prof. D. Fenske for his continuing interest in their work.

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Received: December 10, 2002 [F4656]

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