Calix[4]arene Derivatives of Titanium and Zirconium Alkoxides

Matthias Czakler, Christine Artner, Christian Maurer, and Ulrich Schubert

Institute of Materials Chemistry, Vienna University of Technology, Getreidemarkt 9, A-1060 Vienna, Austria

Reprint requests to Prof. U. Schubert. Fax: +43-(0)1-58801-16599.
E-mail: Ulrich.Schubert@tuwien.ac.at

Dedicated to Professor Hubert Schmidbaur on the occasion of his 80th birthday

Reaction of Ti(OBu)$_4$ or Zr(OBu)$_4$ with *t*butyl-calix[4]arene, calix^{tBu}(OH)$_4$, led to the formation of Ti$_2$(OBu)$_2$[calix^{tBu}O$_3$(OH)]$_2$ and Zr$_3$(OBu)$_8$(calix^{tBu}O$_4$), respectively. Upon *in situ* generation of water in the reaction with Zr(OBu)$_4$, the partially hydrolyzed compound Zr$_4$O(OBu)$_6$(calix^{tBu}O$_4$)$_2$ (BuOH)$_2$ was isolated.

Key words: Titanium Alkoxides, Zirconium Alkoxides, Crystal Structure, Partial Hydrolysis

Introduction

Exchange of the OR groups of titanium and zirconium alkoxides, M(OR)$_4$ (M = Ti, Zr), by an alcohol or phenol R′OH is a straightforward process, especially if the exchange reaction is driven by a stronger bonding of OR′. Among others, this is the case when the reaction with R′OH results in chelating ligands, as for di- and polyols, β-amino [1, 2], β-alkoxy alcohols/phenols [2, 3] or similar. Modification of Ti(OR)$_4$ with 1,2- and 1,3 diols is used for a long time to modify the reactivity of the metal alkoxide [4, 5].

Reactions of M(OR)$_4$ (M = Ti, Zr) with calixarenes, which are reported in this article, are not only interesting with regard to functionalization of the alkoxides (as precursors for sol-gel materials) but also from a structural point of view. Reaction of Ti(OR)$_4$ with O$_2$N–C(CH$_2$OH)$_3$, providing a tripodal, trianionic ligand had resulted in polynuclear compounds, where the oxygen atoms of the O$_2$N–C(CH$_2$O$^−$)$_3$ ligands bridge either two or three titanium atoms [6]. In contrast, many metal complexes of *t*butyl-calix[4]arene, calix^{tBu}(OH)$_4$, (Fig. 1) are known, in which [calix^{tBu}O$_x$(OH)$_{4−x}$]$^{x−}$ ligands are bonded to just one metal [7], among them several titanium [8 – 14] and zirconium derivatives [14 – 17].
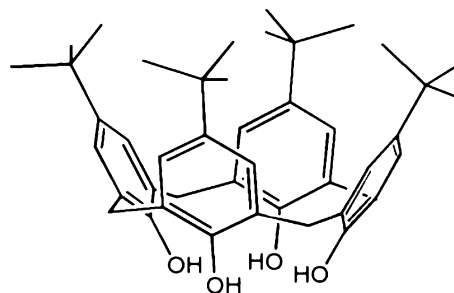

Fig. 1. Cone structure of *t*butyl-calix[4]arene [calix^{tBu}(OH)$_4$].

Results and Discussion

Adding four molar equivalents of Ti(OBu)$_4$ to a suspension of calix^{tBu}(OH)$_4$ in *n*-butanol led to the formation of a red complex, and red crystals of Ti$_2$(OBu)$_2$[calix^{tBu}O$_3$(OH)]$_2$ (**TiCalix**, Fig. 2, Table 1) were eventually obtained. The structure is similar to a calix[4]arene monomethyl ether derivative (with O–4-C$_6$H$_4^t$Bu bridges) which was prepared by another route [14].

Both titanium atoms are octahedrally coordinated and bridged by two OBu ligands. Each calix^{tBu}O$_3$(OH) ligand is coordinated to one titanium atom through three Ti–O bonds and one additional interaction with

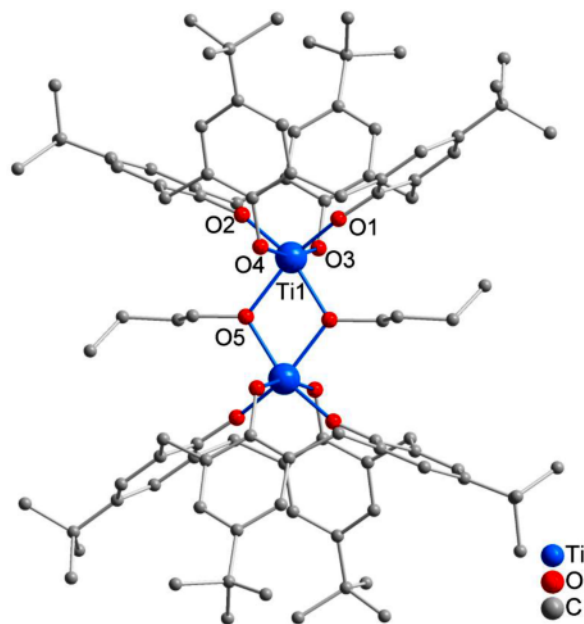Fig. 2 (color online). Molecular structure of $Ti_2(OBu)_2$ $[calix^{tBu}O_3(OH)]_2$ (**TiCalix**). Hydrogen atoms were omitted for clarity.

Table 1. Selected bond lengths (pm) and angles (deg) for **TiCalix**[a].

Ti(1)–O(1)	179.4(3)	O(1)–Ti(1)–O(5)′	93.5(1)
Ti(1)–O(2)	180.7(3)	O(2)–Ti(1)–O(3)	89.7(1)
Ti(1)–O(3)	193.9(3)	O(2)–Ti(1)–O(4)	81.1(1)
Ti(1)–O(4)	224.0(3)	O(2)–Ti(1)–O(5)	92.5(1)
Ti(1)–O(5)	203.5(3)	O(2)–Ti(1)–O(5)′	162.7(1)
Ti(1)–O(5)′	202.2(3)	O(3)–Ti(1)–O(4)	165.0(1)
Ti(1)–O(5)–Ti(1)′	109.8(1)	O(3)–Ti(1)–O(5)	103.4(1)
O(1)–Ti(1)–O(2)	103.3(1)	O(3)–Ti(1)–O(5)′	94.6(1)
O(1)–Ti(1)–O(3)	90.2(1)	O(4)–Ti(1)–O(5)	89.0(1)
O(1)–Ti(1)–O(4)	80.4(1)	O(4)–Ti(1)–O(5)′	97.6(1)
O(1)–Ti(1)–O(5)	159.3(1)	O(5)–Ti(1)–O(5)′	70.2(1)

[a] The label ′ refers to symmetry-equivalent atoms generated by the symmetry operation $-x, -y, z$.

one OH group. The latter was clearly identified by the Ti(1)–O(4) bond length (224 pm) which is substantially longer than that of Ti(1)–O(1), Ti(1)–O(2) and Ti(1)–O(3) (180, 181 and 194 pm, respectively). Ti(1)–O(1) and Ti(1)–O(2) are shorter than Ti(1)–O(3) because they are in a *trans* position to the OBu bridges. The structure of **TiCalix** is a variation of the well-known dimeric structures of $[Ti(\mu\text{-}OR)(OR)_2XY]_2$, where XY represents either a chelating ligand or a combination of an anionic (X) and a neutral ligand

(Y) [18]. In the case of **TiCalix**, the positions of the two terminal OR groups and that of X are occupied by the anionic part of the $calix^{tBu}O_3(OH)$ ligand and that of the neutral ligand Y by the OH group.

Two signals were observed for the CH_2 groups of the $calix^{tBu}O_3(OH)$ ligands in the ^{1}H NMR spectrum. Thus, proton exchange of the OH group is fast on the NMR timescale. This was also found in the ^{13}C NMR spectrum, where only one signal for the CH_3 and CH_2 groups of the butoxo ligand were found, and two signals each for the aromatic carbon atoms.

Derivatives of zirconium alkoxides have, in most cases, different structures than the corresponding titanium alkoxides, because the bigger Zr atoms allow a larger structural variability and because of reactivity differences. Reaction of $calix^{tBu}(OH)_4$ with $Zr(OBu)_4$ in the same molar ratio as in the reaction with $Ti(OBu)_4$ resulted indeed in a compound with different composition and structure, namely $Zr_3(OBu)_8(calix^{tBu}O_4)$ (**Zr3Calix**, Fig. 3, Table 2).

The basic structural motif of **Zr3Calix** is a Zr_3 triangle, which is capped by two μ_3-OBu ligands. The calixarene ligand in **Zr3Calix** is completely deprotonated; three oxygen atoms of the $calix^{tBu}O_4$ ligand are bonded to Zr(1), while the fourth is bridging Zr(1) and Zr(2). The other two edges of the Zr_3 triangle are bridged by μ_2-OBu groups. The coordination spheres
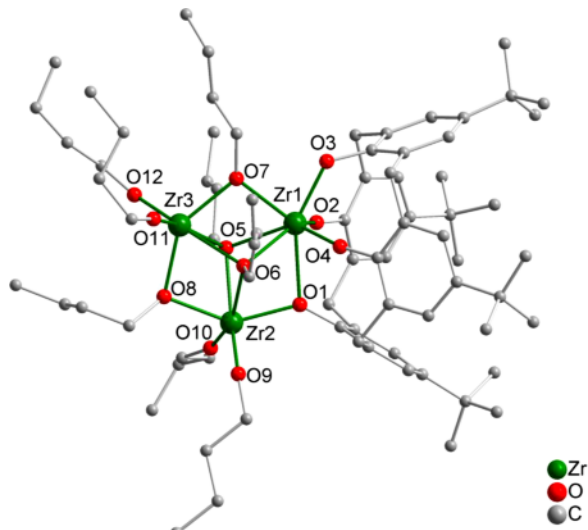

Fig. 3 (color online). Molecular structure of $Zr_3(OBu)_8$ $(calix^{tBu}O_4)$ (**Zr3Calix**). Hydrogen atoms were omitted for clarity.

Table 2. Selected bond lengths (pm) and angles (deg) for **Zr3Calix**.

Zr(1)–O(1)	242.1(2)	Zr(2)–O(10)	190.7(2)
Zr(1)–O(2)	195.9(2)	Zr(3)–O(5)	222.8(2)
Zr(1)–O(3)	202.7(2)	Zr(3)–O(6)	229.3(2)
Zr(1)–O(4)	195.1(2)	Zr(3)–O(7)	212.5(2)
Zr(1)–O(5)	234.1(1)	Zr(3)–O(8)	213.8(2)
Zr(1)–O(6)	232.8(2)	Zr(3)–O(11)	190.8(2)
Zr(1)–O(7)	223.4(2)	Zr(3)–O(12)	191.5(2)
Zr(2)–O(1)	206.7(2)	Zr(2)–O(1)–Zr(1)	98.76(6)
Zr(2)–O(5)	229.7(2)	Zr(2)–O(6)–Zr(3)	93.11(5)
Zr(2)–O(6)	227.5(2)	Zr(2)–O(6)–Zr(1)	95.73(5)
Zr(2)–O(8)	217.5(2)	Zr(3)–O(6)–Zr(1)	95.02(5)
Zr(2)–O(9)	191.5(2)	Zr(3)–O(5)–Zr(2)	94.27(5)
Zr(2)–O(10)	190.7(2)	Zr(3)–O(5)–Zr(1)	96.45(5)
Zr(2)–O(5)	229.7(2)	Zr(2)–O(5)–Zr(1)	94.79(5)
Zr(2)–O(6)	227.5(2)	Zr(3)–O(7)–Zr(1)	102.82(6)
Zr(2)–O(8)	217.5(2)	Zr(3)–O(8)–Zr(2)	100.53(6)
Zr(2)–O(9)	191.5(2)		

Fig. 4 (color online). Molecular structure of $Zr_4O(OBu)_6$ $(calix^{tBu}O_4)_2(BuOH)_2$ (**Zr4Calix2**). Hydrogen atoms and disordered atoms were omitted for clarity.

of the Zr atoms, a distorted square face mono-capped trigonal prism for Zr(1) and distorted octahedra for Zr(2) and Zr(3), are completed by terminal OBu ligands.

Zr3Calix has a local C_s symmetry. In the ^{1}H NMR spectrum, two signals were found for the *t*-butyl groups of the calixarene at 0.93 and 1.02 ppm, and one signal for the other two symmetry-related *t*-butyl groups at 1.59 ppm. The hydrogen atoms of the OCH$_2$ of the calixarene show geminal coupling with a large shift between axial and equatorial. Four different doublets can thus be found in the NMR spectrum (at 3.59, 3.64, 5.23, and 5.32 ppm) with a coupling constant of around 12 Hz. Therefore, it can be assumed that the C_s symmetry is retained in solution. In the ^{13}C NMR spectrum the number of signals of the calix^{tBu}O$_4$ ligand reflects the mirror symmetry (one signal overlaps with the C_6D_6 resonance). The signals of the OBu ligands partly overlap in the ^{1}H and ^{13}C NMR spectra. A smaller number of signals than expected were therefore observed for the latter.

To obtain a calixarene-substituted zirconium oxo cluster, zirconium butoxide was reacted with calix^{tBu}(OH)$_4$ in the same molar ratio in the presence of acetic acid. Addition of acetic acid results in the *in situ* generation of water through esterification with *n*-butanol [19]. This reaction led to the formation of the oxo cluster $Zr_4(\mu_3$-O)(OBu)$_6$(calix^{tBu}O$_4$)$_2$(BuOH)$_2$ (**Zr4Calix2**, Fig. 4, Table 3). The outcome of the reaction of Zr(OBu)$_4$, calix^{tBu}(OH)$_4$ and water (diluted in THF) in a ratio of 8 : 1:4 was the same. This is
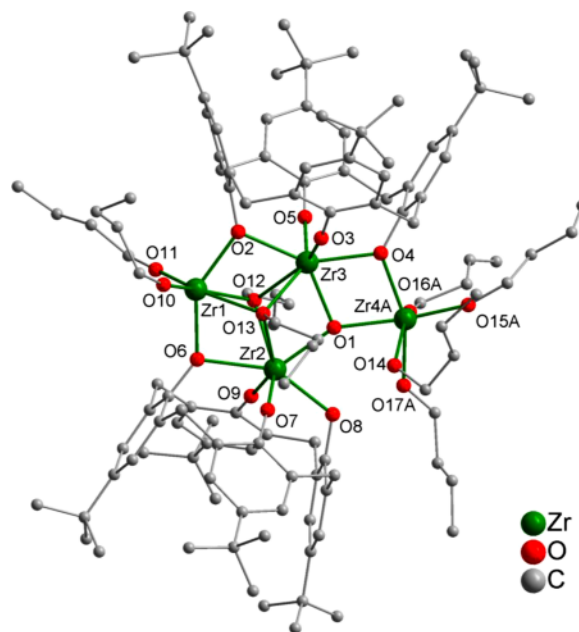
additional proof that acetic acid acts as an *in situ* water source.

The basic structural motif in **Zr4Calix2** is the same as that of **Zr3Calix**, namely a $Zr_3(\mu_3$-OBu)$_2$ unit formed by Zr(1), Zr(2) and Zr(3). Contrary to **Zr3Calix**, a second calix^{tBu}O$_4$ ligand is bonded to this triangular unit. Both calix^{tBu}O$_4$ ligands are bonded in the same manner as in **Zr3Calix**, namely three oxygen atoms are bonded to one Zr atom [O(7)–O(9) to Zr(2) and O(3)–O(5) to Zr(3)], while O(2) and O(6) bridge Zr(1) and Zr(3) or Zr(1) and Zr(2), respectively. This results in symmetrical $Zr_3(\mu_3$-OBu)$_2$(OBu)$_2$(calix^{tBu}O$_4$)$_2$, with two terminal OBu ligands at Zr(1).

The structure of $Zr_3(\mu_3$-OBu)$_2$(OBu)$_2$(calix^{tBu}O$_4$)$_2$ is extended by condensation of a ZrO(OBu)$_2$(BuOH)$_2$ unit through a μ_3-oxo bridge [O(1)] connecting Zr(4) with Zr(2) and Zr(3). The attachment of the ZrO(OBu)$_2$(BuOH)$_2$ unit, however, is not symmetrical. This is due to the additional interaction of Zr(4) with one of the oxygen atoms of *one* calix^{tBu}O$_4$ ligand [O(4) bonded to Zr(3) in Fig. 4]. For steric reasons an interaction with the oxygen atoms of two calix^{tBu}O$_4$ ligands would not be possible. Since the

Table 3. Selected bond lengths (pm) and angles (deg) **Zr4Calix2**. The labels A and B refer to atoms in the disordered positions (see text).

Zr(1)–O(2)	212.3(5)	Zr(4A)–O(16A)	195.9 (2)
Zr(1)–O(6)	210.2(5)	Zr(4A)–O(17A)	203.3(1)
Zr(1)–O(10)	189.6(5)	Zr(4B)–O(1)	212.3(5)
Zr(1)–O(11)	190.0(5)	Zr(4B)–O(8)	213.0(5)
Zr(1)–O(12)	230.8(5)	Zr(4B)–O(14)	205(3)
Zr(1)–O(13)	227.0(5)	Zr(4B)–O(15B)	188(1)
Zr(2)–O(1)	213.3(5)	Zr(4B)–O(16B)	207.9(3)
Zr(2)–O(6)	233.8(5)	Zr(4B)–O(17B)	216.9(2)
Zr(2)–O(7)	196.1(5)	Zr(3)–O(1)–Zr(4B)	150.5(3)
Zr(2)–O(8)	220.4(5)	Zr(3)–O(1)–Zr(2)	103.2(2)
Zr(2)–O(9)	194.3(5)	Zr(4B)–O(1)–Zr(2)	105.4(2)
Zr(2)–O(12)	229.1(5)	Zr(3)–O(1)–Zr(4A)	106.6(2)
Zr(2)–O(13)	225.6(6)	Zr(2)–O(1)–Zr(4A)	149.9(3)
Zr(3)–O(1)	212.0(5)	Zr(1)–O(2)–Zr(3)	100.8(2)
Zr(3)–O(2)	226.9(5)	Zr(4A)–O(4)–Zr(3)	104.2(2)
Zr(3)–O(3)	195.1(6)	Zr(1)–O(6)–Zr(2)	99.4(2)
Zr(3)–O(4)	220.6(5)	Zr(4B)–O(8)–Zr(2)	102.7(2)
Zr(3)–O(5)	194.8(5)	Zr(3)–O(12)–Zr(2)	93.5(2)
Zr(3)–O(12)	228.4(5)	Zr(3)–O(12)–Zr(1)	95.0(2)
Zr(3)–O(13)	228.1(6)	Zr(2)–O(12)–Zr(1)	95.0(2)
Zr(4A)–O(1)	214.3(5)	Zr(2)–O(13)–Zr(1)	97.0(2)
Zr(4A)–O(4)	212.6(5)	Zr(2)–O(13)–Zr(3)	94.5(2)
Zr(4A)–O(14)	267(3)	Zr(1)–O(13)–Zr(3)	96.1(2)
Zr(4A)–O(15A)	195.4(1)		

Fig. 5 (color online). Disordered part of the structure of $Zr_4O(OBu)_6(calix^{tBu}O_4)_2(BuOH)_2$ (**Zr4Calix2**). Hydrogen atoms and disordered atoms were omitted for clarity.

$Zr_3(\mu_3\text{-}OBu)_2(OBu)_2(calix^{tBu}O_4)_2$ part of **Zr4Calix2** is symmetric, the $Zr(OBu)_2(BuOH)_2$ group can also interact with Zr(2) in the same manner. This results in a positional disorder of the $Zr(OBu)_2(BuOH)_2$ group as schematically shown in Fig. 5 (atoms labeled A and B). The two positions were refined in a 0.59 : 0.41 ratio (A : B). A clear distinction between OBu and BuOH groups is not possible because of the disorder, but two Zr–O bond lengths are clearly longer and are therefore assigned to the coordinated alcohol molecules.

Conclusions

Reaction of $Ti(OBu)_4$ with $calix^{tBu}(OH)_4$ resulted in the formation of $Ti_2(OBu)_2[calix^{tBu}O_3(OH)]_2$ (**TiCalix**, Fig. 2) which has the characteristic dimeric structure of titanium alkoxides substituted by chelating ligands. Although the same metal alkoxide : calixarene ratio was used for synthesis, a compound with a lower degree of substitution, namely $Zr_3(OBu)_8(calix^{tBu}O_4)$ (**Zr3Calix**, Fig. 3), was obtained in the corresponding reaction with $Zr(OBu)_4$. This may be a kinetic effect, because the same reaction in the presence of small amounts of water showed that the basic structural motif $Zr_3(\mu_3\text{-}OBu)_2$ can be
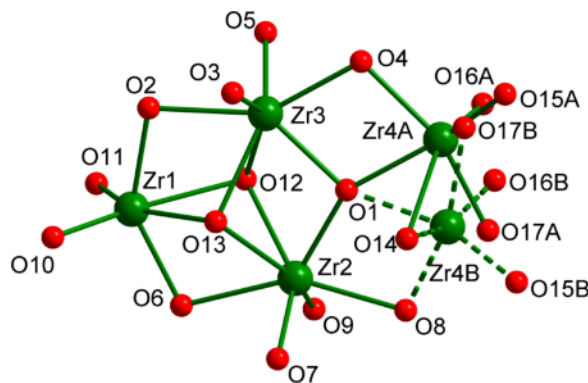
substituted by a second $calix^{tBu}O_4$ unit as well. In the oxo compound $Zr_4O(OBu)_6(calix^{tBu}O_4)_2(BuOH)_2$ (**Zr4Calix2**, Fig. 4) a $ZrO(OBu)_2(HOBu)_2$ unit is condensed to the Zr_3 unit. The relatively low degree of condensation and the fact that the substituted Zr_3 unit is not hydrolyzed shows that the latter appears to be an enduring structural unit. It is also noteworthy that no acetate ligand was coordinated. This shows, not unexpectedly, that $calix^{tBu}O_4$ is the preferred ligand compared to carboxylate.

Experimental

All operations were carried out in inert gas atmosphere using standard Schlenk techniques or a glove box. $Ti(OBu)_4$ and $Zr(OBu)_4$ (used as a 1 : 1 adduct with BuOH) were obtained from Sigma-Aldrich and used as received. *n*-Butanol was purified using standard techniques prior to use. *t*Butyl-calix[4]arene was obtained as described by Gutsche *et al.* [20].

Synthesis of $Ti_2(OBu)_2[calix^{tBu}O_3(OH)]_2$ (*TiCalix*)

$Ti(OBu)_4$ (1.32 mL, 3.88 mmol) was quickly added to a suspension of 630 mg (0.97 mmol) of $calix^{tBu}(OH)_4$ (used as 1 : 1 toluene adduct obtained upon recrystallization [20]) in 4 mL of *n*-butanol. After an immediate change from colorless to yellow, a suspension was obtained. After heating and addition of 4 mL toluene, a red solution was received, from which crystals of **TiCalix** were obtained after 2 weeks. In each of the $calix^{tBu}O_3(OH)$ ligands, one toluene is incorporated (not shown in Fig. 2). Yield 480 mg (66%). – ^{1}H NMR (CDCl$_3$, 250 MHz): $\delta = 0.79$ (br, s, 42 H, CH$_3$), 1.07 – 1.28 (m, 8 H, CH$_2$), 1.34 (s, 36 H, CH$_{3,calix}$), 3.32 (d, $J = 13.09$ Hz, 8 H, CH$_{2,calix}$), 3.42 (broad s, 4 H, CH$_2$O),

4.92 (d, $J = 12.79$ Hz, 8 H, $CH_{2,calix}$), 6.83 (s, 8H, CH), 7.13 ppm (s, 8H, CH). – ^{13}C NMR (CDCl$_3$, 62.9 MHz): $\delta =$ 13.59 (CH_2CH_3), 18.86 (CH_2CH_3), 30.78, 31.51 (CCH_3), 33.54, 34.78 ($CH_{2,calix}$), 35.45 (CH_2CH_2O), 62.52 (CH_2O), 125.78, 125.93 (CCH_2), 128.21, 129.02 (CH_{arom}), 144.36, 146.67 ($CCMe_3$), 157.64, 160.54 ppm (CO).

Synthesis of $Zr_3(OBu)_8(calix^{tBu}O_4)$ (*Zr3Calix*)

Zr(OBu)$_4$ (0.98 mL, 2.14 mmol) was quickly added to a suspension of 347 mg (0.54 mmol) of calix^{tBu}(OH)$_4$ in 2 mL of *n*-butanol under argon. The suspension was heated until a clear solution was obtained and then immediately cooled to room temperature. After 4 days crystals of **Zr3Calix** were obtained. Yield 660 mg (82 %). – ^{1}H NMR (C$_6$D$_6$, 250 MHz): $\delta = 0.89$ (t, $J = 7.30$ Hz, 6 H, CH$_2$CH_3), 0.93 (s, 9 H, CCH_3), 0.95 (t, $J = 7.18$ Hz, 6 H, CH$_2$CH_3), 1.02 (s, 9 H, CCH_3), 1.05 (t, $J = 7.15$ Hz, 6 H, CH$_2$CH_3), 1.12 (t, $J = 7.30$ Hz, 6 H, CH$_2$CH_3), 1.17–1.33 (m, 3 H, CH_2CH$_3$), 1.34–1.58 (m, 9 H, CH_2CH$_3$), 1.59 (s, 18 H, CCH_3), 1.6–1.81 (m, 12 H, CH$_2$CH_2), 1.87–2.01 (m, 2 H, CH_2CH$_2$O), 2.24 (quin, $J = 7.38$ Hz, 2 H, CH_2CH$_2$O), 2.39–2.58 (m, 4 H, CH$_2$), 3.59 (d, $J = 11.88$ Hz, 2 H, OCH$_{2,calix}$), 3.64 (d, $J = 11.87$ Hz, 2 H, CH$_{2,calix}$), 4.17 (t, $J = 6.17$ Hz, 4 H, CH$_2$O$_{term.\ OBu}$), 4.24 (t, $J = 5.78$ Hz, 4 H, CH$_2$O$_{term.\ OBu}$), 4.39–4.49 (m, 2 H, CH$_2$O$_{\mu2\text{-}OBu}$),

4.50–4.62 (m, 2 H, CH$_2$O$_{\mu3\text{-}OBu}$), 4.80–4.92 (m, 2 H, CH$_2$O$_{\mu3\text{-}OBu}$), 5.02 (t, $J = 7.24$ Hz, 2 H, CH$_2$O$_{\mu2\text{-}OBu}$), 5.23 (d, $J = 12.18$ Hz, 2 H, OCH$_{2,calix}$), 5.32 (d, $J = 12.13$ Hz, 2 H, OCH$_{2,calix}$), 7.08 (m, 4 H, CH$_{arom}$), 7.49 ppm (m, 4 H, CH$_{arom}$). – ^{13}C NMR (C$_6$D$_6$, 62.9 MHz): $\delta = 13.52$, 13.76, 14.15 (CH_2CH$_3$), 19.10, 19.25, 19.34 (CH_2CH$_3$), 30.74, 31.08, 31.96, 33.15, 34.07, 34.22 (CCH_3), 34.72, 36.01, 36.34, 36.50 (CH_2CH$_2$O), 70.09, 70.82, 71.30, 72.04 (CH_2O), 123.83, 124.48, 125.30, 126.02 (CH_{arom}), 129.39, 132.28, 134.16 (CCH_2), 140.16, 141.76, 143.00 ($CCMe_3$), 153.22, 157.00, 157.42 ppm (CO$_{arom}$).

Synthesis of $Zr_4(\mu_3\text{-}O)(OBu)_6(calix^{tBu}O_4)_2(BuOH)_2$ (*Zr4Calix2*)

Zr(OBu)$_4$ (815 mL, 1.78 mmol) was added to a mixture of 330 mg (0.45 mmol) of calix^{tBu}(OH)$_4$ and 25.5 mL (1.78 mmol) of acetic acid in 2 mL of *n*-butanol. The suspension was heated under stirring until a clear solution was obtained. After cooling to room temperature, crystals of **Zr4Calix2** had formed after 18 weeks from the mother liquor. Yield 360 mg (70 %).

The same crystals were obtained in a reaction without acetic acid, where water was added instead. In this reaction, 754 mg (1.16 mmol) of calix^{tBu}(OH)$_4$ were suspended in 3 mL of *n*-butanol. To this suspension, 4.25 mL (9.3 mmol)

	TiCalix	Zr3Calix	Zr4Calix2
Empirical formula	C$_{120}$H$_{158}$O$_{12}$Ti$_2$	C$_{76}$H$_{123}$O$_{12}$Zr$_3$	C$_{120}$H$_{177}$O$_{17}$Zr$_4$
M_r	1888.2	1502.40	2256.5
Crystal system	triclinic	orthorhombic	monoclinic
Space group	$P\bar{1}$	$P2_12_12_1$	$P2_1/c$
a, pm	1262.96(9)	16.5246(8)	1303.39(3)
b, pm	1346.57(10)	21.1702(9)	4931.52(12)
c, pm	1798.78(13)	21.9871(10)	1866.79(5)
α, deg	85.990(3)	90	90
β, deg	73.640(3)	90	91.9870(10)
γ, deg	64.020(3)	90	90
V, pm^3 10^6	2633.6(3)	7691.7(6)	11991.9(5)
Z	1	4	4
$D_{calcd.}$, Mg m^{-3}	1.19	1.30	1.25
μ, mm^{-1}	0.2	0.5	0.4
Crystal size, mm^3	$0.4 \times 0.3 \times 0.2$	$0.72 \times 0.64 \times 0.43$	$0.57 \times 0.37 \times 0.36$
θ_{max}, deg	22.59	25	25.03
No. measured refl.	21 201	142 609	123 565
Refl. unique/ref. param.	6831/699	13 545/841	20 496/1360
Obs. refl. [$I > 2\sigma(I)$]	4840	13 147	15 935
R [$F^2 > 2\sigma(F^2)$]^a/wR $(F^2)^b$	0.0593/0.1742	0.0209/0.0635	0.096/0.2312
Gof^c	1.026	1.112	1.179
a/b (weighting scheme)^b	0.0921/3.2969	0.0390/2.8125	0.0524/97.5620
$\Delta\rho_{max/min}$, e 10^{-6} pm^{-3}	0.77/−0.62	0.76/−0.54	1.16/−0.92

Table 4. Crystal data and refinement details for **TiCalix**, **Zr3Calix** and **Zr4Calix2**.

^{a} $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; ^{b} $wR = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$, $w = [\sigma^2(F_o^2) + (aP)^2 + bP]^{-1}$, where $P = (\text{Max}(F_o^2, 0) + 2F_c^2)/3$; ^{c} GoF $= S = [\Sigma w(F_o^2 - F_c^2)^2/(n_{obs} - n_{param})]^{1/2}$.

of $Zr(OBu)_4$ was quickly added. The mixture was heated until a clear solution was obtained. After cooling to room temperature, 1.16 mL (4.64 mmol) of a 4 molar solution of water in THF was added. Crystals of **Zr4Calix2** suitable for single-crystal XRD were obtained after 16 weeks. Yield 800 mg (60 %). – ^{1}H NMR (C_6D_6, 250 MHz): δ = 0.56 (t, J = 7.5 Hz, 3 H, CH_2CH_3), 0.83 – 0.90 (m, 9 H, CH_2CH_3), 0.91 (s, 18 H, CCH_3), 0.93 – 0.96 (m, 12 H, CH_2CH_3), 0.97 (s, 18 H, CCH_3), 1.15 – 1.38 (m, 16 H, CH_2CH_3), 1.44 – 1.65 (m, 16 H, CH_2CH_2O), 1.54 (s, 18 H, CCH_3), 1.56 (s, 18 H, CCH_3), 2.76 – 2.92 (broad, 2 H, OH), 3.51 (d, J = 12.2 Hz, 2 H, CH_2Ph), 3.63 (d, J = 12.5 Hz, 2 H, CH_2Ph), 3.66 (d, J = 12.5 Hz, 2 H, CH_2Ph), 3.71 (d, J = 13.1 Hz, 2 H, CH_2Ph), 4.00 (t, J = 6.7 Hz, 10 H, CH_2CH_2O), 4.22 (t, J = 6.2 Hz, 2 H, CH_2O), 4.35 (t, J = 6.3 Hz, 2 H, CH_2O), 5.19 (d, J = 12.0 Hz, 2 H, CH_2Ph), 5.21 (d, J = 12.0 Hz, 2 H, CH_2Ph), 5.26 – 5.34 (m, 2H, CH_2O), 5.42 (d, J = 12.3 Hz, 2 H, CH_2Ph), 5.53 (d, J = 12.5 Hz, 2 H, CH_2Ph), 7.02 – 7.13 (m, 8 H, CH_{arom}), 7.44 – 7.52 ppm (m, 8 H, CH_{arom}). – ^{13}C NMR (C_6D_6, 62.9 MHz): δ = 12.56, 13.85, 14.05, 14.11 (CH_2CH_3), 18.92, 19.06, 19.13, 19.72 (CH_2CH_3), 30.77, 30.83, 31.90 (CCH_3), 33.25 (CH_2), 33.29 (CH_2), 34.07 (CMe_3), 34.36 (CMe_3), 34.98 (CMe_3), 35.22 (CMe_3), 36.21 (CH_2Ph), 36.29 (CH_2Ph), 67.29 (CH_2O), 71.67 (CH_2O), 71.92 (CH_2O), 72.06 (CH_2O), 73.52 (CH_2O), 74.70 (CH_2O), 123.93 (CCH_2), 124.18 (CCH_2), 124.52 (CCH_2), 124.99 (CCH_2), 125.40 (CCH_2), 125.62 (CCH_2), 126.00 (CCH_2), 129.64, 129.71, 129.86, 130.30, 130.45, 131.05, 131.79, 132.17, 132.89, 133.45 (CH_{arom}), 142.13, 142.27, 142.36, 143.70, 143.96 ($CCMe_3$), 151.69, 152.44, 156.75, 157.28, 157.44 ppm (CO).

Structure analyses by X-ray diffraction

All measurements were performed at 100 K using MoK_α (λ = 71.073 pm) radiation. Data were collected on a Bruker AXS SMART APEX II four-circle diffractometer with κ-geometry with ϕ and ω scans and different frame widths. The data were corrected for polarization and Lorentz effects, and an empirical absorption correction (SADABS [21]) was employed. The cell dimensions were refined with all unique reflections. SAINT+ software [22] was used to integrate the frames. Details of the X-ray investigations are given in Table 4.

The structures were solved by the Patterson method (SHELXS-97 [23, 24]). Refinement was performed by the full-matrix least-squares method based on F^2 (SHELXL-97 [24, 25]) with anisotropic displacement parameters for all non-hydrogen atoms. Hydrogen atoms were inserted in calculated positions and refined riding with the corresponding atom.

CCDC 1006911 (**TiCalix**), 1006912 (**Zr3Calix**) and 1006913 (**Zr4Calix2**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.

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