

A facile route to hetero-bimetallic Ti(IV)-alkali metal calix[4]arene complexes

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Deprotonation of calix[4]arenes by alkali metal in methanol using simple benchtop procedures is effective in the formation of novel monomeric and dimeric titanium(IV) complexes. For the larger alkali metal cations, K⁺ and Cs⁺, favourable complexation within the π -basic calix[4]arene cavity facilitates the formation of monomeric titanium(IV) complexes when oligomer formation is inhibited by an acetylacetonate ligand. In contrast, the smaller Li⁺ and Na⁺ ions preferentially form dimeric complexes with *exo*-bridging alkali and titanium(IV) metal centres. A dimeric complex is also obtained for potassium in the absence of acetylacetonate. The solid state structures of the K–Ti and Na–Ti calix[4]arene dimer complexes show different structural characteristics depending on the nature of the alkali metal.

Introduction

A substantial number of transition metal calix[4]arene ("R–L[OH]₄", R = group at the *p*-position) complexes have been prepared using metathesis reactions involving alkali metal calix[4]arene complexes with various transition metal chlorides under anhydrous conditions.¹ This approach has exclusively involved fully deprotonated calix[4]arenes or their partially O-alkyl derivatives (R–L[OH]_{4–n}[OR'_n]). To our knowledge, there have been no reports of the use of partially deprotonated calix[4]arenes as precursors to transition metal complexes. One cautionary consideration in the use of partially deprotonated/metallated systems arises from the unpredictable equilibrium distribution of alkali metal intermediates and possible differences in their reactivities with the transition metal precursors. For example, attempts to make the lithium di-anions of a calix[4]arene in DMSO results instead in a mixture of mono- and tri-substituted anions (¹H and ⁷Li NMR spectroscopy).² On this basis, such behaviour makes partially metallated systems unattractive as intermediates *en route* to transition metal complexes, although some advances have been made in establishing the nature of such species (see below).

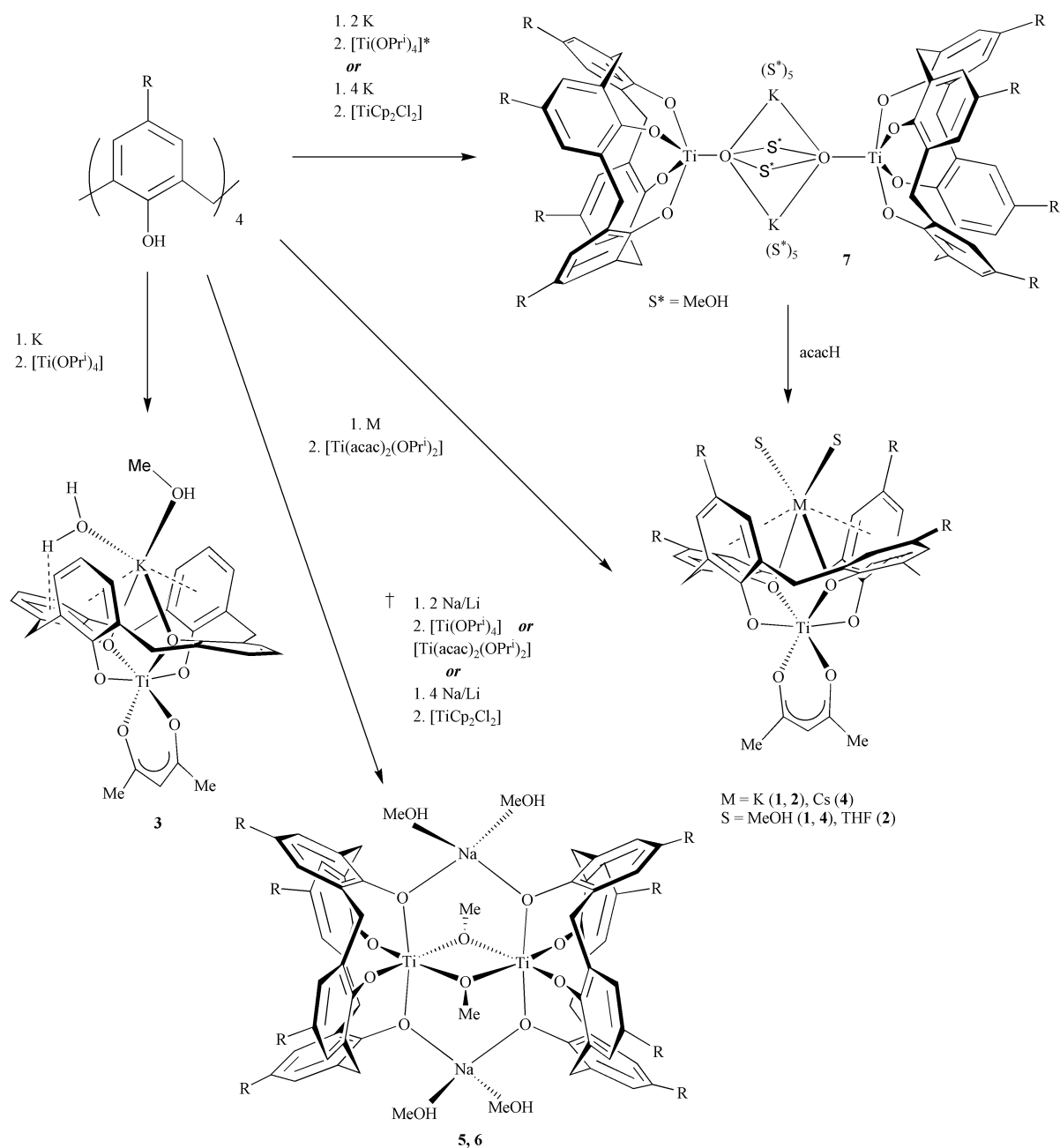
An important property of calix[4]arenes is their two distinctly different binding sites, *endo* and *exo* with respect to the cavity, which further hampers ascertaining the nature of the above-mentioned metallated species. The binding location of the alkali metal and its dependence on both the size of the alkali metal, and the choice of reaction solvent, has been the subject of several theoretical investigations.³ In the *endo*-position, an alkali metal cation can interact with the π -basic cavity of the calix[4]arene whilst also interacting with phenol/phenolate groups, whereas in the *exo*-position alkali metal complexation can occur only through phenol/phenolate groups. Recent structural characterisations of fully metallated alkali metal calix[4]arenes have revealed a mixture of *endo*- and *exo*-complexation of Li⁺, Na⁺ and K⁺ ions.⁴ No structural evidence for *endo*-complexation of these ions has been observed in the partially metallated systems. Structures of partially metallated lithium, sodium and potassium calix[4]arene complexes show *exo*-complexation.^{5–8} Mono-metallation of H–L[OH]₄ with Rb⁺ results in an *endo*-complex but the ¹Bu–L[OH]₄ analogue is an *exo*-complex,⁸ while the Cs⁺ complexes of calix[4]arene mono-anions (R = H, ¹Bu) have *endo*-structures.^{7,9} Overall, the variety

of structural types for partially alkali metallated calixarenes in the solid-state provide no clear indication of what structure such species might have in solution.

Floriani *et al.* have suggested that alkali metal cations can influence the coordination and reactivity of calix[4]arenes with transition metal centres.¹⁰ In this context, Cs⁺ and Ba²⁺ have had a remarkable influence on the reactivity of *p-tert*-butyl-calix[6]arene towards the uranyl ion¹¹ and titanium, respectively.¹² Potassium similarly activates calix[5]arene towards reaction with titanium.¹³ Another consideration in devising synthetic strategies for preparing transition metal calixarene complexes is the possible formation of binuclear, and higher oligomeric complexes. This is highlighted by the reaction of ¹Bu–L[OH]₄ with titanium(IV) precursors such as TiCl₄¹⁴ and Ti(NMe₂)₄,¹⁵ which results in the formation of metallo-bridged species. Undoubtedly the facile elimination of all four ligands from the titanium reagent is favoured by the acidic protons of ¹Bu–L[OH]₄. One strategy for preventing metallo-bridging has been to impose steric and functional limitations by using 1,3-dialkylated calixarene derivatives.¹⁶ Alternatively calixarene complexes devoid of bridging phenolate moieties can be formed by employing the steric buttressing effect of bulky ligands on the metal precursor reagents.^{17–19}

In this paper we report on the influence of alkali metal identity on the formation of novel monomeric and dimeric titanium(IV) complexes arising from reactions of R–L[OH]₄ (R = ¹Bu or H), in concert with titanium(IV) precursors having controlled reactivity. Our synthetic strategy involves partial deprotonation of the calix[4]arene with alkali metal, which disrupts the strong H-bonded array of the calix[4]arene phenolic groups and solubilises the resulting calix[4]arene anion.

The strategy for gaining access to mononuclear titanium(IV) complexes involved using a titanium(IV) reagent possessing at least one chelating ligand. The retention of a chelating ligand in the product provides steric protection against the formation of the common metallo-bridged structures and predisposes the titanium(IV) centre to chelate to a single calix[4]arene. This strategy was successful when using the potassium or caesium substrates, but the lithium and sodium substrates resulted in dimeric complexes, with concomitant loss of the chelating acetylacetonate ligand (acac). As anticipated, in the absence of the acetylacetonate chelate, the potassium substrate gave a dimer structure. Interestingly, the potassium dimer solid-state



† No structure was established for Li

* [Ti(OPrⁱ)₄] premixed with one equivalent of TMEDA

Scheme 1

structure is different from its sodium counterpart, indicating that the structural organisation of the dimers depends on the nature of the alkali metal. We have previously reported, in brief, the preparations of complexes **1** and **2**.²⁰

Results and discussion

Synthesis and characterisation

Reaction of 'Bu-L[OH]₄ with one equivalent of potassium in methanol, followed by the addition of one equivalent of [Ti(acac)₂(OPrⁱ)₂], afforded complex **1**, Scheme 1, which is readily soluble in chloroform, dichloromethane, toluene, THF, or benzene. In the absence of the alkali metal, no reaction was observed between R-L[OH]₄ (R = H or 'Bu) and [Ti(acac)₂(OPrⁱ)₂] in refluxing methanol, THF or toluene. The difference in reactivity would therefore seem to arise from the disruption of the strong hydrogen-bonded array of the neutral calix[4]-

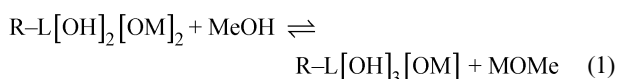
arene upon formation of the mono-anion.²¹ Complex **2** formed upon recrystallisation of **1** in THF, but was also accessible directly by the reaction of K-selectride with 'Bu-L[OH]₄ in THF followed by the addition of [Ti(acac)₂(OPrⁱ)₂]. Compound **3** was prepared as for **1**, except H-L[OH]₄ was substituted for 'Bu-L[OH]₄, and DME was required for successful crystallisation. The *endo*-caesium complex **4** was prepared indirectly, by metathesis, to avoid the expense and handling hazard of caesium metal. Thus **4** was made by the reaction of one equivalent of sodium metal with 'Bu-L[OH]₄ in methanol followed by addition of one equivalent of CsCl, then one equivalent of [Ti(acac)₂(OPrⁱ)₂]. All complexes were prepared in modest to good yields.

When the alkali metal ion was K⁺, (**1**, **2**, **3**) or where Cs⁺ (**4**) was introduced by metathesis of the preformed metal complex, monomeric titanium complexes formed, as summarised in Scheme 1. However, in the presence of Li⁺ or Na⁺ ions, no analogous complexes could be isolated. Instead, addition of

one equivalent of $[\text{Ti}(\text{acac})_2(\text{OPr}^t)_2]$ to solutions of the lithium or sodium mono-anions of $\text{R-L}[\text{OH}]_4$ ($\text{R} = \text{H}$ or $t\text{Bu}$) in methanol precipitated the respective calix[4]arene starting material. In the case of lithium substantial re-precipitation of calix[4]arenes was observed immediately after the addition of one equivalent of $[\text{Ti}(\text{acac})_2(\text{OPr}^t)_2]$, but for sodium, precipitation of calix[4]arenes occurred over some time. Changing the solvent system to THF, isopropanol, or toluene did not influence the course of the reaction.

Changing the ratio of sodium or lithium to the calix[4]arene gave a different result. The addition of two equivalents of either metal to $\text{R-L}[\text{OH}]_4$ followed by addition of $[\text{Ti}(\text{acac})_2(\text{OPr}^t)_2]$ gave a mixed Li–Ti, **5**, ($\text{R} = t\text{Bu}$) or Na–Ti, **6**, ($\text{R} = \text{H}$) complex, as shown in Scheme 1, although only the Na–Ti complex **6** yielded crystals suitable for X-ray structural determination, which revealed a dimeric structure. On the basis of the similar ^1H NMR spectrum of the Li–Ti complex, we assume that it has a similar dimeric structure (see below), although any discussion on the atom-to-atom connectivity for this complex would be speculative. These dimeric complexes could also be prepared by the addition of two equivalents of Li or Na to $\text{R-L}[\text{OH}]_4$ in methanol, followed by addition of one equivalent of $[\text{Ti}(\text{OPr}^t)_4]$, Scheme 1. Attempts to produce potassium–titanium dimers using the same approach were unsuccessful, yielding only insoluble titanium hydrolysis products. However, pre-mixing $[\text{Ti}(\text{OPr}^t)_4]$ with one equivalent of TMEDA prior to addition to a solution of calix[4]arene potassium complex, produced the K–Ti calix[4]arene dimeric complex, **7** ($\text{R} = t\text{Bu}$). Presumably, TMEDA momentarily protects $[\text{Ti}(\text{OPr}^t)_4]$ from side reactions arising from hydrolysis by adventitious water. The need to protect $[\text{Ti}(\text{OPr}^t)_4]$, in the case of potassium, is probably due to the strongly basic nature of the solution. Eqn. (1) outlines the species likely to be present in dimethylated calix[4]arene solutions in methanol ($\text{M} = \text{Li}, \text{Na}, \text{K}$).

Traces of hydroxide ions may also be produced, due to a similar equilibrium with any traces of water present in the solvent. The greater ionic character of K^+ , compared with Na^+ and Li^+ , may contribute to a higher activity of the deprotonated $\text{R-L}[\text{OH}]_4$ species in such solvolysis reactions. Evidently, for potassium, the equilibrium lies farthest to the right, so that an increased concentration of methoxide/hydroxide ions favours irreversible titanium solvolysis/hydrolysis. The introduction of just one equivalent of TMEDA seems to inhibit competing solvolysis/hydrolysis reactions of titanium sufficiently to allow the formation of the K–Ti calix[4]arene dimer to supervene.



A second synthetic route to the dimeric structures was devised, *viz.* the addition of four equivalents of alkali metal to $\text{R-L}[\text{OH}]_4$ followed by the addition of one equivalent of $[\text{TiCp}_2\text{Cl}_2]$, which gave each compound in yields similar to the aforementioned synthetic route. In this modified synthesis, the basic nature of the solution facilitates cleavage of both Cp ligands from $[\text{TiCp}_2\text{Cl}_2]$. Base cleavage of both Cp ligands from $[\text{TiCp}_2\text{Cl}_2]$ is consistent with previous reports that Cp groups are cleaved from titanocene reagents under basic conditions.²² Our ability to synthesise the K–Ti dimer from $[\text{TiCp}_2\text{Cl}_2]$ highlights an important factor in the formation of the K–Ti dimer, namely that it involves slow release of titanium into the reaction system. In our first synthesis, this is controlled by the chelating TMEDA ligand, and in the second, by the gradual solvolysis/hydrolysis of $[\text{TiCp}_2\text{Cl}_2]$.

Interestingly, the addition of $[\text{Ti}(\text{OPr}^t)_4]$ to $\text{R-L}[\text{OH}]_4$ ($\text{R} = \text{H}, t\text{Bu}$) that had been deprotonated using one equivalent of alkali metal in methanol, did not yield the dimers **5–7**. Different products were formed, as evident by the different solubilities,

colour and crystallisation behaviour. In the case of potassium, the new product could be crystallised and X-ray diffraction data was collected on a single crystal, albeit weakly diffracting and no meaningful solution was obtained.

Whilst the formation of the K–Ti calix[4]arene dimer **7** required at least 2:1:1 stoichiometry of potassium, calixarene and $[\text{Ti}(\text{OPr}^t)_4]$, respectively, reaction mixtures containing larger ratios of potassium were more stable, with a delayed onset of irreversible titanium hydrolysis. This effect was also observed for preparation of the complexes containing lithium and sodium, but was much more pronounced in the case of potassium.

Particularly noteworthy is that the K–Ti dimers did not form in the presence of acac, even in the presence of excess potassium metal. Hence, for potassium, formation of the monomeric acac complex seems to represent a more stable structure than the dimeric alternative. The higher stability of the K–Ti-acac complex, **1**, was demonstrated by the facile conversion of K–Ti dimers to the K–Ti-acac monomers (in *ca.* 98% yield) by the addition of one equivalent of acetylacetone, Scheme 1. In contrast, the Na–Ti dimers could not be converted to the K–Ti-acac monomeric complex by similarly adding one equivalent of $\text{K}(\text{acac})$.

Solid state structures

Of the dimer products, only the K–Ti combination with $t\text{Bu-L}[\text{OH}]_4$ afforded crystals suitable for X-ray structure determination, compound **7**, although the crystals were weakly diffracting and the structure is of limited precision. For the Na–Ti combination, **6**, X-ray quality crystals were obtained using $\text{H-L}[\text{OH}]_4$, and for the Li–Ti combination no X-ray quality crystals could be grown using either of the calixarenes, $\text{H-L}[\text{OH}]_4$ or $t\text{Bu-L}[\text{OH}]_4$.

The structure of compound **6** (Fig. 1)²³ revealed a crystallographically imposed centrosymmetric dimeric arrangement, with two distorted octahedral titanium(IV) centres, each attached to four phenolato oxygen atoms of a calix[4]arene, and two bridging methoxy ligands. The sodium atoms have a tetrahedral coordination geometry, consisting of one phenolato oxygen atom from different calix[4]arene molecules and two methanol ligands. There are six methanol solvates per dimer,

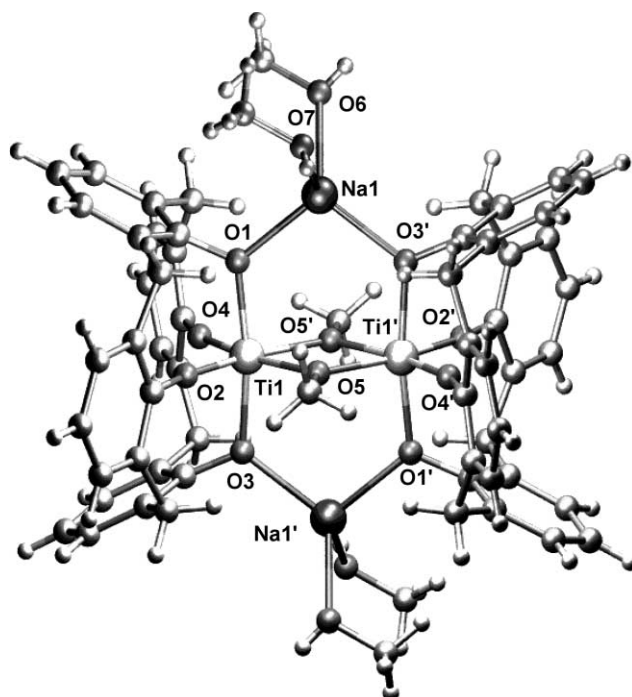


Fig. 1 Molecular projection of **6**. A disordered methanol molecule resides in the cavity of each calixarene, and for clarity are not shown.

Table 1 Selected bond distances (Å) and angles (°) for **6**; molecules lie on inversion centres and the primed atoms are generated by the symmetry operation

Ti1–O(1, 3)	2.0051(14), 2.0137(14)
Ti1–O(2, 4)	1.8096(13), 1.8211(14)
Ti1–O(5, 5')	2.0209(13), 2.0187(14)
Na1–O(1, 3)	2.2766(15), 2.2685(15)
Na1–O(6, 7)	2.305(2), 2.3639(19)
Ti1 ... Ti1'	3.2757(6)
O1–Ti1–O(2, 3, 4, 5, 5')	87.34(6), 171.39(6), 87.32(6), 93.47(6), 93.41(6)
O2–Ti1–O(3, 4, 5, 5')	87.29(6), 100.88(6), 93.47(6), 164.87(6)
O3–Ti1–O(4, 5, 5')	87.09(6), 93.55(6), 93.53(6)
O4–Ti1–O(5, 5')	165.88(6), 94.24(6)
O5–Ti1–O5'	71.64(6)
O1–Na1–O(3', 6, 7)	103.85(6), 113.39(7), 116.99(6)
O3–Na1–O(6, 7)	119.47(7), 116.99(7)
O6–Na1–O7	91.48(8)
Ti1–O5–Ti1'	108.36(6)

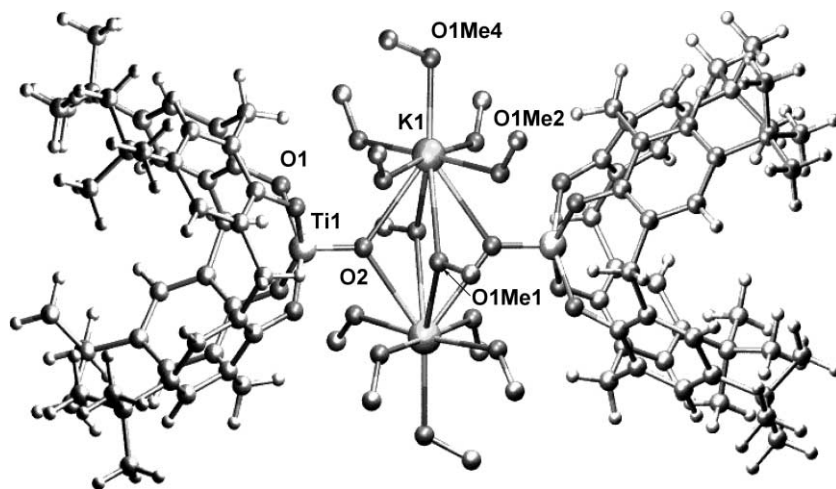


Fig. 2 Molecular projection of **7** showing only one set of pairs of disordered potassium atoms and methanol molecules, and the bridging methanol molecules. A disordered methanol molecule resides in the cavity of each calixarene, and for clarity is not shown.

four are coordinated to the sodium centres and two disordered methanols are located within the calixarene cavities. Selected bond lengths and angles for **6** are included in Table 1. A similar Na–Ti dimer has been reported recently, which consists of tetrahedral sodium and octahedral oxo-bridged titanium centres linking calix[4]arene units. Additionally sodium atoms occupy *endo*-positions relative to the calixarene cavities.²⁴ The Ti–O and Na–O distances in **6** range from 1.8096(13)–2.0187(14) Å and 2.2685(15)–2.3639(19) Å respectively. These distances are very similar to those for the above-mentioned complex *viz.* 1.988(2)–2.086(2), and 2.277(3)–2.368(4) Å.

While refinement of the structure of **7** was inherently difficult due to disorder and weak data, it nevertheless revealed the overall atom-to-atom connectivity and spatial arrangement of a dimeric complex, which also has a crystallographically imposed inversion centre. The central core consists of a rhombus of alternating potassium and μ_3 oxo-centres, with each oxygen atom in an apical position in a square-pyramidal titanium(IV) geometry. The basal plane ligands are the four phenolate oxygen centres from a calix[4]arene which is in a symmetrical cone conformation. Additional μ_2 bridging methanol ligands connect the potassium centres, thereby defining another rhombus of alternating K and O atoms, whose plane is perpendicular to the oxo ligands. Notably, the bridging methanol and potassium cations and associated methanol ligands are disordered over two sets of positions related to each other by a 90° rotation along the principle axis of the molecule. The expanded coordination sphere of the potassium centres, each with nine ligands, two bridging oxo, two bridging methanol and five terminal methanol solvates, is best described as capped square antiprismatic, Fig. 2.²³ Intramolecular hydrogen bonding is also prevalent, with calixarene–methanol O1 ... O1Me2 distance

2.60 Å, and additional interactions between bridging oxo- and bridging methanol ligands, O2 ... O1Me1, 2.66 Å. Overall there are 22 methanol solvates per dimer: 12 are coordinated to potassium centres, two are located in the cavities of the calix[4]arenes, and the remaining 8 are located in the interstitial sites in the structure.

The ¹H NMR spectrum of **6** is inconsistent with its solid-state structure. Present are the characteristic pair of methylene doublets usually observed for calix[4]arene organised in the cone conformation, but the aryl and ^tBu protons of the calixarenes appear as broad singlets, despite the identification of two chemically inequivalent aryl proton environments in the crystal structure. Hence, although the complexation of calix[4]arene in the cone conformation is indeed reflected in the ¹H NMR spectrum, its unsymmetrical conformation is not evidenced on the NMR time scale. For complex **7**, equivalences of aryl and ^tBu protons are expected in the ¹H NMR spectrum and this is indeed the case. The similarity of ¹H NMR spectra for all three dimers in solution does not reflect the difference in connectivity found in the structure of **6** and **7**. For the dimers **6** and **7**, structural organisation depends on the alkali metal, as does the coordination of the titanium centres. On this basis, it is unclear what structure the Li–Ti complex, **5**, would assume but, given the tendency for lithium–calixarene complexes to dimerize,²⁵ the postulation of at least dimers is not unreasonable.

The structures of complexes **6** and **7** give insight into the ease of the conversion of the K–Ti dimer to the K–Ti-acac monomer compared with the Na–Ti dimer. For complex **7**, titanium has a square-pyramidal coordination, with an *oxo*-bridge between titanium and potassium centres. Hydrogen bonding between the potassium's methanol solvates and the calixarene possibly stabilises the *oxo*-bridging. We have previously

prepared similar structures using group 2 cations in place of potassium²⁰ but, unlike **7**, they are insoluble in methanol. The solubility of **7** in methanol may arise from formation of solvent-separated ion pairs. This aside, the formation of the K–Ti–acac monomer is not surprising given that it results in the more favourable octahedral coordination for titanium(IV) centres and that the ambient Hacac may disrupt any dimers present in solution *en route* to the monomeric species. For the Na–Ti dimer **6** there is no conversion to a monomer on addition of Kacac. A methanol solution of the Na–Ti calixarene complex is also less likely to form solvent-separated ion pairs, since the smaller Na⁺ cation is more polarising and the dimeric Na–Ti structure (unlike the K–Ti dimer) already has titanium in an octahedral coordination. However, the selective formation/crystallisation of the Na–Ti dimer, even in the presence of Kacac, could simply be a manifestation of solubility differences. The formation of the *oxo*-bridged dimer exclusively for the larger K⁺ cation may relate to limitations on accommodating large cations around the central core.

Our findings show that for alkali metals smaller than potassium, no monomeric complexes containing *endo*-alkali metal, and *exo*-titanium form from methanol, with these metals preferring to assume *exo*-bridged dimeric structures. However for the larger potassium and caesium cations, monomeric *endo*-potassium/caesium *exo*-titanium complexes result, as evidenced by the ready formation of the complexes **1–4**. A rationalisation for this may be adduced from the structures of **1–4**.

Complexes **1** and **4**, have crystallographically imposed 2-fold symmetry whereas compound **2** has no such symmetry, however the atom-to-atom connectivity is similar in each therefore a detailed discussion of the structures is restricted mainly to complex **1**. The titanium(IV) centres, as expected, are octahedral, coordinating to all four O-centres of the calix[4]arene. This, coupled with the bidentate ligand *exo* to the calix[4]arene cavity, and the regular octahedral stereochemistry of the titanium centre, necessitates pinching of the calix[4]arene ring into an elliptical conformation. The potassium ion is accommodated in the calix[4]arene cavity, ligated by two solvent molecules, and two O-centres of the calixarene from opposite phenolate moieties, with close π -interactions to the other two opposing phenolate rings, Fig. 3.²³ Tables 2 and 3 summarise important bond distances and angles for **1** and **4**, and **2** and **3**, respectively. Although Cs⁺ is much larger than K⁺, the overall complex structure is the same, Fig. 4.²³ The K⁺– η^6 -arene-(centroid) distances for **1** and **2** are 3.142 and 3.180, 3.253 Å

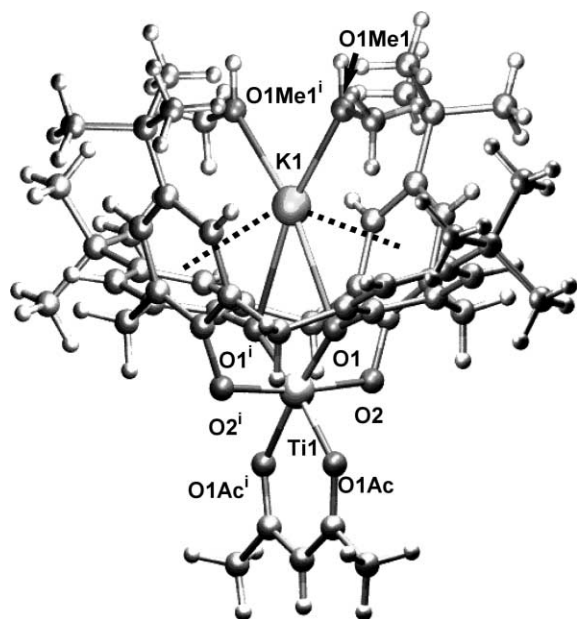


Fig. 3 Molecular projection of **1**; broken lines represent K $\cdots\pi$ interactions.

Table 2 Selected bond distances (Å) and angles (°) for **1** and **4**, M = K and Cs respectively; molecules lie on C₂ axes and primed atoms refer to those atoms generated by the symmetry axis

	1	4
Ti1–O1	1.8307(19)	1.83(3)
Ti1–O2	1.9907(18)	1.989(2)
Ti1–O1Ac	1.999(2)	1.973(4)
M1–O1	2.833(2)	3.137(3)
M1–O1Me1	2.68(3)	3.014(5)
O1–Ti1–O1 ⁱ	94.24(13)	95.9(2)
O1–Ti1–O2	86.51(8)	88.3(1)
O1–Ti1–O2 ⁱ	88.75(8)	87.2(1)
O1–Ti1–O1Ac	91.45(9)	89.7(2)
O1–Ti1–O1Ac ⁱ	173.76(9)	174.4(2)
O2–Ti1–O2	173.02(11)	173.2(2)
O2–Ti1–O1Ac	91.45(9)	93.6(1)
O2–Ti1–O1Ac ⁱ	173.76(9)	91.4(1)
O1–M–O1 ⁱ	56.53(8)	51.2(9)
O1–M–O1Me1	108.78(8)	111.0(1)
O1–M–O1Me1 ⁱ	165.29(8)	162.1(1)
O1Me1–M–O1Me1 ⁱ	85.91(15)	86.8(2)

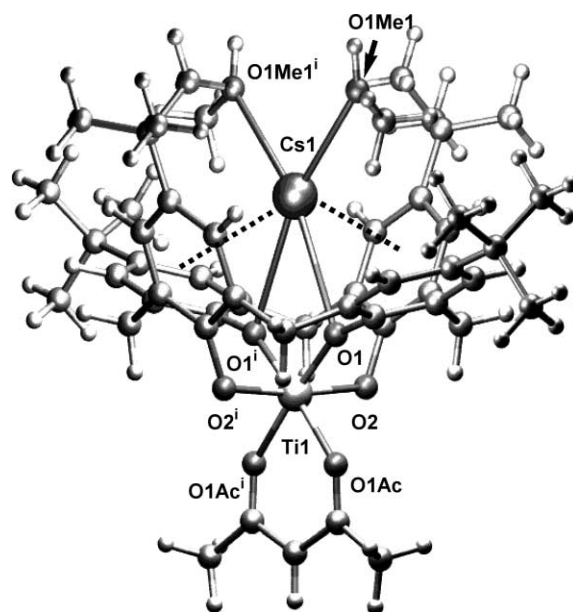


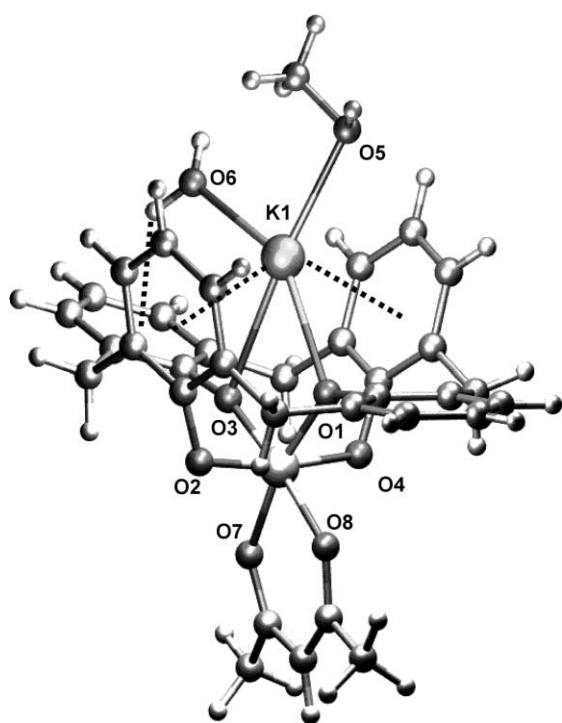
Fig. 4 Molecular projection of **4**; broken lines represent Cs $\cdots\pi$ interactions.

respectively, which are similar to values reported previously for a mixed *endo*-*exo*-potassium *exo*-titanium dimeric calix[4]arene complex (3.217 Å).²⁴ For complex **4** the Cs⁺– η^6 -arene-(centroid) distance is 3.353 Å, which is also similar to values reported previously for *endo*-caesium calix[4]arene complex, *viz.* 3.35 Å.⁹ The pitch angles of the planes defined by the calixarene phenyl groups relative to the plane defined by the four calixarene oxygens are: 18.2(5) and 70.1(5)° for **1**, 12.0(5), 67.7(5), 13.2(5) and 66.1(5)° for **2**, and 21.4(5) and 67.0(5)° for complex **4**.

The structure of **3** shows significant differences from those of **1**, **2**, and **4**, Fig. 5.²³ In particular the calix[4]arene conformation is considerably distorted in **3** which may relate to the absence of bulky 'Bu groups, coupled with crystal packing forces. The pitch angles of the planes defined by the calixarene phenyl groups relative to the plane defined by the four calixarene oxygens are 9.7(5), 75.1(5), 30.1(5) and 71.9(5)°. The *endo*-potassium, (K⁺– η^6 -arene(centroid) 3.022, 3.079 Å) coordinates only one methanol, the other coordination site being occupied by a water molecule, which appears to be involved in HOH $\cdots\pi$ interaction (arene(centroid) \cdots H distance at 2.314 Å), Fig. 5.²³ Similar interactions have been reported

Table 3 Selected bond distances (Å) and angles (°) for **2** and **3**

	2	3
Ti1–O(1, 3)	1.8593(16), 1.8547(16)	1.875(1), 1.825(1)
Ti1–O(2, 4)	1.9503(17), 1.9622(17)	1.990(1), 1.991(1)
Ti1–O(7, 8)	1.9989(17), 2.0130(17)	1.982(2), 2.011(1)
K1–O(1, 3)	2.7476(17), 2.7479(17)	2.697(1), 2.928(1)
K1–O(5, 6)	2.706(2), 2.693(2)	2.667(2), 2.696(2)
O1–Ti1–O(2, 3, 4, 7, 8)	87.89(7), 90.86(7), 87.44(7), 173.94(7), 91.04(7)	88.25(6), 94.34(6), 85.59(6), 167.57(6), 88.90(6)
O2–Ti1–O(3, 4, 7, 8)	87.81(7), 172.90(7), 94.79(7), 92.04(7)	85.91(6), 173.03(6), 100.65(6), 88.97(6)
O3–Ti1–O(4, 7, 8)	86.91(7), 94.66(7), 178.09(7)	88.05(6), 94.94(6), 173.86(6)
O4–Ti1–O(7, 8)	90.37(7), 93.40(7)	86.47(6), 97.41(6)
O7–Ti1–O8	83.45(7)	82.65(6)
O1–K1–O(3, 5, 6)	57.56(5), 110.84(6), 162.04(6)	57.50(4), 122.80(5), 145.81(5)
O3–K1–O(5, 6)	168.40(7), 104.62(6)	171.17(5), 88.39(4)
O5–K1–O6	86.98(7)	91.23(5)

**Fig. 5** Molecular projection of **3**; broken lines represent K $\cdots \pi$ and HOH $\cdots \pi$ interactions.

previously for calix[4]arene complexes.²⁶ The Ti–O and Group 1–O distances are unremarkable²⁴ ranging from 1.83(3)–2.0130(17) Å and 2.667(2)–2.928(1) Å (M = K), 3.014(5)–3.137(3) Å (M = Cs).

¹H NMR spectra of **1**, **2**, **3** and **4** in chloroform solutions are all consistent with the X-ray structures, giving the characteristic set of doublets for the methylene protons and two signals each for the *t*-Bu protons and aryl protons (as expected for calix[4]arene complexed in the unsymmetrical pinched cone conformation).

The formation of both the monomeric and dimeric alkali metal–titanium complexes presumably relate to both the solubilisation and increased reactivity imparted to calix[4]arenes by mono/di-alkali metallation. Adding [Ti(acac)₂(OPr^{*i*})₂] to calixarenes in the presence of potassium or caesium ions forms *endo*-potassium/caesium, *exo*-titanium complexes, where the favourable chelation of the titanium ion by the calix[4]arene, and by acac, relegates the potassium/caesium cation to bind in the *endo*-position. The elliptical distortion resulting from octahedral titanium binding brings two opposing phenyl groups of calix[4]arene into close proximity, this distortion contributing to the favourable bonding of potassium/caesium ions within the calixarene cavity, even in the presence of competing methanol solvation. The *endo*-complexation of a caesium

cation by calix[4]arene itself has been observed previously, however these complexes were formed in CH₃CN^{7,9} and CHCl₃,²⁷ both being comparatively weaker donor solvents. For potassium, no previous *endo*-complexes have been observed in the absence of other cations binding *exo*-, whereas for Rb⁺ *endo/exo* complexation with R–L[OH]₄ is dependent on R: *endo*-complexation occurs where R = H, and *exo*-complexation for R = *t*-Bu.⁸ Notably the *endo*-Rb⁺ cation in the H–L[OH]₄ complex also coordinates *exo*- to a second calixarene unit (this has also been observed for analogous caesium complexes). Therefore the change in complexation mode for *p*-*t*-Bu–L[OH]₄ is likely to result from steric hindrance by the *p*-*t*-Bu groups, which lowers the accessibility of the *endo*-metal for stabilising external interactions with solvent or donor atoms of another calixarene, resulting in *exo*-coordination being preferable overall.

For the smaller potassium cation, the elliptical distortions resulting from *exo*-titanium complexation are required to make its bonding within the calix[4]arene cavity energetically favourable. Without significant pinching of the calix[4]arene, *endo*-positioned potassium ions would be unable to coordinate with more than one aromatic ring in a polyhaptic mode. In contrast, *endo*-complexation of the larger caesium cation (ionic radii 1.67 Å vs. 1.38 Å) with *p*-*t*-Bu–L[OH]₄, has shown polyhaptic coordination to all four aromatic rings without the need for calixarene distortions, pointing to the better size complementarity.

Our inability to obtain analogous sodium and lithium complexes, under the same conditions, suggests that the bonding of the smaller alkali metals by the calix[4]arene cavity is not competitive with *exo*-complexation in methanol, THF, isopropanol or toluene, even with the favourable energetics associated with chelation of titanium(IV) and the accompanying pinching distortions of the calix[4]arene cavity. Whereas Li⁺ or Na⁺ ions may be solvated by up to six methanols in solution, on entering the cavity they could interact with only the two phenolates of the calixarene and two methanol solvates. Unlike the case for K⁺, both Li⁺ and Na⁺ are too small to interact significantly with the opposite phenyl rings in a polyhaptic fashion, even when they are brought into closer proximity by binding of octahedral coordinated titanium(IV) centres. This view has been evidenced previously in a published Na–Ti dimer structure consisting of tetrahedral sodium and octahedral *oxo*-bridged titanium centres linking calix[4]arene units, in which additional sodium atoms occupy *endo*-positions but do not participate in cation $\cdots \pi$ interactions.²⁴ Essentially, for Li⁺ and Na⁺, the desolvation penalty for entering the calixarene cavity can not be compensated by $\pi \cdots \pi$ arene interactions.

Notwithstanding these arguments, mixed transition–alkali metal calix[4]arene complexes have been prepared, where sodium and lithium atoms are found within the calix[4]arene cavity. Their synthesis involves firstly coordinating the transition metal and then using an alkali metal metathesis reaction to

bind the alkali metal. Under these circumstances, no competing coordination is available to the alkali metal. From the crystal structures, a series of complexes consisting of Ta(v) coordinated in the *exo*-position and K, Na or Li in the *endo*-position,¹⁰ the interaction of the alkali metal cation with the arene system of the calix[4]arene cavity varies from bis- η^6 -coordination for potassium to a single η^6 -coordination for sodium and single η^3 -coordination for lithium. In these systems tantalum(v), like titanium(iv) in our case, is octahedrally coordinated, binding through all four calix[4]arene phenolates and causing similar elliptical calix[4]arene distortions, bringing opposing phenyl groups closer together, and almost parallel. These results illustrate the comparatively weak bonding of lithium and sodium ions by the calix[4]arene cavity. This explains why the chemistry reported here does not extend to the use of sodium and lithium, which presumably prefer *exo*-O-bonding to *endo*- π /O-bonding.

Conclusions

Our simple synthetic strategy has led to the formation of novel monomeric and dimeric calixarene complexes. The size complementarity of the calix[4]arene cavity with potassium and caesium cations, in the presence of *exo*-bound Ti(acac), evidently allows desolvation energies in methanol to be comparable with the energies of *endo*-cavity complexation. This balance enables the formation of monomeric titanium(iv) calixarene complexes. The chemistry illustrates the potential for synergistic metal binding to calix[4]arenes from competitive donor solvents, and has implications in designing reactions for other transition metal complexes of the same calixarene, and indeed, larger calixarenes, or to other types of polyphenolic systems, perhaps of biological origin which are known to feature a mixture of *oxo*- and aromatic binding sites. In the absence of acac, *exo*-bound potassium/titanium dimers form. This also occurs with the smaller alkali metal cations, which failed to bind within the calixarene cavity.

Experimental

All reactions were carried out in air. [Ti(acac)₂(OPr^t)₂] (75%, HOPr^t), [Ti(OPr^t)₄] (97%, HOPr^t), K-selectride (1 M, THF), dimethoxyethane, CsCl, potassium, sodium and lithium were all obtained from Aldrich and used as received. Reagent grade methanol was used, *p*-*tert*-butyl-calix[4]arene and calix[4]arene were synthesised according to the literature.²⁸ Crystal data: Data for **1**, **2** and **6** were collected at 150(2) K on an Enraf-Nonius Kappa CCD diffractometer with Mo-K α radiation. The structures were solved by direct methods (SHELXS-97) and refined with a full matrix least-square fit refinement on F^2 (SHELXS-97). Data for **3**, **4** and **7** were collected at 150(2) K on a Bruker-AXS SMART 1000 CCD diffractometer with Mo-K α radiation, and the structures were solved by direct methods (SIR92) and refined with full matrix least-squares refinements on F (RAELS).

Synthesis of 1

To a suspension of 'Bu-L[OH]₄ (0.5 g, 0.77 mmol) in methanol (15 ml) was added potassium metal (0.04 g, 1.0 mmol). The mixture was stirred, giving a clear pale yellow solution on complete reaction of the potassium. The addition of [Ti(acac)₂(OPr^t)₂] (0.4 ml, 75 %, 0.82 mmol) gave an orange solution, which was evaporated by boiling to incipient crystallisation. On slow cooling to 0 °C orange-yellow prisms of **1** deposited (0.60 g, 72 %). A crystal suitable for X-ray structure determination was selected from this sample.

Syntheses of 2 and 3

2 and **3** were prepared as for **1** except that for **2** dry THF and potassium selectride (1 M in THF) were used in place of

methanol and potassium metal. For **3**, calix[4]arene was used in place of 'Bu-L[OH]₄, and dimethoxyethane (~1 ml) was added after concentrating the solution to ~5 ml. These methods gave orange-yellow prisms of **2** (0.45 g, 56 %) and **3** (0.46 g, 63 %). Crystals suitable for X-ray structure determination were selected from these samples.

Synthesis of 4

To a suspension of 'Bu-L[OH]₄ (0.5 g, 0.77 mmol) in methanol (50 ml) was added sodium metal (0.02 g, 0.85 mmol). The mixture was stirred, affording a clear pale yellow solution on complete reaction of the sodium. CsCl (0.14 g, 0.83 mmol) was then dissolved in this solution by heating. From this point onward the procedure followed that for the preparation of **1**, affording orange-yellow prisms of **4** (0.7 g, 81%).

Syntheses of 5–7

Full experimental details are given for the syntheses of **7**, the syntheses of **5** and **6** being similar. To a suspension of 'Bu-L[OH]₄ (0.50 g, 0.77 mmol) in methanol (30 ml) was added potassium (0.070 g, 1.8 mmol). The mixture was stirred affording a clear pale yellow solution on complete reaction of the metal. [Ti(OPr^t)₄] (0.25 ml, 97%, 0.84 mmol) and TMEDA (0.15 ml, 1 mmol), were mixed and then diluted in ~5 ml methanol, and this solution was added to the solution of potassium calix[4]arene. If a solid formed, the mixture was heated to boiling, and sufficient methanol was added until the solid dissolved completely. Otherwise, the solution was evaporated by boiling. On slow cooling to 0 °C, pale yellow prisms deposited (0.60 g, 90%). Procedures for the syntheses of **5** and **6** were analogous, except that for **6**, H-L[OH]₄ was used in place of 'Bu-L[OH]₄, and neat [Ti(OPr^t)₄] was added to a solution of the alkali metal calix[4]arene complex. This gave **6** as colourless prisms (0.50 g, 76%) and **5** as pale yellow needles (0.56 g, 89%). ¹H NMR spectra were obtained immediately from the freshly prepared crystals. The samples were observed to crumble on prolonged exposure to air. After such exposure, the materials no longer dissolved completely in chloroform. Crystalline samples left in their mother liquor, but exposed to air, decomposed over several weeks.

¹H NMR: (300 MHz): **1** δ 7.13 (s, 4 H, aryl), 6.91 (s, 4 H, aryl), 5.94 (s, 1 H, CH), 4.53 (d, 4H, J = 15 Hz, CH₂), 3.45 (s, 24 H, methanol), 3.12 (d, 4 H, J = 15 Hz, CH₂), 2.00 (s, 6 H, CH₃), 1.37 (s, 18 H, 'Bu), 1.10 (s, 18 H, 'Bu) **2** 7.13 (s, 4 H, aryl), 6.93 (s, 4 H, aryl), 5.93 (s, 1 H, CH), 4.52 (d, 4 H, J = 15 Hz, CH₂), 3.69 (m, 12 H, THF), 3.14 (d, 4 H, J = 15 Hz, CH₂), 1.98 (s, 6 H, CH₃), 1.83 (m, 12 H, THF), 1.37 (s, 18 H, 'Bu), 1.10 (s, 18 H, 'Bu), **3** 7.11 (d, 4 H, J = 7.5 Hz, aryl), 6.93 (d, 4 H, J = 7.5 Hz, aryl), 6.74 (t, 2 H, J = 6 Hz, aryl), 6.44 (t, 2 H, J = 6 Hz, aryl), 6.00 (s, 1 H, CH), 4.55 (d, 4 H, J = 15 Hz), 3.21 (s, 3 H, methanol), 3.15 (d, 4 H, J = 15 Hz, CH₂), 2.04 (s, 6 H, CH₃), 4 7.08 (4 H, s, aryl), 6.92 (4 H, s, aryl), 5.92 (1 H, s, CH), 4.52 (4 H, d, J = 13.5 Hz, CH₂), 3.42 (18 H, s, methanol), 3.09 (4 H, d, J = 13.5 Hz, CH₂), 2.00 (6 H, s, CH₃), 1.35 (18 H, s, 'Bu), 1.13 (18 H, s, 'Bu), **5** 6.95 (s, 16 H, aryl), 4.65 (d, 8 H, J = 12 Hz, CH₂), 3.03 (d, 8 H, J = 12 Hz, CH₂), 1.16 (s, 72 H, 'Bu), **6** 6.94 (d, 16 H, J = 12 Hz, aryl), 6.48 (t, 8 H, J = 9 Hz, CH₂), 4.65 (d, 8 H, J = 12 Hz, CH₂), 3.47, (s, 24 H, OCH₃), 3.08, (d, 8 H, J = 12 Hz, CH₂), **7** 6.95 (s, 16 H, aryl), 4.62 (d, 8 H, J = 12 Hz, CH₂), 3.35, (s, 66 H, methanol), 3.08 (d, 8 H, J = 12 Hz, CH₂), 1.16 (s, 72 H, 'Bu).

Crystal data

1 C₄₉H₅₉KO₆Ti.8(CH₃OH), M = 1087.3, monoclinic, a = 14.2018(5), b = 21.9002(9), c = 21.284(8) Å, β = 106.461(2)°, U = 6302.1(4) Å³, T = 150(2) K, space group $C2/c$, Z = 4, μ (Mo-K α) = 0.259 mm⁻¹, 12718 reflections collected, 4209 unique (R_{int} = 0.0385). The final R = 0.0503, and wR = 0.1324

$[I > 2\sigma(I)]$. **2** $C_{49}H_{59}KO_6Ti_3(THF)$, $M = 1047.27$, monoclinic, $a = 13.8800(2)$, $b = 20.3074(3)$, $c = 21.3492(3)$ Å, $\beta = 96.309(2)^\circ$, $U = 5981.18$ (15) Å³, $T = 150(2)$ K, space group $P2_1/n$, $Z = 4$, $\mu(Mo-K\alpha) = 0.265$ mm⁻¹, 66468 reflections collected, 11731 unique, ($R_{int} = 0.082$). Final $R = 0.0562$, and $wR = 0.1455$ [$I > 2\sigma(I)$]. **3** $C_{33}H_{27}KO_6Ti_3CH_3OH \cdot H_2O$, $M = 656.6$, orthorhombic, $a = 12.190(2)$, $b = 15.107(3)$, $c = 16.424(3)$ Å, $U = 3025$ (1) Å³, $T = 150(2)$ K, space group $P 21 21 21$, $Z = 4$, $\mu(Mo-K\alpha) = 0.467$ mm⁻¹, 38999 reflections collected, 7294 unique, ($R_{int} = 0.048$). Final $R = 0.033$, and $wR = 0.047$ [$I > 2\sigma(I)$]. **4** $C_{49}H_{59}C_{10}S_6O_6Ti_6(CH_3OH)$, $M = 1117.1$, monoclinic, $a = 13.622(5)$, $b = 22.248(7)$, $c = 21.168(7)$ Å, $\beta = 105.12(1)^\circ$, $U = 6193(6)$ Å³, $T = 150(2)$ K, space group $C2/c$, $Z = 4$, $\mu(Mo-K\alpha) = 0.761$ mm⁻¹, 29958 reflections collected, 7399 unique ($R_{int} = 0.030$). The final $R = 0.061$, and $wR = 0.093$ [$I > 2\sigma(I)$].

6 $C_{58}H_{46}Na_2O_{10}Ti_2 \cdot 6(CH_3OH)$, $M = 1236.98$, monoclinic, $a = 12.1807(2)$, $b = 14.9482(2)$, $c = 16.5026(3)$ Å, $\beta = 94.770(2)^\circ$, $U = 2994.38(8)$ Å³, $T = 150(2)$ K, space group $P2_1/n$, $Z = 4$, $\mu(Mo-K\alpha) = 0.351$ mm⁻¹, 53795 reflections collected, 5880 unique ($R_{int} = 0.0758$). The final $R = 0.0406$, and $wR = 0.1117$ [$I > 2\sigma(I)$].

7 $C_{44}H_{53}KO_5Ti_11(CH_3OH)$, $M = 1101.4$, tetragonal, $a = 15.558(3)$, $c = 26.922(8)$ Å, $U = 6157(4)$ Å³, $T = 150(2)$ K, space group $I422$, $Z = 4$, $\mu(Mo-K\alpha) = 0.248$ mm⁻¹, 2208 reflections collected, 2163 unique ($R_{int} = 0.015$). The final $R = 0.125$, and $wR = 0.176$ [$I > 2\sigma(I)$].

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See <http://www.rsc.org/suppdata/dt/b3/b310635g/> for crystallographic data in CIF or other electronic format.

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