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Group 1 and mixed Group 1 and 2 metal complexes of dianionic *p-tert*-butylcalix[4]arenes

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Group 1 and related complexes of 1,3-*O,O′*-disubstituted *p-tert*-butylcalix[4]arene dianions [^{t}Bu-calix[4](OR)$_2$(O)$_2$]$^{2-}$ are reported. Reaction of ^{t}Bu-calix[4](OMe)$_2$(OH)$_2$ with NaH, K, Rb or Cs gave dimeric [M$_2${^{t}Bu-calix[4](OMe)$_2$(O)$_2$}]$_2$ (M = Na **1**, K **2**, Rb **3** or Cs **4**). The X-ray structure of **1** shows that two Na$^+$ ions are *exo*-bound between the two calix[4]arene ligands while the other two are *endo*-bound within the calix[4]arene cavities. Reaction of ^{t}Bu-calix[4](OMe)$_2$(OH)$_2$ with ^{n}BuLi (2 equiv.) gave a mixture of dimeric and monomeric compounds. Complex **1** is cleaved by 15-crown-5 forming [Na$_2${^{t}Bu-calix[4](OMe)$_2$(O)$_2$}(15-crown-5)]. The complexes **2**–**4** are cleaved by dibenzo-18-crown-6 forming [M$_2${^{t}Bu-calix[4](OMe)$_2$(O)$_2$}(dibenzo-18-crown-6)]. Reactions of ^{t}Bu-calix[4](OR)$_2$(OH)$_2$ (R = CH$_2$Ph or SiMe$_3$) with Li or Na reagents gave monomeric [M$_2${^{t}Bu-calix[4](OR)$_2$(O)$_2$}]. The reaction of **1** with CsCl gave [NaCs{^{t}Bu-calix[4](OMe)$_2$(O)$_2$}]$_2$ **13** in which the two Cs$^+$ ions are *endo*-bound. Reaction of **1** with CaCl$_2$ formed [Na$_2$Ca{^{t}Bu-calix[4](OMe)$_2$(O)$_2$}$_2$].

Introduction

Functionalised (either at the 'lower rim' oxygens or the 'upper rim' carbons) and non-functionalised calixarenes have received intense attention over the past 20 years.[1–4] Most of this interest has focussed on the calix[4]arene series (which contain four phenolic residues) and these are the subject of our present contribution. Calixarene research has focussed on several key areas, with much of the initial work concentrating on the application of functionalised calix[4]arenes as receptor molecules through *endo*-binding of substrates within their cavities (for classification purposes these could be labelled 'supramolecular' or 'coordination chemistry' applications).[1–3] From an organometallic and organometallic-related standpoint, dianionic di-O-alkyl functionalised calix[4]arenes have served as novel and versatile O-donor ligand platforms (tri- and tetra-anionic homologues have also received attention) and much new transition metal[3–5] and post-transition metal[6] chemistry has emerged.

We had initially been interested in the use of dianionic calix[4]arenes as platforms for Group 4 imido chemistry[7] and in the course of these studies isolated and structurally characterised a homoleptic (in that there are no ligands other than the calix[4]arenes themselves), tetrametallic sodium derivative [Na$_2${^{t}Bu-calix[4](OMe)$_2$(O)$_2$}]$_2$ **1** which was the subject of a preliminary communication.[8] As described below we have subsequently been interested to explore the synthesis and structures of other Group 1 (and also Group 2) metal derivatives of dianionic di-O-functionalised calix[4]arenes of the form [^{t}Bu-calix[4](OR)$_2$(O)$_2$]$^{2-}$ where R = Me, CH$_2$Ph or SiMe$_3$ (the abbreviations adopted here for the derivatised *p-tert*-butylcalix[4]arenes is that previously employed by Floriani and Floriani-Moro[4]).

Most related published work has been on Group 1 *non*-O-alkylated anionic calix[4]arenes,[1a] the first being Harrowfield's [Cs{^{t}Bu-calix[4](OH)$_3$(O)}(MeCN)] which has the Cs$^+$ cation bound *endo* to the lower rim (*i.e.*, within the calixarene cavity and not simply O-bound as might have been expected).[9] This was followed by Bock's report[10] of a dimeric, trilithiated derivative of ^{t}Bu-calix[4](OH)$_4$, a structurally related analogue of which is Davidson's[11] fully deprotonated octa-lithium species [Li$_4${^{t}Bu-calix[4](O)$_4$}(HMPA)$_2$]$_2$ (HMPA = hexamethylphosphoramide). This has six Li$^+$cations *exo*-bound between the fused calix[4]arenes and a further two Li$^+$cations *endo*-bound with additional π-interactions to the phenolic rings. Hanna and Gutsche have reported potassium derivatives of mono-O-deprotonated calix[4]arene and *p-tert*-butylcalix[4]arene,[12] and Thuéry *et al.* described sodium and cesium analogues of non-functionalised calix[4]arene;[13] in both of these reports there is incomplete deprotonation of the calixarene O–H groups. Floriani and coworkers[14] have recently reported the metallation/transmetallation reactions of *p-tert*-butylcalix-[4]arenes with certain Group 1 and 2 metals. The fully tetra-O-deprotonated compounds [M$_4${^{t}Bu-calix[4](O)$_4$}(THF)$_2$] (M = Li, Na, K) were reported and X-ray structures of THF- or pyridine-solvated derivatives for M = Na or K were described. These structures were reminiscent of that described by Davidson *et al.* for [Li$_4${^{t}Bu-calix[4](O)$_4$}(HMPA)$_2$]$_2$ although they clearly differ in specific details. Floriani and coworkers also described metallation reactions of di-O-alkylated ^{t}Bu-calix[4](OR)$_2$(OH)$_2$ (R = Me or C$_5$H$_9$ (cyclopentyl)) with ^{n}BuLi or M/naphthalene (M = Na, K).[14] The products, formulated as monomeric "[^{t}Bu-calix[4](OR)$_2$(OM)$_2$]", were not examined or discussed in any detail. Instead, some were used to prepare a series of novel Group 2 derivatives of the type [M{^{t}Bu-calix[4](OC$_5$H$_9$)$_2$(O)$_2$}-(L)] (M = Mg, Ca, Ba; L = THF, DME or TMEDA) and the mixed-metal compounds [Na$_2$Ba{^{t}Bu-calix[4](OR)$_2$(O)$_2$}$_2$] (R = Me or C$_5$H$_9$) which were analysed in detail. The contribution by Floriani prompted us to report our own related and complementary syntheses of Group 1 (and some mixed-metal) derivatives of di-O-alkylated *p-tert*-butylcalix[4]arenes. Part of this work has been communicated.[8] Note that for certain complexes, despite repeated recrystallisations, a satisfactory elemental analysis could not be obtained. However, we believe that the combined spectroscopic data (NMR, solution molecular weight measurements and ES mass spectrometry) and the fact that the compounds are members of homologous series give sufficient confidence in the assigned compositions in these instances.

Results and discussion

Synthesis of Group 1 complexes [M$_2${^{t}Bu-calix[4](OMe)$_2$(O)$_2$}]$_n$ (*n* = 1 or 2)

Our efforts focussed mainly on derivatives of the dimethyl ether ^{t}Bu-calix[4](OMe)$_2$(OH)$_2$. For comparison ^{t}Bu-calix[4](OCH$_2$-Ph)$_2$(OH)$_2$ and ^{t}Bu-calix[4](OSiMe$_3$)$_2$(OH)$_2$ were also employed,

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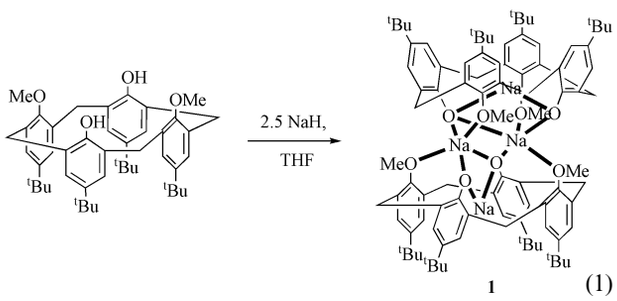
Table 1 Selected bond distances (Å) and angles (°) for $[Na_2\{^tBu\text{-calix}[4](OMe)_2(O)_2\}]_2$ **1** [8]

Na(1)–C(1)	2.792(3)	Na(2)–O(1A)	2.538(4)
Na(1)–C(13)	2.800(6)	Na(2)–O(2)	2.129(4)
Na(1)–C(20)	2.900(5)	Na(2)–O(3)	2.343(4)
Na(1)–C(27)	2.797(5)	Na(2)–O(4)	2.376(4)
Na(1)–O(2)	2.281(4)	Na(2)–O(4A)	2.259(4)
Na(1)–O(4)	2.283(4)		
O(1A)–Na(2)–O(3)	138.53(15)	O(2)–Na(2)–O(4)	88.55(15)
O(1A)–Na(2)–O(4)	127.84(14)	O(2)–Na(2)–O(4A)	163.32(17)
O(2)–Na(2)–O(1A)	90.84(15)	O(3)–Na(2)–O(4)	93.65(15)
O(2)–Na(2)–O(3)	89.86(15)		

but to a lesser extent. All three compounds were prepared according to previously described methods.[15,16]

Reaction of ^{t}Bu-calix[4](OMe)$_2$(OH)$_2$ with 2.5 equivalents of NaH in THF at room temperature afforded a brown suspension. Filtration and crystallisation from THF at −25 °C afforded $[Na_2\{^tBu\text{-calix}[4](OMe)_2(O)_2\}]_2$ **1** in 70% isolated yield (eqn. (1)). Crystallisation from THF at room temperature



(1)

afforded diffraction-quality crystals of **1**·6(THF) which lose THF very readily. The molecular structure of **1** is shown in Fig. 1 and selected bond lengths and angles are listed in Table 1.[17] The THF molecules of crystallisation show no bonding contacts to the Na^+ ions and occupy interstitial sites in the crystal lattice. This accounts for the ease with which THF can be removed from samples of **1**.

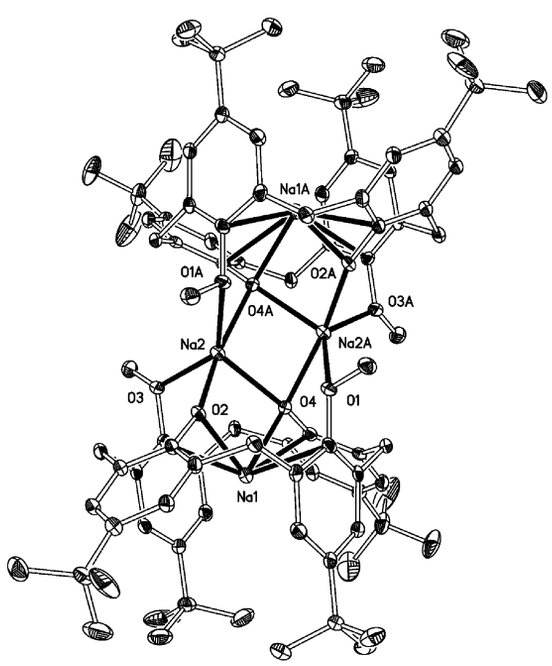


Fig. 1 Molecular structure of $[Na_2\{^tBu\text{-calix}[4](OMe)_2(O)_2\}]_2$ **1**. Displacement ellipsoids are drawn at the 50% probability level. H atoms and THF molecules of crystallisation omitted for clarity. Atoms carrying the suffix 'A' are related to their counterparts by the symmetry operator $1 - x, y, 3/2 - z$.[17]

Molecules of **1** are dimeric in the solid state and lie on crystallographic two-fold axes. Two *exo*-bound Na^+ cations bridge the two ^{t}Bu-calix[4](OMe)$_2$(O)$_2$ units and there are two *endo*-bound Na^+ cations encapsulated in the ^{t}Bu-calix[4](OMe)$_2$(O)$_2$ cavities. The *exo*-bound Na^+ cations [Na(2) and Na(2A)] possess an approximate trigonal bipyramidal coordination geometry coordinated to two ether O-donors and three aryloxide O-donors. The *endo*-bound Na^+ cations [Na(1) and Na(1A)] are bonded to the aryloxide O-groups of a calix[4]arene unit and exhibit bonding contacts[18] to the four phenol ring *ipso* (O-bound) carbons of a calix[4]arene unit. Na(1) and Na(1A) also feature $Na^+ \cdots$ arene ring π contacts to the ether phenol rings. The ether phenol rings bonded to O(1) and O(1A) exhibit η^3-coordination and the ether phenol rings bonded to O(3) and O(3A) exhibit η^5-coordination. The Na–O and Na $\cdots$ C distances lie within reported ranges.[19] The ^{t}Bu-calix[4](OMe)$_2$(O)$_2$ units posses partial flattened cone conformations. The two aryloxide rings are "flattened" with an angle of 75.1° between the normals to their planes (Fig. 2). The two ether rings are "inverted" and the normals to these planes form an angle of 176.2°. The individual $Na_2\{^tBu\text{-calix}[4](OMe)_2(O)_2\}$ moieties in **1** posses local C_1 symmetry because of the relative orientation of the second $Na_2\{^tBu\text{-calix}[4](OMe)_2(O)_2\}$ unit (*i.e.* the two ether rings [bearing O(1) and O(3)] and two aryloxide rings [bearing O(2) and O(4)] are inequivalent, as are the OMe groups).

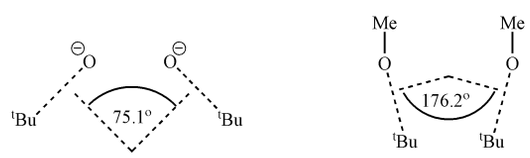


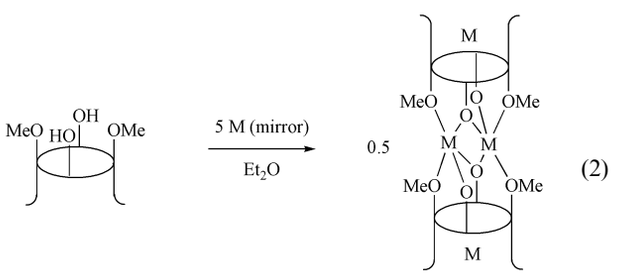
Fig. 2 Angles between the normals to least squares best-fit planes for the aryloxide- and ether-rings of $[Na_2\{^tBu\text{-calix}[4](OMe)_2(O)_2\}]_2$ **1**.

The positive ion electrospray (ES) mass spectrum (THF–MeOH) showed an ion envelope centered at 1376 Da which is assigned to a dimeric species $[\mathbf{1} - 3Na + 4H]^+$ consistent with partial ion-exchange of the parent complex. A cryoscopic solution molecular weight determination in benzene gave a molecular weight of 1442 g mol^{-1} (calculated value for dimeric **1** = 1441 g mol^{-1}). The IR spectrum (KBr/Nujol) showed no ν(OH) bands. The data indicate that the dimeric structure found for **1** in the solid state persists in solution, and that **1** contains fully O-deprotonated ^{t}Bu-calix[4](OMe)$_2$(O)$_2$ ligands.

The room-temperature ^{1}H and ^{13}C NMR spectra of **1** are sharp, featuring resonances for two different *tert*-butyl groups, a single OMe group and a pair of mutually-coupled methylene hydrogens attached to a single type (*i.e.* chemical environment) of methylene carbon. Unfortunately no resonances were observed in the ^{23}Na NMR spectrum. This is possibly due to a broadening of the ^{23}Na resonances due to a fluxional process (see below) and/or an unsymmetrical environment about the quadrupolar ^{23}Na nuclei (I = 3/2).[20] Cooling a sample in toluene-d$_8$ to 183 K caused a broadening of all of the ^{1}H resonances (but those for the residual protio-solvent remained sharp

indicating that the broadening is due to the slowing down of a fluxional process). However, a low-temperature limiting spectrum could not be attained in the available (solvent-determined) temperature range. The room-temperature NMR data imply that the $Na_2\{^tBu\text{-calix}[4](OMe)_2(O)_2\}$ units possess local C_{2v} symmetry on the NMR timescale. This is at odds with the dimeric structure established in the solid state and assumed to persist in solution on the basis of the cryoscopic solution molecular weight determination in benzene. The low-temperature toluene-d_8 data imply that there is in fact a facile, fluxional process which averages the local $^tBu\text{-calix}[4](OMe)_2(O)_2$ environment. Two fluxional processes are likely, namely effective rotation of the $^tBu\text{-calix}[4](OMe)_2(O)_2$ units with respect to each other, or effective translation of the $^tBu\text{-calix}[4](OMe)_2(O)_2$ units with respect to each other. Intramolecular and dissociation–association pathways are in principle possible for both of these. The available data cannot distinguish between them.

Reaction of $^tBu\text{-calix}[4](OMe)_2(OH)_2$ with an excess (5 equivalents per protio-ligand) of K, Rb or Cs metal in Et_2O afforded compounds analogous to **1**, namely $[M_2\{^tBu\text{-calix}[4](OMe)_2(O)_2\}]_2$ (M = K **2**, Rb **3** or Cs **4**) in 82–87% isolated yield (eqn. (2)). Repeated attempts to obtain diffraction-quality crystals failed (as they did for all the other compounds described hereafter) and we have used combinations of cryoscopic solution molecular weight measurements, ES mass spectrometry, elemental analyses and multinuclear NMR spectroscopy (the so-called "sporting methods") to characterise the new compounds. We are also able to draw upon the structure of **1** and those of other main group metallated calix[4]arenes (with *exo* and/or *endo*-coordination of the metal ions) referred to in the Introduction for establishing basic structural motifs. For these reasons the structures of $[M_2\{^tBu\text{-calix}[4](OMe)_2(O)_2\}]_2$ (eqn. (2)) are shown only in schematic form implying the likely *endo*- or *exo*-coordination of the metals and their dimeric nature.



(2)

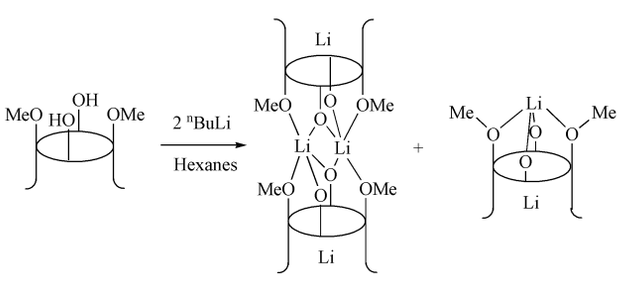
M = K **2**, Rb **3** or Cs **4**

The dimeric nature of complexes **2**–**4** was established by cryoscopic solution molecular weight measurements in benzene which agreed to within ±6–8% of the expected values for the proposed structures. The ES mass spectra (THF–MeOH) showed monomeric $^tBu\text{-calix}[4](OMe)_2(O)_2$ derived cations retaining one or two alkali metal ions. Thus there was cleavage of the original dimers but at most only partial H^+/M^+ ion exchange occurred in the fragments so formed. We show later that all four of the dimeric compounds **1**–**4** can be cleanly cleaved with the appropriate crown ethers.

The ^{133}Cs NMR spectrum of $[Cs_2\{^tBu\text{-calix}[4](OMe)_2(O)_2\}]_2$ **4** in C_6D_6 features resonances at −21.5 ppm (fwhm = 527 Hz) and −135.9 ppm (fwhm = 345 Hz). That at −21.5 ppm is consistent with an O-bound Cs^+ cation[9] and is assigned to the *exo*-bound bridging Cs^+ cations. The resonance at −135.9 ppm is consistent with a Cs^+ cation bound within a calix[4]arene cavity[9] and is assigned to the *endo*-bound Cs^+ cations.

The variable-temperature ^1H and ^{13}C NMR spectra of **2**–**4** show clear evidence for fluxionality. The spectra for all three compounds are rather similar and that for $[K_2\{^tBu\text{-calix}[4](OMe)_2(O)_2\}]_2$ **2** will be discussed by way of example. At 298 K the ^1H NMR spectrum of **2** is comparable to that described for **1** except that the resonance for the methylene hydrogens appear as two very broad signals (no coupling resolvable); the singlets assigned to the OMe and two types of *tert*-butyl groups are also slightly broad compared to the signals for residual protio solvent. On heating the sample to 363 K the spectrum sharpened significantly (showing clear local C_{2v} symmetry for the $^tBu\text{-calix}[4](OMe)_2(O)_2$ fragments on the NMR timescale) and the methylene hydrogens now appeared as two well-resolved doublets. The ^{13}C NMR spectrum could not be observed at this temperature, probably due to temperature-dependent nuclear relaxation effects. Cooling a sample of **2** to 193 K caused substantial broadening and also partial decoalescence of certain signals in the ^1H NMR spectra. For example, at 193 K the *tert*-butyl resonances appeared as three broad signals in the relative ratios 18H : 9H : 9H (with respect to the two OMe groups assigned an intensity of 6H). This is consistent with the proposed dimeric structure (eqn. (2)) which is based on that of **1** as established by X-ray diffraction. Thus, there is clearly a lowering of the effective C_{2v} symmetry implied by the high-temperature limiting spectrum (363 K) upon cooling to 193 K. The methylene resonances appeared as a series of very broad multiplets at 193 K, whereas the OMe groups still appeared as a broad singlet (6H). Clearly the compound is still significantly fluxional at this temperature.

Reaction of $^tBu\text{-calix}[4](OMe)_2(OH)_2$ with two equivalents of *n*-butyllithium (chosen instead of Li metal or LiH for experimental convenience) in hexanes afforded a white solid (**5**) in 87% isolated yield (eqn. (3)). The spectroscopic data for samples of "**5**" show that it consists of two species to which we assign dimeric and monomeric structures, *i.e.* $[Li_2\{^tBu\text{-calix}[4](OMe)_2(O)_2\}]_2$ **5-I** and $[Li_2\{^tBu\text{-calix}[4](OMe)_2(O)_2\}]$ **5-II**. These are present in a *ca.* 1 : 1 ratio as judged by integration of the ^1H NMR spectrum. The dimeric structure proposed for **5-I** is broadly analogous to that established above for the heavier congeners $[M_2\{^tBu\text{-calix}[4](OMe)_2(O)_2\}]_2$ (M = Na, K, Rb, Cs); the species **5-II** is analogous to the monomeric compounds $[M_2\{^tBu\text{-calix}[4](OR)_2(O)_2\}]$ (M = Li or Na, R = CH_2Ph; M = Na, R = $SiMe_3$) which will be discussed later, along with supporting evidence from solution cryoscopic molecular weight measurements. The presence of at least a dimeric component in **5** is supported by the ES mass spectrum which showed a partially ion-exchanged species centered at *m*/*z* = 1360 Da assigned as $[\mathbf{5\text{-}I} - 3Li + 4H]^+$. A further envelope centered at *m*/*z* = 683 Da could be assigned as partially ion-exchanged monomeric species $[\mathbf{5\text{-}II} - Li + 2H]^+$ (although this could arise from cleavage of a dimer as seen in the ES mass spectra for some of the compounds **1**–**4**).



5-I **5-II** (3)

The room-temperature ^1H NMR spectrum of **5** contains two sets of $^tBu\text{-calix}[4](OMe)_2(O)_2$ ligand resonances, one of which is somewhat broader than the other (which is sharp), especially in the methylene proton region. The intensity ratio of the two sets of resonances is *ca.* 2 (broader resonances) : 1, thus implying a molecular ratio of 1 : 1 (provided that the broader set corresponds to dimeric **5-I**). The ^7Li NMR spectrum has two slightly broad resonances at −1.03 (fwhm = 8 Hz) and −2.56 (fwhm = 16 Hz) ppm in a ratio of *ca.* 2 : 1 by integration. This

spectrum implies that within the two species **5-I** (containing 4 Li^+) and **5-II** (containing 2 Li^+) there is either fast exchange of Li^+ cations between *endo* and *exo* sites, or that the well-established[20] narrow chemical shift range observed in ^{7}Li NMR spectroscopy does not separate out the two chemically different nuclei. An interpretation that one resonance corresponds to *both* types of *endo*-bound Li^+ and the other to *both* types of *exo*-bound Li^+ is not likely given the very different integrated intensities for the two signals.

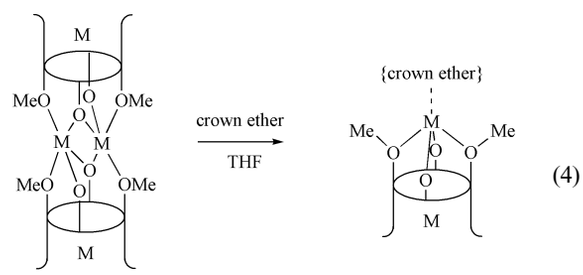
Heating the sample of **5** to 378 K afforded no change in the resonances assigned to the monomeric complex **5-II** (which are fully consistent with a C_{2v} symmetric structure). The resonances assigned to the dimeric complex **5-I** sharpen and coalesce as temperature is increased. At 378 K the latter set of resonances are consistent with a dimeric structure consisting of two equivalent ^{t}Bu-calix[4](OMe)$_2$(O)$_2$ units locked in cone conformations exhibiting effective C_{2v} symmetry on the NMR timescale. The appearances of the **5-I** sub-spectrum at 378 K is completely analogous to those of **1** (at ambient temperature) and **2**–**4** (at elevated temperatures). There is no evidence for exchange between **5-I** and **5-II** at 378 K. The fluxional process(es) for **5-I** is (are) therefore judged to be intramolecular (non-dissociative) in nature. This result might also apply to the dynamic processes for the heavier congeners **1**–**4**.

Decreasing the temperature from 298 to 193 K also afforded no change in the resonances assigned to the monomeric complex **5-II**. However, certain resonances for dimeric **5-I** broaden and decoalesce. At 193 K the resonances are consistent with a dimeric structure consisting of two inequivalent ^{t}Bu-calix[4](OMe)$_2$(O)$_2$ units locked in cone conformations and exhibiting overall molecular C_s symmetry. The appearance of the resonances implies that one ^{t}Bu-calix[4](OMe)$_2$(O)$_2$ unit possesses a mirror plane bisecting the phenoxide rings (equivalent OMe groups) and one ^{t}Bu-calix[4](OMe)$_2$(O)$_2$ unit possesses a mirror plane bisecting the methyl ether rings (inequivalent OMe groups). Eight broad resonances are observed in the region 7.80–6.80 ppm assigned to the *m*-C_6H_2 aryl protons. The diastereotopic methylene group resonances are observed as eight broad doublets in the region 5.20–2.80 ppm. Broad singlets at 3.98 and 2.95 ppm are assigned to the inequivalent OMe groups of one ^{t}Bu-calix[4](OMe)$_2$(O)$_2$ unit. The broad singlet at 3.50 ppm is assigned to the OMe group of the ^{t}Bu-calix[4](OMe)$_2$(O)$_2$ unit possessing equivalent methoxy groups. The *tert*-butyl groups are observed as six broad singlets (two integrating as 18H and four as 9H) in the region 1.80–0.80 ppm. The low-temperature NMR data for **5-I** conclusively establish it as (at least) dimeric, and imply that the molecular structure (with two different ^{t}Bu-calix[4](OMe)$_2$(O)$_2$ units) is somewhat different to that of **1** (and possibly **2**–**4**). This difference, and the fact that a monomeric species is also formed for **5**, is undoubtedly a consequence of the very small ionic radius of lithium.

Dimer-splitting reactions of Group 1 complexes [M$_2${^{t}Bu-calix[4](OMe)$_2$(O)$_2$}]$_2$

In a preliminary exploration of the effect of external Lewis base, a sample of **5** was dissolved in pyridine-d$_5$ giving a clear solution. The ^{1}H NMR spectrum suggested the presence of a single calixarene-containing species giving rise to sharp resonances conforming to molecular C_{2v} symmetry. Two resonances (relative intensity 1 : 1) were seen in the ^{7}Li NMR spectrum at −1.9 (fwhm = 31 Hz) and −5.4 ppm (fwhm = 45 Hz). Assuming that the species present in solution is monomeric and of the type [Li$_2${^{t}Bu-calix[4](OMe)$_2$(O)$_2$}(py-d$_5$)$_x$], then these resonances could be assigned to the chemically inequivalent *exo*- and *endo*-bound Li^+cations. Regardless of this tentative interpretation, it is apparent that effective donors (*i.e.* those able to bind well to alkali metal ions) may be able to cleave dimeric species of the type [M$_2${^{t}Bu-calix[4](OMe)$_2$(O)$_2$}]$_2$ **1**–**5-I**. Studies were therefore undertaken of the reactions of these compounds with polydentate donors (specifically crown ethers[21] of varying cavity size) to prepare well-defined monomeric derivatives.

No reaction of [Li$_2${^{t}Bu-calix[4](OMe)$_2$(O)$_2$}]$_x$ **5** with 12-crown-4 (cyclo-(CH$_2$CH$_2$O)$_4$) was observed, even in the presence of an excess of the crown ether. However, reaction of [Na$_2${^{t}Bu-calix[4](OMe)$_2$(O)$_2$}]$_2$ **1** with 15-crown-5 (cyclo-(CH$_2$CH$_2$O)$_5$) in THF gave monomeric [Na$_2${^{t}Bu-calix[4]-(OMe)$_2$(O)$_2$}(15-crown-5)] **6** as a white solid in 91% isolated yield (eqn. (4)). The compound **6** was insufficiently soluble in benzene to obtain a cryoscopic solution molecular weight measurement, but the positive ion ES mass spectrum (THF–MeOH) showed an ion envelope at 919 Da assigned to the species [**6** − Na + 2H]$^+$ consistent with partial ion-exchange of the parent complex. These data are consistent with the formulation of **6** as a monomeric species. An interpretation of **6** as dimeric with two 15-crown-5 ligands associating with the rather sterically protected *exo*-bound Na^+ cations (see Fig. 1) is rather unreasonable, especially since it is known that THF (present in the crystals of **1** used for the structure determination) does not associate at all with **1**. The general structure proposed for **6** (shown in eqn. (4)) is purposely drawn so as not to specify the coordination mode of the crown ether ligand because this appears to be temperature-dependent.

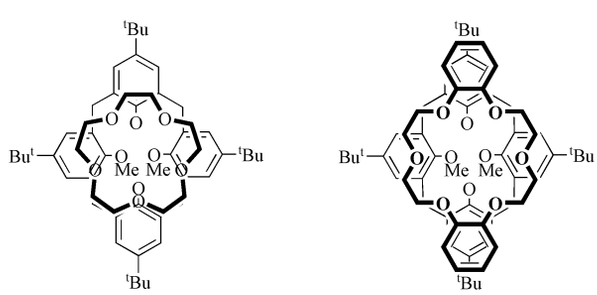


(4)

M = Na **1**, K **2**, Rb **3** or Cs **4**

crown ether = 15-crown-5, M = Na **6**
crown ether = dibenzo-18-crown-6, M = K **7**, Rb **8** or Cs **9**

The low-temperature limiting ^{1}H NMR spectrum of **6** at 193 K (toluene-d$_8$) is consistent with a monomeric complex [Na$_2${^{t}Bu-calix[4](OMe)$_2$(O)$_2$}(κ^5-15-crown-5)] **6a** in which the crown ether is κ^5-bound (Fig. 3(a)). Thus, the crown ether methylene group protons are observed as two broad singlets at 3.30 and 2.95 ppm in a 1 : 1 ratio. This indicates that the "up" and "down" (with respect to the Na$_2${^{t}Bu-calix[4](OMe)$_2$(O)$_2$} moiety) methylene protons are inequivalent as required for κ^5 coordination. The equivalent nature of the individual sets of "up" and "down" protons implies that the crown ether unit is



(a) (b)

Fig. 3 (a) Relative orientation of the 15-crown-5 and ^{t}Bu-calix[4](OMe)$_2$(O)$_2$ units in the low-temperature isomer of [Na$_2${^{t}Bu-calix[4](OMe)$_2$(O)$_2$}(15-crown-5)] **6** as judged by NMR spectroscopy (Na^+ ions not illustrated). (b) Relative orientation of the dibenzo-18-crown-6 and ^{t}Bu-calix[4](OMe)$_2$(O)$_2$ units in the low-temperature isomer of [M$_2${^{t}Bu-calix[4](OMe)$_2$(O)$_2$}(dibenzo-18-crown-6)] (M = K **7**, Rb **7** or Cs **7**) as judged by NMR spectroscopy (metal ions not illustrated).

effectively rapidly rotating about the local (with regard to the 15-crown-5) C_5 axis. This net "rotation" makes each crown ether CH_2 group equivalent, but maintains the ligand's overall orientation with regard to the $Na_2\{^tBu\text{-calix}[4](OMe)_2(O)_2\}$ unit. The ^1H NMR data at 193 K show also that the $Na_2\{^tBu\text{-calix}[4](OMe)_2(O)_2\}$ unit itself possesses local C_s symmetry with a plane of symmetry bisecting the phenoxide rings. This is as expected from Fig. 3(a): the average local C_5 symmetry of the crown ether destroys the local C_{2v} symmetry expected for an isolated $Na_2\{^tBu\text{-calix}[4](OMe)_2(O)_2\}$ moiety, leaving only one of the two mirror planes intact. Four broad singlets at 7.55, 7.48, 7.40 and 7.33 ppm are assigned to the *m*-C_6H_2 protons. The two inequivalent methylene groups afford, as expected, two sets of mutually coupled doublets (these are observed at 5.94 and 5.00 ppm but the other doublets are obscured). The ^{t}Bu-calix[4](OMe)$_2$(O)$_2$ O-methyl groups are equivalent; the *tert*-butyl groups appear as three singlets in the ratio 18H : 9H : 9H.

Increasing the temperature affords a decrease in intensity of the resonances assigned to $[Na_2\{^tBu\text{-calix}[4](OMe)_2(O)_2\}(\kappa^5\text{-15-crown-5})]$ **6a** and an increase in the intensity of resonances assigned to a second isomer, $[Na_2\{^tBu\text{-calix}[4](OMe)_2(O)_2\}(\kappa^1\text{-15-crown-5})]$ **6b** possessing a κ^1-bound 15-crown-5. The absence of a coalescence–decoalescence event implies that going from **6a** to **6b** is a temperature-dependent equilibrium process and not a temperature dependent intramolecular fluxional process. At 253 K complex **6b** is the sole species observed. The crown ether methylene group protons are observed as a time-averaged singlet at 3.50 ppm indicating that the "up" and "down" methylene protons are equivalent on the NMR timescale (effective local D_{5h} symmetry for the crown ether). The ^{t}Bu-calix[4](OMe)$_2$(O)$_2$ resonances are consistent with this moiety possessing effective C_{2v} symmetry on the NMR timescale. The chemical shifts of the ^{t}Bu-calix[4](OMe)$_2$(O)$_2$ unit are not the same as those of $[Na_2\{^tBu\text{-calix}[4](OMe)_2(O)_2\}]_2$ **1** at this temperature (in the same solvent), showing that complex **6b** is not a simple mixture of **1** and uncoordinated 15-crown-5. A κ^1-bonding mode has been observed previously in 15-crown-5 alkali metal chemistry.[22]

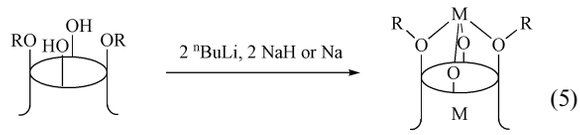
Dimeric calix[4]arene complexes of the larger alkali metals, namely $[M_2\{^tBu\text{-calix}[4](OMe)_2(O)_2\}]_2$ (M = K **2**, Rb **3** and Cs **4**), are cleaved by the larger cavity crown ether, dibenzo-18-crown-6 (eqn. (4)). Isolated yields of $[M_2\{^tBu\text{-calix}[4](OMe)_2(O)_2\}$(dibenzo-18-crown-6)] (M = K **7**, Rb **8** and Cs **9**) were in the range 84–92%. All three compounds give partially ion-exchanged cation envelopes $[M - M' + 2H]^+$ (M′ = K, Rb or Cs) in their ES mass spectra (THF–MeOH) and showed similar variable-temperature NMR behaviour in toluene-d_8. The ^1H NMR spectra for $[K_2\{^tBu\text{-calix}[4](OMe)_2(O)_2\}$(dibenzo-18-crown-6)] **7** will be discussed by way of illustration of the behaviour of all three compounds.

At 298 K complex **7** shows a sharp ^{t}Bu-calix[4](OMe)$_2$(O)$_2$ sub-spectrum (characteristic of local C_{2v} symmetry). The methylene hydrogens of the dibenzo-18-crown-6 are considerably broadened, and its C_6H_4 protons are reasonably sharp. Cooling to 218 K results in no significant change in the ^{t}Bu-calix[4](OMe)$_2$(O)$_2$ sub-spectrum whereas the resonances for the dibenzo-18-crown-6 sharpen appreciably. The sub-spectrum of this moiety consists of four mutually-coupled multiplets (intensity 4H each) for the four different methylene hydrogen environments, and there are also two doublets (intensity 4H) for the C_6H_4 protons. The ^{t}Bu-calix[4](OMe)$_2$(O)$_2$ and dibenzo-18-crown-6 units therefore both possess the proposed overall molecular C_{2v} symmetry of the resultant complex. The orientation of the dibenzo-18-crown-6 with respect to the ^{t}Bu-calix[4](OMe)$_2$(O)$_2$ unit is illustrated in Fig. 3(b). The dibenzo-18-crown-6 methylene resonances therefore correspond to two pairs of "up" and two pairs of "down" (with respect to the $K_2\{^tBu\text{-calix}[4](OMe)_2(O)_2\}$ moiety) protons. Increasing the temperature from 298 to 378 K afforded little change in the ^{t}Bu-calix[4](OMe)$_2$(O)$_2$ sub-spectrum. The resonances assigned to the crown ether C_6H_4 protons protons are also little affected. However, the crown ether methylene proton resonances coalesce, and at 378 K they appear as two mutually coupled sharp triplets at 3.93 and 3.86 ppm. The symmetry and distribution of the crown ether resonances are consistent with effective D_{2h} symmetry on the NMR timescale. The overall fluxional process is therefore one of dissociation (either partial or complete) followed by recoordination; a simple net rotation process would not exchange the "up" and "down" crown ether methylene hydrogens.

The dynamic behaviour for **8** and **9** (as evidenced by ^1H NMR spectroscopy) is analogous to those for the potassium complex just described. For the cesium species $[Cs_2\{^tBu\text{-calix}[4](OMe)_2(O)_2\}$(dibenzo-18-crown-6)] **9**, however, one also has access to ^{133}Cs NMR. The ^{133}Cs NMR spectrum of **9** at 298 K features resonances at 41.0 ppm (fwhm = 89 Hz) and −170.0 ppm (fwhm = 23 Hz). The resonance at 41.0 ppm is consistent with an O-bound Cs^+ cation and is assigned to the *exo*-bound Cs^+(the precursor complex $[Cs_2\{^tBu\text{-calix}[4](OMe)_2(O)_2\}]_2$ **4** has its *exo*-bound ^{133}Cs resonance at −21.5 ppm).[9] The resonance at −170.0 ppm is consistent with a Cs^+ cation bound within a ^{t}Bu-calix[4](OMe)$_2$(O)$_2$ cavity and is assigned to the *endo*-bound Cs^+ (compound **4** had its *endo*-bound ^{133}Cs resonance at −135.9 ppm). The very different ^{133}Cs shifts for **9** compared to those of **4** are consistent with a substantial disruption of the original dimeric structure of **4**.

Synthesis of Li and Na complexes $[M_2\{^tBu\text{-calix}[4](OR)_2(O)_2\}]$ (R = CH_2Ph or $SiMe_3$)

We have briefly examined metallation reactions of the bis-(benzyl) and bis(trimethylsilyl)ethers ^{t}Bu-calix[4](OR)$_2$(OH)$_2$ (R = CH_2Ph or $SiMe_3$) (eqn. (5)). Thus reaction of ^{t}Bu-calix-[4](OCH$_2$Ph)$_2$(OH)$_2$ with 2 equivalents of ^{t}BuLi in pentane gave $[Li_2\{^tBu\text{-calix}[4](OCH_2Ph)_2(O)_2\}]$ **10** in 83% isolated yield; the corresponding reaction with sodium sand in Et_2O gave $[Na_2\{^tBu\text{-calix}[4](OCH_2Ph)_2(O)_2\}]$ **11** in 68% isolated yield. Both compounds were found to be monomeric in benzene solution according to cryoscopic molecular weight measurements (experimental values agreed with calculated ones to within 9% of the expected value), and both compounds give partially ion-exchanged cation envelopes $[M - M' + 2H]^+$ (M′ = Li or Na) in their ES mass spectra (THF–MeOH).



(5)

R = CH_2Ph or $SiMe_3$

R = CH_2Ph, M = Li **10** or Na **11**
R = $SiMe_3$, M = Na **12**

The ^1H and ^{13}C NMR spectra (C_6D_6) of **10** and **11** were consistent with the proposed structures, featuring all of the appropriate resonances for ^{t}Bu-calix[4](OCH$_2$Ph)$_2$(O)$_2$ moieties possessing local C_{2v} symmetry; cooling samples (toluene-d_8) to 183 K gave no significant broadening of the resonances. The ^7Li spectrum of **10** showed a single resonance at −3.0 ppm (fwhm = 21 Hz). As discussed above for the monomeric component of **5**, namely $[Li_2\{^tBu\text{-calix}[4](OMe)_2(O)_2\}]$ **5-II**, this could be attributable to rapid exchange between *endo* and *exo* sites, or to accidental signal overlap. Either way, the shift for the Li^+ ions in **10** (−3.0 ppm) and **5-II** (−2.6 ppm) are very similar, and at least consistent with both possessing monomeric structures. As for **1**, no ^{23}Na NMR resonances could be observed for **11**.

That the ^{t}Bu-calix[4](OCH$_2$Ph)$_2$(O)$_2$ ligand promotes exclusively monomeric derivatives for Li and Na, while the dimethyl homologue more favours dimeric ones could be attributed to the extra steric hindrance associated with the larger benzyl substituents. Alternatively, additional M ⋯ C_{ipso}

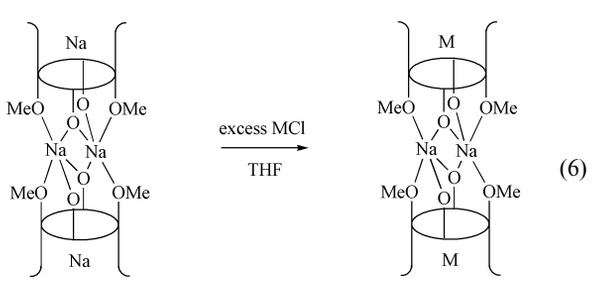
(or similar) interactions involving the benzylic aromatic ring could play a stabilising role (such interactions are well established in alkali metal structural chemistry).[19,23]

Reaction of ^{t}Bu-calix[4](OSiMe$_3$)$_2$(OH)$_2$ with ^{n}BuLi under a variety of conditions gave only mixtures of products. However, reaction with two equivalents of NaH in THF yielded [Na$_2${^{t}Bu-calix[4](OSiMe$_3$)$_2$(O)$_2$}$_2$] **12** in 71% isolated yield. The solution molecular weight estimated by cryoscopic methods in benzene (841 g mol^{-1}) is in extremely good agreement with that expected for a monomeric species (837 g mol^{-1}) of the type indicated in eqn. (5). The ES mass spectrum (THF–MeOH) was less helpful due to hydrolysis of the O–SiMe$_3$ linkages. The ^{1}H and ^{13}C NMR spectra were fully consistent with a C_{2v}-symmetric compound (down to 183 K in toluene-d$_8$); once again no ^{23}Na resonances could be detected. The monomeric nature of **12** is almost certainly attributable to the bulky nature of the trimethylsilyl groups.

Transmetallation reactions of [Na$_2${^{t}Bu-calix[4](OMe)$_2$(O)$_2$}]$_2$

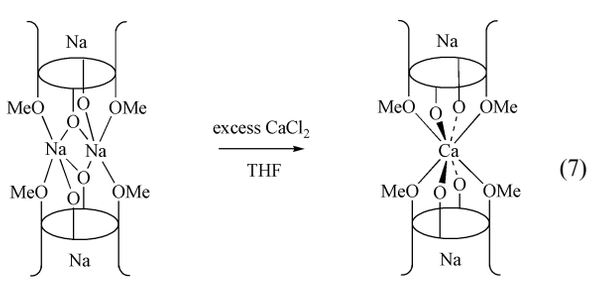
As indicated in the Introduction, Floriani and coworkers[14] have recently reported that *in-situ* generated "[^{t}Bu-calix[4](O C$_5$H$_9$)$_2$(ONa)$_2$]" undergoes transmetallation reactions with [MI$_2$(THF)$_4$] (M = Ca, Ba) to form, after addition of TMEDA, the monomeric compounds [M{^{t}Bu-calix[4](OC$_5$H$_9$)$_2$(O)$_2$}(TMEDA)]. A similar reaction protocol afforded the mixed Group 1/Group 2 metal species [BaNa$_2${^{t}Bu-calix[4](OR)$_2$(O)$_2$}]$_2$ (R = Me or C$_5$H$_9$ (X-ray structure)). This latter compound has *endo*-bound Na$^+$ ions and the *exo*-bound, eight-coordinate Ba^{2+} fuses the two Na{^{t}Bu-calix[4](OR)$_2$(O)$_2$} moieties together.

We have independently carried out transmetallation reactions of [Na$_2${^{t}Bu-calix[4](OMe)$_2$(O)$_2$}]$_2$ **1** with an excess (*ca.* 20 equivalents) of the following Group 1 and 2 metal halides: KCl, RbCl, CsCl and CaCl$_2$ (eqns. (6) and (7)). The reactions of **1** with CsCl (forming **13**) and CaCl$_2$ (forming **16**) went to completion (as judged by ^{1}H NMR spectroscopy) after refluxing in THF for 200 h; those with KCl and RbCl went to 90% and 95% completion (forming **14** and **15**, respectively). This could indicate a reduced thermodynamic driving force for the latter two reactions (since the difference in lattice energies between NaCl and the heavier Group 1 metal halides decreases up the group), or alternatively kinetic factors. However, use of larger excesses of metal halide or extended reaction times did not appear to drive the reactions to completion.



(6)

1 M = Cs **13**, Rb **14** or K **15**



(7)

1 **16**

The compound **13** is assigned a dimeric structure [CsNa{^{t}Bu-calix[4](OMe)$_2$(O)$_2$}]$_2$ with the Cs$^+$ cations exclusively occupying *endo* (cone-encapsulated) positions. The ^{1}H and ^{13}C NMR data are consistent with local C_{2v} symmetry for the ^{t}Bu-calix[4](OMe)$_2$(O)$_2$ moieties within a centrosymmetric dimeric structure. The ES mass spectrum (THF–MeOH) once again showed extensive ion exchange, but the presence of a dimer-based cation envelope assigned as [M − 2Cs – Na + 4H]$^+$ (*m*/*z* = 1376 Da) is at least consistent with **13** adopting a dimeric structure. The *endo* coordination of Cs$^+$ is conclusively supported by the ^{133}Cs NMR spectrum which shows a single resonance at −180.0 ppm (fwhm = 192 Hz). The exclusive location of Cs$^+$ between the cones echoes nicely the original report by Harrowfield *et al.*[9a] on [Cs{^{t}Bu-calix[4](OH)$_3$(O)}(MeCN)] which can be viewed as a monomeric analogue of **13** in which a proton formally takes the place of the Na$^+$ in our compounds. The NMR spectra of **14** and **15** resemble those of **13** and similar structures are assumed with the Na$^+$ ions occupying *exo* positions between the two M{^{t}Bu-calix[4](OMe)$_2$(O)$_2$} (M = cone-encapsulated K or Rb) moieties.

As shown in eqn. (7) [Na$_2${^{t}Bu-calix[4](OMe)$_2$(O)$_2$}$_2$] **1** undergoes a clean and quantitative metathesis with CaCl$_2$ forming trinuclear [CaNa$_2${^{t}Bu-calix[4](OMe)$_2$(O)$_2$}]$_2$ **16**. The reaction is similar to that reported by Floriani and coworkers[14] for [BaI$_2$(THF)$_4$] and a structure with the large, dicationic Ca^{2+} sandwiched in an eight-coordinate manner between two [Na{^{t}Bu-calix[4](OMe)$_2$(O)$_2$}]$^-$ moieties seems the most likely. The ^{1}H and ^{13}C NMR and other spectroscopic data are fully consistent with the proposed centrosymmetric structure.

Conclusions

We have reported the synthesis of Group 1 dimetallated derivatives of dialkyl ether *p-tert*-butyl calix[4]arenes and have studied their structural and solution properties. Dimeric and monomeric and mixed-metal complexes were described together with solution dynamical data for certain crown ether adducts of the cleaved dimers. This present study compliments that very recently described by Floriani *et al.*[14] for the Group 1 tetrametallated *tetra*-phenolic *p-tert*-butylcalix[4]arenes and Group 2 metallated dialkyl ether *p-tert*-butyl calix[4]arenes.

Experimental

General methods and instrumentation

All air- and moisture-sensitive manipulations were performed using standard Schlenk-line (Ar) and dry-box (N$_2$) techniques. Solvents were pre-dried over 4Å molecular sieves and refluxed over potassium (hexane, THF) and sodium–potassium alloy (1 : 3 w/w) (diethyl ether, pentane) under N$_2$. Solvents were distilled at atmospheric pressure and stored in Teflon valve ampoules. Deuterated solvents were dried over sodium (C$_7$D$_8$), potassium (C$_6$D$_6$) or calcium hydride (CDCl$_3$, CD$_2$Cl$_2$, C$_5$D$_5$N) 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. Mirrors were prepared from heating the appropriate weight of bulk metal in a rigorously dried Schlenk tube under a static vacuum (1 × 10^{-2} mbar).

^{1}H and ^{13}C-{^{1}H} NMR spectra were recorded on Varian Unity Plus 500, Varian Mercury 300, and Bruker DPX 300 spectrometers. Spectra are referenced internally to residual protio-solvent (^{1}H) 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. IR spectra were recorded on Perkin Elmer 1600 and Perkin Elmer 1710 spectrometers as Nujol mulls between KBr windows. All data are quoted in wavenumbers (cm^{-1}). Mass

spectra were recorded on Micromass Autospec 500, AEI MS902, and Finnigan MAT 900 XLT spectrometers. All data are quoted in mass/charge ratio (*m*/*z*). Elemental analyses were carried out by the analytical laboratory at the Inorganic Chemistry Laboratory, Oxford, and the School of Chemistry, Nottingham.

Literature preparations

The compounds ^{t}Bu-calix[4](OMe)$_2$(OH)$_2$ and ^{t}Bu-calix-[4](OCH$_2$Ph)$_2$(OH)$_2$ were prepared by modification of the method reported by Reinhoudt and coworkers.[15] The compound ^{t}Bu-calix[4](OSiMe$_3$)$_2$(OH)$_2$ was prepared by modification of the method reported by Schmutzler and coworkers.[16]

[Na$_2${^{t}Bu-calix[4](OMe)$_2$(O)$_2$}]$_2$ (1)

A solution of ^{t}Bu-calix[4](OMe)$_2$(OH)$_2$ (5.000 g, 7.38 mmol) in THF (50 cm^3) was added to NaH (0.441 g, 18.46 mmol) at rt. The mixture was stirred at rt for 20 h to give a brown suspension. This was filtered and the solid extracted with THF (20 cm^3) to give a light yellow solution. Removal of volatiles under reduced pressure and recrystallisation from THF (−25 °C) afforded a white solid. Filtration, washing with THF (2 × 5 cm^3) and removal of volatiles under reduced pressure afforded [Na$_2${^{t}Bu-calix[4](OMe)$_2$(O)$_2$}]$_2$ **1** as a white solid. Yield: 4.292 g (70%).

^{1}H NMR (C$_6$D$_6$, 300.1 MHz, 298 K): δ 7.35 (8H, s, *m*-C$_6$H$_2$), 6.90 (8H, s, *m*-C$_6$H$_2$), 4.49 (8H, d, ^2J = 12 Hz, CH$_2$), 3.53 (12H, s, OMe), 3.25 (8H, d, ^2J = 12 Hz, CH$_2$), 1.50 (36H, s, CMe$_3$), 0.95 (36H, s, CMe$_3$). ^{13}C-{^{1}H} NMR (C$_6$D$_6$, 75.5 MHz, 298 K): δ 163.0 (C*q*-C$_6$H$_2$), 153.3 (C*q*-C$_6$H$_2$), 146.6 (C*q*-C$_6$H$_2$), 136.1 (C*q*-C$_6$H$_2$), 132.7 (C*q*-C$_6$H$_2$), 132.0 (C*q*-C$_6$H$_2$), 126.1 (*m*-C$_6$H$_2$), 124.0 (*m*-C$_6$H$_2$), 63.0 (OMe), 34.1 (*C*Me$_3$), 33.8 (*C*Me$_3$), 33.1 (CH$_2$), 32.5 (C*Me*$_3$), 31.2 (C*Me*$_3$). ES mass spectrum (THF–MeOH): 1376 [M − 3Na + 4H]$^+$ 5%, 699 [M − {^{t}Bu-calix[4](OMe)$_2$(O)$_2$} − 3Na + 2H]$^+$ 100%. IR (KBr plates, Nujol): 1752 (w), 1596 (m), 1430 (s), 1376 (m), 1361 (s), 1345 (m), 1320 (m), 1307 (m), 1287 (m), 1237 (m), 1205 (s), 1180 (w), 1170 (m), 1122 (m), 1098 (m), 1011 (s), 967 (w), 943 (w), 917 (w), 876 (s), 830 (m), 810 (m), 796 (m), 774 (m), 750 (w), 708 (w), 698 (w), 658 (w), 642 (w), 557 (m), 526 (w), 492 (m), 431 (m). Cryoscopic molecular weight (C$_6$H$_6$, g mol^{-1}) (calc.): 1442 (1441). Anal. (calc. for C$_{92}$H$_{116}$Na$_4$O$_8$): C 75.3 (76.6), H 8.5 (8.1) Na 6.4 (6.4)%.

[K$_2${^{t}Bu-calix[4](OMe)$_2$(O)$_2$}]$_2$ (2)

A solution of ^{t}Bu-calix[4](OMe)$_2$(OH)$_2$ (0.250 g, 0.37 mmol) in diethyl ether (50 cm^3) was added to K (mirror, 0.071 g, 1.79 mmol) at −70 °C. The mixture was stirred at rt for 20 h to give a brown suspension. This was filtered to give a white solid which was dissolved in THF (50 cm^3) and filtered to give a colourless solution. Removal of volatiles under reduced pressure afforded [K$_2${^{t}Bu-calix[4](OMe)$_2$(O)$_2$}]$_2$ **2** as a white solid. Yield: 0.245 g (87%).

^{1}H NMR (C$_7$D$_8$, 500.1 MHz, 363 K): δ 7.26 (8H, s, *m*-C$_6$H$_2$), 7.09 (8H, s, *m*-C$_6$H$_2$), 4.30 (8H, d, ^2J = 12.5 Hz, CH$_2$), 3.61 (12H, s, OMe), 3.31 (8H, d, ^2J = 12.5 Hz, CH$_2$), 1.45 (36H, s, CMe$_3$), 1.01 (36H, s, CMe$_3$). ^{13}C-{^{1}H} NMR (C$_6$D$_6$, 125.7 MHz, 298 K): δ 143.8 (C*q*-C$_6$H$_2$), 134.9 (C*q*-C$_6$H$_2$), 128.9 (*m*-C$_6$H$_2$), 123.7 (*m*-C$_6$H$_2$), 32.0 (*C*Me$_3$), 31.8 (*C*Me$_3$), 30.6 (C*Me*$_3$), 29.2 (C*Me*$_3$), resonances not observed: 4 × C*q*-C$_6$H$_2$, OMe, CH$_2$. ES mass spectrum (THF–MeOH): 753 [M − {^{t}Bu-calix[4](OMe)$_2$(O)$_2$} − 2K + H]$^+$ 10%. IR (KBr plates, Nujol): 1595 (m), 1358 (w), 1287 (m), 1236 (w), 1203 (m), 1169 (w), 1121 (w), 1098 (w), 1017 (s), 964 (w), 943 (w), 916 (w), 877 (s), 830 (w), 803 (m), 778 (w), 721 (m), 640 (w), 558 (w), 523 (w), 491 (w), 428 (w). Cryoscopic molecular weight (C$_6$H$_6$, g mol^{-1}) (calc.): 1379 (1506). Anal. (calc. for C$_{92}$H$_{116}$K$_4$O$_8$): C 70.6 (73.4), H 8.0 (7.8), K 10.3 (10.4)%.

[Rb$_2${^{t}Bu-calix[4](OMe)$_2$(O)$_2$}]$_2$ (3)

A solution of ^{t}Bu-calix[4](OMe)$_2$(OH)$_2$ (0.250 g, 0.37 mmol) in diethyl ether (50 cm^3) was added to Rb (mirror, 0.152 g, 1.79 mmol) at −70 °C. The mixture was stirred at rt for 20 h to give a brown suspension. This was filtered to give a white solid which was dissolved in THF (50 cm^3) and filtered again to give a colourless solution. Removal of volatiles under reduced pressure afforded [Rb$_2${^{t}Bu-calix[4](OMe)$_2$(O)$_2$}]$_2$ **3** as a white solid. Yield: 0.254 g (82%).

^{1}H NMR (C$_7$D$_8$, 500.1 MHz, 363 K): δ 7.22 (8H, s, *m*-C$_6$H$_2$), 7.16 (8H, s, *m*-C$_6$H$_2$), 4.25 (8H, d, ^2J = 12.3 Hz, CH$_2$), 3.58 (12H, s, OMe), 3.38 (8H, d, ^2J = 12.3 Hz, CH$_2$), 1.45 (36H, s, CMe$_3$), 1.03 (36H, s, CMe$_3$). ^{13}C-{^{1}H} NMR (C$_6$D$_6$, 125.7 MHz, 298 K): δ 150.2 (C*q*-C$_6$H$_2$), 145.7 (C*q*-C$_6$H$_2$), 135.0 (*m*-C$_6$H$_2$), 125.8 (*m*-C$_6$H$_2$), 33.9 (*C*Me$_3$), 33.7 (*C*Me$_3$), 32.6 (C*Me*$_3$), 31.1 (C*Me*$_3$), resonances not observed: 4 × C*q*-C$_6$H$_2$, OMe, CH$_2$). ES mass spectrum (THF–MeOH): 1438 [M − 3Rb + 4H]$^+$ 1%, 761 [M − {^{t}Bu-calix[4](OMe)$_2$(O)$_2$} − 3Rb + 2H]$^+$ 20%. IR (KBr plates, Nujol): 1594 (w), 1360 (m), 1290 (m), 1238 (m), 1207 (m), 1174 (m), 1122 (m), 1104 (m), 1019 (m), 875 (m), 796 (m). Cryoscopic molecular weight (C$_6$H$_6$, g mol^{-1}) (calc.): 1791 (1691). Anal. (calc. for C$_{92}$H$_{116}$Rb$_4$O$_8$): C 64.9 (65.3), H 6.6 (7.0), Rb 19.8 (20.2)%.

[Cs$_2${^{t}Bu-calix[4](OMe)$_2$(O)$_2$}]$_2$ (4)

A solution of ^{t}Bu-calix[4](OMe)$_2$(OH)$_2$ (0.250 g, 0.37 mmol) in diethyl ether (50 cm^3) was added to Cs (mirror, 0.235 g, 1.77 mmol) at −70 °C. The mixture was stirred at rt for 20 h to give a red suspension. This was filtered to give a white solid which was dissolved in THF (50 cm^3) and filtered again to give a colourless solution. Removal of volatiles under reduced pressure afforded [Cs$_2${^{t}Bu-calix[4](OMe)$_2$(O)$_2$}]$_2$ **4** as a white solid. Yield: 0.285 g (83%).

^{1}H NMR (C$_6$D$_6$, 500.1 MHz, 353 K): δ 7.24 (8H, s, *m*-C$_6$H$_2$), 7.23 (8H, s, *m*-C$_6$H$_2$), 4.40 (8H, d, ^2J = 12.0 Hz, CH$_2$), 3.43 (12 H, s, OMe), 3.42 (8H, d, ^2J = 12.0 Hz, CH$_2$), 1.39 (32H, s, CMe$_3$), 1.02 (32H, s, CMe$_3$). ^{13}C-{^{1}H} NMR (C$_6$D$_6$, 125.7 MHz, 298K): δ 149.2 (C*q*-C$_6$H$_2$), 145.1 (C*q*-C$_6$H$_2$), 136.7 (*m*-C$_6$H$_2$), 126.1 (*m*-C$_6$H$_2$), 35.7, (*C*Me$_3$), 35.4 (*C*Me$_3$), 34.3 (C*Me*$_3$), 33.0 (C*Me*$_3$), resonances not observed: 4 × C*q*-C$_6$H$_2$, OMe, CH$_2$. ^{133}Cs NMR (C$_6$D$_6$, 65.6 MHz, 298 K): δ −21.5 (fwhm = 527 Hz, *exo*), −135.9 (fwhm = 345 Hz, *endo*). ES mass spectrum (THF–MeOH): 809 [M − {^{t}Bu-calix[4](OMe)$_2$(O)$_2$} − 3Cs + 2H]$^+$ 5%. IR (KBr plates, Nujol): 1592 (s), 1360 (s), 1290 (s), 1239 (m), 1204 (s), 1177 (w), 1126 (m), 1104 (w), 1017 (s), 945 (w), 872 (m), 806 (m), 750 (w), 523 (w). Cryoscopic molecular weight (C$_6$H$_6$, g mol^{-1}) (calc.): 2001 (1881). Anal. (calc. for C$_{92}$H$_{116}$Cs$_4$O$_8$): C 55.0 (58.7), H 7.0 (6.2)%.

[Li$_2${^{t}Bu-calix[4](OMe)$_2$(O)$_2$}]$_x$ [*x* = 1 (5-II) or 2 (5-I)]

A solution of ^{n}BuLi (2.5 M in hexanes), (0.30 cm^3, 0.74 mmol) was added dropwise to a solution of ^{t}Bu-calix[4](OMe)$_2$(OH)$_2$ (0.250 g, 0.37 mmol) in hexanes (75 cm^3) at −70 °C. Stirring at rt for 20 h gave a white suspension. This was filtered and the solid washed with hexanes (2 × 5 cm^3). Removal of volatiles under reduced pressure afforded [Li$_2${^{t}Bu-calix[4](OMe)$_2$(O)$_2$}]$_x$ (*x* = 1 **5-II** or 2, **5-I**) as a white solid. Yield: 0.220 g (87%).

^{1}H NMR (**5-I**) (C$_7$D$_8$, 500.1 MHz, 378 K): δ 7.25 (8H, s, *m*-C$_6$H$_2$), 6.87 (8H, s, *m*-C$_6$H$_2$),4.44 (8H, d, ^2J = 13.0 Hz, CH$_2$), 3.49 (12H, s, OMe), 3.30 (8H, d, ^2J = 13.0 Hz, CH$_2$), 1.42 (36H, s, CMe$_3$), 0.99 (36H, s, CMe$_3$). ^{1}H NMR (**5-I**) (C$_7$D$_8$, 500.1 MHz, 288 K): δ 7.38 (4H, s, *m*-C$_6$H$_2$), 7.23 (4H, s, *m*-C$_6$H$_2$), 7.01 (4H, s, *m*-C$_6$H$_2$), 6.85 (4H, s, *m*-C$_6$H$_2$), 4.56 (4H, d, ^2J = 12.5 Hz, CH$_2$), 4.40 (4H, d, ^2J = 12.5 Hz, CH$_2$), 3.53 (12H, s, OMe), 3.40 (4H, d, ^2J = 12.5 Hz, CH$_2$), 3.26 (4H, d, ^2J = 12.5 Hz, CH$_2$), 1.54 (18H, s, CMe$_3$), 1.38 (18H, s, CMe$_3$), 1.10 (18H, s, CMe$_3$), 0.95 (18H, s, CMe$_3$). ^{1}H NMR (**5-I**) (C$_7$D$_8$, 500.1 MHz, 193 K): δ 8.00–6.50 (8 × *m*-C$_6$H$_2$), 5.02 (2H, d, ^2J = 12.0 Hz, CH$_2$), 4.75

(2H, d, ^2J = 12.0 Hz, CH_2), 4.25 (2H, d, ^2J = 12.0 Hz, CH_2), 4.08 (2H, d, ^2J = 12.0 Hz, CH_2), 3.95 (3H, s, OMe), 3.62 (2H, d, ^2J = 12.0 Hz, CH_2), 3.52 (2H, d, ^2J = 12.0 Hz, CH_2), 3.50 (6H, s, OMe), 3.41 (2H, d, ^2J = 12.0 Hz, CH_2), 2.95 (2H, d, ^2J = 12.0 Hz, CH_2), 2.84 (3H, s, OMe), 1.62 (18H, s, CMe_3), 1.50 (9H, s, CMe_3), 1.35 (9H, s, CMe_3), 1.22 (9H, s, CMe_3), 1.18 (9H, s, CMe_3), 0.95 (18H, s, CMe_3). ^{1}H NMR (**5-II**) (C_7D_8, 500.1 MHz, 298 K): δ 7.33 (8H, s, *m*-C_6H_2), 6.90 (8H, s, *m*-C_6H_2), 4.53 (8H, d, ^2J = 13.0 Hz, CH_2), 3.46 (12H, s, OMe), 3.26 (8H, d, ^2J = 13.0 Hz, CH_2), 1.47 (36H, s, CMe_3), 0.99 (36H, s, CMe_3).

^{13}C-{^{1}H} NMR (**5-I** and **5-II**) (C_6D_6, 125.7 MHz, 298 K): δ 161.9 (C*q*-C_6H_2, **5-I** or **5-II**), 160.4 (C*q*-C_6H_2, **5-I** or **5-II**), 152.5 (C*q*-C_6H_2, **5-I** or **5-II**), 151.9 (C*q*-C_6H_2, **5-I** or **5-II**), 147.8, (C*q*-C_6H_2, **5-I** or **5-II**), 147.6 (C*q*-C_6H_2, **5-I** or **5-II**), 146.8 (C*q*-C_6H_2, **5-I** or **5-II**), 135.8 (C*q*-C_6H_2, **5-I** or **5-II**), 133.9 (C*q*-C_6H_2, **5-I** or **5-II**), 133.6 (C*q*-C_6H_2, **5-I** or **5-II**), 132.7 (C*q*-C_6H_2, **5-I** or **5-II**), 132.3 (C*q*-C_6H_2, **5-I** or **5-II**), 131.6 (C*q*-C_6H_2, **5-I** or **5-II**), 130.0 (C*q*-C_6H_2, **5-I** or **5-II**), 126.5 (*m*-C_6H_2, **5-I**), 126.3 (*m*-C_6H_2, **5-II**), 125.8 (*m*-C_6H_2, **5-I**), 125.7 (*m*-C_6H_2, **5-I**), 125.5 (*m*-C_6H_2, **5-I**), 125.2 (*m*-C_6H_2, **5-II**), 65.3 (OMe, **5-II**), 64.9 (OMe, **5-I**), 34.1 (*C*Me_3, **5-I** or **5-II**), 34.0 (*C*Me_3, **5-I** or **5-II**), 33.9 (*C*Me_3, **5-I** or **5-II**), 33.8 (*C*Me_3, **5-I** or **5-II**), 33.2 (CH_2, **5-I**), 33.1 (CH_2, **5-I**), 32.9 (CH_2, **5-II**), 32.5 (C*Me*$_3$, **5-I**), 32.2 (C*Me*$_3$, **5-II**), 31.9 (C*Me*$_3$, **5-I**), 31.5 (C*Me*$_3$, **5-I**), 31.3 (C*Me*$_3$, **5-II**), 31.2, (C*Me*$_3$, **5-I**), resonances not observed: 4 × C*q*-C_6H_2, 2 × *C*Me_3. ^{7}Li NMR (C_7D_8, 194.3 MHz, 298 K): δ −1.03 (fwhm = 8 Hz), −2.56 (fwhm = 16 Hz). ES mass spectrum (THF–MeOH): 1360 [**5-I** − 3Li + 4H]$^+$ 5%, 683 [**5-II** − Li + 2H]$^+$ 30%. IR (KBr plates, Nujol): 1748 (w), 1601 (m), 1393 (w), 1362 (m), 1323(m), 1301(m), 1208 (m), 1167 (m), 1126 (w), 1091 (m), 1023 (m), 994 (m), 982 (w), 940 (w), 920 (w), 873 (s), 829 (m), 811 (m), 797 (m), 769 (m), 759 (m), 704 (m), 663 (w), 639 (w), 605 (w), 589 (w), 566 (w), 535 (m), 484 (m). Anal. (calc. for $C_{92}H_{116}Li_4O_8$): C 80.0 (80.2), H 8.3 (8.4), Li 1.5 (2.0)%.

[Na_2{^{t}Bu-calix[4](OMe)$_2$(O)$_2$}(15-crown-5)] (6)

15-crown-5 (0.030 g, 27.4 μl, 0.14 mmol) was added dropwise to a THF (20 cm^3) solution of [Na_2{^{t}Bu-calix[4](OMe)$_2$(O)$_2$}]$_2$ **1** (0.100 g, 0.07 mmol) at rt. After 30 min removal of volatiles under reduced pressure afforded [Na_2{^{t}Bu-calix[4](OMe)$_2$(O)$_2$}(15-crown-5)] **6** as a white solid. Yield: 0.12 g (91%).

^{1}H NMR (C_7D_8, 500.1 MHz, 193 K): δ 7.55 (2H, s, *m*-C_6H_2), 7.48 (2H, s, *m*-C_6H_2), 7.40 (2H, s, *m*-C_6H_2), 7.33 (2H, s, *m*-C_6H_2), 5.94 (2H, d, CH_2), 5.00 (2H, d, CH_2), 4.28 (6H, s, OMe), 3.30 (10H, s, OCH_2), 2.95 (10H, s, OCH_2), 1.75 (9H, s, CMe_3), 1.62 (9H, s, CMe_3), 1.15 (18H, s, CMe_3). ^{1}H NMR (C_7D_8, 500.1 MHz, 193 K): δ 7.31 (4H, s, *m*-C_6H_2), 6.87 (4H, s, *m*-C_6H_2), 4.43 (4H, d, ^2J = 13.0 Hz, CH_2), 3.52 (6H, s, OMe), 3.49 (20H, s, OCH_2), 3.19 (4H, d, ^2J = 13.0 Hz, CH_2), 1.45 (18H, s, CMe_3), 0.92 (18H, s, CMe_3). ^{13}C-{^{1}H} NMR (C_7D_8, 125.7 MHz, 338 K): δ 163.3 (C*q*-C_6H_2), 155.5 (C*q*-C_6H_2), 146.8 (C*q*-C_6H_2), 137.6 (C*q*-C_6H_2), 136.3 (C*q*-C_6H_2), 132.1 (C*q*-C_6H_2), 126.2 (*m*-C_6H_2), 124.3, (*m*-C_6H_2), 71.4, (OCH_2), 63.0 (OMe), 34.3 (*C*Me_3), 44.0 (*C*Me_3), 33.3 (CH_2), 32.6 (C*Me*$_3$), 31.4 (C*Me*$_3$). ES mass spectrum (THF–MeOH): 919 [M − Na + 2H]$^+$ 1%, 699 [M − (15-crown-5) − Na + 2H]$^+$ 1%. IR (KBr plates, Nujol): 1596 (m), 1358 (m), 1291 (m), 1251 (w), 1206 (m), 1123 (s), 1015 (m), 946 (m), 874 (m), 831 (w), 803 (m), 775 (w), 644 (w), 558 (w), 492 (w), 431 (w). Anal. (calc. for $C_{56}H_{78}Na_2O_9$): C 67.8 (71.4), H 8.2 (8.3), Na 4.8 (4.9)%.

[K_2{^{t}Bu-calix[4](OMe)$_2$(O)$_2$}(dibenzo-18-crown-6)] (7)

A solution of dibenzo-18-crown-6 (0.050 g, 0.14 mmol) in THF (10 cm^3) was added dropwise to a solution of [K_2{^{t}Bu-calix[4](OMe)$_2$(O)$_2$}]$_2$ **2** (0.100 g, 0.07 mmol) in THF (25 cm^3) at rt. After stirring at rt for 30 min. removal of volatiles under reduced pressure afforded [K_2{^{t}Bu-calix[4](OMe)$_2$(O)$_2$}(dibenzo-18-crown-6)] **7** as a white solid. Yield: 0.143 g (92%).

^{1}H NMR (C_7D_8, 500.1 MHz, 363 K): δ 7.29 (4H, s, *m*-C_6H_2), 7.01 (4H, s, *m*-C_6H_2), 6.79 (4H, dd, ^3J = 6.0, ^4J = 3.5 Hz, C_6H_4), 6.65 (4H, dd, ^3J = 6.0, ^4J = 3.5 Hz, C_6H_4), 4.45 (4H, d, ^2J = 12.0 Hz, CH_2), 3.87 (8H, t, ^3J = 8.0 Hz, OCH_2), 3.83 (8H, t, ^3J = 8.0 Hz, OCH_2), 3.45 (6H, s, OMe), 3.20 (4H, d, ^2J = 12.0 Hz, CH_2), 1.42 (18H, s, CMe_3), 0.97 (18H, s, CMe_3). ^{1}H NMR (C_7D_8, 500.1 MHz, 223 K): δ 7.51 (4H, s, *m*-C_6H_2), 7.17 (4H, s, *m*-C_6H_2), 6.82 (4H, dd, ^3J = 6.0, ^4J = 3.5 Hz, C_6H_4), 6.24 (4H, dd, ^3J = 6.0, ^4J = 3.5 Hz, C_6H_4), 5.12 (4H, m, OCH_2), 4.77 (4H, d, ^2J = 12.0 Hz, CH_2), 3.67 (4H, m, OCH_2), 3.52 (4H, m, OCH_2), 3.38 (6H, s, OMe), 3.34 (4H, d, ^2J = 12.0 Hz, CH_2), 3.07 (4H, m, OCH_2), 1.58 (18H, s, CMe_3), 1.03 (18H, s, CMe_3). ^{13}C-{^{1}H} NMR (C_7D_8, 125.7 MHz, 223 K): δ 164.7 (C*q*-C_6H_2), 157.4 (C*q*-C_6H_2), 148.1 (C*q*-C_6H_2), 145.3 (C*q*-C_6H_2), 136.6 (C*q*-C_6H_2), 132.0 (C*q*-C_6H_2), 129.6 (C*q*-C_6H_4), 126.1 (*m*-C_6H_2), 125.2 (*m*-C_6H_2), 120.5 (C_6H_4), 110.7 (C_6H_4), 67.4 (OCH_2), 67.2 (OCH_2), 62.6 (OMe), 34.0 (*C*Me_3), 33.8 (*C*Me_3), 32.6 (C*Me*$_3$), 32.5 (CH_2), 31.1 (C*Me*$_3$). ES mass spectrum (THF–MeOH): 1075 [M − K + 2H]$^+$ 1%, 715 [M − {dibenzo-18-crown-6} − K + 2H]$^+$ 10%. IR (KBr plates, Nujol): 1594 (m), 1359 (m), 1332 (w), 1289 (m), 1251 (m), 1212 (m), 1168 (w), 1123 (m), 1059 (m), 1019 (m), 942 (m), 877 (m), 831 (w), 805 (m), 780 (w), 738 (s), 642 (w), 601 (w), 558 (w), 491 (w). Anal. (calc. for $C_{66}H_{82}K_2O_{10}$): C 70.1 (71.2), H 7.7 (7.4), K 6.5 (7.0)%.

[Rb_2{^{t}Bu-calix[4](OMe)$_2$(O)$_2$}(dibenzo-18-crown-6)] (8)

A solution of dibenzo-18-crown-6 (0.042 g, 0.12 mmol) in THF (10 cm^3) was added dropwise to a solution of [Rb_2{^{t}Bu-calix[4](OMe)$_2$(O)$_2$}]$_2$ **3** (0.100 g, 0.06 mmol) in THF (25 cm^3) at rt. After stirring at rt for 30 min. removal of volatiles under reduced pressure afforded [Rb_2{^{t}Bu-calix[4](OMe)$_2$(O)$_2$}(dibenzo-18-crown-6)] **8** as a white solid. Yield: 0.121 g, (89%).

^{1}H NMR (C_7D_8, 500.1 MHz, 363 K): δ 7.32 (4H, s, *m*-C_6H_2), 7.18 (4H, s, *m*-C_6H_2), 6.78 (4H, dd, ^3J = 6.0, ^4J = 3.5 Hz, C_6H_4), 6.62 (4H, dd, ^3J = 6.0, ^4J = 3.5 Hz, C_6H_4), 4.53 (4H, d, ^2J = 11.5 Hz, CH_2),3.92 (8H, t, ^3J = 8.0 Hz, OCH_2), 3.90 (8H, t, ^3J = 8.0 Hz, OCH_2), 3.42 (6H, s, OMe), 3.25 (4H, d, ^2J = 11.5 Hz, CH_2), 1.40 (18H, s, CMe_3), 0.98 (18H, s, CMe_3). ^{1}H NMR (C_7D_8, 500.1 MHz, 233 K): δ 7.49 (4H, s, *m*-C_6H_2), 7.25 (4H, s, *m*-C_6H_2), 6.80 (4H, dd, ^3J = 6.0, ^4J = 3.5 Hz, C_6H_4), 6.42 (4H, dd, ^3J = 6.0, ^4J = 3.5 Hz, C_6H_4), 5.12 (4H, m, OCH_2), 4.83 (4H, d, ^2J = 11.5 Hz, CH_2), 3.73 (4H, m, OCH_2), 3.52 (4H, m, OCH_2), 3.41 (6H, s, OMe), 3.38 (4H, d, ^2J = 11.5 Hz, CH_2), 3.10 (4H, m, OCH_2), 1.55 (18H, s, CMe_3), 1.02 (18H, s, CMe_3). ^{13}C-{^{1}H} NMR (C_7D_8, 125.7 MHz, 233 K): δ 166.2 (C*q*-C_6H_2), 158.3 (C*q*-C_6H_2), 148.2 (C*q*-C_6H_2), 145.6 (C*q*-C_6H_2), 136.2 (C*q*-C_6H_2), 130.8 (C*q*-C_6H_2), 129.2 (C*q*-C_6H_4), 126.2 (*m*-C_6H_2), 126.0 (*m*-C_6H_2), 120.7 (C_6H_4), 111.0 (C_6H_4), 67.6, (OCH_2), 67.3 (OCH_2), 62.8 (OMe), 34.1 (*C*Me_3), 33.9 (*C*Me_3), 32.8 (C*Me*$_3$), 32.4 (CH_2), 31.3 (C*Me*$_3$). ES mass spectrum (THF–MeOH): 1121 [M − Rb + 2H]$^+$ 1%, 761 [M − {dibenzo-18-crown-6} − Rb + 2H]$^+$ 20%. IR (KBr plates, Nujol): 1594 (s), 1505 (m), 1359 (m), 1327 (w), 1288 (m), 1254 (s), 1221(m), 1166(w), 1131 (s), 1103 (w), 1068 (m), 1016 (m), 944(s), 907 (w), 876 (m), 850 (w), 830 (w), 806 (m), 781 (m), 740 (s), 640 (w), 601(m), 560 (m), 523 (w), 489(m), 430 (w). Anal. (calc. for $C_{66}H_{82}Rb_2O_{10}$): C 65.6 (65.7), H 6.6 (6.9), Rb 13.5 (14.2)%.

[Cs_2{^{t}Bu-calix[4](OMe)$_2$(O)$_2$}(dibenzo-18-crown-6)] (9)

A solution of dibenzo-18-crown-6 (0.038 g, 0.11 mmol) in THF (10 cm^3) was added dropwise to a solution of [Cs_2{^{t}Bu-calix[4](OMe)$_2$(O)$_2$}]$_2$ **4** (0.100 g, 0.05 mmol) in THF (25 cm^3) at rt. After stirring at rt for 30 min. removal of volatiles under reduced pressure afforded [Cs_2{^{t}Bu-calix[4](OMe)$_2$(O)$_2$}(dibenzo-18-crown-6)] **9** as a white solid. Yield: 0.131 g (84%).

^{1}H NMR (C_7D_8, 500.1 MHz, 378 K): δ 7.32 (4H, s, *m*-C_6H_2), 7.27 (4H, s, *m*-C_6H_2), 6.83 (4H, dd, ^3J = 5.5, ^4J = 3.5 Hz, C_6H_4), 6.60 (4H, dd, ^3J = 5.5, ^4J = 3.5 Hz, C_6H_4), 4.42 (4H, d, ^2J = 12.5

Hz, CH_2), 3.93 (8H, t, ^3J = 8.0 Hz, OCH_2), 3.75 (8H, t, ^3J = 8.0 Hz, OCH_2), 3.50 (6H, s, OMe), 3.33 (4H, d, ^2J = 12.5 Hz, CH_2), 1.50 (18H, s, CMe_3), 1.05 (18H, s, CMe_3). ^{133}Cs NMR (C_6D_6, 65.6 MHz, 298 K): δ 41.0 (fwhm = 89 Hz, *exo*), −169.7 (fwhm = 23 Hz, *endo*). ES mass spectrum (THF–MeOH): 1169 [M − Cs + 2H]$^+$ 2%, 809 [M − {dibenzo-18-crown-6} − Cs + 2H]$^+$ 20%. IR (KBr plates, Nujol): 1593 (s), 1360 (m), 1289 (m), 1256 (s), 1233 (w), 1218 (w), 1131 (s), 1061 (m), 1017 (m), 941 (m), 872 (m), 806 (w), 740 (s), 599 (w), 522 (w). Anal. (calc. for $C_{66}H_{82}Cs_2O_{10}$): C 57.2 (60.9), H 6.4 (6.0)%.

[Li_2{^{t}Bu-calix[4](OCH$_2$Ph)$_2$(O)$_2$}$_2$] (10)

^{t}BuLi (1.7 M in pentane), (7.09 cm^3, 12.1 mmol) was added dropwise to a solution of ^{t}Bu-calix[4](OCH$_2$Ph)$_2$(OH)$_2$ (5.000 g, 6.03 mmol) in pentane (100 cm^3) at −70 °C. The reaction mixture was stirred at rt for 20 h to give a yellow suspension. The reaction mixture was filtered and washed with pentane (10 cm^3) to give a light yellow solution. Removal of volatiles under reduced pressure afforded [Li_2{^{t}Bu-calix[4](OCH$_2$Ph)$_2$(O)$_2$}$_2$] **10** as a light yellow solid. Yield: 4.220 g (83%).

^{1}H NMR (C_6D_6, 300.1 MHz, 298 K): δ 7.25 (2H, ap. t, ap. J = 7.7 Hz, *p*-C_6H_5), 7.07 (4H, t, ^3J = 7.7 Hz, *m*-C_6H_5), 7.03 (4H, s, *m*-C_6H_2), 6.58 (4H, ap. d, ap. J = 7.7 Hz, *o*-C_6H_5), 6.51 (4H, s, *m*-C_6H_2), 4.68 (4H, s, OC$H_2C_6H_5$), 4.23 (4H, d, ^2J = 13.0 Hz, CH_2), 2.72 (4H, d, ^2J = 13.0 Hz, CH_2), 1.26 (18H, s, CMe_3), 0.86 (18H, s, CMe_3). ^{13}C-{^{1}H} NMR (C_6D_6, 75.5 MHz, 298 K): δ 159.9 (C*q*-C_6H_2 or *i*-C_6H_5), 148.4 (C*q*-C_6H_2 or *i*-C_6H_5), 147.1 (C*q*-C_6H_2 or *i*-C_6H_5), 135.4 (C*q*-C_6H_2 or *i*-C_6H_5), 135.1 (C*q*-C_6H_2 or *i*-C_6H_5), 134.4 (C*q*-C_6H_2 or *i*-C_6H_5), 134.0 (C*q*-C_6H_2 or *i*-C_6H_5), 131.5 (*o*-C_6H_5), 128.1 (*m*-C_6H_5), 127.4 (*p*-C_6H_5), 125.7 (*m*-C_6H_2), 124.0 (*m*-C_6H_2), 78.1 (O*C*H$_2$C$_6$H$_5$), 33.9 (*C*Me$_3$), 33.6 (*C*Me$_3$), 33.0 (CH_2), 32.0 (C*Me*$_3$), 31.1 (C*Me*$_3$). ^{7}Li NMR (C_6D_6, 194.3 MHz, 298 K): δ −3.0 (fwhm = 21 Hz). ES mass spectrum (THF–MeOH): 835 [M − Li + 2H]$^+$ 10%. IR (KBr plates, Nujol): 1750 (w), 1599 (m), 1303 (m), 1209 (m), 1186 (m), 1123 (m), 1094 (m), 971 (w), 949 (w), 936 (w), 915 (m), 872 (m), 826 (m), 793 (m), 751 (s), 697 (s), 562 (m), 528 (w), 483 (w), 434 (w), 403 (w). Cryoscopic molecular weight (C_6H_6, g mol^{-1}) (calc.): 873 (841). Anal. (calc. for $C_{58}H_{66}Li_2O_4$): C 82.2 (82.8), H 7.9 (7.9) Li 1.4 (1.6)%.

[Na_2{^{t}Bu-calix[4](OCH$_2$Ph)$_2$(O)$_2$}$_2$] (11)

A solution of ^{t}Bu-calix[4](OCH$_2$Ph)$_2$(OH)$_2$ (0.250 g, 0.30 mmol) in diethyl ether (10 cm^3) was added to Na (sand, 0.014 g, 0.60 mol) at −70 °C. The reaction mixture was stirred at rt for 45 h to give a light yellow suspension. The reaction mixture was filtered and washed with diethyl ether (5 cm^3) to give a light yellow solution. Removal of volatiles under reduced pressure and recrystallisation from thf (−25 °C) afforded a light yellow solid. Filtration, washing with thf (−25 °C) (2 × 2.5 cm^3) and removal of volatiles under reduced pressure afforded [Na_2-{^{t}Bu-calix[4](OCH$_2$Ph)$_2$(O)$_2$}$_2$] **11** as a white solid. Yield: 0.178 g (68%).

^{1}H NMR (C_6D_6, 300.1 MHz, 298 K): δ 7.28 (2H, ap. t, J = 7.7 Hz, *p*-C_6H_5), 7.13 (4H, t, ^3J = 7.7 Hz, *m*-C_6H_5), 7.05 (4H, s, *m*-C_6H_2), 6.76 (4H, ap. d, J = 7.7 Hz, *o*-C_6H_5), 6.58 (4H, s, *m*-C_6H_2), 4.75 (4H, s, OC$H_2C_6H_5$), 4.12 (4H, d, ^2J = 13.0 Hz, CH_2), 2.72 (4H, d, ^2J = 13.0 Hz, CH_2), 1.26 (18H, s, CMe_3), 0.89 (18H, s, CMe_3). ^{13}C-{^{1}H} NMR (C_6D_6, 75.5 MHz, 298 K): δ 162.2 (C*q*-C_6H_2 or *i*-C_6H_5), 151.7 (C*q*-C_6H_2 or *i*-C_6H_5), 146.2 (C*q*-C_6H_2 or *i*-C_6H_5), 136.2 (2 × overlapping) (C*q*-C_6H_2 or *i*-C_6H_5), 132.3 (C*q*-C_6H_2 or *i*-C_6H_5), 131.7 (C*q*-C_6H_2 or *i*-C_6H_5), 130.7 (*o*-C_6H_5), 127.8 (*m*-C_6H_5), 127.7 (*p*-C_6H_5), 125.5 (*m*-C_6H_2), 123.3 (*m*-C_6H_2), 77.2 (O*C*H$_2$C$_6$H$_5$), 33.9 (*C*Me$_3$), 33.5 (*C*Me$_3$), 32.9 (CH_2), 32.1 (C*Me*$_3$), 31.0 (C*Me*$_3$). ES mass spectrum (THF–MeOH): 851 [M − Na + 2H]$^+$ 50%. IR (KBr plates, Nujol): 1596 (w), 1329 (m), 1308 (w), 1288 (m), 1208 (w), 1188 (m), 1120 (w), 1096 (m), 967 (m), 942 (w), 916 (m), 874 (m), 827 (w), 798 (w), 753 (m), 697 (m), 647 (w), 615 (w), 598 (w), 570 (w), 554 (m), 523 (w), 494 (m). Cryoscopic molecular weight (C_6H_6, g mol^{-1}) (calc.): 951 (873). Anal. (calc. for $C_{58}H_{66}Na_2O_4$): C 80.0 (79.8), H 7.8 (7.6) Na 5.3 (5.3)%.

[Na_2{^{t}Bu-calix[4](OSiMe$_3$)$_2$(O)$_2$}$_2$] (12)

A solution of ^{t}Bu-calix[4](OSiMe$_3$)$_2$(OH)$_2$ (5.000 g, 5.77 mmol) in THF (25 cm^3) was added to NaH (0.277 g, 11.55 mmol) at rt. The reaction mixture was stirred at rt for 100 h to give a white suspension. The reaction mixture was filtered and the washed with thf (10 cm^3) to give a colourless solution. Removal of volatiles under reduced pressure and recrystallisation from thf (−25 °C) afforded a white solid. Filtration, washing with thf (−25 °C), (2 × 5 cm^3) and removal of volatiles under reduced pressure afforded [Na_2{^{t}Bu-calix[4](OSiMe$_3$)$_2$(O)$_2$}$_2$] **11** as a white solid. Yield: 3.425 g (71%).

^{1}H NMR (C_6D_6, 300.1 MHz, 298 K): δ 7.08 (4H, s, *m*-C_6H_2), 6.61 (4H, s, *m*-C_6H_2), 4.20 (4H, d, ^2J = 13.0 Hz, CH_2), 2.98 (4H, d, ^2J = 13.0 Hz, CH_2), 1.32 (18H, s, CMe_3), 0.87 (18H, s, CMe_3), 0.26 (18H, s, $SiMe_3$). ^{13}C-{^{1}H} NMR (C_6D_6, 75.5 MHz, 298 K): δ 161.1 (C*q*-C_6H_2), 148.5 (C*q*-C_6H_2), 144.2 (C*q*-C_6H_2), 134.4 (C*q*-C_6H_2), 132.8 (C*q*-C_6H_2), 132.1 (C*q*-C_6H_2), 124.8 (*m*-C_6H_2), 123.3 (*m*-C_6H_2), 33.8 (*C*Me$_3$), 33.6 (*C*Me$_3$), 33.5 (CH_2), 32.1 (C*Me*$_3$), 31.0 (C*Me*$_3$), 0.4 ($SiMe_3$). ES mass spectrum (THF–MeOH): 671 [M − 2TMS − Na + 4H]$^+$ 10%. IR (KBr plates, Nujol): 1595 (w), 1260 (s), 1199 (w), 1096 (s), 1018 (s), 916 (w), 871 (m), 845 (w), 799 (s), 595 (w), 559 (w). Cryoscopic molecular weight (C_6H_6, g mol^{-1}) (calc.): 841 (837). Anal. (calc. for $C_{50}H_{70}Na_2O_4Si_2$): C 70.3 (71.7), H 8.6 (8.4) Na 5.5 (5.5)%.

[NaCs{^{t}Bu-calix[4](OMe)$_2$(O)$_2$}]$_2$ (13)

A solution of [Na_2{^{t}Bu-calix[4](OMe)$_2$(O)$_2$}]$_2$ **1** (0.250 g, 0.18 mmol) in THF (10 cm^3) was added to CsCl (0.583 g, 3.50 mmol) at rt. The mixture was stirred at 65 °C under reduced pressure for 200 h and then filtered and washed with THF (10 cm^3) to give a colourless solution. Removal of volatiles under reduced pressure afforded [NaCs{^{t}Bu-calix[4](OMe)$_2$(O)$_2$}]$_2$ **13** as a white solid. Yield: 0.274 g (85%).

^{1}H NMR (C_6D_6, 300.1 MHz, 298 K): δ 7.32 (8H, s, *m*-C_6H_2), 7.18 (8H, s, *m*-C_6H_2), 4.86 (8H, d, ^2J = 12.0 Hz, CH_2), 3.84 (12H, s, OMe), 3.37 (8H, d, ^2J = 12.0 Hz, CH_2), 1.45 (32H, s, CMe_3), 0.96 (32H, s, CMe_3). ^{13}C-{^{1}H} NMR (C_6D_6, 75.5 MHz, 298 K): δ 164.1 (C*q*-C_6H_2), 157.0 (C*q*-C_6H_2), 146.2 (C*q*-C_6H_2), 136.6 (C*q*-C_6H_2), 131.6 (C*q*-C_6H_2), 131.0 (C*q*-C_6H_2), 126.2 (*m*-C_6H_2), 125.5 (*m*-C_6H_2), 64.3 (OMe), 34.0 (*C*Me$_3$), 33.8 (*C*Me$_3$), 32.7 (CH_2), 32.5 (C*Me*$_3$), 31.1 (C*Me*$_3$). ^{133}Cs NMR (C_6D_6, 65.5 MHz, 298 K): δ −180.05 (fwhm = 192 Hz, *endo*). ES mass spectrum (THF–MeOH): 1376 [M − 2Cs − Na + 4H]$^+$ 5%, 699 [M − {^{t}Bu-calix[4](OMe)$_2$(O)$_2$} − 2Cs − Na + 2H]$^+$ 1%. IR (KBr plates, Nujol): 1754 (w), 1594 (m), 1480 (s), 1433 (m), 1391 (w), 1359 (m), 1289 (m), 1237 (m), 1203 (m), 1180 (w), 1124 (m), 1093 (m), 1015 (m), 966 (w), 941 (w), 888 (w), 874 (m), 828 (w), 802 (m), 776 (w), 752 (w), 704 (m), 663 (m), 637 (m), 599 (w), 570 (w), 559 (m), 523 (m), 490 (m), 468 (w), 449 (w), 428 (m). Anal. (calc. for $C_{92}H_{116}Cs_2Na_2O_8$): C 66.3 (66.5), H 7.2 (7.0) Na 2.9 (2.8)%.

[NaRb{^{t}Bu-calix[4](OMe)$_2$(O)$_2$}]$_2$ (14)

A solution of [Na_2{^{t}Bu-calix[4](OMe)$_2$(O)$_2$}]$_2$ **1** (0.250 g, 0.18 mmol) in THF (10 cm^3) was added to RbCl (0.423 g, 3.50 mmol) at rt. The mixture was stirred at 65 °C under reduced pressure for 200 h and then filtered. Removal of volatiles under reduced pressure afforded a mixture of [NaRb{^{t}Bu-calix-[4](OMe)$_2$(O)$_2$}]$_2$ **14** and [Na_2{^{t}Bu-calix[4](OMe)$_2$(O)$_2$}]$_2$ **1** in a 95:5 ratio as judged by ^{1}H NMR spectroscopy.

^{1}H NMR for **14** (C_6D_6, 300.1 MHz, 298 K): δ 7.34 (8H, s, *m*-C_6H_2), 7.08 (8H, s, *m*-C_6H_2), 4.67 (8H, d, ^2J = 12.0 Hz, CH_2), 3.70 (12H, s, OMe), 3.29 (8H, d, ^2J = 12.0 Hz, CH_2), 1.48 (32H, s, CMe_3), 0.93 (32H, s, CMe_3).

[NaK{^{t}Bu-calix[4](OMe)$_2$(O)$_2$}]$_2$ (15)

A solution of [Na$_2${^{t}Bu-calix[4](OMe)$_2$(O)$_2$}]$_2$ **1** (0.250 g, 0.18 mmol) in THF (10 cm^3) was added to KCl (0.261 g, 3.50 mmol) at rt. The mixture was stirred at 65 °C under reduced pressure for 200 h and then filtered. Removal of volatiles under reduced pressure afforded a mixture of [NaK{^{t}Bu-calix[4](OMe)$_2$(O)$_2$}]$_2$ **15** and [Na$_2${^{t}Bu-calix[4](OMe)$_2$(O)$_2$}]$_2$ **1** in a 90:10 ratio as judged by ^{1}H NMR spectroscopy.

^{1}H NMR for **15** (C_6D_6, 300.1 MHz, 298 K): δ 7.35 (8H, s, *m*-C_6H_2), 7.02 (8H, s, *m*-C_6H_2), 4.60 (8H, d, ^2J = 12.0 Hz, CH_2), 3.66 (12H, s, OMe), 3.28 (8H, d, ^2J = 12.0 Hz, CH_2), 1.49 (32H, s, CMe_3), 0.91 (32H, s, CMe_3)

[Na$_2$Ca{^{t}Bu-calix[4](OMe)$_2$(O)$_2$}$_2$] (16)

A solution of [Na$_2${^{t}Bu-calix[4](OMe)$_2$(O)$_2$}]$_2$ **1** (0.250 g, 0.18 mmol) in THF (10 cm^3) was added to $CaCl_2$ (0.393 g, 3.50 mmol) at rt. The mixture was stirred at 65 °C under reduced pressure for 200 h. The mixture was then filtered and washed with THF (10 cm^3) to give a colourless solution. Removal of volatiles under reduced pressure afforded [Na$_2$Ca{^{t}Bu-calix[4](OMe)$_2$(O)$_2$}$_2$] **16** as a white solid. Yield: 0.229 g (86%).

^{1}H NMR ($CDCl_3$, 300.1 MHz, 298 K): δ 7.09 (8H, s, *m*-C_6H_2), 6.64 (8H, s, *m*-C_6H_2), 4.49 (8H, d, ^2J = 12 Hz, CH_2), 3.31 (12H, s, OMe), 3.06 (8H, d, ^2J = 12 Hz, CH_2), 1.31 (36H, s, CMe_3), 0.89 (36H, s, CMe_3). ^{13}C-{^{1}H} NMR ($CDCl_3$, 75.5 MHz, 298 K): δ 161.4 (C*q*-C_6H_2), 155.4 (C*q*-C_6H_2), 145.9 (C*q*-C_6H_2), 135.7 (C*q*-C_6H_2), 133.6 (C*q*-C_6H_2), 132.3 (C*q*-C_6H_2), 124.9 (*m*-C_6H_2), 123.2 (*m*-C_6H_2), 63.7 (OMe), 33.9 (*C*Me_3), 33.6 (*C*Me_3), 32.6 (CH_2), 32.1 (C*Me*$_3$), 31.1 (C*Me*$_3$). ES mass spectrum (THF–MeOH): 1376 [M − Ca − Na + 4H]$^+$ 5%, 699 [M − {^{t}Bu-calix[4](OMe)$_2$(O)$_2$} − Ca − Na + 2H]$^+$ 100%, 715 [M − {^{t}Bu-calix[4](OMe)$_2$(O)$_2$} − 2Na + H]$^+$ 1%. IR (KBr plates, Nujol): 1483 (w), 1363 (m), 1300 (m), 1260 (m), 1204 (w), 1188 (m), 1170 (m), 1120 (m), 1101 (m), 1020 (w), 874 (m), 811 (s), 801 (m), 668 (s). Anal. (calc. for $C_{92}H_{116}CaNa_2O_8$): C 76.4 (76.9), H 8.9 (8.1)%.

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