# Polymetallated 4-*tert*-Butylcalix[4]arene Complexes of Sodium and Potassium Stabilized by Crown Ethers: Syntheses, Structures and Activation of Carbon Dioxide

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4-*tert*-Butylcalix[4]arene and 18-crown-6 react with NaH in THF to form the complex [(18-crown-6)(THF)$Na_4$(4-*tert*-butylcalix[4]arene-4H)$]_2$·3THF (**1**). Analogously, the reaction with 4-*tert*-butyltetrathiacalix[4]arene in DMF results in the formation of [(18-crown-6)Na(dmf)$_{1.5}]_2$[(4-*tert*-butyltetrathiacalix[4]arene-4H)$_2$$Na_6$(dmf)$_2$] (**2**) The X-ray analysis of **1** shows an $Na_6O_6$ skeleton consisting of two fused open heterocubanes. Two $Na^+$ ions are encapsulated in the cavities of the calix[4]arene units. Additionally, two peripheral $Na^+$ ions, each surrounded by a crown ether and one THF ligand, are connected to the central $Na_6O_6$ skeleton by one bridging oxygen of the calix[4]arene. In contrast, **2** contains the highly symmetrical anion [(4-*tert*-butyltetrathiacalix[4]arene-4H)$_2$$Na_6$(dmf)$_2]^{2-}$ and crown-ether-stabilized cations. While **1** shows a dynamic process in solution above 40 °C, the structure of the highly symmetrical compound **2** remains stable at higher temperatures. The solid-state structure of the potassium complex [(dibenzo-18-crown-6)$K_4$(4-*tert*-butylcalix[4]arene-4H)(THF)$_3]_2$·4THF (**4**) is similar to **1**; however, the calix[4]arene units in the open heterocubane structure of **4** are shifted less than half a diameter to one another than in the sodium complex **1**. According to the $^1H$ NMR spectra complex **3a**, containing 18-crown-6, has a very similar structure to the related complex **4**. Both **1** and **4** absorb carbon dioxide in THF and are active $CO_2$-transfer reagents towards 2-fluoropropiophenone; complex **2** is much less active. This clearly demonstrates the subtle influence of the structure of the alkali metal complexes on the $CO_2$ reactivity in these types of compounds.

## Introduction

Calixarenes and their metal complexes have attracted great interest during the last 20 years due to a number of attractive aspects in different areas. A great number of derivatives have been synthesized, structurally characterized and used for application in supramolecular chemistry (especially host-guest complexes), for selective metal coordination, as models for simulating catalytic oxide surfaces, and as catalysts and sensors.[1−7]

Interactions with alkali metal ions have been intensively investigated mainly due to their importance for the separation of the alkali metals and as models for metal-ion transport.[8] The first complex of the monoanion of 4-*tert*-butylcalix[4]arene with $Cs^+$ was described 1991 by Harrowfield.[9] In 1993 Atwood isolated a monometallated sodium complex in which two oxygens of the calixarene unit chelate to the metal.[10] A number of other alkali metal complexes with monoanionic and dianionic calixarenes are also known.[11−13] Recently, Harrowfield described partially deprotonated thiacalixarene complexes of the Li−Cs series,[14] and in 1995 Bock et al. published the molecular structure of [$Li_3$(calix[4]arene-3H)($NH_3$)$]_2$ the first alkali metal complex of a multiply deprotonated calix[4]arene.[15]

Surprisingly little is known about alkali metal complexes with fully deprotonated calix[4]arenes of the type [$M_4$(4-*tert*-butylcalix[4]arene-4H)(solv)$_x]_2$, which are useful building blocks for the preparation of transition metal complexes. The first complex of this type with Li as the metal center was described by Davidson.[16] Recently, Floriani,[17] and Fromm[18] prepared and structurally elucidated polymetallated alkali metal complexes with Li, Na and K using different synthetic procedures. Partial hydrolysis of the lithium derivative resulted in the formation of the doubly protonated Li complex.[18] Furthermore, the syntheses and structures of dialkylated alkali metal calix[4]arene complexes were recently described, and their reaction with crown ethers in solution investigated by NMR spectroscopy.[19]

It is well-known that alkali-metal phenolates react with carbon dioxide to form complexes of hitherto unknown structures which can undergo self-carboxylation to form salicylic acid or the *para*-hydroxybenzoic acid. Additionally, some alkali-metal phenolates are also able to carboxylate

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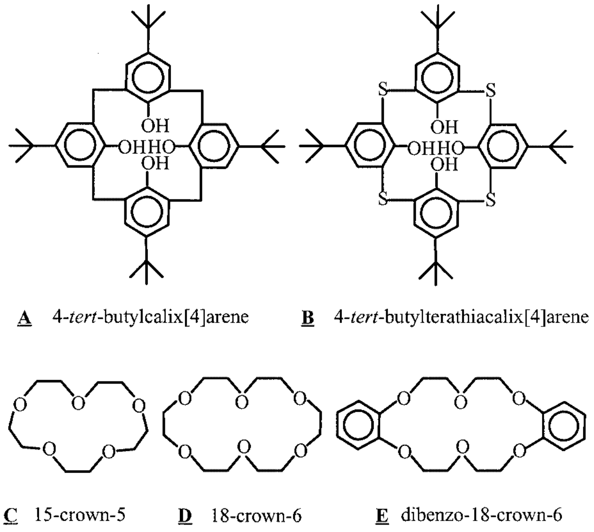
activated aliphatic C−H bonds in dipolar aprotic solvents to form aliphatic carboxylic acids upon hydrolysis.[20−24]

Generally, calixarene alkali metal complexes containing phenolate groups linked in the two *ortho* positions by methylene groups should be of great interest in $CO_2$ chemistry, especially for the design of metal complexes which could be active in both the fixation and the activation of carbon dioxide. To the best of our knowledge, this aspect of calixarene metal chemistry has been completely ignored so far.

Here we report on the synthesis and molecular structures of new polymetallated sodium and potassium calix[4]arene complexes in combination with crown ethers, which act as competitive ligands. Our aim was to construct soluble systems which would be active in both $CO_2$ fixation and in carboxylation reactions of activated aliphatic C−H bonds.

## Results and Discussion

Scheme 1 displays the starting calix[4]arene **A** and its sulfur-bridged analogue **B**, as well as the three crown ethers used as co-ligands.



Scheme 1. The calix[4]arenes **A** and **B** and the crown ethers **C**−**E** used as ligands

### Sodium Complexes with 4-*tert*-Butylcalix[4]arene (1 and 2)

In the absence of traces of water sodium hydride readily reacts with the calix[4]arene **A** in THF to form completely deprotonated products. In the presence of 15-crown-5 (**C**), which is tailor-made for $Na^+$, the resulting reaction product is insoluble even in polar solvents such as THF, DMF or DMSO. We assume, therefore, that the fully deprotonated calixarene-containing sodium complex consists either of separated ions, which cannot be solvated effectively in organic solvents, or forms a polymeric structure.

However, with 18-crown-6 (**D**) as co-ligand, a crown ether which does not "fit" effectively to $Na^+$,[25] complex **1** was obtained as a THF-soluble product. From this solution we isolated well-shaped single crystals containing three non-coordinated molecules of THF per dimeric unit [18-crown-6)(THF)$Na_4$(4-*tert*-butylcalix[4]arene-4H)$]_2$. THF is very easily eliminated from this complex at 0 °C or by bubbling a stream of inert gas through the solution. Complex **1** is formed in a very selective reaction in high yields. Even if an excess of 18-crown-6 was used as a competitor ligand for the calix[4]arene, only complex **1** was formed. This shows that the sodium strongly prefers the charged ligand to the neutral one. Single crystals were grown from THF solution and the structure of **1** was confirmed crystallographically with the molecular structure illustrated in Figure 1.

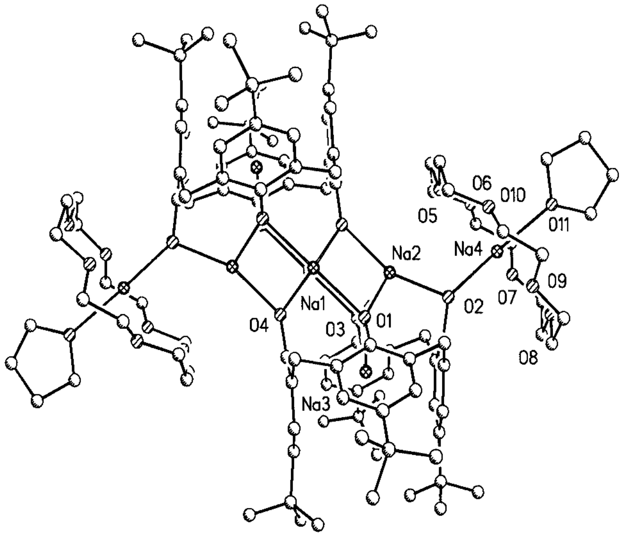


Figure 1. Molecular structure of [(18-crown-6)(THF)$Na_4$(4-*tert*-butylcalix[4]arene-4 H)$]_2$·3THF (**1**); non-coordinated THF and hydrogen atoms have been omitted for clarity; selected bond lengths (Å): Na(1)−O(1) 2.275(3), Na(1)−O(3) 2.281(3), Na(1)−O(4) 2.292(3), Na(2)−O(1) 2.383(3), Na(2)−O(2) 2.199(3), Na(2)−O(3) 2.359(3), Na(2)−O(4A) 2.232(3), Na(3)−O(1) 2.327(3), Na(3)−O(3) 2.356(3), Na(4)−O(2) 2.216(3), Na(4)−O(5) 2.802(4), Na(4)−O(6) 2.805(4), Na(4)−O(7) 2.661(4), Na(4)−O(8) 2.714(4), Na(4)−O(9) 2.672(4), Na(4)−O(10) 2.820(4), Na(4)−O(11) 2.381(4), Na(1)···Na(1A) 2.931(3), Na(1)···Na(2) 3.152(2); selected bond angles (°): O(11)−Na(4)−O(5) 99.60(14), O(11)−Na(4)−O(6) 84.2(2), O(11)- Na(4)−O(7) 86.9(2), O(11)−Na(4)−O(8) 83.13(13), O(11)−Na(4)−O(9) 86.1(2), O(11)−Na(4)−O(10) 81.6(2), (11)−Na(4)−O(2) 177.7(2), O(1)−Na(1)−O(3A) 171.68(12), O(1)−Na(1)−O(4A) 93.73(11), O(1)−Na(1)−O(4) 90.77(10), O(2)−Na(2)−O(4A) 153.33(12), O(2)−Na(2)−O(1) 101.50(11), O(2)−Na(2)−O(3) 102.82(11), O(1)−Na(2)−O(3) 86.91(10), Na(1)−O(1)−Na(3) 118.7(3), Na(1A)−O(3)−Na(3) 117.3(3)

Figure 2 shows the $Na_6O_6$ skeleton of **1**, with the Na(1)−O(4)−Na(1A)−O(4A)−plane fusing two heterocubane units. Since there are no bonding interactions between Na(3) and O(4) or Na(3A) and O(4A), two "open" heterocubane units result.

Compound **1** can be considered as an intermediate between the fully lithiated compound (with the coordination number 4 for Li)[18] and the potassium compound (open heterocubane structure), reflecting also the intermediate size of the Na cation between Li and K.

Furthermore, in **1** the two calix[4]arene units are shifted by half a diameter with respect to one another. This is different to the reported pyridine-stabilized sodium complex

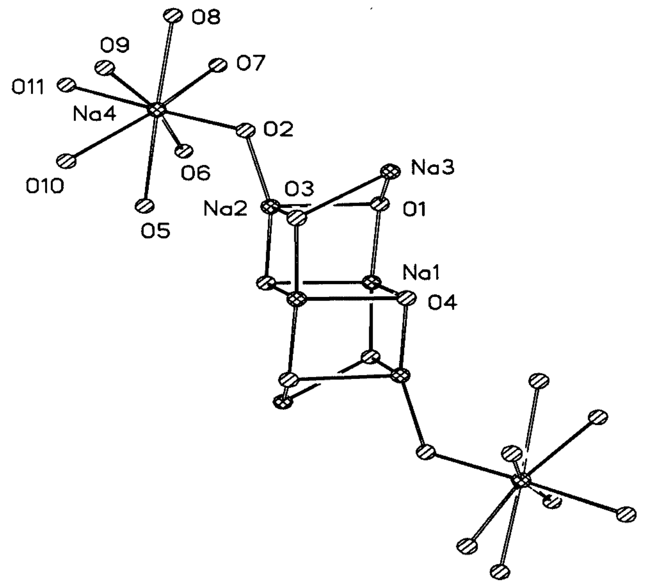


Figure 2. $Na_8O_8$ cluster core of **1** with the central $Na_6O_6$ skeleton

[(pyridine)$_4$Na$_4$(4-*tert*-butylcalix[4]arene-4H)]$_2$·THF in which this shift is very small.[10] Consequently, the sodium atoms in the plane fusing the two heterocubanes exhibit coordination numbers of four in **1**, in contrast to the above pyridine complex where these $Na^+$ ions have a coordination number of five.

In the central $Na_6O_6$ skeleton the oxygen atoms of the calix[4]arene are situated at the corners of a deformed rhomb, in contrast to their positions in the free calix[4] arene where these oxygens occupy the corners of a square.[26] Na(3) and Na(3A) are encapsulated in the cavities of the calix[4]arenes and are in contact with the aromatic π-systems of two calix[4]arene phenyl rings. These rings are almost parallel to each other and the Na−C bond lengths (between 2.931 and 3.500 Å) are similar to previously reported values.[18,19]

The peripheral Na(4) and Na(4A) atoms, with a coordination number of eight, each surrounded by the six oxygens of 18-crown-6 and one THF oxygen, are linked to the central $Na_6O_6$ skeleton by only one bridging calixarene phenolate. The six crown ether oxygens adopt almost coplanar positions with the sodium ion out of this plane (deviation from the least-squares plane: 0.15 Å, shifted in the direction of the coordinated phenolate). Furthermore, the coordinated THF and the oxygen of the phenolate group lie *trans* to each other, perpendicular to the plane formed by the crown ether. This type of coordination is, in principle, well-known for symmetric 18-crown-6 sodium complexes of the type [(18-crown-6)NaL$_2$]X (L = THF,[27−30] $H_2O$[31,32] with different anions; for a review see ref.[33]). Moreover, asymmetric types of the composition [(18-crown-6)Na(X)] (L = THF or 1,3-dioxolane; X = anionic ligand) have recently been found as well.[34−36]

The Na−O(crown) distances in **1** [between 2.661(4) and 2.805(4) Å] are considerably longer than the Na−O(THF) distance [2.381(4) Å]. These values lie in a typical range for the above type of asymmetric compounds. As expected, the Na−O(phenolate) distance [2.216(3) Å] is the shortest Na−O bond due to the anionic nature of the $Na_6O_6$ skeleton containing the calixarene units.

The $^1$H NMR spectrum in [D$_8$]THF at room temperature suggests that the structure found in the solid state is also maintained in solution at ambient temperature (Figure 3). As expected for this structure three signals of *tert*-butyl groups in a 2:1:1 ratio (at δ = 0.76, 0.95 and 1.29 ppm), and four signals for the *meta*-protons of the phenolates at δ = 6.27, 6.54, 6.84 and 6.90 ppm are observed at 20 °C. Furthermore, four doublets belonging to the bridging methylene groups at δ = 2.71, 2.82, 3.77 and 4.73 ppm appear.

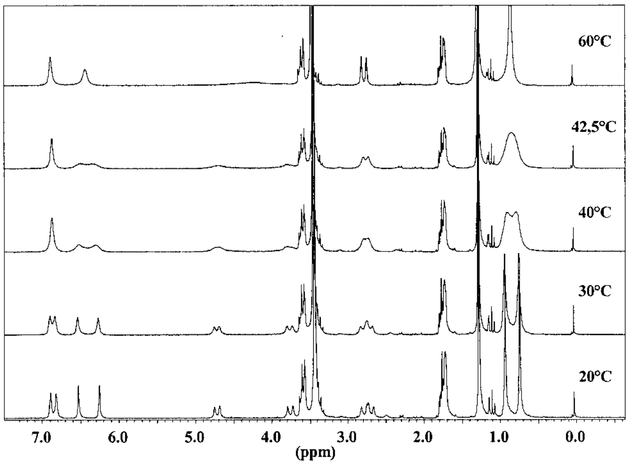


Figure 3. Temperature-dependent $^1$H NMR spectra of **1** in [D$_8$]THF

Increasing the temperature results in a significant change of the NMR spectra. At 42.5 °C the two signals at higher field coalesce and at higher temperatures only two signals for the *tert*-butyl protons in a ratio of 2:2 (at δ = 0.82 and 1.25 ppm) appear. The signals of the *meta*-protons of the phenolates (at δ = 6.40 and 6.84 ppm) and of the bridging $CH_2$ (at δ = 2.74 and 4.19 ppm) show the same behavior, indicating that at higher temperature two pairs of equivalent phenolates exist in the molecule.

The reversible nature of the temperature-dependent $^1$H NMR spectra implies a dynamic process, the activation energy of which ($\Delta H$ = 65.0 ± 0.5 kJ·mol$^{-1}$) can be calculated from the temperature of coalescence and the separation of the signals in the $^1$H NMR spectra.

One possibility to explain this dynamic behavior would be the dissociation of **1** into the ions [Na(18-crown-6)]$^+$ and [(4-*tert*-calix[4]arene-4H)Na$_3$]$_2^-$. However, this process can be excluded because in this case three different species would exist in solution above 40 °C: the starting compound **1** and the ionic compounds [Na(18-crown-6)]$^+$ and [(4-*tert*-butylcalix[4]arene)Na$_3$]$_2^-$. This is not in agreement with the simple $^1$H NMR pattern at high temperatures. However, a translation process involving the translation of one calix[4]-arene unit in the direction defined by the Na(2)−Na(2A) axis, and the translation of the other calix[4]arene in the opposite direction, could explain the NMR spectroscopic data. Simultaneously, the sodium ions Na(4) and Na(4A) would undergo a 1,3-shift. An alternative process would be the synchronized rotation of both calix[4]arene units in **1** around their central axis. The rhomb of Na(1)−Na(2)−Na(1A)−Na(2A) may be fixed during this process in which **1** would act in solution as a "temperature-dependent molecular slide clutch". A similar process, with an activation enthalpy, $\Delta H^{\ominus}$, of 45 kJ·mol$^{-1}$ was recently found for a mononuclear Zn calixarene complex.[37] Although the NMR spectroscopic data do not allow us to distinguish between the translation and the rotation process in **1**, it is reasonable to favor the translation process, since a rotation would require more activation energy than a simple transition process.

The reaction of the sulfur-bridged calix[4]arene **B** with $NaN(SiMe_3)_2$ in the presence of 18-crown-6 in a molecular ratio of 1:4:1 in THF results in an insoluble product. Recrystallization from DMF gives well-shaped single crystals of the composition [(18-crown-6)Na(dmf)$_{1.5}$]$_2$[(4-*tert*-butyltetrathiacalix[4]arene-4H)$_2$Na$_6$(dmf)$_2$] (**2**). Complex **2** contains the same molecular ratio between calix[4]arene, sodium and 18-crown-6 as **1**; however the $^1$H NMR spectrum of **2** exhibits only a simple pattern indicating a high symmetry of the molecule.

Unfortunately, due to the poor crystal quality only the structural motif could be determined by X-ray analysis. However, the complex is undoubtedly an ionic compound consisting of two [(dmf)$_n$Na$^+$(18-crown-6)]$^+$ ($n$ = 1, 2) cations and the anion [(dmf)$_2$Na$_6$(4-*tert*-butyltetrathiacalix[4]arene$_2$]$^{2-}$. Figure 4 displays the structure motif of the anionic part.

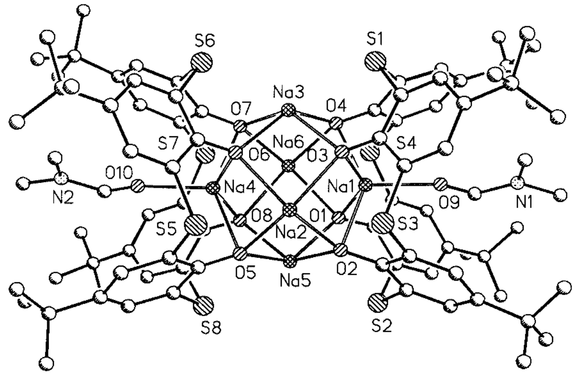


Figure 4. Structural motif of the [(4-*tert*-butyltetrathiacalix[4]arene-4H)$_2$Na$_6$(dmf)$_2$]$^{2-}$ anion of **2**; the counterions [(dmf)$_2$Na(18-crown-6)]$^+$, [(dmf)Na(18-crown-6)]$^+$ and the hydrogen atoms have been omitted for clarity

Complex **2** contains two perpendicular mirror planes, one of which consists of Na(2), Na(3), Na(5) and Na(6), and the other S(1), S(2), S(6) and S(8). The central unit of the structure is an octahedron with Na(1), Na(2), Na(3), Na(4), Na(5) and Na(6) at the corners. Every plane of the octahedron is capped by an oxygen of the phenolate rings. The sodium atoms Na(3), Na(2) Na(5), and Na(6) form square pyramids, with the Na ions at the apex and four oxygens in the base. In addition, the oxygen atoms of the calix[4]arene phenolates are located at the corners of a cube and the 4-*tert*-butyltetrathiacalix[4]arene moieties are in an eclipsed arrangement. There is no interaction of the Na$^+$ ions with the free electron-pairs of the sulfur atoms. In contrast to the sodium-calixarene complex **1**, where a sodium atom is found inside the cavities, the cavities of **2** contain a DMF molecule, which coordinates to Na(1) and Na(4).

The two counterions [(dmf)Na$^+$(18-crown-6)] and [(dmf)$_2$Na$^+$(18-crown-6)] have different coordination environments. In [(dmf)Na$^+$(18-crown-6)] the crown ether oxygens are arranged in a "boat form" with the sodium ion below the plane. The coordination of six oxygens of the crown ether and one DMF molecule results in a coordination number of seven for the sodium ion. This arrangement is similar to that in compound **5** and will be discussed in more detail below.

The structural motif of the other cation [(dmf)$_2$Na$^+$(18-crown-6)] is typical of the above-mentioned group of symmetrical [(18-crown-6)NaL$_2$]$^+$ complexes,[27−33] with a hexagonal-bipyramidal arrangement of the eight oxygen ligands surrounding the sodium ion. The sodium ion is situated in the center of the plane formed by the six oxygens of the crown ether compound. In addition, the two DMF ligands lie *trans* to each other.

The $^1$H NMR spectrum in [D$_8$]THF is in agreement with this highly symmetrical structure found in the solid state: besides the DMF protons only one singlet for the protons of the *tert*-butyl groups (at $\delta$ = 1.14 ppm), one singlet for the *meta* CH groups of the aromatic rings (at $\delta$ = 7.42 ppm) and one singlet for the OCH$_2$ groups of the crown ether (at $\delta$ = 3.59 ppm), with the expected intensities, were observed. According to the $^1$H NMR spectrum, this structure is maintained even at higher temperatures.

### Potassium Complexes with 4-*tert*-Butylcalix[4]arene and Crown Ethers

The reaction of **A** with $KN(SiMe_3)_2$ and 18-crown-6 (**D**) in a molar ratio of 1:4:1 in THF afforded a mixture of the two compounds **3a** and **3b** even if the molecular ratio of **A**/18-crown-6 was varied from 1:1 to 1:2. Complex **3a** crystallized as large, colorless crystals of the composition [(18-crown-6)K$_4$(4-*tert*-butylcalix[4]arene-4H)(THF)$_n$], and **3b** crystallized as fine needles. Separation of **3a** from the reaction mixture was possible by repeated decanting of **3a** from the suspension followed by washing the crystals with THF at −78 °C. According to the $^1$H NMR spectrum the purity of **3a** was greater than 95%. However, since **3a** could not be isolated as single crystals suitable for X-ray crystallography, we performed a similar reaction with the closely related dibenzo-18-crown-6 instead of 18-crown-6 to get better crystals of this type of compound.

Reaction of ligand **A** with $KN(SiMe_3)_2$ and dibenzo-18-crown-6 (**E**) in a molar ratio of 1:4:1 in THF did indeed yield the complex [(dibenzo-18-crown-6)K$_4$(4-*tert*-butylcalix[4]arene-4H)(THF)$_3$]$_2$·4THF (**4**) in a mixture with a second product of the composition [(dibenzo-18-crown-

6)$_2$K$_4$(4-*tert*-butylcalix[4]arene-4H)] (according to the $^1$H NMR spectrum of the reaction mixture). Single crystals of compound **4** grown from THF were suitable for X-ray analysis. Figure 5 shows the molecular structure and contains selected bond lengths and bond angles in the figure caption; Figure 6 shows the $K_8O_8$ core.

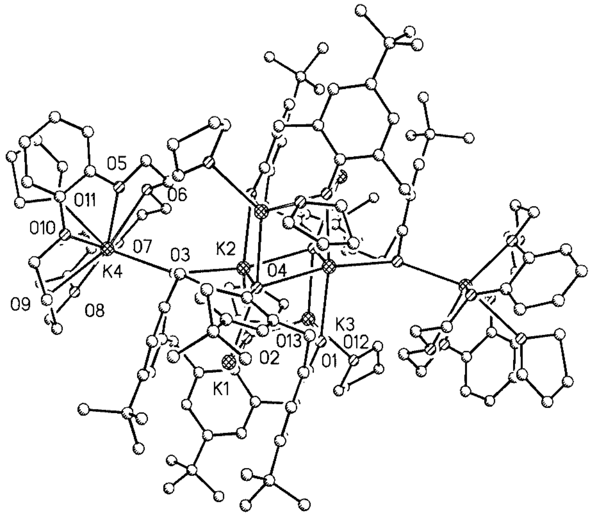


Figure 5. Molecular structure of **4**; non-coordinated THF and hydrogen atoms have been omitted for clarity; selected bond lengths (Å): K(1)−O(2) 2.704(4), K(1)−O(4) 2.842(4), K(2)−O(2) 2.619(4), K(2)−O(3) 2.599(4), K(2)−O(4) 2.574(4), K(3)−O(1A) 2.702(4), K(2)−K(2A) 3.477(2), K(3)−O(1) 2.744(4), K(3)−O(2) 2.678(4), K(3)−O(12) 2.776(7), K(3)−O(13) 2.833(6), K(3)−K(2A) 2.6391(18Å, K(4)−O(3) 2.681(4), K(4)−O(5) 2.827(5), K(4)−O(6) 2.779(4), K(4)−O(7) 2.797(5) Å, K(4)−O(8) 2.848(5), K(4)−O(9) 2.812(5), K(4)−O(10) 2.841(5), K(4)−O(11) 2.758(8)

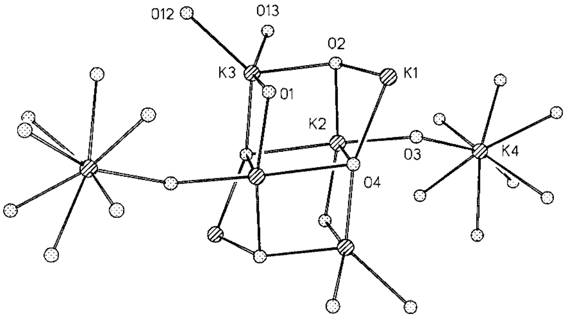


Figure 6. The $K_8O_8$ core in **4** with the central $K_6O_6$ skeleton and the two peripheral $K^+$ ions (each surrounded by the crown ether oxygens and one oxygen of THF) bridged by O(3) and O(3A), respectively

The molecular structure of **4** shows some similarities to the sodium compound **1**. In both complexes the central $M_6O_6$ moiety consists of two fused open heterocubanes where the corners are occupied alternately by alkali metal cations and oxygens of the calix[4]arenes. However, there are remarkable differences in the details of the structure. In contrast to **1**, the central heterocubane units in **4** are arranged nearly perpendicularly, and the peripheral [(THF)K(4)(dibenzo-18-crown-6)]$^+$ unit interacts with the phenolate oxygen bridge O(3) of the central skeleton and not with O(2) as found in **1**.

The calixarene oxygens coordinate to the central potassium rhomb containing K(2), K(3), K(2A) and K(3A). K(2) and K(2A) have coordination numbers of five, with a distorted square-pyramidal arrangement of the phenolate oxygen atoms. K(3) and K(3A) also have a coordination number of five due to three phenolate oxygen atoms and two coordinated THF molecules.

The two calix[4]arene units are shifted less than half a diameter with respect to one another, therefore the [(THF)K(dibenzo-18-crown-6)]$^+$ moieties are much closer to the central $K_6O_6$ skeleton.

The structure of **4** is very similar to the reported structures of the complexes [(THF)$_5$K$_4$(4-*tert*-butylcalix[4]arene-4 H)]$_2$·4THF[17] and [(THF)$_5$K$_4$(4-*tert*-butylcalix[4]arene-4 H)]$_2$·THF.[18] The most remarkable difference consists in the different coordination of the peripheral ions K(4) and K(4A), indicating the influence of the crown ether ligand: as they are surrounded by the crown ether oxygens and one THF, both K(4) and K(4A) are only coordinated to one calix[4]arene oxygen bridge, in contrast to the previously described THF-stabilized complexes, where two oxygen bridges link these $K^+$ ions.

K(1) and K(1A) inside the calix[4]arene cores are bonded to only two oxygen atoms of the phenolates, although they also interact with the π-electron systems of the two nearly parallel phenolates. The K(1)−C$_{aromat}$ distances lie within reported ranges[18] [2.931(3)−3.435(4) Å for the first ring and 3.058(4)−3.152(3) Å for the second ring]. However, there are also contacts to the *ipso* carbon atoms of the other two phenyl rings [K(1)−C$_{ipso}$ = 2.977(3) and 2.964(5) Å].

The structure of the crown ether part is very similar to that in the sodium compound **1**. The coordination number of the potassium ion is eight, and the crown ether oxygens are arranged in an almost coplanar arrangement. The potassium ion lies above this plane, with a deviation of 0.53 Å. This structural motif is known for 18-crown-6 complexes of both sodium and potassium.[38] The K−O(crown) distances in **4** vary between 2.779(4) and 2.848(5) Å. As expected for the coordination of an anionic oxygen ligand, the K−O distance to the bridging calix[4]arene moiety [K(1)−O(3) 2.681(4) Å] is significantly shorter than the other K−O distances.

The $^1$H NMR spectrum of **4** is in agreement with the structure found in the solid state and is very similar to that of **3a**, which contains 18-crown-6 instead of dibenzo-18-crown-6. Therefore, we assume that **3a** has a similar nonionic cluster-like structure to that of complex **4**.

The temperature-dependent $^1$H NMR spectra of complex **3a** give evidence for an interesting reversible reaction. At ambient temperature three chemically different *tert*-butyl protons in a molecular ratio 2:1:1 are observed at δ = 1.15, 1.11 and 1.08 ppm. Upon warming, the signals of the *tert*-butyl protons and the *meta* protons of the phenolate groups become more and more equal and, in a simultaneous process, the intensity of the original signals of **3a** disappears, while new signals of a highly symmetric compound appear without coalescence. At 55 °C the $^1$H NMR spectrum contains only signals for chemically equivalent phenolate groups. Therefore, we assume that a reversible, temperature-dependent dissociation of compound **3a** may proceed according to Equation (1):

$$\mathbf{3a} \rightleftarrows 2\,[\mathrm{K(18\text{-}crown\text{-}6)(THF)_2}]^+ + [\mathrm{K_3(calix[4]arene\text{-}4H)}]_2^{2-} \qquad (1)$$

Due to the similarities with the $^1$H NMR spectrum of the anion of **2** we suggest that the anion $[\mathrm{K_3(calix[4]arene\text{-}4H)}]_2^{2-}$ could have a similar molecular structure.

One of the reasons for the different behavior between the sodium complex **1** and the potassium complex **3a** in solution at increasing temperatures may be the different coordinating ability of 18-crown-6 to $Na^+$ and $K^+$, which favors the formation of an ionic product for $K^+$.

### Fixation of $CO_2$ by 1, 2 and 4 and $CO_2$-Transfer Reaction with 2-Fluoropropiophenone

Sodium phenolate reacts with carbon dioxide to give a product of unknown structure which is able to carboxylate activated aliphatic C−H bonds in dipolar aprotic solvents.[13−17] Therefore it may be expected that some of the above alkali metal calix[4]arene complexes containing four linked phenolate rings should, in principle, be capable of carboxylating activated C−H bonds.

Compound **1** reacts rapidly with $CO_2$ in THF. If water is not excluded very carefully the resulting products are $NaHCO_3$ and compound **5** [Equation (2)], which could be obtained as single crystals from THF.

$$\mathbf{1} + 3\,CO_2 + 3\,H_2O \rightarrow \underset{\mathbf{5}}{[\mathrm{Na(18\text{-}crown\text{-}6)}][\mathrm{(calix[4]arene\text{-}H)}]} + 3\,NaHCO_3$$

The X-ray structure of **5** (Figure 7) shows that the compound contains a single deprotonated [calix[4]arene-3H]$^-$ anion that is connected to the counterion [Na(18-crown-6)]$^+$ by a phenolate bridge of the calix[4]arene monoanion [Na−O(3) = 2.454(5) Å]. The other three oxygens of the calixarene unit do not coordinate [Na−O distances: Na···O(1) 4.869(5), Na···O(2) 3.507(6), Na···O(4) 3.984(4) Å]. The O···O distances between the calixarene oxygens of O(1)···O(2) [2.932(6) Å], O(1)···O(4) [2.669(6) Å], O(2)···O(3) [2.597(6) Å], and O(3)···O(4) [2.528(6) Å] are typical for intramolecular hydrogen bonds. The much shorter separations between the phenolate oxygen atom O(3) and its neighboring atoms O(2) and O(4) suggests rather strong intramolecular hydrogen bonds between these atoms. In contrast, the other O···O distances are significantly longer, although they are also in the range of hydrogen bonds. A more detailed discussion about the nature of the hydrogen-bond system is, however, not possible, because the hydrogen atoms were not found in the Fourier map. In this connection it is interesting to note that, in the known monometallated sodium compound of **A**,[10] containing methanol as co-ligand, and the tetrathia analogue **B**,[14] with water and THF as co-ligands, the calixarene units also form an intramolecular hydrogen-bond system. However, in these complexes the two calixarene oxygens act as bidentate chelating ligands, in contrast to **5**, where only one oxygen of the calixarene is coordinated. This reflects again the stronger ligand-effect of the crown ether compared with the other ligands in the above complexes. The coordinated 18-crown-6 is folded away from the calix[4]arene moiety, so there is no space for another THF molecule to coordinate to the sodium cation, which has a coordination number of seven. The structure of the crown ether part in **5** is very different from that in complex **1**, where the oxygens form a coplanar arrangement: the crown ether oxygens in **5** form a "distorted boat" with the plane formed by O(6), O(7), O(9), and O(10). The sodium ion lies below this plane, whereas the other two oxygens [O(5) and O(8)] are above the plane, with very different deviations from the least-square plane [1.86 Å for O(5) and 0.80 Å for O(8)]. According to a search of the Cambridge Crystallographic Database a few other 18-crown-6 complexes of sodium exist in which an analogous arrangement has been found.[39,44] It is, however, noteworthy that the six calixarene oxygens in similar sodium complexes can assume a chair form as well.[41,42]

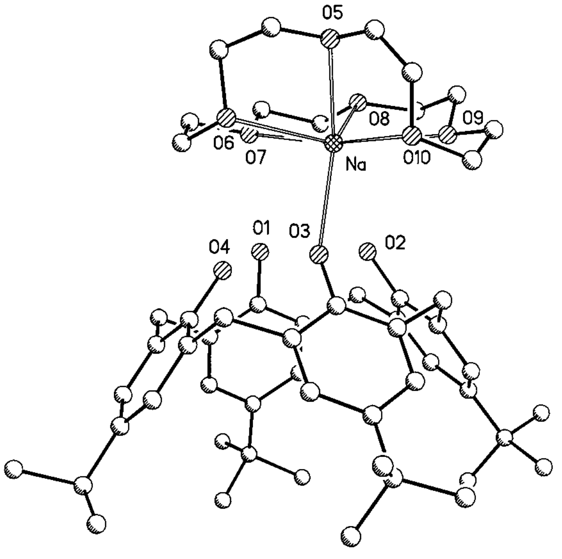


Figure 7. [Na(18-crown-6)(4-*tert*-butylcalix[4]arene-H)]·$OEt_2$ (**5**); the non-coordinated ether and the hydrogen atoms have been omitted for clarity; selected bond lengths (Å): Na−O(3) 2.454(4), Na−O(5) 2.522(5), Na−O(6) 2.612(6), Na−O(7) 2.532(5), Na−O(8) 2.574(5), Na−O(9) 2.586(5), Na−O(10) 2.703(6); selected bond angles (°): O(3)−Na−O(5) 148.2(2), O(3)−Na−O(6) 94.8(2), O(3)−Na−O(7) 89.2(2), O(3)−Na−O(8) 113.4(2), O(3)−Na−O(9) 101.6(2), O(3)−Na−O(10) 97.4(2), Na(1)−O(1)−Na(3) 118.7(3)

Compound **5** displays a simple NMR spectrum. In the $^1$H NMR spectrum only one singlet is observed for the *tert*-butyl groups (at $\delta = 1.17$ ppm) and for the *meta* protons of the calix[4]arene unit (at $\delta = 6.87$ ppm). The OH protons appear at $\delta = 13.39$ ppm. Furthermore, two doublets of the calix[4]arene $CH_2$ protons were observed at $\delta = 3.07$ and 5.52 ppm. The crown ether $CH_2$ protons give a signal at $\delta = 3.62$ ppm. From these data we can conclude that, in solution, the (18-crown-6)$Na^+$ moiety jumps from one phenol oxygen to another.

In contrast to these results, the reaction of **1** with carbon dioxide, with strict exclusion of moisture, proceeds differently. When a solution of **1** in hot THF under an atmosphere of $CO_2$ is quickly cooled down in a dry ice bath, a clear solution is obtained, although the starting compound is only sparingly soluble in cold THF. This is the first evidence for the formation of a reaction product with $CO_2$. In the $^1H$ NMR spectrum the signals of **1** disappear upon uptake of carbon dioxide and a set of new signals appear at $\delta = 1.17$ (s), 3.07 (d), 3.62 (s), 5.52 (d) and 6.87 ppm (br). The $CO_2$-containing complex could not be isolated because the weakly coordinated $CO_2$ is easily eliminated during work up. The final product is again the complex **1**. This clearly demonstrates that the $CO_2$ fixation is a reversible reaction. The same behavior was observed for **2**, meaning that both **1** and **2** are able to act as reversible $CO_2$ carriers.

To prove that the $CO_2$ products are capable of transferring their $CO_2$ to activated aliphatic C−H bonds we investigated the reactions of **1**, **2** and **4** in THF with 2-fluoropropiophenone under an atmosphere of carbon dioxide. After 24 h the reaction mixture was treated with dimethyl sulfate to yield the methyl ester of the unstable 3-ketocarboxylic acid. For comparison, the same reaction was carried out with sodium phenolate, which is known to act as a $CO_2$-transfer reagent.

Figure 8 shows that in all four reactions 2-benzoyl(2-fluoro)methylpropionate was formed, although in veryy different yields. Whereas sodium phenolate/$CO_2$ and **2**/$CO_2$ show very little activity (9% and 8% yield, respectively), the systems **1**/$CO_2$ and **4**/$CO_2$ are very efficient $CO_2$-transfer reagents that form the carboxylation product in a highly selective reaction (about 90%).

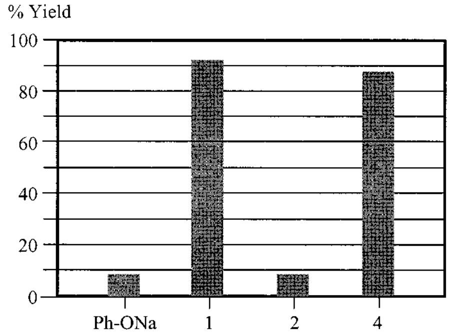


Figure 8. Carboxylation of 2-fluoropropiophenone by the complexes **1**/$CO_2$, **2**/$CO_2$, **4**/$CO_2$ and PhONa/$CO_2$ (for comparison) in THF at ambient temperature; reaction time: 24 h, molar ratio: 2-fluoropropiophenone/complex = 1:4; the yield was determined by $^{19}F$ NMR spectroscopy

Although the reasons for the remarkable difference in the carboxylation reactivity are hitherto unknown, the following points attract attention. Generally, $CO_2$-transfer reactions between NaOPh/$CO_2$ and substrates containing aliphatic activated C−H bonds such as acetone or acetophenone only proceed efficiently if dipolar aprotic solvents are used as solvent; the activity in THF is very low.[23] The reaction with 2-fluoropropiophenone confirms this (Figure 8). To explain this solvent-dependent activity, we assume that dipolar aprotic solvents (such as DMF, DMSO or *N*-methyl-ε-caprolactam) are stronger ligands than THF and can additionally split the Na−O bonds of the NaOPh oligomer in solution. This could result in more-reactive species which carboxylate activated C−H bonds much better than the "closed" heterocubane system found in complexes of the type (LNaOPh)[23,24] or polymeric NaOPh.[24] In contrast, **1** and **4** are complexes with "open" heterocubane structures in which the Na−O bonds should be more reactive in carboxylation reactions of activated aliphatic C−H bonds. The different structure of **2**, which exhibits a highly symmetrical anionic structure, could then explain why **2** is less active.

## Conclusions

Sodium and potassium complexes of calix[4]arenes and crown ethers yield different types of stable molecular structures depending on the diameter of the alkali metal cations, the different size of the cavities of the calix[4]arenes and the different efficiency of the coordination by additional crown ether ligands. Even a relatively small difference of the size in the cavities of **A** ($C-CH_2 = 1.516-1.581$ Å) and **B** ($C-S = 1.777$ Å) results in a completely different structure type for complexes **1** and **2**, even though the ratio between 18-crown-6, $Na^+$ ions and calix[4] arene is the same. While **1** shows a dynamic process in solution above 40 °C, the structure of the highly symmetrical compound **2** remains stable at higher temperatures.

The structure of the potassium compound **4** is also different from the related sodium complex **1**. In **4** the calix[4]arene units are less shifted with respect to the plane fusing the two heterocubane units, and the coordination of the peripheral $[(THF)K(dibenzo\text{-}18\text{-}crown\text{-}6)]^+$ is also different. Temperature-dependent $^1H$ NMR spectra suggest, in this case, that a dissociation process proceeds resulting in the formation of ionic species.

Compounds **1** and **4**, containing the calix[4]arene **A**, are active $CO_2$-transfer reagents towards 2-fluoropropiophenone, in contrast to **2**, which contains the calix[4]arene **B**. This clearly demonstrates the subtle influence of the structure of the alkali-metal complexes on the $CO_2$ reactivity in these types of compounds.

## Experimental Section

Due to the sensitivity of the substances to moisture and partly to air all manipulations were carried out under an atmosphere of argon. The solvents DMF and DMSO were dried with molecular sieves and THF with benzophenone/sodium, and freshly distilled before use.

4-*tert*-Butyltetrathiacalix[4]arene was prepared from 4-*tert*-butylphenol and sulfur in a solution of tetraethylene glycol dimethyl ether.[20] 4-*tert*-Butylcalix[4]arene, sodium hydride, $NaN(SiMe_3)_2$, $KN(SiMe_3)_2$, 4-*tert*-butylphenol, dibenzo-18-crown-6, 15-crown-5 and 18-crown-6 were purchased from Aldrich and tetraethylene glycol dimethyl ether from Merck-Schuchardt.

Most of the synthesized complexes contain extremely weakly bound THF in the crystals which is extremely easily released when not in contact with the mother liquor. In addition, THF is very easily eliminated from complex **1** even at −78 °C in a stream of inert gas. The other complexes (except **2** and **5**) eliminate solvent when handled at 0 °C. This resulted in problems in obtaining microanalyses for **1**, **3a**, and **4** from the bulk material. Furthermore, only approximate yields (%) could be calculated on the basis of complex compositions due to loss of non-coordinated volatile solvents. These problems are well-known for alkali metal compounds of calixarenes containing volatile ligands.[12,14,18]

$^{1}$H and $^{13}$C NMR spectra were recorded on a Bruker AC 200 F spectrometer. Mass spectra were recorded on a Finnigan MAT SSQ 710.

**[(18-Crown-6)(THF)Na$_4$(4-*tert*-butylcalix[4]arene-4H)]$_2$·3THF (1):** 18-Crown-6 (0.33 g, 1.25 mmol) and sodium hydride (0.13 g, 5.42 mmol) were added to a suspension of **A** (0.81 g, 1.25 mmol) in THF (50 mL). The reaction mixture was stirred and heated in a water bath to reflux. Hydrogen gas was liberated while the starting materials gradually dissolved. The hot solution was filtered through a Schlenk frit. Complex **1** crystallized from the filtrate. The colorless crystals lost non-coordinated THF and formed an amorphous powder. Yield: 1.3 g (ca. 95% based on the composition [(18-crown-6)(THF)Na$_4$(4-*tert*-butylcalix[4]arene-4H)]$_2$. $^{1}$H NMR (200 MHz, [D$_8$]THF, 20 °C): δ = 0.76 (s, 9 H, *t*Bu), 0.95 (s, 9 H, *t*Bu), 1.29 (s, 18 H, *t*Bu), 2.71 (d, $^{2}J_{H,H}$ = 13.1 Hz, 2 H, CH$_2$), 2.82 (d, $^{2}J_{H,H}$ = 13.6 Hz, 2 H, CH$_2$), 3.45 (s, 24 H, CH$_2$O), 3.77 (d, $^{2}J_{H,H}$ = 13.6 Hz, 2 H, CH$_2$), 4.73 (d, $^{2}J_{H,H}$ = 13.3 Hz, 2 H, CH$_2$) 6.27 (s, 2 H, *m*-CH), 6.54 (s, 2 H, *m*-CH), 6.84 (s, 2 H, *m*-CH), 6.90 (s, 2 H, *m*-CH) ppm. $^{1}$H NMR (200 MHz, [D$_8$]THF, 60 °C): δ = 0.86 (s, 18 H, *t*Bu), 1.25 (s, 18 H, *t*Bu), 2.74 (d, $^{2}J_{H,H}$ = 13.3 Hz, 4 H, CH$_2$), 3.38 (s, 24 H, OCH$_2$), 4.19 (br., 4 H, CH$_2$), 6.40 (s, 4 H, *m*-CH), 6.84 (s, 4 H, *m*-CH) ppm. $^{13}$C{$^{1}$H} NMR (50.3 MHz, [D$_8$]THF, 60 °C): δ = 32.1, 32.6 (CH$_3$, *t*Bu), 33.9 (CH$_2$), 34.8 (C, *t*Bu), 70.5 (CH$_2$O), 123.6, 134.3 (br., *o*-C), 125.7, 132.1 (*m*-CH), 129.3, 163.7 (*ipso*-C). Well-shaped crystals suitable for the X-ray analysis crystallized from a solution in THF.

**[(18-Crown-6)Na(dmf)$_{1.5}$]$_2$[(4-*tert*-butyltetrathiacalix[4]arene-4H)$_2$Na$_6$(dmf)$_2$] (2):** 18-Crown-6 (0.33 g, 1.25 mmol) and sodium hydride (0.13 g, 5.42 mmol) were added to a suspension of **B** (0.90 g, 1.25 mmol) in THF (50 mL). The reaction mixture was stirred and heated in a water bath to reflux. Hydrogen gas was liberated during the reaction. The resulting white precipitate was separated from the reaction mixture by filtration through a Schlenk frit. Single crystals for X-ray analysis of **2** were obtained by recrystallization of the precipitate from a solution in DMF. Yield: 2.85 g (91%) of colorless needles of **2**. $C_{119}H_{171}N_5Na_8O_{25}S_8$: calcd. C 56.90, H 6.86, N 2.79, S 10.21; found C 56.07, H 6.81, N 3.21, S 9.44. $^{1}$H NMR (200 MHz, [D$_7$]DMF, 30 °C): δ = 1.14 (s, 36 H, *t*Bu), 3.59 (s, 24 H, OCH$_2$), 7.43 (s, 8 H, *m*-CH) ppm. $^{13}$C{$^{1}$H} NMR (50.3 MHz, [D$_7$]DMF, 30 °C): δ = 32.0 (CH$_3$, *t*Bu), 33.6 (C, *t*Bu), 70.5 (CH$_2$O), 126.3, 134.3, 132.3, 135.9, 171.1 (*ipso*-C) ppm.

**[(18-Crown-6)K$_4$(4-*tert*-butylcalix[4]arene-4H)(THF)$_n$] (3a):** A suspension of **1** (0.81 g, 1.25 mmol) in THF (50 mL) was reacted with 18-crown-6 (0.33 g, 1.25 mmol) and KN(SiMe$_3$)$_2$ (1.07 g, 5.38 mmol). Large colorless crystals of **3a** were decanted from a suspension of fine needles of **3b**. The crystals of **3a** were washed with THF at −78 °C in order to remove impurities of **3b** from the surface of the crystals. The colorless crystals very easily lost non-coordinated THF when not in contact with the mother liquor and formed an amorphous powder. Yield: 0.04 g of the amorphous product **3a** approximately 3% based on the composition [(18-crown-6)K$_4$(4-*tert*-butylcalix[4]arene-4H)]. According to the $^{1}$H NMR spectrum the purity of the product was greater than 95%.
**3a:** $^{1}$H NMR (200 MHz, [D$_8$]THF, 10 °C): δ = 1.08 (s, 9 H, *t*Bu), 1.11 (s, 9 H, *t*Bu), 1.15 (s, 18 H, *t*Bu), 2.67 (br., CH$_2$), 3.45 (s, 24 H, CH$_2$O), 4.44 (br., CH$_2$), 6.63 (s, 4 H, *m*-CH), 6.91 (s, 4 H, *m*-CH) ppm. $^{1}$H NMR (200 MHz, [D$_8$]THF, 55 °C): δ = 1.12 (s, 36 H, *t*Bu), 2.67 (br., CH$_2$), 3.46 (s, 24 H, CH$_2$O), 4.44 (br., CH$_2$), 6.82 (s, 8 H, *m*-CH) ppm.
**3b:** $^{1}$H NMR (200 MHz, [D$_8$]THF, 10 °C): δ = 1.11 (s, 36 H, *t*Bu), 2.70 (br., 4 H, CH$_2$), 3.46 (s, 48 H, CH$_2$O), 4.50 (br., 4 H, CH$_2$), 6.66 (s, 8 H, *m*-CH) ppm.

**[(Dibenzo-18-crown-6)K$_4$(4-*tert*-butylcalix[4]arene-4 H)(THF)$_3$]$_2$·4THF (4):** Dibenzo-18-crown-6 (0.45 g, 1.25 mmol) and KN(SiMe$_3$)$_2$ (1.07 g, 5.38 mmol) were added to a suspension of **1** (0.81 g, 1.25 mmol) in THF (50 mL). The reaction mixture was stirred and heated in a water bath to reflux while the starting materials gradually dissolved. The hot solution was filtered through a Schlenk frit. Compound **4** crystallized from the filtrate as a mixture with "K$_4$(4-*tert*-butylcalix[4]aren-4H)(dibenzo-18-crown-6)$_2$(THF)$_n$". The large colorless crystals of **4** were separated from the fine needles of the by-product by pouring off the suspension. The colorless crystals lost non-coordinated THF and formed an amorphous powder. Yield: 0.44 g of a white amorphous crude product. (ca. 25% based on the composition [(dibenzo-18-crown-6)K$_4$(4-*tert*-butylcalix[4]arene-4H)(THF)$_3$]$_2$. $^{1}$H NMR (200 MHz, [D$_8$]THF, 10 °C): δ = 1.09 (s, 9 H, *t*Bu), 1.10 (s, 9 H, *t*Bu), 1.15 (s, 18 H, *t*Bu), 3.00 (d, $^{2}J_{H,H}$ = 11.7 Hz, 2 H, CH$_2$), 3.92 (br., 8 H, O-CH$_2$), 3.99 (br., 8 H, O-CH$_2$), 4.46 (br., 2 H, CH$_2$), 6.73 (br., 8 H, *m*-CH), 6.82 (br., 8 H, *o*-C$_6$H$_4$) ppm.

**[(18-Crown-6)Na](4-*tert*-butylcalix[4]arene-H)·OEt$_2$ (5):** Carbon dioxide gas and water (54 µL, 3.0 mmol) were added to a suspension of crude product of **1** (1.07 g, 1.0 mmol) in THF (50 mL). The reaction mixture was then stirred and heated in a water bath to reflux. The hot solution was filtered through a Schlenk frit. The complex **5·THF** crystallized from the clear filtrate. Single crystals of **5·OEt$_2$** suitable for X-ray analysis were obtained by recrystallization of **5·THF** from diethyl ether. Yield: 0.54 g (58%) of colorless **5·THF**. $C_{56}H_{79}NaO_{10}$: calcd. C 71.92, H 8.52; found C 71.46, H 8.98. $^{1}$H NMR (200 MHz, [D$_8$]THF, 25 °C): δ = 1.17 (s, 36 H, *t*Bu), 3.07 (d, $^{2}J_{H,H}$ = 12.1 Hz, 4 H, CH$_2$), 3.62 (s, 24 H, O-CH$_2$), 5.52 (d, $^{2}J_{H,H}$ = 12.1 Hz, 4 H, CH$_2$), 6.87 (br., 8 H, *m*-CH), 13.39 (s, 3 H, OH) ppm. $^{13}$C{$^{1}$H} NMR (50.3 MHz, [D$_8$]THF, 25 °C): δ = 32.1 (CH$_3$, *t*Bu), 34.1, 35.1, 70.8 (O-CH$_2$), 124.8, 131.2, 139.4, 154.2 (*ipso*-C) ppm.

**Reaction of 1 with CO$_2$:** A suspension of **1** (1.0 mmol) in THF (50 mL) under a carbon dioxide atmosphere was refluxed, resulting in a clear solution which was quickly cooled down in a dry ice bath. No precipitation was observed. $^{1}$H NMR (200 MHz, [D$_8$]THF, 25 °C): δ = 1.17 (s, 36 H, *t*Bu), 3.07 (d, $^{2}J_{H,H}$ = 12.0 Hz, 4 H, CH$_2$), 3.62 (s, 24 H, O-CH$_2$), 5.52 (d, $^{2}J_{H,H}$ = 12.0 Hz, 4 H, CH$_2$), 6.87 (s, 8 H, *m*-CH) ppm. Carbon dioxide was liberated from this product during warming of the solution to reflux under an atmosphere of argon. The NMR spectroscopic data of the resulting precipitate were identical to those of the starting compound **1**.

**Carboxylation of 2-Fluoropropiophenone:** A suspension of **1** (1.0 mmol), **2** (1.0 mmol) or **4** (1.0 mmol) in THF (30 mL) was warmed to reflux under an atmosphere of carbon dioxide. The solution was then quickly put in a dry ice cooling bath. 2-Fluoropropiophenone (0.152 g, 1.0 mmol) was then added from a syringe. The reaction mixture was shaken for 24 h followed by addition of dimethyl sulfate (0.69 g, 5.5 mmol) and $Na_2CO_3$ (0.5 g). The mixture was then shaken for 24 h. Yield of 2-fluoro-2-benzoyl-methylpropionate (as determined by $^{19}F$ NMR spectroscopy): 92% for **1**/$CO_2$; 8% for **2**/$CO_2$; 89% for **4**/$CO_2$. $^1H$ NMR (200 MHz, $CDCl_3$, 25 °C): $\delta = 1.86$ (d, $^3J_{H,F} = 22.6$ Hz, 3 H, $CH_3$), 3.76 (s, 3 H, $COOCH_3$), 7.42−8.04 (m, 5 H, Ph) ppm. $^{13}C\{^1H\}$ NMR (50.3 MHz $CDCl_3$, 25 °C): $\delta = 20.9$ (d, $^2J_{F,C} = 23.3$ Hz, $CH_3$), 53.1 (COO$C$H$_3$), 97.0 (d, $^1J_{F,C} = 195.1$ Hz, CF), 20.9 (d, $^2J_{F,C} = 23.3$ Hz, $CH_3$), 128.5 (CH), 129.6 (d, $^4J_{F,C} = 5.6$ Hz, *m*-CH), 130.0 (d, $^3J_{F,C} = 20.4$ Hz, *i*pso-C), 133.8 (CH), 168.7 (d, $^2J_{F,C} = 25.6$ Hz, *C*OOCH$_3$), 191.6 (d, $^2J_{F,C} = 25.2$ Hz, C=O) ppm. $^{19}F$ NMR (188.3 MHz, $CDCl_3$, $CFCl_3$, 25 °C): $\delta = -151.9$ (q, $^3J_{H,F} = 22.6$ Hz) ppm. MS (EI): *m*/*z* = 210 [$M^+$], 179 [$M^+ - OCH_3$], 151 [$M^+ - COOCH_3$], 105 [PhCO]. GC-IR: $\nu(C{=}O) = 1777\ cm^{-1}$, $\nu(COOCH_3) = 1712\ cm^{-1}$.

Carboxylation with **2**/$CO_2$ yielded the product in very low yield. Upon reaction with dimethyl sulfate, white crystals of 4-*tert*-butyltetrathiacalix[4]arene tetramethyl ether[44] crystallized as the first product from the reaction mixture. $^1H$ NMR (200 MHz, $CDCl_3$, 25 °C): $\delta = 1.28$ (s, 36 H, *t*Bu), 3.42 (s, 12 H, $OCH_3$), 7.42 (s, 8 H, *m*-CH) ppm.

**Crystal Structure Determination:** The intensity data for the compounds were collected on a Nonius KappaCCD diffractometer, using graphite-monochromated Mo-$K_\alpha$ radiation. Data were corrected for Lorentz and polarization effects, but not for absorption effects.[45,46] The structures were solved by direct methods (SHELXS[47]) and refined by full-matrix least-squares techniques against $F_o^2$ (SHELXL-97[48]). All hydrogen atoms were included at calculated positions with fixed thermal parameters. All non-hydrogen atoms were refined anisotropically.[48] The *R*1 values are relatively high, since the compounds are large systems that contain both slightly disordered coordinated and non-coordinated solvent molecules. In addition, *tert*-butyl groups cause high anisotropic displacement parameters. This is typical for a number of similar compounds.[14,18] Very recently the general reasons for the difficulties in obtaining low *R*1 values have been discussed in detail.[14]

Since the quality of the data of both modifications of compound **2** is too low, we will only publish the conformation of the molecule and the crystallographic data. We have not deposited the data with the Cambridge Crystallographic Data Center. Although the *R*1 value for **4** is also high, the estimated standard derivations (e.s.d.) for the bond lengths and angles are small (see Figure 5), therefore the structural data have been deposited. XP (SIEMENS Analytical X-ray Instruments, Inc.) was used for structure representations

**Crystal Data for 1:**[49] $C_{148}H_{224}Na_8O_{29}$, $M_r = 1325.60\ g{\cdot}mol^{-1}$, colorless prism, size $0.40 \times 0.35 \times 0.32\ mm^3$, triclinic, space group $P\bar{1}$, $a = 16.6116(6)$, $b = 17.3483(9)$, $c = 17.9319(9)$ Å, $\alpha = 97.769(2)°$, $\beta = 105.557(2)°$, $\gamma = 115.616(2)°$, $V = 4297.3(3)$ Å$^3$, $T = -90$ °C, $Z = 2$, $\rho_{calcd.} = 1.024\ g{\cdot}cm^{-3}$, $\mu(Mo\text{-}K_\alpha) = 0.86\ cm^{-1}$, $F(000) = 1432$, 11345 reflections in *h*(0/17), *k*(−19/17), *l*(−19/18), measured in the range $4.93° \leq \Theta \leq 23.31°$, completeness $\Theta_{max} = 91.3\%$, 11345 independent reflections, 8317 reflections with $F_o > 4\sigma(F_o)$, 946 parameters, 0 restraints, $R1_{obs} = 0.087$, $wR^2_{obs} = 0.246$, $R1_{all} = 0.118$, $wR^2_{all} = 0.2704$, GOOF = 1.092, largest difference peak and hole: 0.523/−0.426 e·Å$^{-3}$.

**Crystal Data for 2:** $C_{108}H_{136}N_{20}Na_8O_5S_8$, $M_r = 2234.77\ g{\cdot}mol^{-1}$, colorless prism, size $0.04 \times 0.03 \times 0.03\ mm^3$, monoclinic, space group $P2_1/n$, $a = 12.8900(1)$, $b = 32.1789(5)$, $c = 33.4040(4)$ Å, $\beta = 94.988(8)°$, $V = 13803.0(3)$ Å$^3$, $T = 20$ °C, $Z = 4$, $\rho_{calcd.} = 1.075\ g{\cdot}cm^{-3}$, $\mu(Mo\text{-}K_\alpha) = 2.05\ cm^{-1}$, $F(000) = 4720$, 77462 reflections in *h*(−15/12), *k*(−38/41), *l*(−32/43), measured in the range $1.22° \leq \Theta \leq 27.41°$, completeness $\Theta_{max} = 87.3\%$, 27449 independent reflections.

**Crystal Data for 4:**[49] $C_{168}H_{232}K_8O_{30}$, $M_r = 3044.34\ g{\cdot}mol^{-1}$, colorless prism, size $0.32 \times 0.28 \times 0.20\ mm^3$, monoclinic, space group $P2_1/n$, $a = 16.7197(2)$, $b = 18.9198(5)$, $c = 27.1965(6)$ Å, $\beta = 97.489(1)°$, $V = 8529.8(3)$ Å$^3$, $T = -90$ °C, $Z = 2$, $\rho_{calcd.} = 1.185\ g{\cdot}cm^{-3}$, $\mu(Mo\text{-}K_\alpha) = 2.69\ cm^{-1}$, $F(000) = 3264$, 62897 reflections in *h*(−21/18), *k*(−24/19), *l*(−34/35), measured in the range $1.31° \leq \Theta \leq 27.45°$, completeness $\Theta_{max} = 97.5\%$, 19016 independent reflections, $R_{int} = 0.096$, 10537 reflections with $F_o > 4\sigma(F_o)$, 803 parameters, 4 restraints, $R1_{obs} = 0.132$, $wR^2_{obs} = 0.347$, $R1_{all} = 0.214$, $wR^2_{all} = 0.395$, GOOF = 1.280, largest difference peak and hole: 3.123/−1.179 e·Å$^{-3}$.

**Crystal Data for 5:**[49] $C_{56}H_{79}NaO_{10}{\cdot}C_4H_{10}O$, $M_r = 1009.30\ g{\cdot}mol^{-1}$, colorless prism, size $0.32 \times 0.30 \times 0.28\ mm^3$, monoclinic, space group $P2_1$, $a = 12.6427(5)$, $b = 12.7316(3)$, $c = 18.4929(6)$ Å, $\alpha = 90.00°$, $\beta = 94.233(1)°$, $\gamma = 90.00°$, $V = 2968.5(2)$ Å$^3$, $T = -90$ °C, $Z = 2$, $\rho_{calcd.} = 1.129\ g{\cdot}cm^{-3}$, $\mu(Mo\text{-}K_\alpha) = 0.82\ cm^{-1}$, $F(000) = 1096$, 4475 reflections in *h*(0/14), *k*(0/14), *l*(−20/20), measured in the range $2.21° \leq \Theta \leq 23.26°$, completeness $\Theta_{max} = 99.4\%$, 4475 independent reflections, 3732 reflections with $F_o > 4\sigma(F_o)$, 648 parameters, 7 restraints, $R1_{obs} = 0.068$, $wR^2_{obs} = 0.171$, $R1_{all} = 0.100$, $wR^2_{all} = 0.201$, GOOF = 1.129, Flack-parameter −0.1(9), largest difference peak and hole: 0.544/−0.319 e·Å$^{-3}$.

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[49] CCDC-216538 (**1**), -216539 (**4**), and -216540 (**5**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: (internat.) + 44-1223-336-033; or deposit@ccdc.cam.ac.uk).

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