endo-, *exo*-Cavity hydride isomerism for an aluminium complex of dimetallated 1,3-dimethyl ether *p-tert*-butylcalix[4]arene

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Reaction of 1,3-dimethyl ether *p-tert*-butylcalix[4]arene 1 with H_3AlNMe_3 in toluene gives an isomeric mixture of monomeric five-coordinate metallocalixarene species derived from dimetallation with the metal centres attached to four oxygens and a hydride either *exo* (2a) or *endo* (2b) to the calixarene cavity; 2a is converted to thermodynamically favoured 2b in the presence of H_3AlNMe_3, with the chloro-analogue of 2a, 3 (formed exclusively from the reaction of 1 and $AlCl_3$) preferentially affording 2b when treated with NaH.

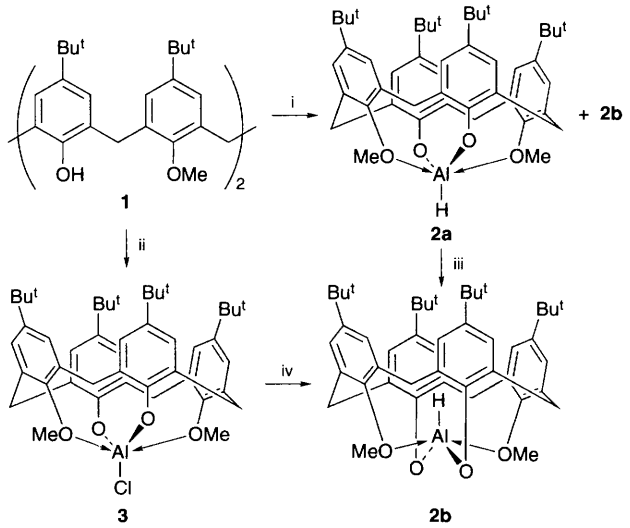
Calixarenes[1] are versatile reagents capable of acting as receptor molecules *via endo*-binding in their cavities, and as polyphenolic/phenolate O-centred ligands towards metal ions with the resulting complexes also capable of acting as receptors.[1,2] Such metal complexation can block the conformational tumbling of the calixarene and has mainly been focused on *p-tert*-butylcalix[4,6,8]arenes rather than O-alkylated analogues where the limited studies include the formation or Zr complexes of a partially O-methylated calixarene, notably 1,3-dimethyl ether *p-tert*-butylcalix[4]arene **1**,[3] the Na complex of tetramethyl ether *p-tert*-butylcalix[4]arene,[4] and $AlMe_3$ complexes of permethyl ethers of *p-tert*-butylcalix[*n*]arenes (*n* = 4, 8).[5] $AlMe_3$ completely metallates all the O-phenolic centres of calix[*n*]arenes (*n* = 4,[6] 6,[7]) yielding Al-rich complexes with some residual Me groups attached to the metal centres. In contrast the NMe_3 adduct of alane, H_3AlNMe_3, reacts with *p-tert*-butylcalix[4]arene to yield a divergent receptor system arising from linking two calix[4]arenes through the O-rims by two metal centres.[8]

Herein we explore aluminium chemistry of **1** demonstrating its potential to act as a bulky tetradentate dianionic ligand for Al with an auxiliary hydride ligand either *endo* or *exo* with respect to the cavity of the calixarene, which by necessity, is in the cone conformation rather than the 1,3-alternate form. We note that Lattman *et al.* have identified an *endo*-hydride attached to O-complexed phosphorus for the reaction product of *p-tert*-butylcalix[4]arene with $P(NHMe_2)_3$,[9] and an oxomolybdenum complex of *p-tert*-butylcalix[4]arene has an *endo*-bound water molecule.[10] In addition, as a class of aluminium alkoxohydrides the present compounds are unusual.[3,11]

Reaction of **1** with an excess of H_3AlNMe_3 in toluene at −80 °C then warming to room temp. gives a mixture of the *exo*, (**2a**) or endo, (**2b**), isomers (Scheme 1). The *exo* isomer has been structurally authenticated for a single crystal, and the NMR data infer the two isomers have identical symmetry in solution. Treatment of the *exo*-chloro analogue **3** (derived from the reaction of **1** with $AlCl_3$) with excess NaH in thf yields exclusively compound **2b**. Conversion of **2a** to **2b** is effective using H_3AlNMe_3 in benzene under reflux, Scheme 1, with the reaction of **1** with 2 equiv. of H_3AlNMe_3 (**1** added to H_3AlNMe_3) in toluene at −80 °C affording predominantly the kinetically favoured *exo* isomer **2a** (ratio 85 : 15). Addition of an ethereal solution of AlH_3 to **1** in Et_2O at 0 °C gives a 80:20 mixture. No reaction was observed when **1** was treated with either 2 equiv. of H_3GaNMe_3, or with 2 equiv. of $GaCl_3$.

The *exo* to *endo* isomerisation is unlikely to be an intramolecular process and most likely involves the formation of the ubiquitous $[AlH_4]^-$ species and an Al calixarene cation when formed from **2a** in the presence of H_3AlNMe_3. The forcing conditions for chloride/hydride exchange yielding **3** presumably predetermines the formation of the thermodynamically favoured *endo* isomer. Other chemistry developed, *vide infra* is consistent with **2a,b** being isomers. Compound **2a** preferentially hydrolyses under mild conditions as established by exposing a benzene solution containing a mixture of **2a,b** to air with the ^1H NMR spectrum corresponding to **2a** diminishing at the expense of the appearance of resonances for **1**. Moreover, **2a** forms an inclusion complex with CH_2Cl_2 but not so for **2b**.

In the solid state molecules of **2a** together with the included CH_2Cl_2 have approximately C_{2v} symmetry, Fig. 1, as is the case for molecules of **3**, but this is not extended to the included toluene which has the *meta*-H-atom directed towards the metal centre.‡ Presumably a similar binding of toluene would prevail in a toluene adduct of **2a**. In addition to the included toluene in **3** there is a toluene in the bulk lattice. For comparative purposes we also established the X-ray structure of $\mathbf{1}\cdot 3C_6H_5Me$ which now has the methyl group of the included toluene directed towards the centre of the cavity, Fig. 2, in a similar way to the Na complex of tetramethyl ether *p-tert*-butylcalix[4]arene·toluene.[4] An earlier structure determination of **1** had the cavity devoid of solvent molecules.[12] The asymmetric unit in the present structure is half the supermolecule of $\mathbf{1}\cdot C_6H_5Me$ the other half generated by a C_2 symmetry axis, and a full molecule of toluene in the lattice, all toluene molecules being well ordered.



Scheme 1 *Reagents and conditions*: i, H_3AlNMe_3, toluene, $-NMe_3$, $-2H_2$; ii, $AlCl_3$, CH_2Cl_2, −2HCl; iii, H_3AlNMe_3, benzene; iv, NaH, thf, −NaCl

The different orientations of toluene in the cavities of **1** and **3** relates to differences in the pitch of the cavity controlled mainly by hydrogen bonding within the O_4 rim or by metal complexation. In **1** the calixarene pitch is higher with the dihedral angle between the opposite aromatic rings of the calixarene 39.2 (anisole groups) and 91.0° (phenol groups) *cf.* 26.2, 99.1° for unsolvated molecules of **1**.[12] Corresponding values for **3** and **2a** are 46.5, 44.5 and 110.2, 105.6°, which compare with 47 and 108° for the bis-calixarene derived from H_3AlNMe_3 and *p-tert*-butylcalix[4]arene, the similar acute angles being important in the uptake of included CH_2Cl_2 (see below).[8] The phenolic protons in **1** (not located) are possibly disordered around the O_4 rim, the O···O distances at 2.76, 2.86 Å being similar to those of the unsolvated analogue.[12] The CH_2Cl_2 in **2a** is involved in nonclassical C–H···π-arene hydrogen bonding[13] whereby the H-atoms of the solvent interact symmetrically with two opposite aromatic rings (anisole groups), C–H···centroid distances, 2.48, 2.61 Å. Indeed the two compounds have similar arrangements of a pair of opposite aromatic rings for complementarity with CH_2Cl_2. In a related bis-calixarene complex based on complexation of Zn^{II} the dihedral angles are less disparate at 110 and 121° and included CH_2Cl_2 is disordered in a shallower cavity.[14]

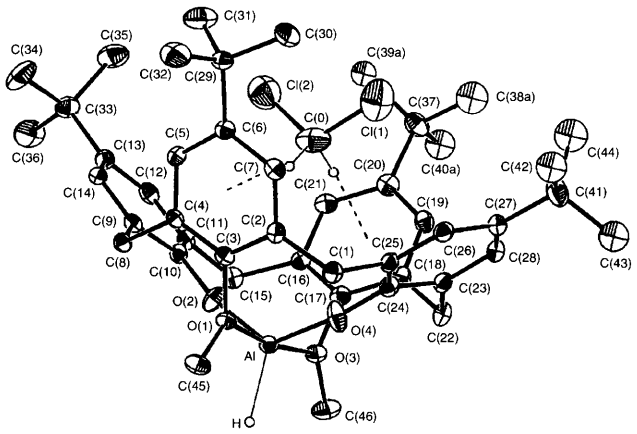


Fig. 1 Crystal structure of **2a**·CH_2Cl_2. Selected distances (Å) and angles (°): Al–O(1,2,3,4),H 2.077(9), 1.690(8), 2.137(9), 1.684(9), 1.68(7), O(1)–Al–O(2,3,4),H 88.2(4), 171.1(3), 88.4(4), 94(3), O(2)–Al–O(3,4),H 88.1(4), 124.1(5), 115(2), O(3)–Al–O(4),H 87.1(4), 95(3), O(4)–Al–H 121(2) [Corresponding values for **3**·2 C_6H_5Me: Al–Cl,O(1,2,3,4) 2.11(1), 2.18(1), 1.69(1), 2.18(1), 1.76(1), Cl(1)–Al–O(1,2,3,4) 91.7(6), 117.0(8), 93.0(6), 117.4(6), O(1)–Al–O(2,3,4) 88.78(8), 174.9(7), 91.7(8), O(2)–Al–O(3,4) 87.5(8), 125.6(9), O(3)–Al–O(4) 87.8(8)].

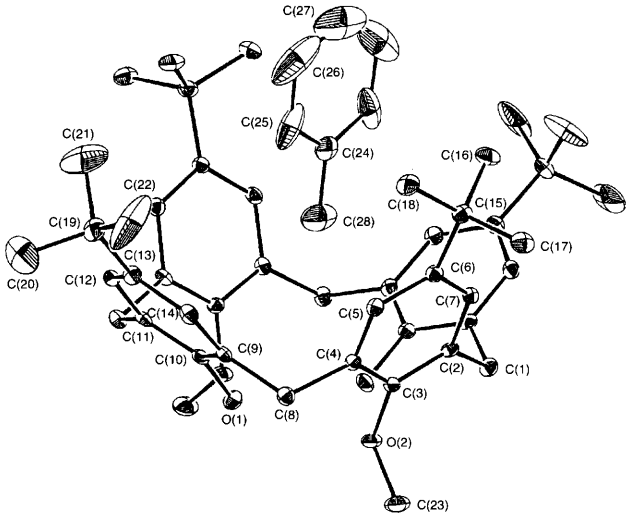


Fig. 2 Crystal structure of **1**·$3C_6H_5Me$

Al centres in **2a** and **3** are distorted trigonal bipyramidal with the two equatorial bonds to the phenolate O-centres [1.69, 1.73 Å (mean)], and the two axial Al–O dative bonds are significantly longer at 2.11, 2.18 Å (mean). The terminal equatorial Al–H and Al–Cl bonds at 1.68(7) and 2.11(1) Å are unexceptional. Molecular mechanics of **2a,b** using the Insight II (Version 2.3.7): Discover 3 Minimisation Package,[15] gave the *endo* isomer (square-pyramidal environment with the hydride apical) 21 kcal mol^{-1} (cal = 4.184 J) more favourable than the *exo* isomer in accordance with the above kinetic *vs.* thermodynamic considerations for the two compounds.

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Footnotes

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‡ *Crystal structure determinations*: (Rigaku AFC7R diffractometer, crystal mounted in a capillary). **1**·$3C_6H_5Me$: $C_{67}H_{84}O_4$, monoclinic, space group *C*2/*c* (no. 15), a = 24.034(5), b = 10.995(6), c = 23.351(5) Å, β = 108.14(2)°, U = 5863(4) Å^3, D_c = 1.080, μ = 0.65 cm^{-1} (no correction), Z = 4, Mo-Kα radiation, 5453 unique reflections [2633 observed, $I > 3.0\sigma(I)$], T = 173 K, 323 parameters, R = 0.066, R_w = 0.075 (unit weights). **2a**·CH_2Cl_2: $C_{47}H_{61}AlCl_2O_4$, triclinic, space group $P\bar{1}$ (no. 2), a = 13.313(3), b = 16.087(3), c = 12.912(2) Å, α = 102.79(2), β = 117.84(1), γ = 97.33(2)°, U = 2297(1) Å^3, D_c = 1.139, μ = 2.0 cm^{-1} (no correction), Z = 2, Mo-Kα radiation, 8078 unique reflections [3552 observed, $I > 2.5\sigma(I)$], T = 298 K, 497 parameters, R = 0.077, R_w = 0.114 (σ weights). **3**·$2C_6H_5Me$: $C_{60}H_{74}AlClO_4$, triclinic, space group $P\bar{1}$ (no. 2), a = 13.285(6), b = 18.212(6), c = 13.095(5) Å, α = 93.50(4), β = 116.84(2), γ = 77.04(3)°, U = 2752(1) Å^3, D_c = 1.112 μ = 1.29 cm^{-1} (no correction), Z = 2, Mo-Kα radiation, 5437 unique reflections [1658 observed, $I > 3.0\sigma(I)$], T = 208 K, 325 parameters, R = 0.140, R_w = 0.153 (σ weights). Solutions by direct methods with refinements on F. The structure of **3** is of low accuracy but nevertheless it unequivocally established the nature of the complex. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Information for Authors, Issue No. 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 182/168.

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