Aluminium-fused Bis-*p-tert*-butylcalix[4]arene: A Double Cone with Two π-Arene···H Interactions for Included Methylene Chloride

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Treatment of *p-tert*-butylcalix[4]arene **1** with $[H_3Al(NMe_3)]_2$ results in trimetallation and deprotonation by the tertiary amine, yielding the bis(calix[4]arene), $[\{(\mathbf{1} - H_4)Al\}_2]^{2-}$ $[HNMe_3]^+{}_2$, **2**, which has been isolated with included methylene chloride; distorted five-coordinate O-bound aluminium centres [Al–O 1.74(1)–2.35(1) Å] fuse the slightly flattened cone calixarene units with the methylene chloride H-atoms residing over two opposite aromatic rings in each cone, C···ring centroid 3.54 Å.

Calixarenes[1,2] form inclusion complexes with a variety of small molecules, *e.g.* toluene[3] and *tert*-butylammonium ion[4] in *p-tert*-butylcalix[4]arene **1**. They can also form O-bound complexes with a variety of metal cations,[5–10] or complexes with metal–π-aromatic ring interactions, recently identified for Cs^+ with **1**.[11] In addition, O-functionalised ferrocene derivatives are known.[12] Transition metal and lanthanide metal calixarene chemistry[6–10] is more extensive than main group chemistry, which is restricted to phosphorus,[13] Na^+,[14] Cs^+,[11] and Al^{3+}.[15] For the latter, mono-calix[4]arene–trimethylaluminium derivatives have been prepared with doubly flattened partial cone, and alternating conformations,[16] rather than the more common cone conformation.

We show that an alumino-bis(*p-tert*-butylcalix[4]arene) is accessible with both calixarenes in the cone conformation, using the highly reactive tertiary amine adduct of aluminium hydride $[H_3Al(NMe_3)]_2$,[17] where the hydrides and the amines serve as deprotonating agents. The product is a unique example of (*i*) a calix[4]arene with included methylene chloride involved in two C–H···π-arene ring hydrogen bonds, and (*ii*) a bis(calixarene) unit in which the O-complexed species is a main group element. The latter represents a model system for the binding of calix[4]arenes to aluminium oxide surfaces, which is important in some of the potential applications of calixarenes.

The synthesis of the bis(calix[4]arene) $[\{(\mathbf{1} - H_4)Al\}_2]^{2-}\cdot[HNMe_3]^+{}_2$ **2** is shown in Scheme 1;† an excess of $[H_3Al(NMe_3)]_2$ was used so the direct comparison with the analogous reaction involving $(AlMe_3)_2$[15] is valid. Here the product is a mono-calixarene with a partially flattened cone, and is rich in metallating agent, $[\{(\mathbf{1} - H_4)Al_4Me_8\}_2]$.

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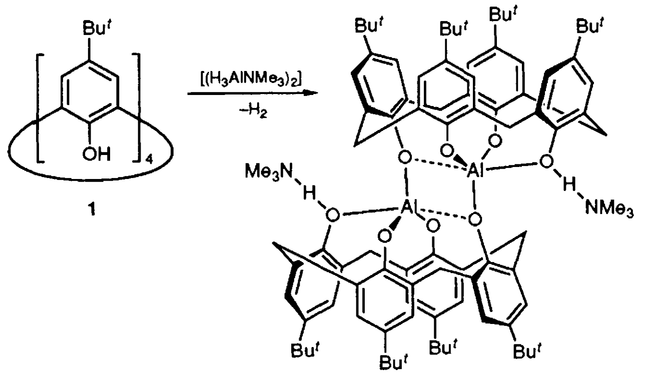
† A solution of $[H_3Al(NMe_3)]_2$ (0.14 g, 0.8 mmol) in toluene (5 ml) was added over 30 min to a suspension of **1** (0.70 g, 1.1 mmol) in toluene (40 ml) at −80 °C with vigorous evolution of gas. Upon warming to room temp. volatile material was removed *in vacuo* yielding a white powder which was washed with hexane (3 × 30 ml) and recrystallised from methylene chloride (40 ml) to yield large colourless crystals of **2**. Yield after vacuum drying 0.54 g (67%); m.p. 195 °C (decomp.); ^1H NMR (360 MHz, $CDCl_3$) δ 1.21 (72H, s, CMe_3), 2.77 (18H, br s, $N(Me_3)$), 3.51 (8H, br d, CH_2), 4.24 (8H, br, d, CH_2), 5.28 (4H, s, Ch_2Cl_2), 7.01 (16H, s, ArH) and 10.33 (2H, br s, ArOH); ^{13}C NMR (90.6 MHz, $CDCl_3$) δ 31.4 (CMe_3), 32.4 (CH_2), 34.8 (CMe_3), 47.2 (NMe_3), 53.4 (CH_2Cl_2), 126.1, 127.4, 145.4 and 152.6 (Ar); IR ν 3140 cm^{-1} (O–H str.); positive ion FAB *m/z* 1462 ($M^{\cdot +}$, 8), 1403 (37), 1344 (100%); Found: C 69.86, H 7.48, N 1.48; calc. for $C_{98}H_{128}N_2Al_2Cl_4O_8$: C 71.0, H 7.78, N 1.69%.



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Scheme 1

Compound **2** was recrystallised with methylene chloride included in each of the cones, and with methylene chloride, and hydrocarbons, as solvents of crystallisation. All solvent species are readily lost *in vacuo*. FAB mass spectrometry (nitrobenzyl alcohol) gave a peak at 1462 (8%) corresponding to $\mathbf{2}^{\cdot +}$ devoid of methylene chloride, and thermogravimetric analysis differentiated the two types of methylene chloride (loss of non-included CH_2Cl_2 at <50 °C, loss of included CH_2Cl_2 at 70–180 °C with 9.9% weight loss; *cf.* 10.4% theoretical). The solid state ^{13}C NMR chemical shift of the included methylene chloride is δ 67.8. This compares with 53.4 for the freshly prepared compound in toluene solution where rapid exchange between included and solvent of crystallisation is likely; detection of solid state ^{13}C NMR signals for the solvent of crystallisation was not possible owing to its rapid dissipation even at room temperature.

Molecules of **2** are centrosymmetric in the solid‡ with the aluminium centres in distorted trigonal bipyramidal environments as part of an Al_2O_2 four-membered ring system in which the associated phenoxides bridge two metal centres, Fig. 1. This is a similar structure to that established for europium and transition metal calix[4]arene species, albeit with different coordination environments.[8-10] Each calixarene unit possesses a residual phenolic proton that is seemingly hydrogen bonded to a molecule of NMe_3 [N(1)···O(2) 2.58(1) Å; $\nu_{O\cdots H\cdots N}$ 3140 cm^{-1}]. The presence of such a hydrogen bond and the steric bulk of the calixarene probably protects the residual phenolic proton from further reaction with the excess of $[H_3AlNMe_3]_2$. Distinction between the various types of phenolate groups in the solid is not apparent in toluene solution on the NMR timescale.

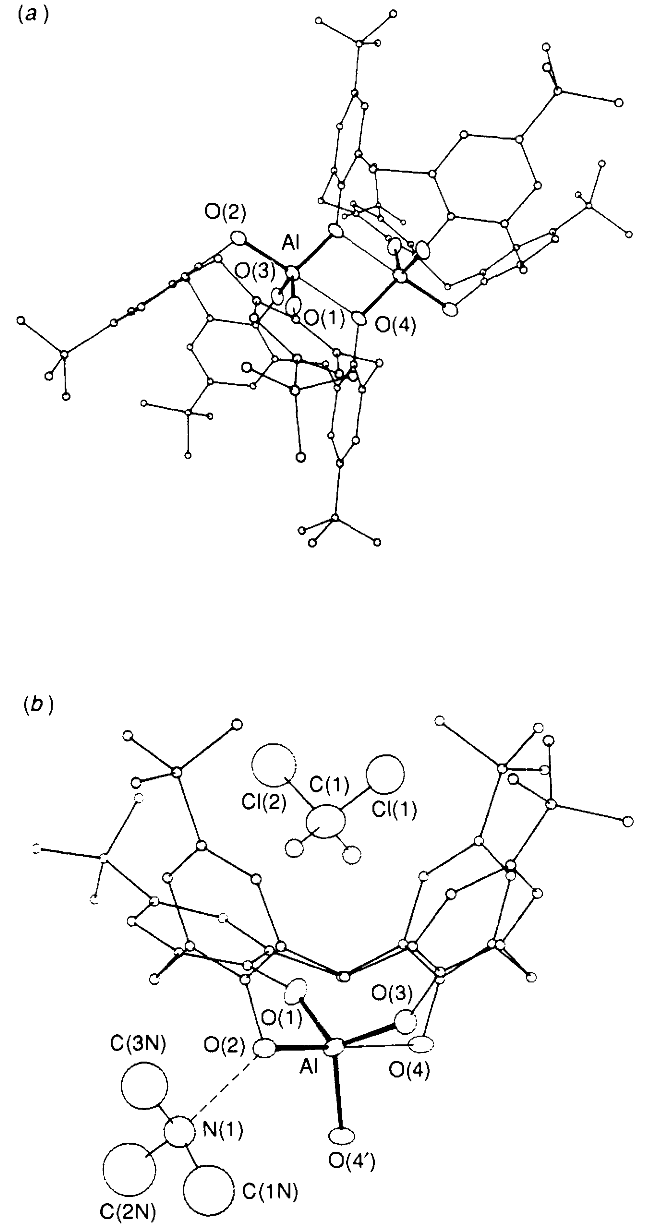

Fig. 1 Projection of (*a*) $[\{(\mathbf{1} - H_4)Al\}_2]^{2-}$ and (*b*) one calix[4]arene unit showing non-hydrogen atoms, included methylene chloride hydrogens excepted. Selected bond distances (Å) and angles (°): Al–O(1,2,3,4) 1.702(7), 1.853(6), 1.750(7), 2.353(7); Al–O(4) 1.753(7), O(1)–Al O(2,3,4) 98.4(3), 122.5(4), 79.8(3); O(2)–Al–O(3,4) 99.1(3), 178.2(3); O(3)–Al–O(4) 82.0(3), O(1)–Al–O(4) 117.3(3), O(2)–Al–O(4) 103.5(3), O(3)–Al–O(4) 110.9(3), O(4)–Al–O(4) 77.3(3).

The cones are slighlty distorted such that the opposite pairs directed towards the methylene chloride have a lower dihedral angle [relative to O(2), O(4), 47°] than the other pairs [O(1), O(3), 108°], allowing the solvent to sit deep in the cone, Fig. 1. Recent theoretical studies[18] describe a similar interaction between chloroform and benzene, energetically favoured by 3.94 kcal mol^{-1} (16.4 kJ mol^{-1}) with a chloroform C···ring centroid distance of 3.36 Å, *cf.* 3.54 Å for C···ring centroid in **2**, which is associated with an H···ring centroid distance of 2.46 Å (assuming C–H = 1.08 Å).[19] Intramolecular C–H···ring centroid distances in the range 2.5–2.7 Å have been reported in certain hydrocarbon structures,[19,20] but a search of the Cambridge Crystallographic Data Base supports the supposition that this is the first example of such in a host–guest complex. Interestingly, H atom π-arene interactions involving water molecules in a calix[4]arene have also been recently established.[21]

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‡ *Crystal structure determination*, $\mathbf{2}\cdot 4CH_2Cl_2\cdot 2C_7H_8\cdot 2C_6H_{14}$ (T = 297 K; Enraf-Nonius CAD4 diffractometer, crystals mounted in capillaries, λ = 1.54178 Å): $C_{124}H_{176}Al_2Cl_8N_2O_8$, M = 2160.4, monoclinic, space group $P2_1/n$,a = 14.637(2), b = 23.023(3), c = 17.249(3) Å, β = 92.59(1)°, U = 5807 Å^3, $F(000)$ = 2324; Z = 4, D_c = 1.24 g cm^{-3}, $\mu(Cu\text{-}K_\alpha)$ = 23.9 cm^{-1}, specimen 0.12 × 0.18 × 0.41 mm, 8134 unique reflections, 4111 with $I > 3.0\,\sigma(I)$ used in the refinement, $2\theta_{max}$ = 110°. The structure was solved by direct methods and refined by full-matrix least-squares analysis with non-hydrogen atoms anisotropic; H-atom details were included as invariants. Unit weights were used and the final residuals were R 0.093; $R_w{}'$ 0.101. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

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