

Trimethyl-aluminium and -gallium derivatives of calix[4]arenes: cone (mono-metallic) or doubly flattened partial cone (tetrametallic) conformations

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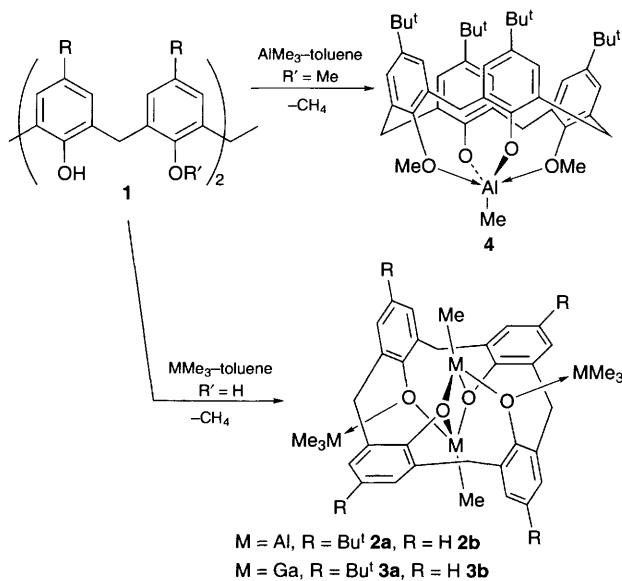
Reaction of calix[4]arene (H₄L) or *p*-Bu^t-calix[4]arene (H₄L') with MMe₃ (M = Al, Ga) in toluene affords fully deprotonated, alkyl-metal rich complexes [(L or L')(M-Me)₂(MMe₃)₂] with the calixarene adopting a doubly flattened partial cone conformation; reaction of 1,3-dimethyl ether *p*-Bu^t-calix[4]arene (H₂L'') with AlMe₃ yields [(L'')AlMe], the metal-bound alkyl group *exo* to the cavity of the calixarene in a cone conformation.

Bu^t-calix[4]arenes can act as poly-phenolic/phenolate O-centred ligands, often with two of them linked by two metal centres and the resulting cavity of each calixarene capable of acting as a receptor.¹⁻³ For example, the reaction of H₃AlNMe₃ with *p*-Bu^t-calix[4]arene yields such a 'divergent' receptor molecule.⁴ Larger calixarenes have greater conformation mobility and are more likely to give monocalixarene species as recently demonstrated for the product of the reaction between calix[6]arene and trimethylaluminium.⁵ However, monocalixarene species are accessible for *p*-Bu^t-calix[4]arene using partially O-alkylated analogues for which a few studies have recently been established, notably zirconium(IV)⁶ and aluminium(III)⁷ complexes of 1,3-dimethyl ether *p*-Bu^t-calix[4]arene **1** (R = Bu^t, R' = Me), Scheme 1. O-permethylated *p*-Bu^t-calix[4]arenes form monocalixarene species with sodium ions,⁸ and with trimethylaluminium, as does the analogous calix[8]arene.⁹

In exploring the group 13 chemistry of calixarene we have authenticated a new class of complexes whereby calix[4]arene and Bu^t-calix[4]arene **1** (R = H, Bu^t; R' = H), yield trimethyl-aluminium and -gallium rich, mono-calix[4]arene species when

treated with MMe₃ (M = Al or Ga), with four metal centres forming a thread through the calixarene which is in an unusual partially flattened double cone conformation. We have also established that treatment of 1,3-dimethyl ether *p*-Bu^t-calix[4]arene **1** (R = Bu^t, R' = Me), with trimethylaluminium also yields a monocalixarene species but only involving one metal centre, with a residual methyl group attached to aluminium exclusively *exo* to the cavity of the calixarene.⁷ The same calixarene with H₃AlNMe₃ yields a similar compound albeit now with the smaller residual hydride group either *exo* or *endo* with respect to the cavity, which by necessity is in the cone conformation for both isomers.⁷ As a class of aluminium alkoxohydrides the present compounds are unusual^{10,11} and it is noteworthy that aluminium phenolates with bulky *ortho*-substituents (an inherent feature of these complexes) are of interest in organic synthesis.¹²

Separate treatment of H₄L' and H₄L, **1** (R = Bu^t, H; R' = H) with excess MMe₃ (M = Al, Ga) in toluene resulted in vigorous exothermic reactions accompanied by gas evolution with the reaction mixtures affording colourless, air-sensitive crystals of [(L)(MMe)₂(MMe₃)₂] (M = Al **2a**, Ga **3a**) and [(L)(MMe)₂(MMe₃)₂] (M = Al **2b**, Ga **3b**), Scheme 1. With a 2 : 1 ratio of MMe₃ to calixarene ill-defined, sparingly soluble



Scheme 1

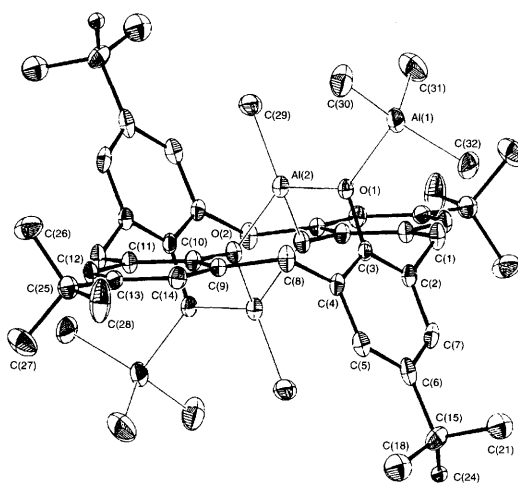


Fig. 1 Crystal structure of **2a** (20% ellipsoids); selected distances (Å) and angles (°) including the corresponding values for **2b** and **3a** [in parentheses (av.)]: Al(1)–O(1) 1.975(6), 1.972(4), [2.19]; Al(1)–C 1.97, 1.97 (av.), [1.95]; Al(2)–Al(2') 2.797(7), 2.828(4), [3.03]; Al(2)–O(1) 1.778(6), 1.766(4), [1.80]; Al(2)–O(2) 1.826(6), 1.837(4), [1.94]; Al(2')–O(2) 1.810(7), 1.819(4), [1.95]; Al(2)–C(29) 1.89(1), 1.909(6), [1.92]; O(1)–Al(1)–C 103.6, 103.5, [99] (av.); C–Al(1)–C 114.3, 114.7, [117] (av.); O(1)–Al(2)–O(2) 104.4(3), 102.8(2), [98]; O(1)–Al(2)–O(2') 102.3(3), 102.7(2), [98]; O(1)–Al(2)–C(29) 113.3(4), 113.4(2), [114]; O(2)–Al(2)–O(2') 79.4(3), 78.6(2), [77]; O(2)–Al(2)–C(29) 124.9(4), 123.6(2), [135]; O(2)–Al(2')–C(29') 126.4(4), 129.0(2), [123]; Al(1)–O(1)–Al(2) 130.1(4), 128.7(2), [129]

powders form. These are possibly polymeric compounds with inter-calixarene O–Al–O bridging which is disrupted in the presence of excess MMe_3 thereby rendering the metalocalixarene species more soluble. Reaction of $\text{H}_2\text{L}''$ **1** ($\text{R} = \text{Bu}^t$, $\text{R}' = \text{Me}$) with AlMe_3 similarly removes all available phenolic protons, but now affording a monometallic species, $[(\text{L}'')\text{AlMe}]$ **4**, even in the presence of excess AlMe_3 , unlike the foregoing compounds which can be considered as $(\text{Al}, \text{Ga})\text{Me}_3$ adducts of the analogous $[(\text{L}' \text{ or } \text{L})(\text{MMe})_2]$ species.

New compounds were characterised using ^1H and ^{13}C NMR spectroscopy which showed that the integrity of the solid-state structures are retained in solution, with the molecules of either C_{2h} or C_{2v} symmetry, and using X-ray crystallography with the structures reported herein,[†] except for compound **3a** which is isostructural with its aluminium analogue.⁷ Crystals were grown from toluene (**2a**, **3b**, **4**) or benzene (**2b**) and except for **4** (see below) molecules lie across inversion centres with half the molecule, **2a**, **b**, or two half molecules, **3b**, as the asymmetric unit. These centrosymmetric structures have the same metal coordination array as a thread passing through the calixarene annulus, Fig. 1. Metal centres of the central planar four-membered M_2O_2 ring also bear a methyl group and a phenolic O-centre which is in turn bound by MMe_3 . Similar organometallic M_2O_2 four-membered rings ($\text{M} = \text{Al}, \text{Ga}$) are invariably formed in reactions of MMe_3 with phenols.^{10,11,13} The calixarene moiety adopts the doubly flattened partial cone conformation which is not conducive to the formation of molecular inclusion complexes, unlike compound **4**, which crystallises with a toluene in the cavity of the calixarene, Fig. 2. Two opposite aromatic rings are coplanar with the other two intersecting the 'flattened' plane with dihedral angles of 113.6, 114.5 and 109°, respectively.

The metal centres in **2a**, **b** and **3b** have distorted tetrahedral geometries, the distortion being more pronounced for the central metal centres which are associated with the strained M_2O_2 rings. Internuclear distances for the different types of Al–O interactions in **2a** and **2b** are similar and similar to those in related compounds.^{7,10,11} In **3b** the Ga–O distances within each Ga_2O_2 ring are similar, 1.95 Å (mean), and similar to those in the related gallium phenoxide, $[\text{GaMe}_2(\mu\text{-OC}_6\text{H}_4\text{OMe-2})_2]$ [1.96(1) Å],¹³ but are significantly longer than the corresponding Al–O distances in **2a**, **b**, 1.82 Å (average). The O–GaMe₃ distances in **3b**, 2.19 Å, are longer than the adjacent O–GaMe distances, 1.80 Å, but are comparable with those seen in related coordination complexes, e.g. $[(\text{GaMe}_3)_2(\text{dibenzo-18-crown-6})]$ [2.20(1) Å].¹⁴ A less pronounced difference is found for the analogous distances in **2a**, **b**, 1.97 and 1.77 Å (av.).

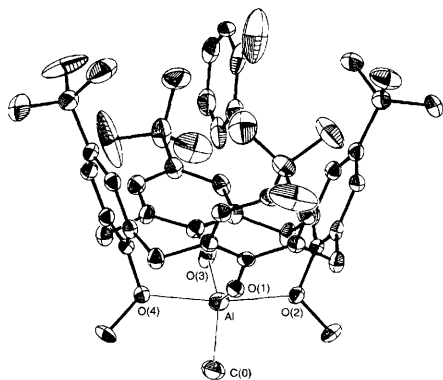


Fig. 2 Crystal structure of **4** showing the cavity included toluene (20% ellipsoids); selected distances (Å) and angles (°): Al–O(1,2,3,4) 1.725(6), 2.149(7), 1.691(7), 2.172(7); Al–C(0) 1.94(1); O(1)–Al–O(2,3,4), C(0) 89.4(3), 120.0(3), 87.5(3), 120.7(4); O(2)–Al–O(3,4), C(0) 87.4(3), 170.8(2), 93.5(3); O(3)–Al–O(4), C(0) 86.6(3), 119.3(4), O(4)–Al–C(0) 95.5(4)

In the solid state, molecules of **4** have approximately C_{2v} symmetry, but this is not extended to the included toluene which is disordered with the major component orientated with the *m*-H atom directed towards the metal centre, Fig. 2, as established for the ordered toluene in the Al–Cl analogue.⁷ Indeed, the distorted trigonal-bipyramidal metal centres in this compound and **4** are the same, as judged by bond distances and angles and the dihedral angle between opposite pairs of aromatic rings, 46.5 and 110.2°, and 43.7 and 108.9° respectively.

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Footnote

[†] *Crystal structure determinations* (Rigaku AFC7R or CAD4 diffractometer, crystal mounted in a capillary). **2a**· C_7H_8 : $\text{C}_{59}\text{H}_{84}\text{Al}_4\text{O}_4$, triclinic, space group $P\bar{1}$ (no. 2), $a = 11.610(6)$, $b = 12.903(6)$, $c = 11.534(5)$ Å, $\alpha = 106.76(5)$, $\beta = 116.02(3)$, $\gamma = 92.75(6)^\circ$, $U = 1458(1)$ Å³, $D_c = 1.10$ g cm⁻³, $\mu = 1.22$ cm⁻¹ (no correction), $Z = 2$, Mo-K α radiation, 5151 unique reflections, $2\theta \leq 50^\circ$ [2168 observed, $I > 3.0\sigma(I)$], $T = 297$ K, $R = 0.086$, $R_w = 0.080$. **2b**· C_7H_8 : $\text{C}_{48}\text{H}_{56}\text{Al}_4\text{O}_4$, monoclinic, space group $P2_1/n$ (no. 14), $a = 11.629(4)$, $b = 16.720(6)$, $c = 12.483(5)$ Å, $\beta = 109.03(3)^\circ$, $U = 2294(1)$ Å³, $D_c = 1.165$ g cm⁻³, $\mu = 1.42$ cm⁻¹ (no correction), $Z \leq 2$, Mo-K α radiation, 4192 unique reflections, $2\theta \leq 50^\circ$ [1752 observed, $I > 2.5\sigma(I)$], $T = 173$ K, $R = 0.055$, $R_w = 0.051$. **3b**: $\text{C}_{36}\text{H}_{44}\text{Ga}_4\text{O}_4$, monoclinic, space group $P2_1/n$ (no. 14), $a = 16.675(6)$, $b = 11.339(5)$, $c = 18.781(6)$ Å, $\beta = 100.33(3)^\circ$, $U = 3493(2)$ Å³, $D_c = 1.576$ g cm⁻³, $\mu = 30.0$ cm⁻¹, $Z = 4$, Mo-K α radiation, $2\theta \leq 40^\circ$ [2214 observed, $I > 3.0\sigma(I)$], $T = 297$ K, 397 parameters, $R = 0.098$, $R_w = 0.111$. **4**· C_7H_8 : $\text{C}_{61}\text{H}_{77}\text{AlO}_4$, triclinic, space group $P\bar{1}$ (no. 2), $a = 18.239(6)$, $b = 13.255(4)$, $c = 13.060(3)$ Å, $\alpha = 63.08(2)$, $\beta = 86.52(2)$, $\gamma = 77.07(3)^\circ$, $U = 2741(2)$ Å³, $D_c = 1.092$ g cm⁻³, $\mu = 0.80$ cm⁻¹ (no correction), $Z = 2$, Mo-K α radiation, 7727 unique reflections, $2\theta \leq 50^\circ$ [2976 observed, $I > 3.0\sigma(I)$], $T = 297$ K, $R = 0.070$, $R_w = 0.072$. 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 182/232.

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