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COMMUNICATION

# Zinc dimerization of *p*-*tert*-butylcalix[4]arene

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Reaction of *p*-*tert*-butylcalix[4]arene, **1**, with excess ZnEt<sub>2</sub> results in complete metallation of the calixarene, or with two equivalents of ZnEt<sub>2</sub> selective dimetallation occurs yielding the bis(calix[4]arene) species [(1-H<sub>2</sub>)Zn]<sub>2</sub>, **2**; distorted four coordinate O-bound zinc centers (Zn-O = 1.896(7) – 1.978(8) Å) fuse the slightly flattened cone conformation calixarene units with methylene chloride included in the divergent cavities.

Covalently bound oligomers of divergent receptor molecules are defined as koilands<sup>1</sup> and their assembly by non-covalent interactions with host molecules are of interest in the construction of new networks. Two or more calixarenes covalently bound by the oxygen atoms of the lower rim are koilands, and some have been prepared via metal/metalloid complexation, as in bis-(calixarene) aluminum(III),<sup>2</sup> niobium(V) titanium(IV),<sup>3</sup> europium(III),<sup>5</sup> and silicon(IV)<sup>1,6,7</sup> species, and in tris(calixarene) silicon species.<sup>7</sup> These moieties are all based on *p*-*tert*-butylcalix[4]arene in the cone conformation and changing the nature of the metal/metalloid centers changes the shape of the cavity, and thus the uptake of small molecules. The same species are also of interest in the binding of calixarenes to hydroxylated surfaces.<sup>2</sup>

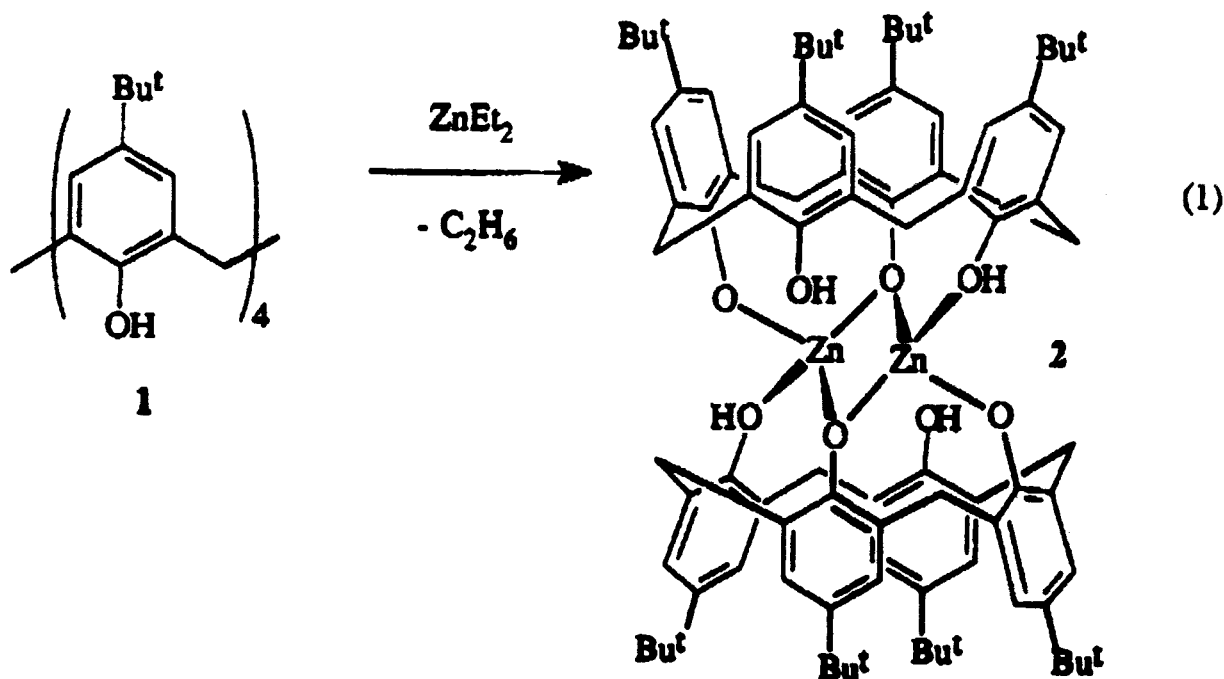
Formation of metal/metalloid fused koilands depends on the choice of metallating reagent. For example we note that the foregoing aluminum species is formed via treatment of H<sub>3</sub>AlNMe<sub>3</sub> with *p*-*tert*-butylcalix[4]arene,<sup>2</sup> whereas using trimethylaluminum results in an aluminum rich, mono-calixarene species with a doubly flattened partial cone conformation.<sup>8</sup> In further exploring the synthesis of koilands we have investigated the reaction

of diethylzinc with *p*-*tert*-butylcalix[4]arene, and report the synthesis of a bis(calixarene) koiland, **2**, and its crystal structure. It is the first structurally authenticated Group 12 metal O-complexed species, and it represents a new structural type of koilands based on the bis(calixarene) system, for which only a few structures have been established.<sup>2,3,4,5</sup>

The synthesis of compound **2** is shown in equation 1;<sup>9</sup> two equivalents of diethylzinc gave the highest yield of **2** and for complete deprotonation of the calixarene four equivalents were required (NMR, IR). Presumably here a mono-calixarene results as for the metallation of **1** using trimethylaluminum,<sup>8</sup> although in contrast there was no evidence for residual alkyl metal groups. Slow hydrolysis of the deprotonated species, which failed to give a single pure compound, gave crystals of compound **2** with methylene chloride included in each of the cones, and with methylene chloride and toluene as solvents of crystallization.

Molecules of **2** are centrosymmetric in the solid<sup>10</sup> with the zinc centers in distorted tetrahedral environments as part of a Zn<sub>2</sub>O<sub>2</sub> four membered ring system in which the associated phenoxides bridge two metal centers, Figure 1. This arrangement differs from that established for europium,<sup>5</sup> transition metals,<sup>3,4</sup> silicon,<sup>6</sup> and aluminum,<sup>3,2</sup> calix[4]arene species. Indeed, it is unique in the way the two calixarenes interact with the metal centers, most notably in having an uncoordinated O-center. The two phenolic protons required by valency considerations are most likely associated with H-bonding involving the uncoordinated O-center and adjacent O-centers, OA...OB 2.57(1) Å, OA...OD 2.53(1) Å, there being only one ν<sub>O...H</sub> band, 3175 cm<sup>-1</sup>. Symmetrical H-bonding is consistent with the molecular symmetry approximating

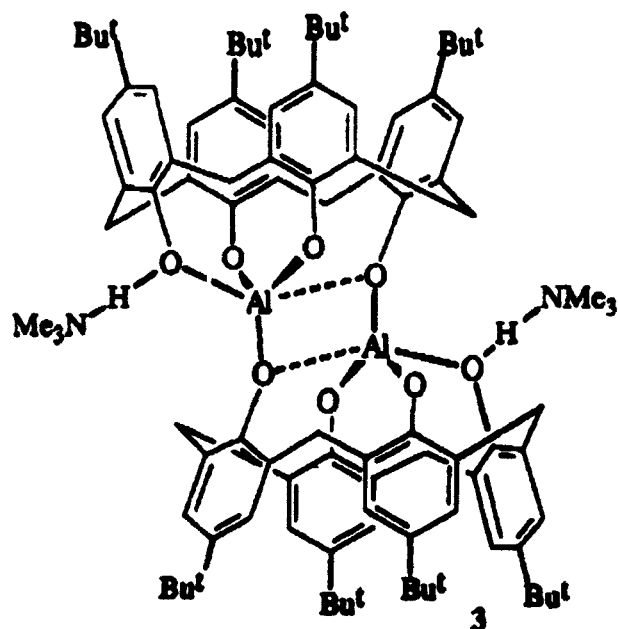
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to  $C_s$  with the mirror plane bisecting the uncoordinated phenol and the bridging phenoxide, Figure 1. The  $Zn_2O_2$  core is planar and overall the geometries of the metal centers are unremarkable.<sup>11</sup> Distinction between the various types of phenolate/phenol groups in the solid is not apparent in toluene solution on the NMR time scale.

As has been noted for compound 3,<sup>2</sup> methylene chloride is included in the cavity, although in the present case it is highly disordered, possibly due to different shapes of the cones. These are distorted such that the opposite pairs associated with the uncoordinated phenol and the bridg-

ing phenoxide have a significantly higher dihedral angle,  $110^\circ$  relative to OAC, than the other pairs associated with the terminal phenoxides/phenols,  $121^\circ$  relative to OBD, Figure 1. The corresponding angles for 3 are more disparate at  $47^\circ$  and  $108^\circ$ ,<sup>2</sup> the former allowing the solvent to sit deeply in the cone resulting in ordered C-H... $\pi$ -arene aromatic ring hydrogen interactions to opposite rings. In 2 there is only one C-H... $\pi$ -arene interaction evident (C...ring-centroid 3.36 Å, cf 3.54 Å in 3). Interestingly, theoretical studies describe a similar C-H... $\pi$ -arene interaction between chloroform and benzene, energetically favored by 3.94 kcal/mol,<sup>12</sup> and C-H... $\pi$ -arene interactions are important in the degradation of  $C_{60}/p$ -tert-butylcalix[8]arene in chlorinated hydrocarbons.<sup>13</sup>



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- 9 A solution of ZnEt<sub>2</sub> (0.604 g, 4.89 mmol) in toluene (20 mL) was added over 30 minutes to a stirred solution of *p*-tert-butylcalix[4]arene (1.43 g, 2.20 mmol) in toluene (40 mL) at 0°C. After warming to room temperature, the reaction mixture was stirred for 2 days. The resulting solution was filtered and the solvent removed *in vacuo* yielding a pale yellow powder which was recrystallised from dichloromethane, then dried *in vacuo* (1.83 g, 63.4%); Mp 312°C (dec.); <sup>1</sup>H NMR (CDCl<sub>3</sub>, 200 MHz) δ 1.29 (36H, s, Bu<sup>1</sup>), 3.46 (4H, m, CH<sub>2</sub>) 4.44 (4H, m, CH<sub>2</sub>) 7.15 (4H, s, ArH), 7.36 (4H, s, ArH), 10.57 (2H, s, OH); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 50.3 MHz) δ 31.5 (b, CH<sub>3</sub>), 33.8 (CCH<sub>3</sub>), 125.4, 127.8, 128.3, 129.1, 138.9 (Ar); anal. found C 61.79, H 6.55: calc. for C<sub>88</sub>H<sub>108</sub>O<sub>8</sub>Zn<sub>2</sub>4CH<sub>2</sub>Cl<sub>2</sub>: C 62.63, H 6.63.
- 10 Crystal structure determination, 2.2CH<sub>2</sub>Cl<sub>2</sub> (T = 297 K; Enraf-Nonius CAD4 diffractometer, crystal mounted in capillaries, λ = 0.71069 Å): C<sub>92</sub>H<sub>116</sub>Zn<sub>2</sub>Cl<sub>8</sub>O<sub>8</sub>, M = 1764.2, triclinic, space group P $\bar{1}$ , a = 12.501(2), b = 14.297(1), c = 14.932(1) Å, α = 74.48(1), β = 79.22(1), γ = 89.55(1)<sup>o</sup>, U = 2524 Å<sup>3</sup>, F(000) = 898; Z = 1, D<sub>c</sub> = 1.16 g cm<sup>-3</sup>, μ(Mo-Kα) = 10.46 cm<sup>-1</sup>, specimen 0.25 × 0.40 × 0.40 mm, 6167 unique reflections, 3566 with I > 3.0 σ(I) used in the refinement, 2θ<sub>max</sub> = 50°. The structure was solved by direct methods and refined by full matrix least squares refinement with non-hydrogen atoms anisotropic; H-atom details were included as invariants. Unit weights were used and the final residuals were R 0.089; R' 0.097.
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