Zinc calixarene complexes for the ring opening polymerization of cyclic esters

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Zinc Calixarene Complexes for the Ring Opening Polymerization of Cyclic Esters

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Reaction of Zn(CsF5)2·toluene (two equivalents) with 1,3-dipropoxy-p-tert-butyl-calix[4]arene (L1H2) led to the isolation of the complex [{Zn(CsF5)2}L1] (1), whilst similar use of Zn(Me)2 resulted in the known complex [{Zn(Me)}2L1] (2). Treatment of L1H2 with in-situ prepared Zn(N(SiMe3)2)2 in refluxing toluene led to the isolation of the compound [ZnN(SiMe3)2L1(Na)] (3). The stepwise reaction of L1H2 and sodium hydride, followed by ZnCl2 and finally NaN(SiMe3)2 yielded the compound [ZnN(SiMe3)2L1] (4). The reaction between three equivalents of Zn(CsF5)2·toluene and oxacalix[3]arene (L2H3) at room temperature formed the compound [{Zn(CsF5)}3L2] (5); heating of 5 in acetonitrile caused the ring opening of the parent oxacalix[3]arene and rearrangement to afford the complex [(L2Zn(CsF5)2(R)(R)OH)·5MeCN] R = CsF5CH2–(p-tertBuPhenolate–CH2OCH2–)2–p-tertBuPhenolate–CH2O–]3- (6). The molecular structures of the new complexes 1, 3 and 6, together with that of the known complex 2, whose solid state structure has not previously been reported, have been determined.

Compounds 1, 3 – 5 have been screened for the ring opening polymerization (ROP) of ε-caprolactone (ε-CL) and rac-lactide. Compounds featuring a Zn—C6F5 fragment were found to be poor ROP pre-catalysts as they did not react with benzyl alcohol to form an alkoxide. By contrast, compound 4, which contains a zinc silylamide linkage, was the most active of the zinc-based calix[4]arene compounds screened and was capable of ROP at ambient temperature with 65 % conversion over 4 h.

Introduction

A great number zinc-based ring opening polymerization (ROP) catalysts have been explored since the seminal work by Coates and co-workers. The majority of these catalysts employ ligand systems such as diphenolates, or Schiff bases, whilst relatively few calixarene-based catalysts for the ROP of either lactides or lactones have been examined. Generally, ligands that are monoanionic are chosen for reaction with zinc precursors as they will inevitably lead to a metal that still contains a viable nucleophilic group for ROP, which may be the reason that p-tert-calix[4]arenes have rarely been utilized. Vigalok and co-workers have had success with zinc alkyl-based calix[4]arenes and although the dialkoxy-calix[4]arene ligand is dianionic when deprotonated its use leads to a dicational complex that can still contain a nucleophilic group. Indeed, in related work, we have accessed a highly selective and immortal magnesium based mononuclear complex [L1Mg(n-Bu)], where L1 is derived from tripropoxy-p-tert-butylicalix[4]arene, which exhibited exceptional activity for the ROP of rac-lactide. Given zinc compounds are often synthesized due to their higher tolerance of water, we have initiated a programme to more fully explore both the coordination chemistry and catalysis of zinc-based calixarenes. Herein, we explore the use of the calix[4]arene ligand L1H2 and the oxacalix-

Results and discussion

Calix[4]arene Complexes

A number of new zinc-containing calix[4]arene complexes have been synthesized and fully characterized. The synthetic procedures are outlined below in Scheme 1.
Scheme 1 Synthesis of zinc compounds 1 – 4. i) 2 Zn(C₆F₅)₂.tol, toluene, reflux, 16 h. ii) 2 ZnMe₂, toluene, RT, 16 h. iii) 1) 2 NaH, THF, 16 h, room temperature, 2) ZnCl₂, THF, 2 h, RT, 3) Na(N(SiMe₃)₂), THF, 2 h, RT. iv) 2 Zn(N(SiMe₃)₂)₂, toluene, reflux, 72 h.

The compound 1,3-dipropoxy-p-tert-butyl-calix[4]arene (L₁H₂) was synthesized as previously described.³⁸,³⁹ Treatment of L₁H₂ with Zn(C₆F₅)₂.toluene (two equivalents) in refluxing toluene led to the isolation of the complex [{Zn(C₆F₅)}₂L₁] (1) in good yield (54 %). A related n-propoxy calix[4]arene derivative, synthesized via treatment with ZnMe₂, was previously employed by Vigalok and co-workers, who reported that calix[4]arene derivatives containing smaller alkyl chains (at the lower rim) led to more complex products, including partial and 1,3-alternate cone conformations.¹² In the case of 1, the cone conformation was isolated exclusively. Crystallization of compound 1 using hot acetonitrile led to the formation of clear blocks on slow cooling to ambient temperature, which proved suitable for single crystal X-ray diffraction studies. Compound 1 crystallizes with two different pentafluorophenyl zinc environments, one outside of the calix[4]arene backbone and the other within the cavity. The exo zinc metal centre is five co-ordinate in a trigonal bipyramidal geometry bonding to all four of the calix[4]arene lower-rim oxygens, whereas the encapsulated zinc is trigonal planar and only binds to the ‘non-propoxy’ oxygen atoms. The pinched-cone calixarene conformation arises due to the propoxy substitution and the spatial requirement of the Zn(2)-bound C₆F₅ group. The Zn(2) to arene distances of ca. 3.0 Å are likely too long for these to be considered as Zn···π interactions. The structure of compound 1 is depicted in Figure 1, with selected bond lengths and angles given in the caption.

Disappointingly, the pre-polymerization screening of compound 1 indicated no reaction between the benzyl alcohol (BnOH) and the Zn—C₆F₅ moiety, which was also the conclusion obtained by Schnee et al and Piedra-Arroni et al when Zn(C₆F₅)₂.toluene was employed in the presence of either BnOH or amine/phosphine respectively.¹³,¹⁴ In such systems, the catalyst was thought to behave as a ‘monomer activator’ rather than proceeding via a ‘co-ordination insertion’ pathway; the lack of activity contrasts with a
number of previous Zn—C₆F₅ containing compounds. To ensure that the polymerization would proceed through a ‘coordination insertion’ mechanism, the pentafluorophenyl moiety was substituted for a more nucleophilic group. To isolate a zinc alkoxide, firstly the methyl zinc derivative (compound 2) was synthesized following the literature procedure. Single crystals of compound 2 suitable for single crystal X-ray diffraction were grown from a saturated petroleum ether solution. The structure of 2 was initially assigned based on ¹H NMR spectroscopic data and is similar to the ethyl derivative. Surprisingly, the crystal structure of 2 (See Figure 2) reveals both the cone and partial cone conformations within the unit cell (although the partial cone is better described as a chair conformation); the ¹H NMR spectrum (CDCl₃) indicates that only the cone conformation is present in solution, which is consistent with the literature data.

The cone conformation of 2 is similar to that observed in compound 1, and again the exo-Zn is trigonal bipyramidal, whilst the endo-Zn is trigonal planar. In the chair conformation, there is a centre of inversion in the middle of the calix[4]arene. The zinc metal centres are in the base of a trigonal pyramid with the n-propoxy oxygen at the apex. Treatment of 2 with alcohol (MeOH, iPrOH) at −80 °C did not form the alkoxide; only starting material was detected. At higher temperatures, free calix[4]arene was formed, suggesting that the alcohol displaced the calix[4]arene; a similar result was reported by Drouin et al.

Zinc silylamides have previously been shown to be active for ROP of L-lactide and as such the synthesis of a calix[4]arene zinc silylamide was targeted. Treatment of L₁H₂ with Zn(N(SiMe₃)₂)₂, which was synthesized in situ, from the sodium salt, in refluxing toluene led to the isolation of compound 3. Rather than the expected formation of a dizinc silylamide species, where one Zn—N(SiMe₃)₂ fragment is present in the cavity, compound 3 contains a sodium cation within the cavity. The sodium cation likely originates from unreacted sodium hexamethyldisilazane.
Single, rod-like, crystals were obtained on prolonged standing of a petroleum ether solution of compound 3 at ambient temperature. The crystal structure was determined by X-ray diffraction (Figure 3).

The zinc centre is bound to three of the oxygens of the calixarene, the two phenolic oxygens and one n-propoxy oxygen. As expected, the dative O—Zn bond length is significantly longer than the other two, viz 2.2760(10) Å vs. 1.9297(10) Å; the N—Zn bond is 1.8929(13) Å. The sodium cation occupies a trigonal pyramid rather than in the trigonal bipyramidal geometry seen for 1. The sodium and zinc centres are 3.1725(7) Å apart. The target dizinc silylamide, compound 4, was synthesized from the reaction between two equivalents of zinc metal centres (See Figure 4). The remaining oxacalix[3]arene ligands are two O atoms and supported with an O—H⋯O H-bond (see Table 1). The resulting 1H NMR spectrum is complex due to lack of symmetry.

For comparison we have prepared the related oxacalixarene complexes. The reaction between three equivalents of \( \text{Zn(C}_6\text{F}_5)_2 \) in toluene and oxacalix[3]arene (1,2H_3) at room temperature led to the formation of compound 5 after removal of volatiles. However, on attempted crystallisation from hot acetonitrile, ring opening of the parent oxacalix[3]arene and rearrangement to complex 6 was observed. The ability of an electrophilic species to open the ether linkages of the oxacalix backbone is not unprecedented, for example Iglesia and co-workers proposed a similar product from a Ti/SiO_2 grafted oxacalix[3]arene,\(^{17}\) however this is the first structurally characterised result.

Unfortunately, suitable single crystals of compound 5 could not be obtained. The 1H NMR spectra are consistent with the complex existing in a partial cone conformation: there are three distinct sets of doublets for each of the methylene bridges and signals overlap. Compound 5 has also been characterised by mass spectroscopy and elemental analysis, both of which are consistent with the structure depicted in chart 2.

The structure of the ring opened oxacalix[3]arene compound 6 was determined by single crystal X-ray diffraction, which revealed the presence of three separate oxacalix[3]arene ligands within the molecule, two of which have been ring opened with formation of two carbon—C_6F_5 bonds and a protonated oxygen which is involved either in hydrogen bonding to an acetonitrile molecule or an oxygen anion that forms two short bonds with two Zn\(^{2+}\) centres (See Figure 4). The remaining oxacalix[3]arene remains intact. There are six zinc metal centres within the compound, one of which is bound to a C_6F_5 ring. The core of the molecule consists of two Zn_2O_4 cubes missing one corner, linked via two O atoms and supported with an O—H⋯O H-bond (see Table 1). The resulting 1H NMR spectrum is complex due to lack of symmetry.

Figure 3 ORTEP representation of compound 3. Hydrogen atoms, tert-butyl groups and disorder have been removed for clarity. Displacement ellipsoids are drawn at the 50 % probability level. Selected bond lengths (Å) and angles (°): Zn(1)—N(1) 1.8929(13), Zn(1)—O(1) 1.9297(10), Zn(1)—O(3) 1.9402(10), Zn(1)—O(2) 2.2760(10), N(1)—Zn(1)—O(1) 131.42(5), N(1)—Zn(1)—O(3) 134.32(5), O(1)—Zn(1)—O(3) 88.46(5), N(1)—Zn(1)—O(2) 109.26(5), O(1)—Zn(1)—O(2) 87.08(4), O(3)—Zn(1)—O(2) 91.34(4).

Chart 2. Oxacalixarene complexes 5 and 6.

Oxacalix[3]arene complexes

For comparison we have prepared the related oxacalixarene complexes. The reaction between three equivalents of \( \text{Zn(C}_6\text{F}_5)_2 \) in toluene and oxacalix[3]arene (1,2H_3) at room temperature led to the formation of compound 5 after removal of volatiles. However, on attempted crystallisation from hot acetonitrile, ring opening of the parent oxacalix[3]arene and rearrangement to complex 6 was observed. The ability of an electrophilic species to open the ether linkages of the oxacalix backbone is not unprecedented, for example Iglesia and co-workers proposed a similar product from a Ti/SiO_2 grafted oxacalix[3]arene,\(^{17}\) however this is the first structurally characterised result.

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with nine separate tert-butyl signals. The $^{19}$F NMR spectrum consists of nine peaks in total for the three C$_6$F$_5$ fragments.

### Table 1. Hydrogen-bond geometry (Å, °) for 6

<table>
<thead>
<tr>
<th>D—H•••A</th>
<th>D—H</th>
<th>H•••A</th>
<th>D•••A</th>
<th>D—H•••A</th>
</tr>
</thead>
<tbody>
<tr>
<td>O19—H19•••O5</td>
<td>1.00</td>
<td>1.84</td>
<td>2.786 (11)</td>
<td>157</td>
</tr>
</tbody>
</table>

#### Polymerization Screening

Compounds 1, 3 – 5 were screened for the polymerization of ε-caprolactone (ε-CL) and rac-lactide. The results are presented in Table 1.

Compounds 1 was screened for the polymerization of ε-caprolactone at room temperature and was found to be inactive when using dichloromethane, tetrahydrofuran or toluene as solvent (Table 2, runs 1 – 3). Only at temperatures greater than 80 °C was compound 1 found to be active for the ROP of ε-caprolactone; attempting polymerization without benzyl alcohol present was detrimental to the catalytic system (Table 2, runs 5 – 7). Furthermore, compound 1 was only active for the ROP of rac-lactide at high temperature. In both cases (ε-caprolactone and rac-lactide) high conversion rates can be achieved at high temperature, however the resulting polymer molecular weight is much lower than expected; this indicates that there are significant *trans*-esterification reactions occurring at such temperatures. Screening of 4, where the C$_6$F$_5$ groups have been replaced with N(SiMe$_3$)$_2$, revealed that the system was active at room temperature and converted 100 equivalents of ε-caprolactone with 65 % completion over 4 h in toluene (Table 2, run 13). The polymer molecular weights were close to the expected values; lower activity was observed using THF. This compares favourably with the ROP activity (43 % over 24 h at 60 °C) observed for the hexanuclear complex [L$_2$Zn$_4$(Zn$_2$CH$_3$CN)$_4$(µ-OEt)$_2$]$_9$.

Compound 3, which differs from compound 4 by replacement of the Zn—N(SiMe$_3$)$_2$ in the calix[4]arene cavity with a sodium cation, was not active under the same conditions as for 4. Compound 5 was only active for the ROP of rac-lactide at high temperatures (100 °C) and gave ε-caprolactone molecular weight much lower than expected. The polymerization using 5 was further complicated due to the probability of forming a species similar to compound 6; the latter was not screened for polymerization. Interestingly, despite the aforementioned *trans*-esterification at high temperatures, all of the zinc compounds screened afforded products with low PDI values (1.06 – 1.48). We also note that for [L$_2$Zn$_4$(Zn$_2$CH$_3$CN)$_4$(µ-OEt)$_2$]$_9$, the use of low co-catalyst loadings resulted in molecular weights far lower than the calculated values, indicating the importance of back biting reactions. Similarly for [L$_2$Zn$_4$(Zn$_2$CH$_3$CN)$_4$(µ-OEt)$_2$]$_9$, the polydispersity (≤ 1.3) was not hampered by such back biting.

### Experimental

All manipulations were carried out under an atmosphere of nitrogen using standard Schlenk and cannula techniques or in a conventional nitrogen-filled glove-box. Solvents were refluxed over an appropriate drying agent, and distilled and degassed prior to use. Elemental analyses were performed by the microanalytical services at London Metropolitan University. NMR spectra were recorded on Bruker Ascend 500/300 MHz spectrometers at 298 K; chemical shifts are referenced to the residual protio impurity of the deuterated solvent. IR spectra (Nujol mulls) were recorded.
Synthesis of L1[NaZnN(SiMe3)2] (3)

Stirred for a further 1 h, NaN(SiMe3)2 (2.73 ml, 1 M solution in THF) was then added and after 1 h, the volatiles were removed in vacuo. The residue was extracted in petroleum ether and on standing (2 h) clear rods of compound 3 formed. (1.32 g, 50 %). MS (EI, m/z): 977 [M]+. Found: C, 68.44; H, 8.72; N, 1.49. C36H32Na2N2O4Si2Zn requires C, 71.55; H, 5.37; N, 2.30 %.

Synthesis of L1(ZnC6F5)2 (1)

1,3-dipropoxy-p-cresol (1.39 g, 10.0 mmol) and bis(pentafluorophenyl)zinc toluene (0.98 g, 2.0 mmol) were dissolved in toluene (30 ml) and refluxed for 16 h. The volatiles were removed in vacuo. The residue was extracted in petroleum ether and on standing (2 h) clear rods of compound 1 formed. (1.32 g, 50 %). MS (EI, m/z): 977 [M]+. Found: C, 68.44; H, 8.72; N, 1.49. C36H32Na2N2O4Si2Zn requires C, 71.55; H, 5.37; N, 2.30 %.

MS (EI, m/z): 977 [M]+. Found: C, 68.44; H, 8.72; N, 1.49. C36H32Na2N2O4Si2Zn requires C, 71.55; H, 5.37; N, 2.30 %.

Synthesis of L1[ZnN(SiMe3)2] (3)

1,3-dipropoxy-p-tetra-butylcalix[4]arene (2.00 g, 2.73 mmol) and sodium hydride (140 mg, 5.83 mmol) were dissolved in THF (30 ml). The solution was stirred for 1 h and then ZnCl2 (0.37 g, 2.73 mmol) was added as a THF solution (15 ml). The solution was stirred for a further 1 h, NaN(SiMe3)2 (2.73 ml, 1 M solution in THF) was then added and after 1 h, the volatiles were removed in vacuo. The residue was extracted in petroleum ether and on standing (2 h) clear rods of compound 3 formed. (1.32 g, 50 %). MS (EI, m/z): 977 [M]+. Found: C, 68.44; H, 8.72; N, 1.49. C36H32Na2N2O4Si2Zn requires C, 71.55; H, 5.37; N, 2.30 %.
C(CH₃)₃, 0.11 (overlapping s, 36H, N(SiMe₃)₃). ¹³C NMR (CDCl₃): δ = 156.3, 148.4, 145.1, 138.0, 131.2, 131.1, 124.8.

Table 3 Crystallographic data for compounds 1, 2, 3 and 6.

<table>
<thead>
<tr>
<th>Compound</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>6</th>
</tr>
</thead>
</table>
| Formula | C₆H₆F₆O₃Zn₂ | C₆H₆F₆O₃Zn₂ | C₆H₆NNaO₃Si₂Zn | C₁₂H₂₆F₁₆O₇Zn₆
| Formula weight | 1195.89 | 891.89 | 979.80 | 5837.84 |
| Crystal system | Triclinic | Triclinic | Triclinic | Triclinic |
| Space group | P 1 | P 1 | P 1 | P 1 |
| Unit cell dimensions | | | | |
| a (Å) | 10.935(3) | 12.440(9) | 10.0724(7) | 16.9733(14) |
| b (Å) | 15.653(4) | 13.4833(9) | 12.3152(9) | 20.4715(17) |
| c (Å) | 18.150(5) | 24.1096(17) | 22.8866(16) | 21.2759(17) |
| α (°) | 95.911(4) | 90.508(5) | 81.897(3) | 91.246(6) |
| β (°) | 105.236(3) | 100.669(6) | 88.440(3) | 109.931(8) |
| γ (°) | 105.822(4) | 113.943(7) | 89.093(3) | 102.477(7) |
| V (Å³) | 2832.4(13) | 3617.2(5) | 2809.3(3) | 6749.0(10) |

Z | 2 | 3 | 2 | 2 |
Temperature (K) | 120(2) | 100(2) | 100(2) | 100(2) |
D (g/cm³) | 1.402 | 1.228 | 1.158 | 1.396 |
Absorption coefficient, μ (mm⁻¹) | 0.869 | 1.036 | 0.530 | 1.135 |
Crystal size (µm³) | 0.18 x 0.05 x 0.02 | 0.050 x 0.10 x 0.02 | 0.18 x 0.13 x 0.05 | 0.11 x 0.02 x 0.01 |
2θmax (°) | 26.0 | 27.5 | 27.5 | 22.5 |
Reflections measured | 24992 | 42558 | 48002 | 60159 |
Unique reflections, Rint | 11859, 0.042 | 16159, 0.075 | 12822, 0.039 | 17582, 0.340 |
Reflections with F² > 2σ(F²) | 7445 | 11427 | 12053 | 5403 |
Transmission factors (max., min.) | 0.983 and 0.859 | 1.00 and 0.757 | 1.00 and 0.747 | 0.994 and 0.885 |
Number of parameters | 888 | 808 | 603 | 1766 |
R₁ [F² > 2σ(F²)] | 0.046 | 0.079 | 0.041 | 0.086 |
wR₁ (all data) | 0.118 | 0.228 | 0.116 | 0.142 |
GOOF, S | 0.989 | 1.041 | 1.055 | 0.807 |
Largest difference peak and hole (e Å⁻³) | 0.387 and -0.337 | 2.818 and -1.586 | 0.901 and -0.806 | 0.505 and -0.448 |

Synthesis of L²Zn(C₆F₅)₃ (5)

A toluene solution (30 ml) of p-tert-butyhexahomotrioxacalix[3]arene (0.50 g, 0.87 mmol) and bis(pentafluoro phenyl)zinc toluene (1.27 g, 2.60 mmol) was stirred at ambient temperature for 12 h. The volatiles removed in vacuo. The residue was extracted into warm light petroleum and compound 5 immediately formed as a white powder. (0.91 g, 79 % yield).

Polymerization methods

ε-Caprolactone

A Schlenk flask (250 ml) was charged with the required quantity of pre-catalyst in a glove box. The required amount of dry, degassed toluene and alcohol (from an alcohol/toluene solution) was added. The solution was heated to the required temperature.

The polymerization was initiated by addition of the ε-
caprolactone and was stirred for the allotted time. Conversion of monomer was determined by $^1$H NMR spectroscopy, and the polymerization was quenched by addition of methanol.

**rac-Lactide**

Solutions of rac-lactide and catalyst were prepared separately using the required solvent. The required amount of alcohol, from a standard alcohol solution in toluene, was added to the catalyst. The rac-lactide solution was added to the catalyst solution and stirred for the allotted time at room temperature under nitrogen. 0.5 – 1.0 mL aliquots were taken out of the stirred solution where required and quenched with 1 drop of 0.1 M HCl. The aliquots were then dried and analysed by $^1$H NMR spectroscopy and GPC.

**Crystallography**

Intensity data were collected on Bruker Apex 2 CCD diffractometer (1) or a Rigaku FR-E+ diffractometer (all others). For 1, data were measured using synchrotron radiation at SRS Daresbury station 9,8; all other data were measured with monochromated Mo-Kα radiation. Structures were determined by the direct methods routines in SHELXS-97 (1, 6) or SIR-92 (2, 3, 11), and were refined by full-matrix least-squares methods on $R^2$ in SHELXL-2013/2014. Non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were included in idealized positions and their $U_{iso}$ values were set to ride on the $U_{eq}$ values of the parent carbon atoms except for H(13) in 6 for which coordinates were refined with an O-H distance restraint. Complex 2 contained a disordered solvent region which was handled using the BYPASS procedure. The crystals of 6 were weakly diffracting, so data were only used to $\theta = 22.5^\circ$ and were of rather poor quality; the connectivity is however clearly determined.

Crystal data and refinement results for all samples are collated in Table 3. CCDC 1014114-1014117 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request cif

**Conclusion**

In conclusion, we have structurally characterized a number of new zinc complexes bearing ligands derived from either 1,3-dipropoxy-p-tert-butyl-calix[4]arene or p-tert-butylhexahomotrioxacalix[3]arene. These include a complex in which there are two different calixarene conformations in the same structure, and an unusual structure bearing an oxacalix[3]arene derived ligand as well as two ring-opened ligands derived from the parent oxacalix[3]arene. Screening for the potential to ROP either ε-caprolactone (ε-CL) and rac-lactide revealed that the presence of a Zn-C$_2$F$_2$ motif was detrimental in the calix[4]arene systems, whilst use of the amide group N(SiMe$_3$)$_2$ proved to be more effective, with a 65 % conversion over 4 h at ambient temperature.

**Notes and references**

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