

Direct Transformation of Six- to Three-Coordinate Phosphorus in *p*-*tert*-Butylcalix[4]arene; the First X-Ray Crystal Structure of a Hypervalent Main Group Atom Bound to a Calixarene

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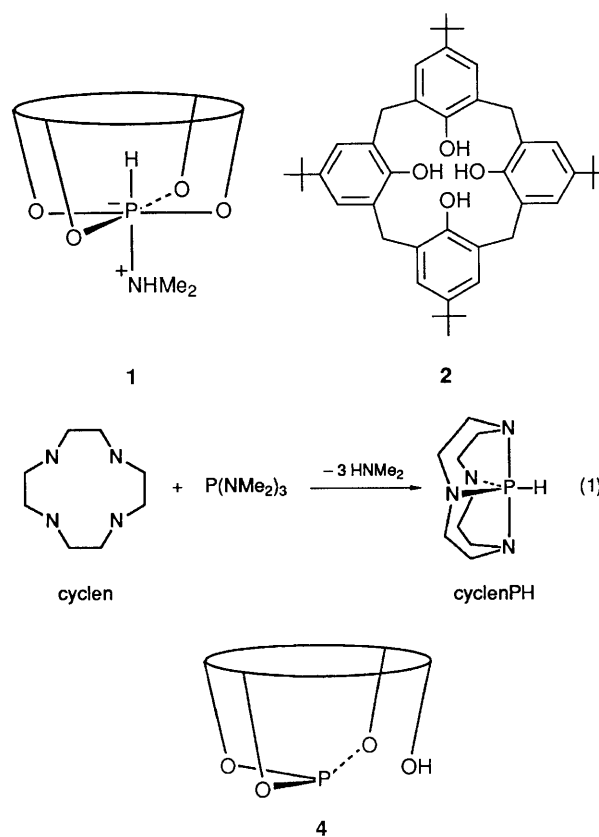
Removal of dimethylamine from the zwitterionic six-coordinate phosphorus species *p*-*tert*-butylcalix[4]areneP(H)NMe₂ **1** leads to the three-coordinate derivative *p*-*tert*-butylcalix[4]arene(H)P **4**; the X-ray structure of Li[*p*-*tert*-butylcalix[4]areneP(H)NMe₂] **3** gives an insight as to why no pentacoordinate species is observed.

We recently reported¹ the synthesis of the novel zwitterionic six-coordinate phosphorus derivative *p*-*tert*-butylcalix[4]areneP(H)NMe₂ **1** via the reaction of *p*-*tert*-butylcalix[4]arene **2** with tris(dimethylamino)phosphine. Remarkably, only two of the amine groups were removed; the third dimethylamine remained coordinated to phosphorus. This was in direct contrast to our expectation that all of the dimethylamine would be lost to give a pentacoordinate species, analogous to the synthesis of cyclenPH. [eqn. (1)];³ cyclen = 1, 4, 7, 10-tetraazacyclododecane. In addition, treatment of **1** with butyllithium led to deprotonation of the amine, leaving the P–H bond intact, to yield the corresponding lithium salt Li[*p*-*tert*-butylcalix[4]areneP(H)NMe₂] **3**.¹ We herein describe our efforts to isolate the pentacoordinate analogue of **1** by removal of the last dimethylamine. In addition, we report the X-ray crystal structure of **3** which is the first structural evidence for a hypervalent main group atom bound to the oxygens of a calixarene. These results suggest that the *p*-*tert*-butylcalix[4]arene ring may not be able to stabilise a pentacoordinate geometry in which all four oxygens are bound to phosphorus.

Heating a sample of **1** (³¹P NMR: δ – 120, ¹J_{PH} 733 Hz)¹ at 320 °C in an inert atmosphere for 2 h (to drive off dimethylamine) yields a product which has a single peak in the ³¹P NMR spectrum at δ + 113, with no observed proton coupling; this value is in the usual trivalent phosphite region.⁴ The *tert*-butyl region of the ¹H NMR spectrum, which showed a singlet for **1**, is now split into three peaks in a 1 : 1 : 2 ratio, and no resonance due to a –NMe₂ group is found. Moreover, a peak in the ν_{OH} region of the IR spectrum (Nujol mull) at 3515 cm^{–1} is observed, which is absent in **1**. These data are consistent with the formation of the three-coordinate phosphorus product *p*-*tert*-butylcalix[4]arene(H)P **4**, rather than a five-coordinate species.† In order to determine if the pentacoordinate form might be observed under more mild conditions, **1** was treated with trifluoroacetic acid. Protonation would be expected initially to cleave one P–O bond yielding a phenol linkage, possibly followed by elimination of dimethylammonium trifluoroacetate. In fact, the dimethylammonium salt is formed in this reaction; however, **4** is formed in this case as well.‡ It appears that there is no pentacoordinate species in which all four oxygens are bound to phosphorus, unless it is an intermediate.

The constraint of the *p*-*tert*-butylcalix[4]arene apparently stabilises a six-coordinate but not a five-coordinate geometry for phosphorus. This is in marked contrast to the constraint imposed by cyclen. Thus, the equilibrium between the closed **5a** and open **5b** tautomers is shifted to the right when the macrocycle is *p*-*tert*-butylcalix[4]arene (E = oxygen) and to the left with cyclen (E = nitrogen).

We obtained the X-ray crystal structure of **3**§ to see if it might give insight into the above observations (all attempts at growing suitable crystals of **1** were fruitless). The structure is



§ Crystal data for **3**: [C₅₄H₇₅O₆NPLi]·2THF, *M_r* = 1016.32. Monoclinic, *P*2₁/*n*, *a* = 18.805(7), *b* = 13.465(5), *c* = 25.197(10) Å, β = 111.13(3)°, *U* = 5951(4) Å³, *Z* = 4, *D_c* = 1.134 g·cm^{–3}, μ = 1.029 cm^{–1}. Of 6295 data collected on Nicolet R3m/V, Mo-Kα, 2θ 3.0–42.0°, at –63 °C, 3509 reflections were observed [*I* > 3.0σ(*I*)]. Data were corrected for Lorentz and polarization effects, but not for absorption. The structure was solved by direct methods using SHELXTL-Plus (G. M. Sheldrick, Structure Determination Software packages, Siemens analytical X-Ray Instruments, Inc. USA, 1990). The hydrogen atom attached to P was located on difference Fourier maps but not refined, while the remaining hydrogens were included using a riding model. All non-hydrogen atoms were refined anisotropically with the BLOC technique converging to *R* = 0.072, *R_w* = 0.075, GOF = 2.35, Δρ: 0.43, –0.39 e·Å^{–3}. 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.

† In an inert atmosphere, **1** (54 mg, 0.075 mmol) was heated to 320 °C for 2 h in the solid-state, yielding pure **4** as a white, air-stable solid (50 mg, 99%). M.p. (nitrogen-filled tube) 385–387 °C. Anal. calcd. for C₄₄H₅₃O₄P: C, 78.08; H, 7.89. Found: C, 78.75; H, 8.44. ¹H NMR (CD₂Cl₂): δ 1.20 (s, 9H), 1.33 (s, 9H), 1.39 (s, 18H), 3.62 (d, ²J_{HH} 15 Hz, 2H), 3.71 (d, ²J_{HH} 17 Hz, 2H), 4.29 (d, ²J_{HH} 17 Hz, 2H), 4.49 (d, ²J_{HH} 15 Hz, 2H), 4.74 (s, OH, 1H), 7.11 (s, 2H), 7.20 (d, ⁴J_{HH} 2 Hz, 2H), 7.25 (s, 2H), 7.26 (d, ⁴J_{HH} 2 Hz, 2H).

‡ In an inert atmosphere, a stirred solution of **1** (35 mg, 0.048 mmol) in CDCl₃ (0.5 ml) was treated dropwise with trifluoroacetic acid (4 μl, 0.05 mmol). Within 15 min, ³¹P and ¹H NMR spectra of the solution indicated the presence of **4** and Me₂NH₂⁺ (as well as a trace of unreacted **1**).

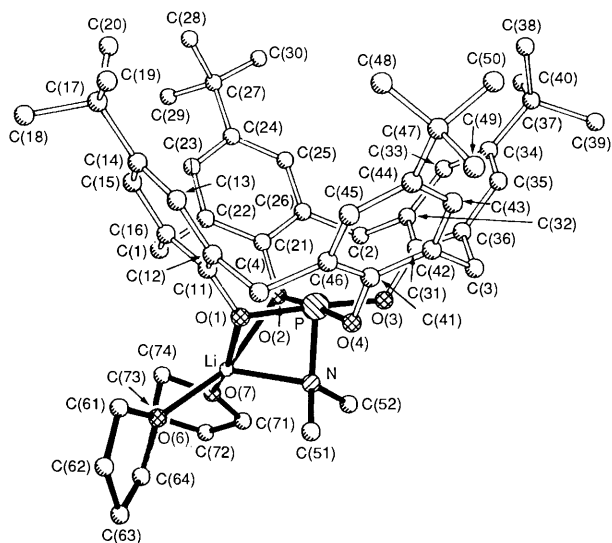
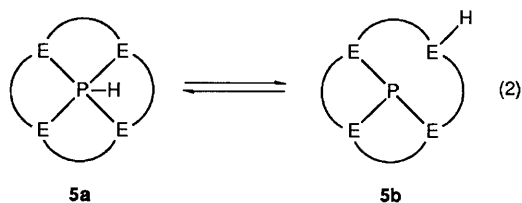


Fig. 1 Computer-generated drawing of $\text{Li}[p\text{-tert-butylcalix-4]areneP(H)NMe}_2$ **3**, tetrahydrofuran solvate, hydrogen atoms omitted for clarity. Selected bond lengths (\AA) and angles ($^\circ$): P–O(1) 1.789(4), P–O(2) 1.803(5), P–O(3) 1.720(5), P–O(4) 1.715(5), P–N 1.763(7), O(1)–C(11) 1.364(9), O(1)–Li 2.248(15), O(2)–C(21) 1.366(10), O(2)–Li 2.071(14), O(3)–C(31) 1.389(10), Li–N 2.052(15), N–C(51) 1.487(9), N–C(52) 1.470(8); O(1)–P–O(2) 86.5(2), O(1)–P–O(3) 175.5(3), O(1)–P–O(4) 91.0(2), O(2)–P–O(3) 90.6(2), O(2)–P–O(4) 175.7(3), O(3)–P–O(4) 91.7(2), O(1)–P–N 84.8(2), O(2)–P–N 84.8(3), O(3)–P–N 91.5(3), O(4)–P–N 91.5(3), P–O(1)–C(11) 120.6(4), P–O(2)–C(21) 122.5(5), P–O(3)–C(31) 124.9(5), P–O(4)–C(41) 124.2(5), P–N–Li 90.1(5), P–N–C(51) 118.1(5), P–N–C(52) 118.1(5), C(51)–N–C(52) 109.1(6).

illustrated in Fig. 1, and selected bond distances and angles are given in the caption. In addition to confirming the basic six-coordinate geometry for phosphorus, with the hydrogen (not shown) inside the basket and the dimethylamino group outside, several key features are evident. The lithium is bonded to two oxygens of the calixarene, as well as to nitrogen. Two molecules of THF are bonded to lithium (there are an additional two molecules of THF not shown, one inside

the basket and one outside). The phosphorus is almost coplanar with the four oxygens, lying 0.054 \AA above (inside the basket) the mean plane of the oxygens [sum of the *cis* O–P–O angles about phosphorus is $359.8(4)^\circ$]. The P–O–C angles are within the usual range.⁵ The P–O(1) and P–O(2) bonds are significantly longer than the other P–O bonds due to the additional complexation of the oxygens to lithium; however, even the P–O(3) and P–O(4) bond lengths are about 0.05 \AA or more longer than in other high-coordinate species.⁶

The geometry about phosphorus in **3** may be the key to the inability to observe a pentacoordinate derivative. The most likely structure of such a species should be a square pyramid (ideal *trans* basal angle of 150°)⁶ with the phosphorus lying out the plane of the four oxygens (either outside or, perhaps, inside the basket) and the hydrogen occupying the unique apical position. This would elongate the P–O bonds even more and alter the P–O–C angles, perhaps to such an extent as to force P–O bond cleavage. For a trigonal bipyramidal geometry, the equatorial O–P–O angle would most likely be too small to accommodate four P–O bonds. Further support for this argument comes from a related structure⁷ in which molybdenum is bonded to all four oxygens of *p-tert-butylcalix-4*arene, as well as to another oxygen (outside the basket) and a loosely bound water (inside the basket). The Mo–O (calixarene) bonds are about 0.15 \AA longer than the P–O bonds in **3**, and the Mo lies $0.337(3) \text{ \AA}$ below (outside the basket) the oxygen plane.

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