

Facile Synthetic Route to Cone-shaped Phosphorylated [CH₂P(O)Ph₂] Calix[4]arenes

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Selective incorporation of one, two or four CH₂P(O)Ph₂ substituents at specific sites in *para-tert*-butylcalix[4]arene was achieved using NaH and an appropriate alkylating agent; the tetrasubstituted compound (structure established by X-ray crystallography) was quantitatively reduced to the corresponding tetraphosphine L⁶ which, by reaction with [Pd(C₆H₄CH₂NMe₂-o)Cl]₂, gave access to the tetranuclear complex [Pd(C₆H₄CH₂NMe₂-o)Cl]₄L⁶.

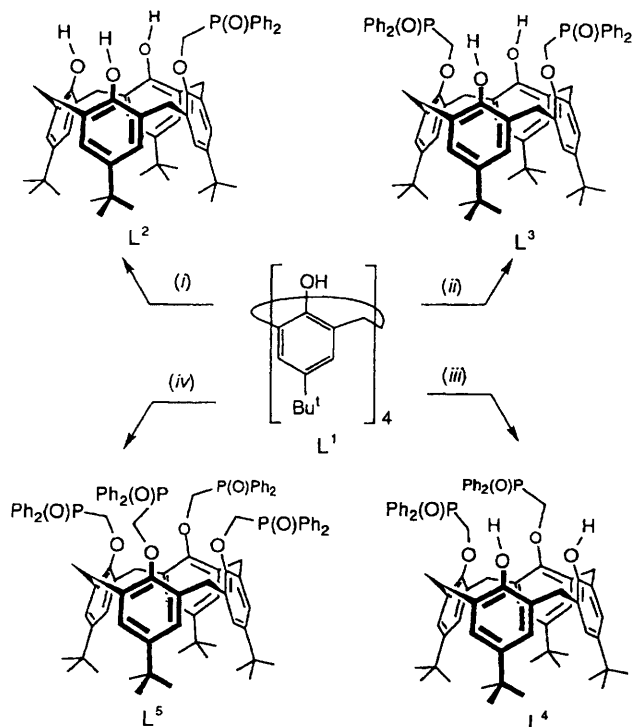
Calixarenes derived from phenolic compounds are valuable pre-organizing matrices for preparation of multifunctional host molecules¹ since they often adopt a cone conformation possessing a well-ordered cavity defined by substituents at the hydroxylic groups. Current and potential applications of such molecules include their use as selective complexing agents² and as sensors for analytical purposes,³ the preparation of new molecular materials,⁴ and homogeneous catalysts containing transition-metal centres.⁵ In view of the many rapid developments in this field, it has become essential to develop efficient methodologies^{1b,6} for the selective functionalisation of the now readily available (HO)_n-calix[*n*]arenes.⁷ Following our previous work on macrocyclic ligands containing pendant phosphine groups, we now describe convenient syntheses of novel *para-tert*-butylcalix[4]arene-derived molecules containing one, two or four CH₂P(O)Ph₂ groups covalently bound to the phenolic oxygen atoms. Such phosphoryl groups offer interesting possibilities as specific complexing agents for a wide variety of metal ions,⁸ notably for lanthanides and actinides, and also constitute valuable precursors for the preparation of phosphine ligands.⁹ It is important to realize that the combination of P(O)R₂ groups with molecular receptors of well-defined stereochemistry and cavity dimension provides new possibilities for the site-selective binding of metal ions whereas receptors with closely-appended phosphino groups are particularly promising materials for the preparation of transition-metal-based catalysts possessing shape-recognition qualities.¹⁰

Treatment of *para-tert*-butylcalix[4]arene L¹ with NaH (3 equivalents) and subsequent reaction with Ph₂P(O)CH₂I¹¹ (2.2 equivalents) in refluxing tetrahydrofuran (thf) gave after 5 d the monofunctionalized calix[4]arene L²† in ca. 50% yield (Scheme 1). The ¹H NMR spectrum of L² displays two distinct AB spin systems of equal intensity for the C₆H₂CH₂C₆H₂ bridges and two OH signals (intensity 2:1). This pattern, together with the chemical shift values of the C₆H₂CH₂C₆H₂ carbon atoms,¹² is fully consistent with the compound existing exclusively in a cone conformation. Under similar conditions but using toluene as solvent (80 °C), a double alkylation reaction occurred, leading to formation of the distally-substituted product L³‡ (yield ca. 80%). As expected for a 1,3-

difunctionalized calix[4]arene in a cone conformation, the ¹H NMR spectrum of L³ displays a single AB spin system for the bridging C₆H₂CH₂C₆H₂ groups; the cone-shaped structure was confirmed by the ¹³C NMR spectrum. It is worth mentioning that treatment of L¹ with K₂CO₃ and Ph₂P(O)CH₂I in acetonitrile selectively yielded L³, but in this case the reaction was much slower than with the NaH-toluene procedure (*ca.* 30 d are required for a complete conversion of L¹). The formation of the proximally disubstituted analogue L⁴ was realized by reacting L¹ with NaH and Ph₂P(O)CH₂O₃SC₆H₄Me-*p*¹³ in a refluxing thf-dmf (9:1, v/v) (dmf = dimethylformamide) mixture for 2 d. However, under these conditions, the yield for L⁴ did not exceed 25%. The ¹H NMR spectrum of L⁴ shows the characteristic signals expected for a 1,2-functionalized calix[4]arene; namely, three AB spin systems for the C₆H₂CH₂C₆H₂ hydrogen atoms (intensity 2:4:2) and two Bu^t signals (18:18). The cone

† Selected data for L²: yield 50%, m.p. > 270 °C (Found: C, 79.4; H, 8.0. C₅₇H₆₇O₅P requires C, 79.3; H, 7.8%; *M* 863). FAB mass spectrum: *M*⁺ 863.1 (calc. 862). $\tilde{\nu}_{\text{max}}/\text{cm}^{-1}$ (OH) 3370m, 3178m. (P=O, tentative assignment) 1202ms; δ_{H} (200 MHz, CDCl₃) 9.76 (1 H, s, OH), 8.87 (2 H, s, OH), 8.10–8.00 and 7.65–7.60 (10 H, m, PPh₂), 7.05 and 6.95 [4 H, AB system, ⁴*J*(AB) 2 Hz, *m*-C₆H₂], 7.03 (4 H, s, *m*-C₆H₂), 5.01 [2 H, d, ²*J*(PH) 3 Hz, OCH₂P(O)Ph₂], 4.64 and 3.39 [4 H, AB system, ²*J*(AB) 13 Hz, C₆H₂CH₂C₆H₂], 4.14 and 3.39 [4 H, AB system, ²*J*(AB) 13 Hz, C₆H₂CH₂C₆H₂], 1.23 (9 H, s, Bu^t), 1.21 (18 H, s, Bu^t), 1.17 (9 H, s, Bu^t); δ_{C} (50 MHz, CDCl₃) 151.68–126.97 (aromatic quaternary C), 132.65–125.43 (aromatic CH), 74.03 [d, *J*(PC) 81 Hz, OCH₂P(O)Ph₂], 34.10, 33.90 and 33.84 [3 s, C(CH₃)₃], 32.83 and 32.17 (2 s, C₆H₂CH₂C₆H₂), 31.47 [br s, C(CH₃)₃], 31.12 [s, C(CH₃)₃]; δ_{P} (81 MHz, CDCl₃, H₃PO₄) 27.9 (s).

‡ Selected data for L³: yield 78%, m.p. > 270 °C (Found: C, 78.2; H, 7.1. C₇₀H₇₈O₆P₂ requires C, 78.0; H, 7.3%; *M* 1077); $\tilde{\nu}_{\text{max}}/\text{cm}^{-1}$ (OH) 3298m, (P=O, tentative assignment) 1206ms (KBr); δ_{H} (200 MHz, CDCl₃) 8.07–7.97 (8 H, m, PPh₂), 7.45–7.44 [12 H, m, P(O)Ph₂], 7.01 (4 H, s, *m*-C₆H₂), 6.56 (4 H, s, *m*-C₆H₂), 5.68 (2 H, s, OH), 4.63 [4 H, d, ²*J*(PH) 6 Hz, OCH₂P(O)Ph₂], 4.12 and 3.16 [8 H, AB system, ²*J*(AB) 13 Hz, C₆H₂CH₂C₆H₂], 1.31 and 0.81 [36 H (1:1), 2 s, Bu^t]; δ_{C} (50 MHz, CDCl₃) 151.43–125.58 (aromatic quaternary C), 132.31–124.97 (aromatic CH), 74.63 [d, *J*(PC) 82 Hz, OCH₂P(O)Ph₂], 33.52 [br s, C(CH₃)₃], 33.31 (s, C₆H₂CH₂C₆H₂), 31.62 and 30.76 [2 s, C(CH₃)₃]; δ_{P} (81 MHz, CDCl₃, H₃PO₄) 25.7 (s).



Scheme 1 (i) NaH (3 equivalents, reflux in thf, 3 h), then $\text{Ph}_2\text{P}(\text{O})\text{CH}_2\text{I}$ (2.2 equivalents, reflux in thf, 5 d); (ii) NaH (5 equivalents, 4 h, toluene, 80 °C), then $\text{Ph}_2\text{P}(\text{O})\text{CH}_2\text{I}$ (2.5 equivalents, toluene, 80 °C, 6 d); (iii) NaH [2.5 equivalents, reflux in thf-dmf (9:1, v/v), 1 h], then $\text{Ph}_2\text{P}(\text{O})\text{CH}_2\text{O}_3\text{SC}_6\text{H}_4\text{Me-p}$ [2.2 equivalents, reflux in thf-dmf (9:1, v/v), 48 h]; (iv) NaH (6 equivalents, toluene, 80 °C, 6 h), then $\text{Ph}_2\text{P}(\text{O})\text{CH}_2\text{O}_3\text{SC}_6\text{H}_4\text{Me-p}$ (4.2 equivalents, toluene, 80 °C, 3 d)

conformation of L^{4*} was again evident from the ^{13}C NMR spectrum.

For the synthesis of the tetrasubstituted compound L^5 ,† the use of the highly reactive tosylated phosphine oxide $\text{Ph}_2\text{P}(\text{O})\text{CH}_2\text{O}_3\text{SC}_6\text{H}_4\text{Me-p}$ proved to be very efficient. Thus, the tetrapode L^5 was obtained in high yield by heating a suspension of L^1 , NaH and $\text{Ph}_2\text{P}(\text{O})\text{CH}_2\text{O}_3\text{SC}_6\text{H}_4\text{Me-p}$ (1:6:4.2) in toluene at 80 °C for 3 d. The cone structure of L^5 was inferred from the ^1H and ^{13}C NMR spectra. In the range –60 to 30 °C, NMR spectra of L^5 show four equivalent phosphines and four

equivalent phenoxy rings. Based on recent studies on the dynamic behaviour of calix[4] arenes,¹⁴ these NMR data may be interpreted in terms of a fast C_{2v} – C_{2v} exchange, rather than simply corresponding to a static C_4 -symmetrical structure. An X-ray diffraction study‡ establishes that, in the solid state, the symmetry of the calixarene matrix is close to C_{2v} (Fig. 1), this structure being characterized by two facing phenoxy rings oriented in an almost parallel fashion [dihedral angle $3(2)^\circ$], with the other two approaching perpendicularity [dihedral angle $97.4(2)^\circ$]. Such arrangements are not unusual for tetrasubstituted calix[4]arenes.¹⁶ One phosphoryl group points inside the cavity created from the four pendant groups, whereas the other three may be regarded as oriented tangentially with respect to the substituent barrel.

Reduction of L^5 with SiH_3Ph at 100 °C (7 d) resulted in quantitative formation of the tetraphosphine L^6 § (Scheme 2). The NMR data of L^6 are fully consistent with a cone conformation. The phosphino groups appear as a sharp singlet in the ^{31}P NMR spectrum (CDCl_3 , δ –20.3).

Ligand L^6 is suitable for the build-up of polynuclear complexes. Thus, reaction of L^6 with 2 equivalents of $[\{\text{Pd}(\text{C}_6\text{H}_4\text{CH}_2\text{NMe}_2\text{-}o)\text{Cl}\}_2]$ in CH_2Cl_2 afforded complex **1**¶ in ca. 85% yield (Scheme 2).

The FAB mass spectrum of **1** displays a peak at 2510.8 (6%), corresponding to a $[\text{M} - \text{Cl}]^+$ ion. As inferred from the presence of a $^4J(\text{P}-\text{NCH}_3)$ coupling constant (2 Hz), each of the palladocyclic fragments is bonded to a phosphorus atom. The ^1H and ^{31}P NMR (CDCl_3) spectra of **1**, measured at 55 °C, indicate equivalence on the NMR time-scale of the four pendant arms and of the four phenoxy rings. Note, the signals of the ^1H NMR spectrum broaden upon lowering the temperature, presumably due to structural dynamic fluctuations in solution. This broadening may be ascribed to hindered rotation around the individual palladium–phosphorus bonds at lower temperatures, as results from steric interactions between the palladocycles and the calixarene fragment.

‡ Crystal data. $\text{C}_{96}\text{H}_{100}\text{O}_8\text{P}_4 \cdot \text{CH}_2\text{Cl}_2$, $M = 1590.69$, triclinic, space group $P\bar{1}$, $a = 14.209(4)$, $b = 22.607(7)$, $c = 13.895(4)$ Å, $\alpha = 95.63(2)$, $\beta = 102.91(2)$, $\gamma = 84.20(2)^\circ$, $U = 4315.1$ Å³, $Z = 2$, $D_c = 1.224$ g cm^{–3}, $F(000) = 1684$, Philips PW1100/16 diffractometer, Cu-K α radiation ($\lambda = 1.5405$ Å), $T = 173$ K, $\mu(\text{Cu-K}\alpha) = 18.229$ cm^{–1}, dimensions $0.35 \times 0.30 \times 0.24$ mm, ω scan, $\theta_{\min} = 3$, $\theta_{\max} = 55^\circ$, 7561 observed data [$I > 3\sigma(I)$], weighting scheme $w = 1/\sigma^2$ where $\sigma^2(F^2) = \sigma_c^2 + (0.08I)^2$. Structure solved using the Enraf–Nonius MOLEN¹⁵ package and refined by full-matrix least squares with anisotropic thermal parameters for all non-hydrogen atoms, final $R = 0.062$ and $R_w = 0.086$. Atomic coordinates, thermal parameters and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1995, Issue 1, pp. xxv–xxx.

§ Selected data for L^6 : yield 84%, m.p. 211.5–212 °C (Found: C, 80.1; H, 7.2. $\text{C}_{96}\text{H}_{100}\text{O}_4\text{P}_4$ requires C, 80.0; H, 7.0%; M 1441); FAB mass spectrum: M^+ 1441.8 (calc. 1441). δ_{H} (200 MHz, CDCl_3) 7.29–7.11 (40 H, m, PPh₂), 6.54 (8 H, s, $m\text{-C}_6\text{H}_2$), 5.07 (8 H, s, OCH_2PPh_2), 4.43 and 2.87 [8 H, AB system, $^2J(\text{AB})$ 13 Hz, $\text{C}_6\text{H}_2\text{CH}_2\text{C}_6\text{H}_2$], 1.01 (36 H, s, Bu^t); δ_{C} (50 MHz, CDCl_3) 153.24 [d, $^3J(\text{PC}) < 3$ Hz, quaternary C–O], 144.73 (aromatic quaternary C), 137.56 [d, $J(\text{PC})$ 15 Hz, quaternary C–P], 133.77, 133.77, 133.77 (aromatic quaternary C), 133.23–124.65 (aromatic CH), 76.27 [d, $J(\text{PC})$ 33 Hz, OCH_2PPh_2], 33.63 [s, $\text{C}(\text{CH}_3)_3$], 32.72 (s, $\text{C}_6\text{H}_2\text{CH}_2\text{C}_6\text{H}_2$), 31.27 [s, $\text{C}(\text{CH}_3)_3$]; δ_{P} (81 MHz, CDCl_3 , H_3PO_4) –20.3 (s).

¶ Selected data for **1**: yield 86% (Found: C, 62.5; H, 5.5. $\text{C}_{132}\text{H}_{148}\text{Cl}_4\text{N}_4\text{O}_4\text{P}_4\text{Pd}_4$ requires C, 62.3; H, 5.9%; M 2546); FAB mass spectrum M^+ 2510.8 [calc. for $(\text{M} - \text{Cl})$ 2510]. δ_{H} (200 MHz, 328 K, CDCl_3) 7.87–7.78 (40 H, 2 m, PPh₂), 6.91–6.16 (16 H, ABMN system, aryl H of dimethylbenzylamine), 6.42 (8 H, s, $m\text{-C}_6\text{H}_2$), 5.66 (8 H, br s, OCH_2PPh_2), 4.49 and 2.70 [8 H, AB system, $^2J(\text{AB})$ 13 Hz, $\text{C}_6\text{H}_2\text{CH}_2\text{C}_6\text{H}_2$], 3.98 (8 H, br s, NCH_2), 2.75 [24 H, d, $^4J(\text{PH})$ 2 Hz, NMe_2], 1.00 (36 H, s, Bu^t); δ_{C} (50 MHz, 328 K, CDCl_3) 153.66, 151.24, 147.95, 142.97, 131.54 and 131.10 (aromatic quaternary C), 137.19, 137.00, 135.05, 131.54, 128.48, 128.29, 125.19, 124.87, 124.78, 123.31 and 121.91 (aromatic CH), 75.65 [d, $J(\text{PC})$ 23 Hz, OCH_2PPh_2], 73.07 (s, NCH_2), 50.19 (s, NMe_2), 33.53 [s, $\text{C}(\text{CH}_3)_3$], 31.69 (s, $\text{C}_6\text{H}_2\text{CH}_2\text{C}_6\text{H}_2$), 31.49 [s, $\text{C}(\text{CH}_3)_3$]; δ_{P} (81 MHz, 328 K, CDCl_3 , H_3PO_4) 33.1 (s).

* Selected data for L^4 : yield 25%, m.p. 255 °C (Found: C, 78.1; H, 7.1. $\text{C}_{70}\text{H}_{78}\text{O}_6\text{P}_2$ requires C, 78.0; H, 7.3%; M 1077). FAB mass spectrum: M^+ 1076.5 (calc. 1076). $\tilde{\nu}_{\text{max}}/\text{cm}^{-1}$ (OH) 3378m (P=O, tentative assignment) 1192s (KBr); δ_{H} (200 MHz, CDCl_3) 8.64 (2 H, s, OH), 7.91–7.82 and 7.56–7.30 [20 H, m, $\text{P}(\text{O})\text{Ph}_2$], 6.89 (4 H, br s, $m\text{-C}_6\text{H}_2$), 6.71 and 6.61 [8 H, AB system, $^4J(\text{AB})$ 2 Hz, $m\text{-C}_6\text{H}_2$], 5.11 and 4.99 [4 H, ABX system, $^2J(\text{AB})$ 14 Hz, $^2J(\text{AX})$ 4 Hz, $^2J(\text{BX})$ 0 Hz, $\text{OCH}_2\text{P}(\text{O})\text{Ph}_2$], 4.82 and 3.25 [2 H, AB system, $^2J(\text{AB})$ 13 Hz, $\text{C}_6\text{H}_2\text{CH}_2\text{C}_6\text{H}_2$], 4.67 and 3.13 [4 H, AB system, $^2J(\text{AB})$ 13 Hz, $\text{C}_6\text{H}_2\text{CH}_2\text{C}_6\text{H}_2$], 4.29 and 3.27 [2 H, AB system, $^2J(\text{AB})$ 14 Hz, $\text{C}_6\text{H}_2\text{CH}_2\text{C}_6\text{H}_2$], 1.19 and 1.00 [36 H (1:1), 2 s, Bu^t]; δ_{C} (50 MHz, CDCl_3) 153.46–127.02 (aromatic quaternary), 132.33–124.91 (aromatic CH), 72.94 [d, $J(\text{PC})$ 80 Hz, $\text{OCH}_2\text{P}(\text{O})\text{Ph}_2$], 33.77 and 33.66 [2 s, $\text{C}(\text{CH}_3)_3$], 32.14, 31.92 and 29.67 (3 s, $\text{C}_6\text{H}_2\text{CH}_2\text{C}_6\text{H}_2$), 31.46 and 31.14 [2 s, $\text{C}(\text{CH}_3)_3$]; δ_{P} (81 MHz, $\text{CH}_2\text{Cl}_2\text{-C}_6\text{D}_6$, H_3PO_4) 26.6 (s).

† Selected data for L^5 : yield 80%, m.p. >270 °C (Found: C, 76.4; H, 6.7. $\text{C}_{96}\text{H}_{100}\text{O}_8\text{P}_4$ requires C, 76.6; H, 6.7%; M 1506); $\tilde{\nu}_{\text{max}}/\text{cm}^{-1}$ (P=O, tentative assignment) 1196s (KBr); δ_{H} (200 MHz, CDCl_3) 7.81–7.72 and 7.37–7.21 (40 H, m, PPh₂), 6.37 (8 H, s, $m\text{-C}_6\text{H}_2$), 5.25 [8 H, s, $\text{OCH}_2\text{P}(\text{O})\text{Ph}_2$], 4.82 and 2.74 [8 H, AB system, $^2J(\text{AB})$ 13 Hz, $\text{C}_6\text{H}_2\text{CH}_2\text{C}_6\text{H}_2$], 0.94 (36 H, s, Bu^t); δ_{C} (50 MHz, CDCl_3) 152.98 [d, $^3J(\text{PC})$ 4 Hz, quaternary C–O], 144.72, 133.43, 133.11 (3 s, aromatic quaternary C), 131.17, 130.98, 128.36, 128.13 and 124.76 (aromatic CH), 71.15 [d, $J(\text{PC})$ 77 Hz, $\text{OCH}_2\text{P}(\text{O})\text{Ph}_2$], 33.54 [s, $\text{C}(\text{CH}_3)_3$], 32.31 (s, $\text{C}_6\text{H}_2\text{CH}_2\text{C}_6\text{H}_2$), 31.20 [s, $\text{C}(\text{CH}_3)_3$]; δ_{P} (81 MHz, CDCl_3 , H_3PO_4) 25.7 (s).

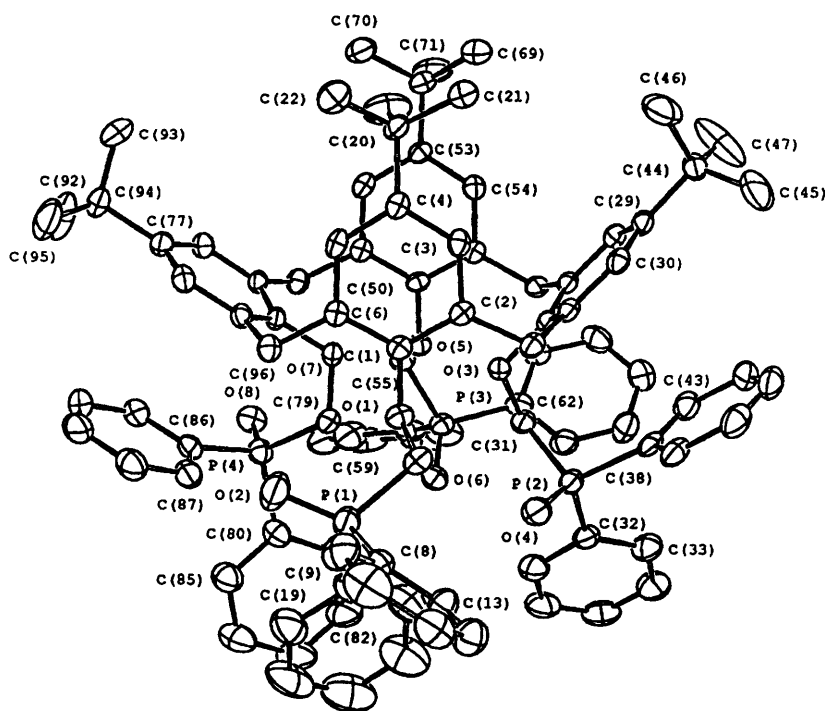
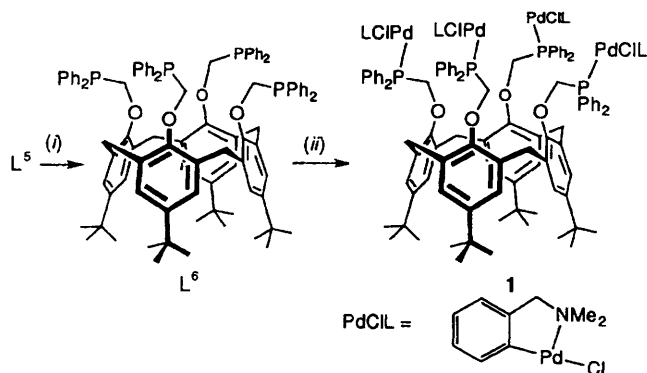


Fig. 1 Molecular structure of L^5 . Selected bond lengths (Å) and angles (°): P(1)–O(2) 1.470(3), P(1)–C(8) 1.804(4), P(1)–C(14) 1.805(4), P(1)–C(7) 1.822(4), P(2)–O(4) 1.477(2), P(2)–C(32) 1.806(3), P(2)–C(38) 1.801(3), P(2)–C(31) 1.827(3), P(3)–O(6) 1.474(2), P(3)–C(56) 1.791(4), P(3)–C(62) 1.796(4), P(3)–C(55) 1.432(4), P(4)–O(8) 1.484(2), P(4)–C(80) 1.802(4), P(4)–C(86) 1.801(4), P(4)–C(79) 1.830(3); P(1)–C(7)–O(1) 112.2(2), P(2)–C(31)–O(3) 115.7(2), P(3)–C(55)–O(5) 110.2(2), P(4)–C(79)–O(7) 117.7(2)



Scheme 2 (i) SiH_3Ph , 100 °C, 7 d; (ii) $[(\text{PdCIL})_2]$ (2 equivalents, CH_2Cl_2 , room temperature, $L = \text{C}_6\text{H}_4\text{CH}_2\text{NMe}_2\text{-o}$)

In summary, this study describes convenient synthetic methodology of new phosphorus-functionalized calix[4]arenes existing in a cone conformation. We emphasize, in particular, the determinant role of the reaction conditions used (base, solvent, alkylating agent) as a means of controlling the degree of alkylation of the calixarene matrix subunit. To the best of our knowledge, compound L^6 is the first example of a tetraphosphine ligand built on the lower rim of a calix[4]arene matrix. In following studies we expect further to exploit the ability of L^6 to form polynuclear transition metal complexes and to establish its potential for construction of heterobimetallic catalysts.

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