Facile Synthetic Route to Cone-shaped Phosphorylated $[CH_2P(O)Ph_2]$ Calix[4]arenes

Cedric Dieleman,[a] Cyrille Loeber,[a] Dominique Matt,*[a] André De Cian[b] and Jean Fischer[b]
[a] *Ecole Européenne des Hautes Etudes des Industries Chimiques de Strasbourg, Groupe de Chimie Inorganique Moléculaire, 1 rue Blaise Pascal, F-67008 Strasbourg Cedex, France*
[b] *Université Louis Pasteur, Laboratoire de Cristallochimie et Chimie Structurale, 4 rue Blaise Pascal, F-67070, Strasbourg Cedex, France*

Selective incorporation of one, two or four $CH_2P(O)Ph_2$ 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 L^6 which, by reaction with $[\{Pd(C_6H_4CH_2NMe_2\text{-}o)Cl\}_2]$, gave access to the tetranuclear complex $[\{Pd(C_6H_4CH_2NMe_2\text{-}o)Cl\}_4L^6]$.

Calixarenes derived from phenolic compounds are valuable pre-organizing matrices for preparation of multifunctional host molecules[1] 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 agents[2] 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 $CH_2P(O)Ph_2$ 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 $P(O)R_2$ 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 L^1 with NaH (3 equivalents) and subsequent reaction with $Ph_2P(O)CH_2I$[11] (2.2 equivalents) in refluxing tetrahydrofuran (thf) gave after 5 d the monofunctionalized calix[4]arene L^2† in *ca.* 50% yield (Scheme 1). The ^1H NMR spectrum of L^2 displays two distinct AB spin systems of equal intensity for the $C_6H_2C\mathit{H}_2C_6H_2$ bridges and two OH signals (intensity 2:1). This pattern, together with the chemical shift values of the $C_6H_2\mathit{C}H_2C_6H_2$ 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 L^3‡ (yield *ca.* 80%). As expected for a 1,3-difunctionalized calix[4]arene in a cone conformation, the ^1H NMR spectrum of L^3 displays a single AB spin system for the bridging $C_6H_2C\mathit{H}_2C_6H_2$ groups; the cone-shaped structure was confirmed by the ^{13}C NMR spectrum. It is worth mentioning that treatment of L^1 with K_2CO_3 and $Ph_2P(O)CH_2I$ in acetonitrile selectively yielded L^3, 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 L^1). The formation of the proximally disubstituted analogue L^4 was realized by reacting L^1 with NaH and $Ph_2P(O)CH_2O_3SC_6H_4Me\text{-}p$[13] in a refluxing thf–dmf (9:1, v/v) (dmf = dimethylformamide) mixture for 2 d. However, under these conditions, the yield for L^4 did not exceed 25%. The ^1H NMR spectrum of L^4 shows the characteristic signals expected for a 1,2-functionalized calix[4]arene; namely, three AB spin systems for the $C_6H_2C\mathit{H}_2C_6H_2$ hydrogen atoms (intensity 2:4:2) and two Bu^t signals (18:18). The cone

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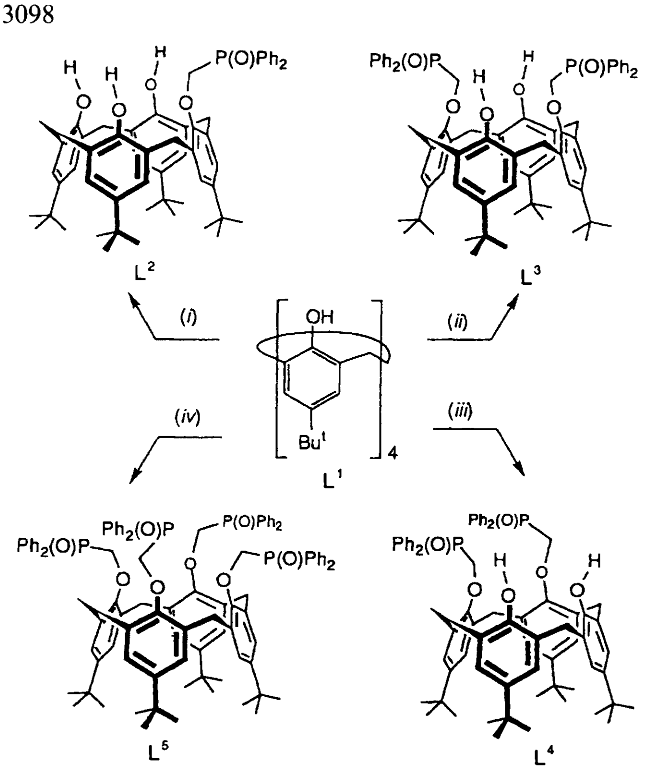
† Selected data for L^2: yield 50%, m.p. > 270 °C (Found: C, 79.4; H, 8.0. $C_{57}H_{67}O_5P$ requires C, 79.3; H, 7.8%; *M* 863). FAB mass spectrum: M^+ 863.1 (calc. 862). $\tilde{\nu}_{max}/cm^{-1}$ (OH) 3370m, 3178m. (P=O, tentative assignment) 1202ms; δ_H(200 MHz, $CDCl_3$) 9.76 (1 H, s, OH), 8.87 (2 H, s, OH), 8.10–8.00 and 7.65–7.60 (10 H, m, PPh_2), 7.05 and 6.95 [4 H, AB system, ^4J(AB) 2 Hz, *m*-C_6H_2], 7.03 (4 H, s, *m*-C_6H_2), 5.01 [2 H, d, ^2J(PH) 3 Hz, $OC\mathit{H}_2P(O)Ph_2$], 4.64 and 3.39 [4 H, AB system, ^2J(AB) 13 Hz, $C_6H_2C\mathit{H}_2C_6H_2$], 4.14 and 3.39 [4 H, AB system, ^2J(AB) 13 Hz, $C_6H_2C\mathit{H}_2C_6H_2$], 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, $CDCl_3$) 151.68–126.97 (aromatic quaternary C), 132.65–125.43 (aromatic CH), 74.03 [d, *J*(PC) 81 Hz, $O\mathit{C}H_2P(O)Ph_2$], 34.10, 33.90 and 33.84 [3 s, $\mathit{C}(CH_3)_3$], 32.83 and 32.17 (2 s, $C_6H_2\mathit{C}H_2C_6H_2$), 31.47 [br s, $C(\mathit{C}H_3)_3$], 31.12 [s, $C(\mathit{C}H_3)_3$]; δ_P(81 MHz, $CDCl_3$, H_3PO_4) 27.9 (s).

‡ Selected data for L^3: yield 78%, m.p. > 270 °C (Found: C, 78.2; H, 7.1. $C_{70}H_{78}O_6P_2$ requires C, 78.0; H, 7.3%; *M* 1077); $\tilde{\nu}_{max}/cm^{-1}$ (OH) 3298m, (P=O, tentative assignment) 1206ms (KBr); δ_H(200 MHz, $CDCl_3$) 8.07–7.97 (8 H, m, PPh_2), 7.45–7.44 [12 H, m, $P(O)Ph_2$], 7.01 (4 H, s, *m*-C_6H_2), 6.56 (4 H, s, *m*-C_6H_2), 5.68 (2 H, s, OH), 4.63 [4 H, d, ^2J(PH) 6 Hz, $OC\mathit{H}_2P(O)Ph_2$], 4.12 and 3.16 [8 H, AB system, ^2J(AB) 13 Hz, $C_6H_2C\mathit{H}_2C_6H_2$], 1.31 and 0.81 [36 H (1:1), 2 s, Bu^t]; δ_C(50 MHz, $CDCl_3$) 151.43–125.58 (aromatic quaternary C), 132.31–124.97 (aromatic CH), 74.63 [d, *J*(PC) 82 Hz, $O\mathit{C}H_2P(O)Ph_2$], 33.52 [br s, $\mathit{C}(CH_3)_3$], 33.31 (s, $C_6H_2\mathit{C}H_2C_6H_2$), 31.62 and 30.76 [2 s, $C(\mathit{C}H_3)_3$]; δ_P(81 MHz, $CDCl_3$, H_3PO_4) 25.7 (s).



Scheme 1 (*i*) NaH (3 equivalents, reflux in thf, 3 h), then $Ph_2P(O)CH_2I$ (2.2 equivalents, reflux in thf, 5 d); (*ii*) NaH (5 equivalents, 4 h, toluene, 80 °C), then $Ph_2P(O)CH_2I$ (2.5 equivalents, toluene, 80 °C, 6 d); (*iii*) NaH [2.5 equivalents, reflux in thf–dmf (9:1, v/v), 1 h], then $Ph_2P(O)CH_2O_3SC_6H_4Me$-*p* [2.2 equivalents, reflux in thf–dmf (9:1, v/v), 48 h]; (*iv*) NaH (6 equivalents, toluene, 80 °C, 6 h), then $Ph_2P(O)CH_2O_3SC_6H_4Me$-*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 $Ph_2P(O)CH_2O_3SC_6H_4Me$-*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 $Ph_2P(O)CH_2O_3SC_6H_4Me$-*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)°], with the other two approaching perpendicularity [dihedral angle 97.4(2)°]. 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 $[\{Pd(C_6H_4CH_2NMe_2\text{-}o)Cl\}_2]$ 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 $[M - Cl]^+$ ion. As inferred from the presence of a $^4J(P\text{–}NCH_3)$ 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.

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[*] Selected data for L^4: yield 25%, m.p. 255 °C (Found: C, 78.1; H, 7.1. $C_{70}H_{78}O_6P_2$ requires C, 78.0; H, 7.3%; *M* 1077). FAB mass spectrum: M^+ 1076.5 (calc. 1076). $\tilde{\nu}_{max}/cm^{-1}$ (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, $P(O)Ph_2$], 6.89 (4 H, br s, *m*-C_6H_2), 6.71 and 6.61 [8 H, AB system, ^4J(AB) 2 Hz, *m*-C_6H_2], 5.11 and 4.99 [4 H, ABX system, ^2J(AB) 14 Hz, ^2J(AX) 4 Hz, ^2J(BX) 0 Hz, $OCH_AH_BP(O)Ph_2$], 4.82 and 3.25 [2 H, AB system, ^2J(AB) 13 Hz, $C_6H_2CH_2C_6H_2$], 4.67 and 3.13 [4 H, AB system, ^2J(AB) 13 Hz, $C_6H_2CH_2C_6H_2$], 4.29 and 3.27 [2 H, AB system, ^2J(AB) 14 Hz, $C_6H_2CH_2C_6H_2$], 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*(PC) 80 Hz, $OCH_2P(O)Ph_2$], 33.77 and 33.66 [2 s, $C(CH_3)_3$], 32.14, 31.92 and 29.67 (3 s, $C_6H_2CH_2C_6H_2$), 31.46 and 31.14 [2 s, $C(CH_3)_3$]; δ_P(81 MHz, CH_2Cl_2–C_6D_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. $C_{96}H_{100}O_8P_4$ requires C, 76.6; H, 6.7%; *M* 1506); $\tilde{\nu}_{max}/cm^{-1}$ (P=O, tentative assignment) 1196s (KBr); δ_H(200 MHz, $CDCl_3$) 7.81–7.72 and 7.37–7.21 (40 H, m, PPh_2), 6.37 (8 H, s, *m*-C_6H_2), 5.25 [8 H, s, $OCH_2P(O)Ph_2$], 4.82 and 2.74 [8 H, AB system, ^2J(AB) 13 Hz, $C_6H_2CH_2C_6H_2$], 0.94 (36 H, s, Bu^t); δ_C(50 MHz, $CDCl_3$) 152.98 [d, ^3J(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*(PC) 77 Hz, $OCH_2P(O)Ph_2$], 33.54 [s, $C(CH_3)_3$], 32.31 (s, $C_6H_2CH_2C_6H_2$), 31.20 [s, $C(CH_3)_3$]; δ_P(81 MHz, $CDCl_3$, H_3PO_4) 25.7 (s).

[‡] Crystal data. $C_{96}H_{100}O_8P_4\cdot CH_2Cl_2$, $M = 1590.69$, triclinic, space group $P\bar{1}$, $a = 14.209(4)$, $b = 22.607(7)$, $c = 13.895(4)$ Å, $\alpha = 95.63(2)$, $\beta = 102.91(2)$, $\gamma = 84.20(2)°$, $U = 4315.1$ Å^3, $Z = 2$, $D_c = 1.224$ g cm^{-3}, $F(000) = 1684$, Philips PW1100/16 diffractometer, Cu-Kα radiation (λ = 1.5405 Å), $T = 173$ K, μ(Cu-Kα) = 18.229 cm^{-1}, dimensions 0.35 × 0.30 × 0.24 mm, ω scan, $\theta_{min} = 3$, $\theta_{max} = 55°$, 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 MOLEN[15] 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. $C_{96}H_{100}O_4P_4$ 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, PPh_2), 6.54 (8 H, s, *m*-C_6H_2), 5.07 (8 H, s, OCH_2PPh_2), 4.43 and 2.87 [8 H, AB system, ^2J(AB) 13 Hz, $C_6H_2CH_2C_6H_2$], 1.01 (36 H, s, Bu^t); δ_C(50 MHz, $CDCl_3$) 153.24 [d, ^3J(PC) < 3 Hz, quaternary C–O], 144.73 (aromatic quaternary C), 137.56 [d, *J*(PC) 15 Hz, quaternary C–P], 133.77, (aromatic quaternary C), 133.23–124.65 (aromatic CH), 76.27 [d, *J*(PC) 33 Hz, OCH_2PPh_2], 33.63 [s, $C(CH_3)_3$], 32.72 (s, $C_6H_2CH_2C_6H_2$), 31.27 [s, $C(CH_3)_3$]; 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. $C_{132}H_{148}Cl_4N_4O_4P_4Pd_4$ requires C, 62.3; H, 5.9%; *M* 2546); FAB mass spectrum M^+ 2510.8 [calc. for (M − Cl) 2510]. δ_H(200 MHz, 328 K, $CDCl_3$) 7.87–7.78 (40 H, 2 m, PPh_2), 6.91–6.16 (16 H, ABMN system, aryl H of dimethylbenzylamine), 6.42 (8 H, s, *m*-C_6H_2), 5.66 (8 H, br s, OCH_2PPh_2), 4.49 and 2.70 [8 H, AB system, ^2J(AB) 13 Hz, $C_6H_2CH_2C_6H_2$], 3.98 (8 H, br s, NCH_2), 2.75 [24 H, d, ^4J(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*(PC) 23 Hz, OCH_2PPh_2], 73.07 (s, NCH_2), 50.19 (s, NMe_2), 33.53 [s, $C(CH_3)_3$], 31.69 (s, $C_6H_2CH_2C_6H_2$), 31.49 [s, $C(CH_3)_3$]; δ_P(81 MHz, 328 K, $CDCl_3$, H_3PO_4) 33.1 (s).

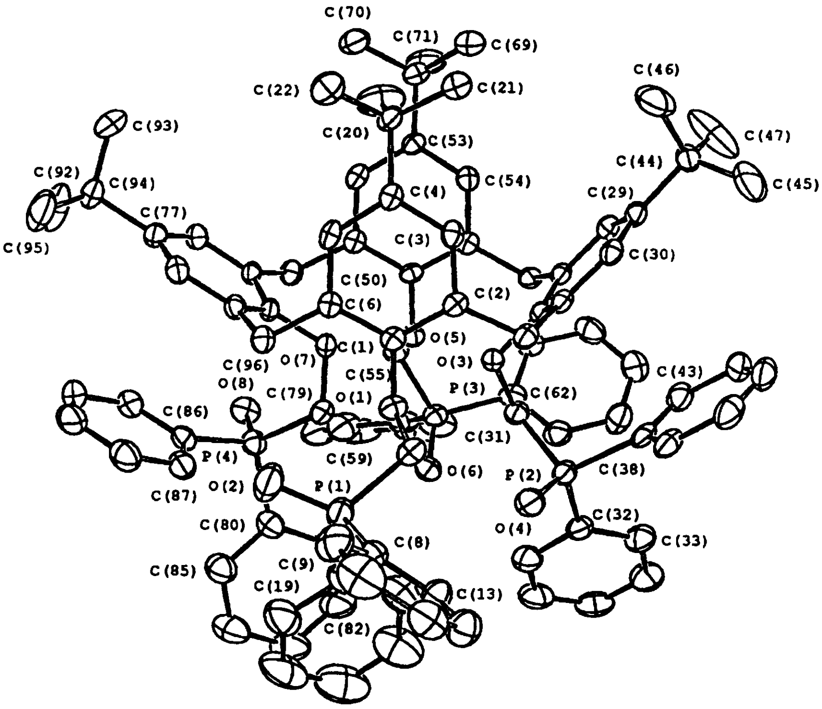
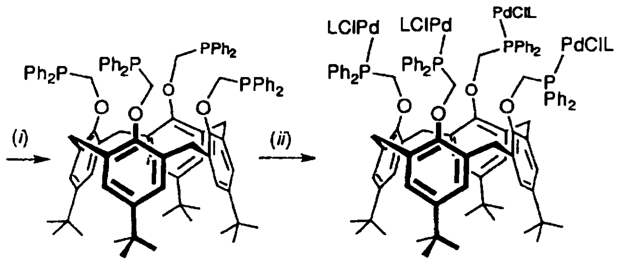


Fig. 1 Molecular structure of L^5. Selected bond lengths (Å) and angles (°): P(1)–O(2) 1.470(3), P(1)–C(8) 1.804(4), P(1)–C(14) 1.805(4), P(1)–C(7) 1.822(4), P(2)–O(4) 1.477(2), P(2)–C(32) 1.806(3), P(2)–C(38) 1.801(3), P(2)–C(31) 1.827(3), P(3)–O(6) 1.474(2), P(3)–C(56) 1.791(4), P(3)–C(62) 1.796(4), 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*) $[(PdClL)_2]$ (2 equivalents, CH_2Cl_2, room temperature, L = $C_6H_4CH_2NMe_2$-*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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