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Arranging phosphoryl ligands on a calixarene platform

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Abstract

Cone calix[4]arenes substituted at the lower rim by one to four $-CH_2P(O)Ph_2$ functionalities have been prepared in moderate to excellent yield, either directly from *p-tert*-butylcalix[4]arene or piecewise from calix[4]arenes containing easily removable protecting groups. The X-ray structure of a calix[4]arene-derived tris–(phosphine oxide) is presented. © 1997 Elsevier Science S.A.

Keywords: Calixarene; Phosphine oxide; Calixphosphine; Calixcrown; Tetraphosphine; X-ray diffraction

1. Introduction

Molecules containing a phosphine oxide functionality continue to attract considerable attention [1–5], especially in view of their potential use as ligands for the recovery of actinides from nuclear waste. Recent developments in this area have been stimulated by the work of Gatrone et al. [6,7] and of Conary et al. [8] using carbamoylphosphine oxides (CMPOs). This class of compound combines a phosphoryl subunit with an amide donor and has been shown to behave as potent extractants of actinides from acidic media. A logical extension to this area would involve the use of macrocyclic matrices functionalized with multiple phosphine oxides, but surprisingly such materials are scarce [9]. In these systems the macrocycle is intended to provide a platform that could promote synergy between the disparate anchored binding functions. Of the many macrocycles that could be considered for use as such platforms, the calix[4]arenes offer many advantages.

The calix[4]arene matrix has been used to support various phosphorus-containing ligands [10–30]. Indeed, we have recently described synthetic methodologies allowing construction of 1,3-difunctionalized *cone*-calix[4]arenes bearing two phosphoryl arms and appended chains equipped with a variety of donor sites (e.g. esters [31], amides [32], ethers [33]). Some of these compounds display valuable extractive properties towards the alkaline cations, and also for other monovalent cations such as Ag^+ or Cu^+ [34,35]. In extending the range of macrocyclic ligands having *exo*-($P=O$) and *exo*-(P(III)) substituents [23,36,37], we now report the preparation of new *p-tert*-butylcalix[4]arene (**1**) derivatives substituted with one or more phosphine oxide moieties. The synthetic strategy developed herein allows attachment of up to four $-CH_2P(O)Ph_2$ groups on the lower rim of the calixarene, according to a predetermined pattern and with retention of the cone conformation. The structure of a triply-phosphorylated compound has been established by X-ray crystallography.

2. Results and discussion

For the phosphoryl-substituted calixarenes described here, the phosphoryl group(s) ($-CH_2P(O)Ph_2$) were tethered to the macrocycle using a two-step approach. In the first step, (i) an appropriate solvent/base couple was used to deprotonate a hydroxy-substituted calixarene precursor. Subsequent alkylation (ii) with $Ph_2P(O)CH_2OTs$ ($Ts = O_2S$-*p*-C_6H_4-Me) or $Ph_2P(O)CH_2I$ afforded the required material. The precursor was either a generic calixarene (i.e., substituted by four hydroxy groups) or contained the same number of hydroxy groups as phosphoryl groups to be introduced. In each case, the isolated calixarene was found

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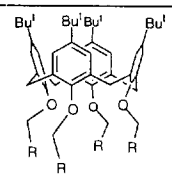
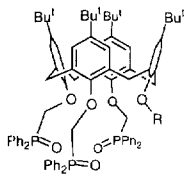
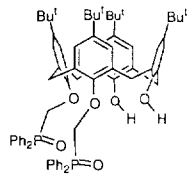
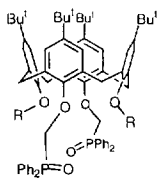
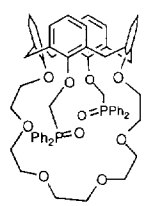
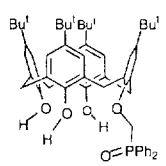
Table 1
Important spectroscopic data of compounds $\mathbf{L^1}$–$\mathbf{L^{11}}$

Compound		R	$\delta(^1H)^a$		$\delta(^{13}C)^a$	$\delta(^{31}P)^b$
			$C_6H_2CH_AH_BC_6H_2$ δ_A; δ_B (J_{AB} / Hz)	Δ_{AB}	$C_6H_2CH_2C_6H_2$	
$\mathbf{L^1}$		$P(O)Ph_2$	4.81; 2.73 (13)	2.08	32.2	25.6
$\mathbf{L^2}$		PPh_2	4.43; 2.87 (13)	1.56	32.7	- 20.4
$\mathbf{L^3}$		Me	4.97; 3.02 (13) 4.21; 3.07 (13)	1.25 0.75	32.2 / 31.5	26.4 23.0
$\mathbf{L^4}$		H	4.97; 3.04 (14) 4.41; 3.11 (13)	1.93 1.30	32.1 / n.f.[c]	25.8 24.1
$\mathbf{L^5}$		Bz	4.69; 2.44 (13) 4.27; 3.00 (13)	2.25 1.27	32.7 / 32.05	23.6 25.4
$\mathbf{L^6}$		/	4.82; 3.25 (13) 4.67; 3.13 (13) 4.29; 3.27 (14)	1.57 1.54 1.02	32.1 31.9 29.7	26.6
$\mathbf{L^7}$		H	4.15; 3.18 (13)	0.97	n.f.[c]	25.6
$\mathbf{L^8}$		Bz	4.48; 2.90 (13)	1.58	32.0	22.2
$\mathbf{L^9}$		Me	4.21; 3.06 (13)	1.15	31.5	24.1
$\mathbf{L^{10}}$		/	4.16; 3.00 (14)	1.16	30.9	24.1
$\mathbf{L^{11}}$		/	4.64; 3.39 (13) 4.14; 3.39 (13)	1.25 0.75	32.8 / 32.2	27.9

[a] In $CDCl_3$.
[b] In $CDCl_3$ except for $\mathbf{L^6}$, $\mathbf{L^9}$ and $\mathbf{L^{10}}$, in CH_2Cl_2/C_6D_6.
[c] Peak not found.

to possess the cone conformation according to conventional analysis by ^1H and ^{13}C NMR spectroscopy (Table 1) [38].

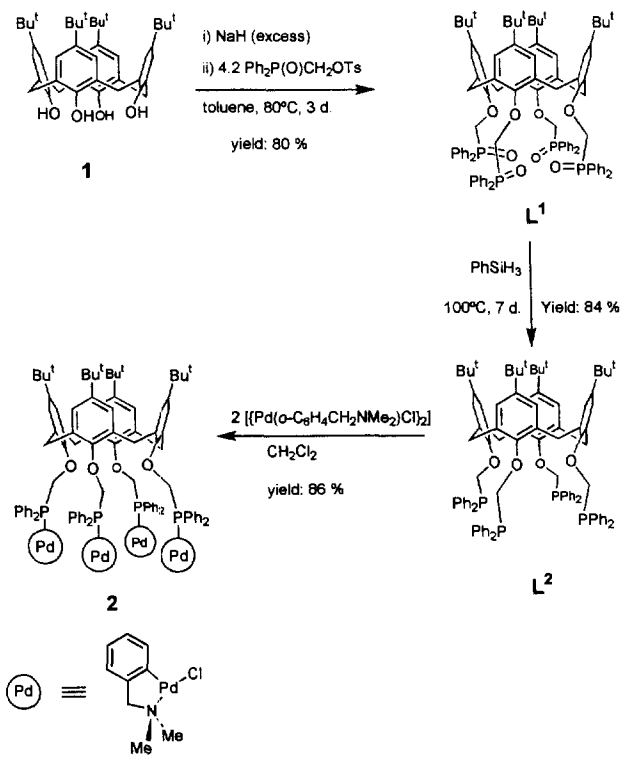
2.1. Attachment of four phosphine oxide residues and their subsequent reduction

Compound $\mathbf{L^1}$ was obtained in 80% yield by reaction of *p-tert*-butylcalix[4]arene (**1**) with NaH and $Ph_2P(O)CH_2OTs$ in toluene at 80°C (Scheme 1). Consistent with a cone conformation, the bridging methylene carbon atoms of $\mathbf{L^1}$ appear as a single peak at 32.22 ppm in the ^{13}C NMR spectrum while the corresponding CH_2 protons give an AB spectrum. The chemical shift difference between the two non-equivalent CH_2 protons ($\Delta_{AB} = \delta_A - \delta_B = 2.08$ ppm, see Table 1) is larger than that found for **1**, suggesting some structural modification of the calixarene. It is likely that

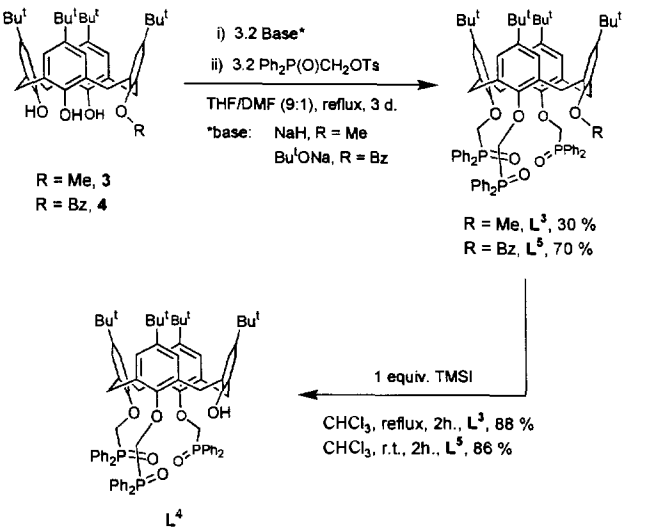
steric crowding by the phosphine groups and/or repulsion between phosphoryl oxygen atoms serve to diminish the cone angle of the calixarene. However, the solid state structure of $\mathbf{L^1}$, which was reported earlier, shows little if any deviation from the normal shape found for cone calixarenes [37].

Compound $\mathbf{L^1}$ can be converted into the corresponding tetra-phosphine $\mathbf{L^2}$ by reaction with phenylsilane used as solvent at 100°C (Scheme 1). Since this reaction requires about one week to reach completion, the temperature should be kept below 110°C in order to avoid decomposition of the resultant phosphine. The ^{31}P NMR spectrum of $\mathbf{L^2}$ shows a singlet at −20.4 ppm indicating equivalence of the four phosphorus atoms. All ^{1}H and ^{13}C NMR spectral data were consistent with a cone conformation. Compound $\mathbf{L^2}$ is the first known example of a cone calix[4]arene bearing four phosphine ligands, although a related compound has been reported by Hamada et al. [13] and tetraphosphites are well known [10,22,39].

Ligand $\mathbf{L^2}$ provides the appropriate complexation domain for binding four transition metal atoms. Thus, reaction of $\mathbf{L^2}$ with $[Pd(C \cap N)Cl]_2$ ($C \cap N = o\text{-}C_6H_4CH_2NMe_2$) (1 Ligand: 2 dimers) gave the tetranuclear complex **2** in quantitative yield. The FAB mass spectrum of **2** shows a peak at 2510.8 (6%) corresponding to the $[M\text{-}Cl]^+$ ion with the expected isotopic profile. The ^{31}P NMR spectrum exhibits a single peak (slightly broad) at 33.1 ppm. The ^{1}H NMR spectrum at room temperature displays broad signals that sharpen on warming, the spectra corresponding then to a C_4-symmetrical species in solution. The broadness of the room temperature peaks is indicative of dynamic equilibration under these conditions. The exact nature of the interconverting species is unknown, but the observation of a non-zero ^{4}J(P-NCH$_2$) coupling constant would appear to exclude fast transfer of 'Pd(C ∩ N)' units between phosphorus atoms.



Scheme 1.



Scheme 2.

2.2. *Preparation of calixarenes bearing three (phosphine oxide) residues*

Attempts to prepare a tris-phosphorylated calixarene from **1** in a single step were unsuccessful and instead it was necessary to employ a protection–deprotection procedure. Such a strategy has been applied for the preparation of other functionalised calixarenes [40,41]. Thus, reaction of the monomethoxy calixarene **3** with NaH and $Ph_2P(O)CH_2OTs$ in THF/DMF (9:1, v/v) afforded $\mathbf{L^3}$ in ca. 30% yield after work-up (Scheme 2). Other non-identified products were formed, and reaction was not optimized. The ^{13}C NMR spectrum of $\mathbf{L^3}$ exhibits two signals for the bridging Ar*C*H$_2$Ar groups, consistent with a C_s-symmetrical molecule, with the observed chemical shifts, 32.19 and 31.50 ppm, being indicative of a cone conformation. Of the two Δ_{AB} values apparent in the ^{1}H NMR spectrum one (Δ_{AB} = 0.75 ppm) is unusually small. Such behaviour is often observed when a small substituent enters the interior of a cavity and thereby causes some deviation from the ideal cone conformation. Regarding the transformation $\mathbf{L^3} \rightarrow \mathbf{L^4}$, it was found that TMSI (trimethylsilyl iodide) selectively cleaves the *O*-methyl bond without affecting the phosphoryl arm. Deprotection was achieved in re-

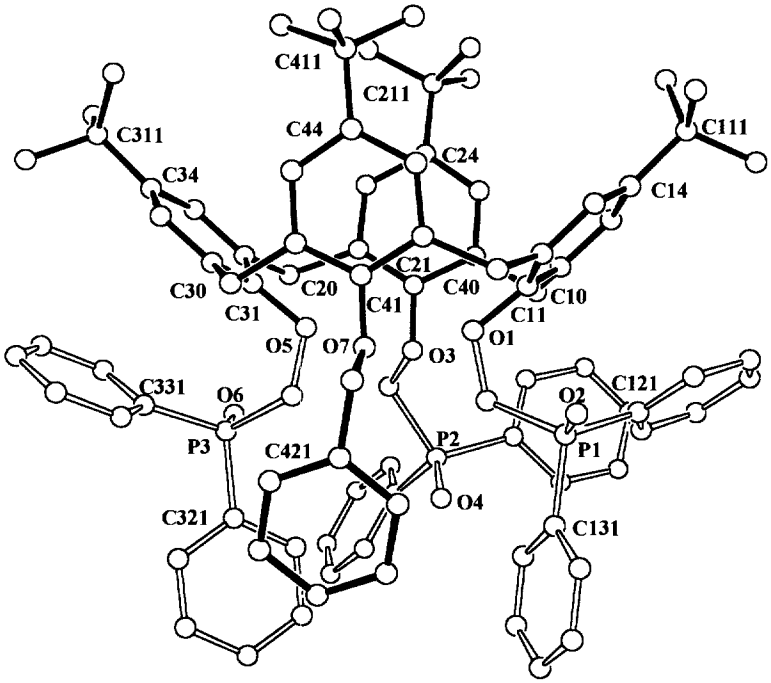


Fig. 1. Molecular structure of L^5 showing the numbering scheme (Ortep-3 [42,43]).

fluxing chloroform during which the cone conformation was retained. The PCH_2 hydrogens of opposite phosphoryl groups, being common to both L^3 and L^4, exhibit a characteristic ABX pattern.

The poor selectivity observed during alkylation of **3** most probably arises because the methoxy group attached to the lower rim penetrates into the cavity and promotes formation of non-cone conformers. It was surmised that this problem could be circumvented by the use of a large protective group. Consequently mono-benzyloxy calixarene **4** was synthesized and found to give much improved selectivity towards formation of the required tris-phosphorylated derivative. In this case conversion of **4** to L^5 was achieved in 70% yield

Table 2
Selected bond lengths (Å) and angles (°) for L^5

P(1)–O(2)	1.486(2)	P(1)–C(121)	1.806(3)
P(1)–C(131)	1.815(3)	P(1)–C(115)	1.838(3)
P(2)–O(4)	1.487(2)	P(2)–C(221)	1.800(3)
P(2)–C(231)	1.810(3)	P(2)–C(215)	1.815(3)
P(3)–O(6)	1.488(2)	P(3)–C(331)	1.807(3)
P(3)–C(321)	1.810(3)	P(3)–C(315)	1.837(3)
O(1)–C(11)	1.389(3)	O(1)–C(115)	1.422(3)
O(3)–C(21)	1.391(3)	O(3)–C(215)	1.433(3)
O(5)–C(31)	1.395(3)	O(5)–C(315)	1.426(3)
O(7)–C(41)	1.393(3)	O(7)–C(415)	1.437(3)
O(2)–P(1)–C(121)	111.79(14)	O(2)–P(1)–C(131)	111.15(13)
C(121)–P(1)–C(131)	106.82(14)	O(2)–P(1)–C(115)	115.66(13)
C(121)–P(1)–C(115)	107.71(14)	C(131)–P(1)–C(115)	103.03(13)
O(4)–P(2)–C(221)	112.63(14)	O(4)–P(2)–C(231)	113.13(13)
C(221)–P(2)–C(231)	106.43(14)	O(4)–P(2)–C(215)	113.83(13)
C(221)–P(2)–C(215)	108.62(14)	C(231)–P(2)–C(215)	101.38(13)
O(6)–P(3)–C(331)	112.36(13)	O(6)–P(3)–C(321)	112.74(13)
C(331)–P(3)–C(321)	107.24(14)	O(6)–P(3)–C(315)	113.63(13)
C(331)–P(3)–C(315)	107.63(13)	C(321)–P(3)–C(315)	102.58(13)
C(11)–O(1)–C(115)	120.3(2)	C(21)–O(3)–C(215)	117.2(2)
C(31)–O(5)–C(315)	119.7(2)	C(41)–O(7)–C(415)	113.3(2)
C(426)–C(421)–C(415)	120.3(3)	–	–

(Scheme 2). However, to prevent accidental displacement of the benzyl group it was necessary to use Bu^{t}ONa in THF/DMF (9:1, v/v) in place of NaH. The protected phosphorylated calixarene $\mathbf{L}^5$ adopts the cone conformation, as deduced from ^{13}C NMR data ($\delta(ArCH_2$ of calix) = 32.74 and 32.05 ppm). The two Δ_{AB} values found for this conformer are 2.25 and 1.27 ppm.

Crystals of $\mathbf{L}^5$ suitable for X-ray diffraction were obtained by slow diffusion of hexane into a solution of $\mathbf{L}^5$ in chlorobenzene. The triclinic unit cell contains two molecules of $\mathbf{L}^5$, four of PhCl, and one of hexane. Fig. 1 shows the structure of $\mathbf{L}^5$, with selected bond distances and angles being given in Table 2. The macrocyclic matrix adopts the usual shape for a calix[4]arene in the cone conformation, since two opposite aryl rings (based on C(21), C(41)) lie essentially parallel (dihedral angle 10.8°) with the other two being almost perpendicular (dihedral angle 89.3°). The P=O bonds associated with the 'orthogonal' arenes (P(1)O(2) and (P(3)O(6)), are directed at a tangent to the cavity defined by the calixarene substituents, while that trans to the benzyl group is directed toward the interior of the cavity (Fig. 2). Interestingly, the C(11) and C(121) aryl rings are sufficiently close together, the C(11)–C(121) and C(12)–C(121) distances being 3.32 and 3.40 Å, respectively, to provide $\pi-\pi$ stacking. The same holds for the C(31) and C(331) aryl rings. Clearly, such structural attributes would cause the P=O bonds to adopt the observed orientations. The benzyl group faces the cavity and augments the cavity wall.

Reaction of $\mathbf{L}^5$ with TMSI in $CHCl_3$ yielded $\mathbf{L}^4$ in quantitative yield under *ambient* conditions (Scheme 2). It is clear therefore that the benzyl protective group is more easily removed than the corresponding methyl function.

2.3. Preparation of calixarenes with two appended phosphoryl groups

Two families of disubstituted calix[4]arenes can be obtained, namely the 1,2 (or proximal) and 1,3 (or distal) derivatized compounds. In seeking to restrict substitution to the required degree, it is important to exert the maximum kinetic control possible over the reaction conditions. Detailed examination of the literature suggests that such control might be obtained by judicious choice of the leaving group for the ensuing SN2 reaction. In particular it is known that, for compounds of the general type $Ph_2P(O)CH_2X$, higher rates of substitution are found for X = tosylate than for the corresponding iodide [44]. We sought therefore to employ this strategy to optimise the preparation of suitably disubstituted calixarenes containing phosphine oxide groups. Some degree of control over the site of substitution can be obtained by careful consideration of the relative concentration of base used for deprotonation, although in practice this procedure is somewhat empirical.

Suitable conditions for the preparation of a proximally disubstituted compound, namely $\mathbf{L}^6$, are illustrated in Scheme 3. Thus, reaction of **1** with 2.5 equiv.

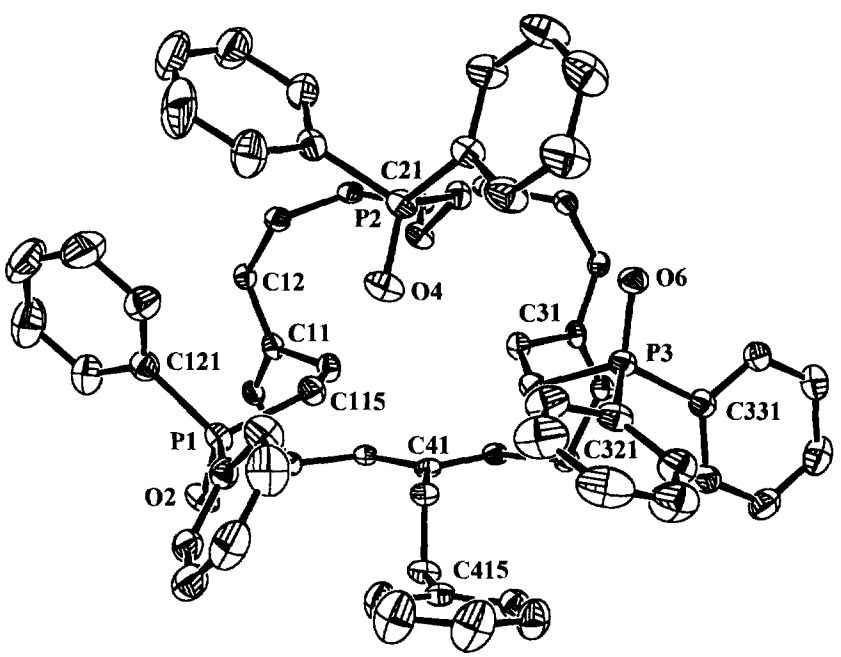
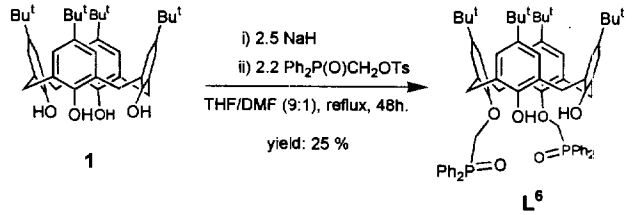
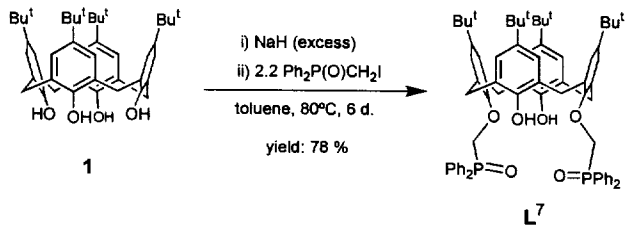


Fig. 2. Partial view (Ortep-3 [42,43]) of $\mathbf{L}^5$ from below showing the orientation of the P=O bonds.



Scheme 3.



Scheme 4.

of NaH and $Ph_2P(O)CH_2OTs$ in refluxing THF-DMF (9:1, v/v) for 2 d gave $\mathbf{L^6}$ in 25% yield after work-up (Scheme 3). Although this reaction is not selective, $\mathbf{L^6}$ is easily separated by column chromatography. Among the products formed, we detected the presence of $\mathbf{L^1}$ and $\mathbf{L^7}$ (see below). There is a single plane of symmetry inherent in such a 1,2-disubstituted calixarene such that the ^{1}H NMR spectrum of $\mathbf{L^6}$ shows three AB spin systems for the bridging methylene groups, with Δ_{AB} values of 1.57, 1.54, and 1.02 ppm. The chemical shifts found for the corresponding carbon atoms lie in the range expected for a cone conformation.

The distally-substituted product $\mathbf{L^7}$ was generated in high yield via a single step upon reacting **1** with excess NaH and $Ph_2P(O)CH_2I$ in toluene at 80°C for 6 d (Scheme 4). It was necessary to use only the stoichiometric amount of $Ph_2P(O)CH_2I$ since it proved difficult to separate excess reagent from the calixarene product. The ^{1}H NMR spectrum of $\mathbf{L^7}$ displays the AB system for the bridging methylene groups, with $\Delta_{AB} = 0.97$ ppm, that we consider characteristic for the cone conformation. The ^{13}C NMR spectrum showed no indica-

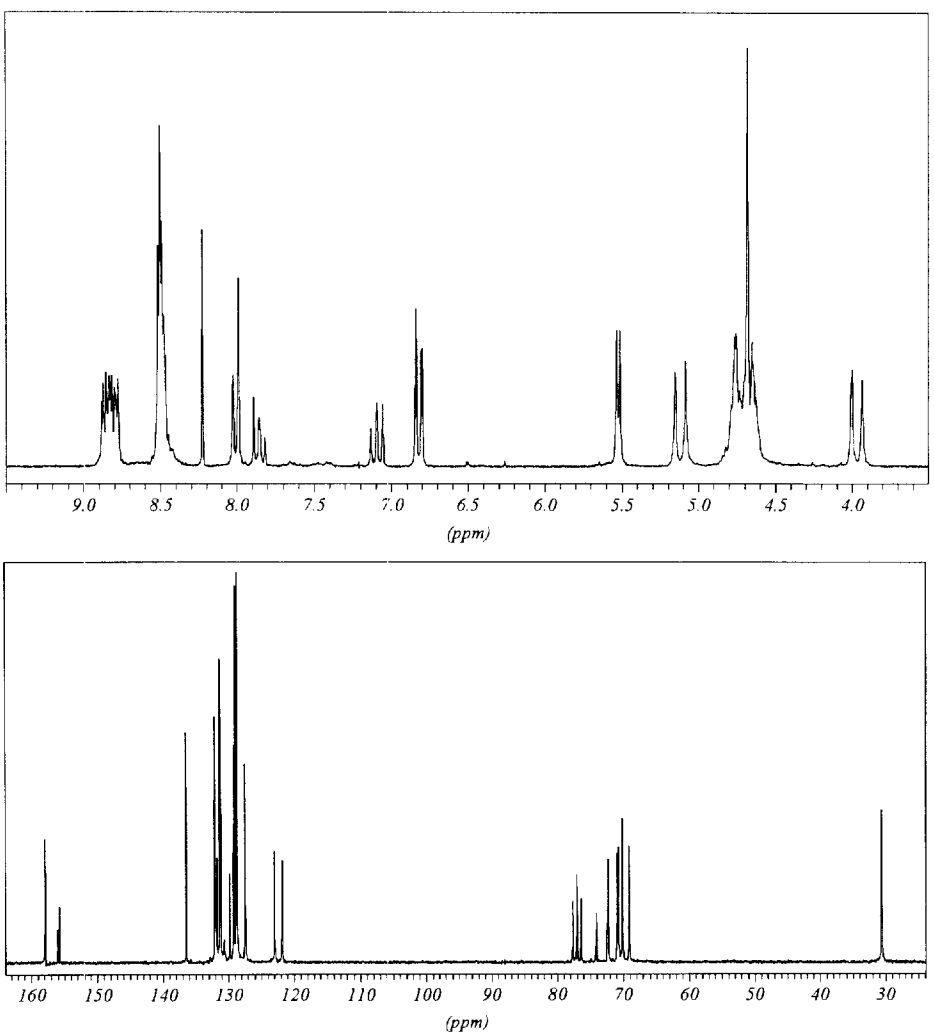
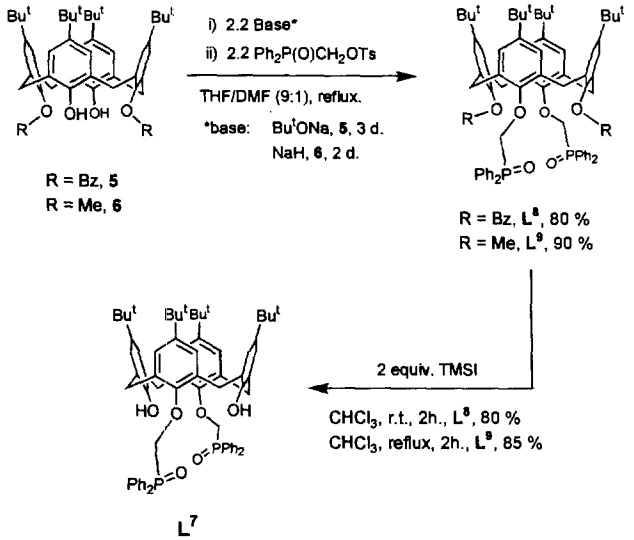


Fig. 3. ^{1}H NMR (top) and ^{13}C NMR (bottom) spectra of calixcrown $\mathbf{L^{10}}$ ($CDCl_3$).

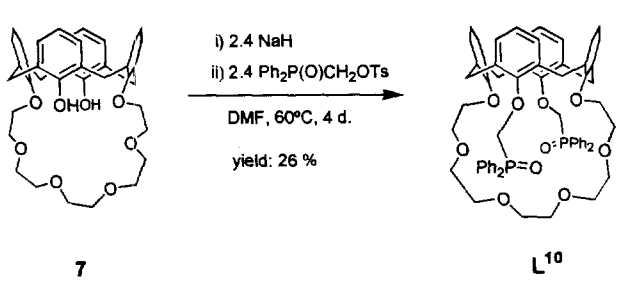


Scheme 5.

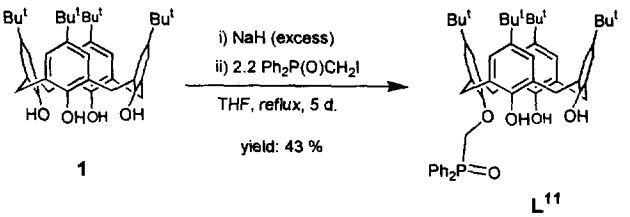
tion of conformers other than the expected cone, although the characteristic $ArCH_2Ar$ signal of the latter was obscured by one of the Bu^t resonances.

An alternative route to $\mathbf{L}^7$, requiring shorter reaction periods, starts from the protected 1,3-dibenzyloxy calixarene **5** (Scheme 5). Double alkylation of **5** was achieved at 80% yield within 3 d using Bu^tONa and $Ph_2P(O)CH_2OTs$ in refluxing THF-DMF (9:1, v/v). Subsequent deprotection of the resultant compound $\mathbf{L}^8$ was accomplished in quantitative yield with TMSI in $CHCl_3$ at room temperature. Similarly the 1,3-dimethoxy-protected calixarene **6** gave the corresponding diphosphorylated compound $\mathbf{L}^9$ in excellent yield (Scheme 5). In the latter case, deprotection had to be performed in *refluxing* $CHCl_3$.

Dialkylation of calixcrown **7** with NaH and $Ph_2P(O)CH_2OTs$ in DMF at 60°C afforded the expected calixcrown-bis(phosphine oxide) $\mathbf{L}^{10}$ in 26% yield (Scheme 6). The surprisingly moderate yield of this reaction is due to partial decomposition of the starting compound under the reaction conditions. Isolation of $\mathbf{L}^{10}$ therefore required purification by chromatography. Both the ^1H NMR spectrum ($\Delta_{AB} = 1.16$ ppm) and the ^{13}C NMR spectra ($\delta(ArCH_2) = 30.91$ ppm) unambiguously indicate the formation of a C_2-



Scheme 6.



Scheme 7.

symmetrical cone conformer (see Fig. 3). An interesting feature of compound $\mathbf{L}^{10}$ is that it contains ten oxygen atoms that roughly define a spherical cavity. Preliminary experiments showed that with potassium isocyanate, $\mathbf{L}^{10}$ forms a 1:1 complex (see experimental part), but the coordinative properties of this ligand will be reported elsewhere.

2.4. Synthesis of a calixarene bearing a solitary phosphoryl group

In order to limit reaction to mono-functionalisation, it was deemed necessary to use only the least reactive alkylating agent, namely $Ph_2P(O)CH_2I$. Selective conversion of **1** into the mono-phosphine oxide $\mathbf{L}^{11}$ was realized by reaction with excess NaH and $Ph_2P(O)CH_2I$ in refluxing THF (Scheme 7). After 5 d the conversion had reached 43%. As expected for this C_s-symmetrical molecule, the ^1H NMR spectrum displays the two AB spin systems for the bridging methylenes. The solid state IR spectrum displays two absorption bands in the OH region, at 3370 and 3178 cm^{-1}. The lower frequency is comparable to that found in **1** (3145 cm^{-1}) and indicates hydrogen bonding for one of the OH groups.

In summary, we have presented a series of functionalisation reactions allowing introduction of one to four $-CH_2P(O)Ph_2$ ligands on a calix[4]arene matrix. Under the conditions used (strong sodium bases, alkylating agents of the type $Ph_2P(O)CH_2X$), cone calixarenes were formed exclusively. Consistent with earlier studies, it was found that the rate of phosphorylation depended upon the nature of the leaving group in the alkylating reagent. In particular, there were marked differences in the rates of alkylation with $Ph_2P(O)CH_2I$ and $Ph_2P(O)CH_2OTs$ which could be exploited to prepare calixarenes bearing the required number of phosphoryl substituents. Using this approach, together with careful selection of the concentration and type of the deprotonating agent, it is possible to selectively prepare a range of lower rim-modified calixarenes. More subtlety is required to prepare the corresponding tris-substituted derivative and we found it necessary to devise a protection/deprotection strategy in this case. The same procedure can be used to increase the yield of the distally substituted bis-(phosphine oxide). It is impor-

tant to note that the deprotection routine using TMSI is specific for cleavage of the benzyloxy or methyloxy group and leaves the $-CH_2P(O)Ph_2$ moiety intact.

The various phosphorylated calixarenes described here can be converted into the corresponding calixphosphines under standard conditions, as outlined for **L¹**. This provides access to a series of compounds that might be expected interesting co-ordinative behaviour towards catalytically active metal centres. We have in fact described the synthesis of one such metal complex. Further studies will concentrate on the ability of these phosphine oxides to bind adventitious cations and on the catalytic properties of calixphosphine-derived platinum metal complexes.

3. Experimental

3.1. Reagents and physical measurements

All manipulations were performed in Schlenk-type flasks under an atmosphere of argon. Solvents were dried by conventional methods and distilled immediately prior to use. $CDCl_3$ was passed down a 5 cm thick alumina column and stored under argon over molecular sieves (4 Å). IR spectra were recorded on a Perkin–Elmer 1600 spectrometer (4000–400 cm^{-1}). Routine ^1H, $^{31}P\{^1H\}$ and $^{13}C\{^1H\}$ NMR spectra were recorded with an FT Bruker WP-200 SY instrument. ^1H NMR spectral data were referenced to residual protiated solvents (7.25 ppm for $CDCl_3$), ^{13}C chemical shifts are reported relative to deuterated solvents (77.0 ppm for $CDCl_3$), and the ^{31}P NMR data are given relative to external H_3PO_4. The mass spectra were recorded on a ZAB HF VG Analytical spectrometer using *m*-nitrobenzyl alcohol or tetraglyme (2,5,8,11,14-pentaoxapentadecane) as a matrix. For column chromatography Geduran SI (E. Merck, 0.040–0.063 mm) was used. Routine thin-layer chromatography analysis were done by using plates coated with Merck Kieselgel 60 GF_{254}. Elemental analyses were performed by the Centre de Recherche Chimie, Strasbourg, analytical service. Compound **L⁹** was prepared using a modification (see below) of the original procedure [45]. Samples of *p-tert*-butylcalix[4]arene (**1**) [46], 5,11,17,23-tetra-*tert*-butyl-25-methoxy-26,27,28-trihydroxycalix[4]arene (**3**) [40], 5,11,17,23-tetra-*tert*-butyl-25-benzyloxy-26,27,28-trihydroxycalix[4]arene (**4**) [40], 5,11,17,23-tetra-*tert*-butyl-25,27-dibenzyloxy-26,28-dihydroxycalix[4]arene (**5**) [47], 5,11,17,23-tetra-*tert*-butyl-25,27-dimethoxy-26,28-dihydroxycalix[4]arene (**6**) [48], 25,27-dihydroxycalix[4]arene-crown-6 (**7**) [41], $Ph_2P(O)CH_2OTs$ (Ts = O_2S-*p*-C_6H_4-Me) [49], $Ph_2P(O)CH_2I$ [44] and $[Pd(o\text{-}C_6H_4CH_2NMe_2)Cl]_2$ [50] were prepared according to literature procedures.

3.2. Syntheses

3.2.1. 5,11,17,23-tetra-tert-butyl-25,26,27,28-tetrakis(diphenylphosphinoylmethoxy)-calix[4]arene (L¹)

A suspension of *p-tert*-butylcalix[4]arene (**1**) (1.000 g, 1.54 mmol) and NaH (0.222 g, 9.24 mmol) in toluene (45 cm^3) was stirred at 80°C for 6h. Then $Ph_2P(O)CH_2OTs$ (2.500 g, 6.47 mmol) was added and the resultant solution was maintained at 80°C for a further 3 d. Excess NaH was decomposed with MeOH (20 cm^3), and the solvent was evaporated in vacuo. The residue was taken up in CH_2Cl_2 (100 cm^3) and washed with 1 N HCl (50 cm^3) then with water (2×50 cm^3). The organic layer was dried with $MgSO_4$, and filtered. After evaporation of the solvent, the solid residue was recrystallised from acetone (−20°C) affording the product as a white powder ($R_f = 0.29$, CH_2Cl_2/MeOH, 95:5, v/v) (1.855 g, 80%), m.p. > 270°C (Found: C, 76.40; H, 6.70. $C_{96}H_{100}O_8P_4$ requires C, 76.60; H, 6.70%; $M_r = 1505.74$). FAB mass spectrum: *m/z* 1505 (100%) (M^+); ν_{max}/cm^{-1} (KBr) 1196s (P=O, tentative assignment). NMR: ^1H ($CDCl_3$), δ 7.80–7.71 and 7.35-7.20 [40H, $P(O)Ph_2$], 6.36 (8H, s, *m*-C_6H_2), 5.24 [8H, s, $OCH_2P(O)$], 4.81 and 2.73 [8H, AB system, ^2J(AB) 13 Hz, $C_6H_2CH_2C_6H_2$], 0.93 (36H, s, Bu^t); $^{13}C\{^1H\}$ ($CDCl_3$), δ 152.95 [d, ^3J(PC) 4 Hz, O–C_{quat}], 144.7, 133.3 and 132.9 (aromatic C_{quat}), 131.1, 130.9, 128.4, 128.1 and 124.7 (aromatic *C*H's), 71.1 [d, *J*(PC) 78 Hz, $OCH_2P(O)$], 33.5 [s, $C(CH_3)_3$], 32.2 (s, $C_6H_2CH_2C_6H_2$), 31.2 [s, $C(CH_3)_3$]; $^{31}P\{^1H\}$ ($CDCl_3$), δ 25.6 [s, $P(O)Ph_2$].

3.2.2. 5,11,17,23-tetra-tert-butyl-25,26,27,28-tetrakis(diphenylphosphinomethoxy)calix[4]arene (L²)

A suspension of **L¹** (0.500 g, 0.33 mmol) in phenylsilane (10 cm^3, 81.00 mmol) was heated at 90–100°C for 7 d. After evaporation of the solvent in vacuo, the residue was taken up in CH_2Cl_2 and the solution was filtered through a layer of silica gel (ca. 5 cm) to remove side products. The filtrate was concentrated to ca. 10 cm^3. Addition of MeOH yielded the product as a white powder ($R_f = 0.64$, CH_2Cl_2) (0.399 g, 84%), m.p. 211.5–212°C (Found: C, 80.11; H, 7.22. $C_{96}H_{100}O_4P_4$ requires C, 79.98; H, 6.99%; M_r = 1441.74). FAB mass spectrum: *m/z* 1441 (2%) (M^+), 1255 (5%) [$(M\text{-}PPh_2)^+$]. NMR: ^1H ($CDCl_3$), δ 7.29–7.11 (40H, PPh_2), 6.54 (8H, s, *m*-C_6H_2), 5.07 (8H, s, OCH_2P), 4.43 and 2.87 [8H, AB system, ^2J(AB) 13 Hz, $C_6H_2CH_2C_6H_2$], 1.02 (36H, s, Bu^t); $^{13}C\{^1H\}$ ($CDCl_3$), δ 153.3 (s, O–C_{quat}), 144.7 (s, aromatic C_{quat}), 137.3 [d, *J*(PC) 15 Hz, P–C_{quat}], 133.7 (s, aromatic C_{quat}), 133.2, 132.8, 128.15 and 124.6 (aromatic *C*H's), 76.0 [d, *J*(PC) 7 Hz, OCH_2P], 33.6 [s, $C(CH_3)_3$], 32.7 (s, $C_6H_2CH_2C_6H_2$), 31.3 [s,

$C(CH_3)_3$]; $^{31}P\{^1H\}$ ($CDCl_3$), δ −20.4 (s, PPh_2). Because of a typographical error, a wrong J(PC) coupling constant was given for the signal at $\delta(^{13}C) = 76.0$ ppm in the preliminary communication (see Ref. [36]).

3.2.3. Tetranuclear palladium complex [{Pd(o-$C_6H_4CH_2NMe_2$)Cl}$_4$L^2] (2)

To a solution of $\mathbf{L^2}$ (0.115 g, 0.08 mmol) in CH_2Cl_2 (50 cm^3) was added a solution of [Pd(o-$C_6H_4CH_2NMe_2$)Cl]$_2$ (0.092 g, 0.17 mmol) in CH_2Cl_2 (50 cm^3). After stirring for 1 h, the solution was concentrated to ca. 10 cm^3 and filtered through celite. Addition of pentane yielded the complex as a pale yellow powder (0.175 g, 86%), m.p. 160–164°C (Found: C, 62.5; H, 5.5. $C_{132}H_{148}Cl_4N_4O_4P_4Pd_4$ requires C, 62.3; H, 5.9%; $M_r = 2545.98$). FAB mass spectrum: m/z 2510.8 (6%) [(M-Cl)$^+$]. NMR: ^1H ($CDCl_3$, 328K), δ 7.87–7.78 (40H, m, PPh_2), 6.91–6.16 (16H, ABMN system, C_6H_4 of dimethylbenzylamine), 6.42 (8H, s, m-C_6H_2), 5.66 (8H, br s, OCH_2P), 4.49 and 2.70 [8H, AB system, ^2J(AB) 13 Hz, $C_6H_2CH_2C_6H_2$], 3.98 (8H, br s, NCH_2), 2.75 [24H, d, ^4J(PH) 2 Hz, $N(CH_3)_2$], 1.00 (36H, s, Bu^t); $^{13}C\{^1H\}$ ($CDCl_3$, 328K), δ 153.7, 151.2, 147.95, 143.0, 131.5 and 131.1 (aromatic C_{quat}), 137.2, 137.0, 135.05, 131.5, 128.5, 128.3, 125.2, 124.9, 124.8, 123.3 and 121.9 (aromatic CH's), 75.65 [d, J(PC) 23 Hz, OCH_2P], 73.1 (s, NCH_2), 50.2 [s, $N(CH_3)_2$], 33.5 [s, $C(CH_3)_3$], 31.7 (s, $C_6H_2CH_2C_6H_2$), 31.5 [s, $C(CH_3)_3$]; $^{31}P\{^1H\}$ ($CDCl_3$, 328K), δ 33.1 (s, PPh_2).

3.2.4. 5,11,17,23-tetra-tert-butyl-25-methoxy-26,27,28-tris(diphenylphosphinoylmetho xy)calix[4]arene (L^3)

5,11,17,23-Tetra-*tert*-butyl-25-methoxy-26,27,28-trihydroxycalix[4]arene (**3**) (2.161 g, 3.26 mmol) was reacted with NaH (0.250 g, 10.43 mmol) for 2 h in a refluxing THF/DMF mixture (9:1, v/v, 200 cm^3). Then $Ph_2P(O)CH_2OTs$ (4.030 g, 10.43 mmol) was added and the resultant solution was further refluxed for 3 d. Methanol (20 cm^3) was added. After filtration, the solvent was evaporated in vacuo. The residue was taken up in CH_2Cl_2 (150 cm^3) and washed with 1 N HCl (50 cm^3) then with water (2 × 50 cm^3). The organic layer was dried with $MgSO_4$ and the solvent was evaporated in vacuo. The compound was purified by flash chromatography using CH_2Cl_2/MeOH (96:4, v/v) as eluent. $\mathbf{L^3}$ was obtained as a white powder in 30% yield ($R_f = 0.18$, CH_2Cl_2/MeOH, 95:5, v/v), m.p. > 270°C (Found: C, 77.34; H, 7.14. $C_{84}H_{91}O_7P_3$ requires C, 77.28; H, 7.03%; $M_r = 1305.58$). FAB mass spectrum: m/z 1305 (40%) [(M + H)$^+$]; ν_{max} cm^{-1} (KBr) 1193s (P=O, tentative assignment). NMR: ^1H ($CDCl_3$), δ 8.14–7.20 [30H, $P(O)Ph_2$], 7.04 and 6.69 (2H + 2H, 2s, m-C_6H_2), 6.29 and 6.25 [4H, AB system, ^2J(AB) < 4 Hz, m-C_6H_2], 5.47 [2H, s, $OCH_2P(O)$], 5.35 and 4.50 [4H, AB system, ^2J(AB) 14 Hz, $OCH_2P(O)$ adjacent to methoxy], 4.97 and 3.02 [4H, AB system, ^2J(AB) 13 Hz, $C_6H_2CH_2C_6H_2$], 4.21 and 3.07 [4H, AB system, ^2J(AB) 13 Hz, $C_6H_2CH_2C_6H_2$], 2.65 (3H, s, OCH_3), 1.31, 1.24 and 0.75 (9H + 9H + 18H, 3s, Bu^t); $^{13}C\{^1H\}$ ($CDCl_3$), δ 155.6 (s, O–C_{quat}), 155.05 [d, ^3J(PC) 7 Hz, O–C_{quat}], 151.6 (s br, O–C_{quat}), 145.6–130.4 (aromatic C_{quat}), 131.8, 131.6, 131.45, 131.3, 131.1, 128.9, 128.7, 128.45, 128.2, 125.4, 125.3, 124.9 and 124.3 (aromatic CH's), 73.7 [d, J(PC) 83 Hz, $OCH_2P(O)$], 70.0 [d, J(PC) 72 Hz, $OCH_2P(O)$], 59.55 (s, OCH_3), 34.1, 33.9 and 33.6 [3s, $C(CH_3)_3$], 32.2 and 31.5 (2s, $C_6H_2CH_2C_6H_2$), 31.7, 31.7 and 31.1 [3s, $C(CH_3)_3$]; $^{31}P\{^1H\}$ ($CDCl_3$), δ 26.4 [s, 2P, $P(O)Ph_2$], 23.0 [s, 1P, $P(O)Ph_2$].

3.2.5. 5,11,17,23-tetra-tert-butyl-25-benzyloxy-26,27,28-tris(diphenylphosphinoylmethoxy)calix[4]arene (L^5)

5,11,17,23-Tetra-*tert*-butyl-25-benzyloxy-26,27,28-trihydroxycalix[4]arene (**4**) (2.409 g, 3.26 mmol) was treated with Bu^{t}ONa (1.002 g, 10.43 mmol) in a refluxing THF/DMF mixture (9:1, v/v, 200 cm^3) for 2h. Then $Ph_2P(O)CH_2OTs$ (4.030 g, 10.43 mmol) was added and the resultant solution was further refluxed for 3 d. After filtration, the solvent was evaporated in vacuo. The residue was taken up in CH_2Cl_2 (150 cm^3) and washed with 1 N HCl (50 cm^3) then with water (2 × 50 cm^3). The organic layer was dried with $MgSO_4$ and the solvent was evaporated in vacuo. The compound was purified by flash chromatography using CH_2Cl_2/MeOH (96:4, v/v) as eluent. Compound $\mathbf{L^5}$ was obtained as a white powder in 70% yield ($R_f = 0.38$, CH_2Cl_2/MeOH, 95:5, v/v), m.p. > 270°C (Found: C, 78.03; H, 6.82. $C_{90}H_{95}O_7P_3$ requires C, 78.24; H, 6.93%; $M_r = 1381.70$). FAB mass spectrum: m/z 1381 (28%) (M^+); ν_{max} cm^{-1} (KBr) 1195s (P=O, tentative assignment). NMR: ^1H ($CDCl_3$), δ 8.15–7.07 (35H, aromatic H's), 6.83 and 6.35 (2H + 2H, 2s, m-C_6H_2), 6.44 and 6.15 [4H, AB system, ^2J(AB) 2 Hz, m-C_6H_2], 5.51 [2H, s, OCH_2Ph or $OCH_2P(O)$], 5.11 and 4.56 [4H, ABX system with X = P, ^2J(AB) 15 Hz, ^3J(AX) 4 Hz, ^3J(BX) 5 Hz, $OCH_2P(O)$ adjacent to benzyl], 4.69 and 2.44 [4H, AB system, ^2J(AB) 13 Hz, $C_6H_2CH_2C_6H_2$], 4.49 [2H, s, $OCH_2P(O)$ or OCH_2Ph], 4.27 and 3.00 [4H, AB system, ^2J(AB) 13 Hz, $C_6H_2CH_2C_6H_2$], 1.15, 1.04 and 0.85 (9H + 9H + 18H, 3s, Bu^t); $^{13}C\{^1H\}$ ($CDCl_3$), δ 154.2 and 153.8 (2s, O–C_{quat}), 151.8 [d, ^3J(PC) 4 Hz, O–C_{quat}], 145.0, 144.5, 139.0, 134.4, 133.6, 133.0, 132.4, 132.0, 131.7 and 130.1 (aromatic C_{quat}), 131.6–124.5 (aromatic CH's), 76.7 (s, OCH_2Ph), 71.7 [d, J(PC) 78 Hz, $OCH_2P(O)$], 70.1 [d, J(PC) 74 Hz, $OCH_2P(O)$], 33.8, 33.6 and 33.5 [3s, $C(CH_3)_3$], 32.7 and 32.05 (2s, $C_6H_2CH_2C_6H_2$), 31.5, 31.3 and 31.1 [3s, $C(CH_3)_3$]; $^{31}P\{^1H\}$ ($CDCl_3$), δ 25.4 [s, 2P, $P(O)Ph_2$], 23.6 [s, 1P, $P(O)Ph_2$].

3.2.6. 5,11,17,23-tetra-tert-butyl-25,26,27-tris(diphenylphosphinoylmethoxy)-28-hydroxycalix[4]arene (L^4)

This compound was obtained via a protection–deprotection procedure starting either from L^3 or L^5. To a solution of 5,11,17,23-tetra-*tert*-butyl-25-alkoxy-26,27,28-tris(diphenylphosphinoylmethoxy)calix[4]arene (alkoxy = OMe, L^3; OCH_2Ph, L^5) (0.57 mmol) in $CHCl_3$ (100 cm^3) was added iodotrimethylsilane (1.71 mmol). The deprotection of L^5 was performed at room temperature while that of L^3 was achieved in refluxing $CHCl_3$. The reaction was monitored by TLC analysis. After completion of the reaction, 1 N HCl (50 cm^3) was added. The aqueous layer was discarded, and the yellow organic layer was washed with a saturated $Na_2S_2O_3$ solution (50 cm^3), then with water (2×50 cm^3). The resultant colourless organic solution was dried with $MgSO_4$. After removal of the solvent, the solid residue was recrystallised from a CH_2Cl_2/hexane mixture. Compound L^4 was obtained as a white powder (88% from L^3, 86% from L^5) ($R_f = 0.18$, CH_2Cl_2/MeOH, 95:5, v/v), m.p. > 270°C (Found: C, 77.16; H, 7.06. $C_{83}H_{89}O_7P_3$ requires C, 77.19; H, 6.94%; M_r = 1291.55). FAB mass spectrum: *m/z* 1291 (37%) [$(M+H)^+$]; ν_{max} cm^{-1} (KBr) 3454m br (OH), 1200s (P=O, tentative assignment). NMR: ^1H ($CDCl_3$), δ 8.00–7.19 [30H, P(O)Ph_2], 6.98 and 6.76 (2H + 2H, 2s, *m*-C_6H_2), 6.37 and 6.34 [4H, AB system, ^2J(AB) < 4 Hz, *m*-C_6H_2], 5.53 (1H, s, OH), 5.47 [2H, s, $OCH_2P(O)$], 5.03 and 4.64 [4H, ABX system with X = P, ^2J(AB) 14 Hz, ^3J(AX) 3 Hz, ^3J(BX) 0 Hz, $OCH_2P(O)$ adjacent to hydroxy], 4.97 and 3.04 [4H, AB system, ^2J(AB) 14 Hz, $C_6H_2CH_2C_6H_2$], 4.41 and 3.11 [4H, AB system, ^2J(AB) 13 Hz, $C_6H_2CH_2C_6H_2$], 1.29, 1.26 and 0.75 (9H + 9H + 18H, 3s, Bu^t); $^{13}C\{^1H\}$ ($CDCl_3$), δ 153.1 [d, ^3J(PC) 6 Hz, O–C_{quat}], 152.7 (s br, O–C_{quat}), 150.8 (s, O–C_{quat}), 145.9–131.3 (aromatic C_{quat}), 132.0, 131.5, 131.3, 128.9, 128.7, 128.5, 128.3, 125.7, 125.5 and 125.0 (aromatic *C*H's), 74.0 [d, *J*(PC) 81 Hz, $OCH_2P(O)$], 71.0 [d, *J*(PC) 74 Hz, $OCH_2P(O)$], 34.0, 33.8 and 33.7 [3s, $C(CH_3)_3$], 32.1 (s, $C_6H_2CH_2C_6H_2$), 31.8, 31.6 and 31.0 [3s, $C(CH_3)_3$] (the second $ArCH_2Ar$ signal is probably overlapping with a Bu^t signal); $^{31}P\{^1H\}$ ($CDCl_3$), δ 25.8 [s, 1P, P(O)Ph_2], 24.1 [s, 2P, P(O)Ph_2].

3.2.7. 5,11,17,23-tetra-tert-butyl-25,26-bis(diphenylphosphinoylmethoxy)-27,28-dihydroxycalix[4]arene (L^6)

A suspension of *p-tert*-butylcalix[4]arene (**1**) (0.500 g, 0.77 mmol) and NaH (0.046 g, 1.92 mmol) in a refluxing THF/DMF mixture (9:1, v/v, 20 cm^3) was stirred for 1 h. Then $Ph_2P(O)CH_2OTs$ (0.654 g, 1.69 mmol) was added and the resultant solution was refluxed for a further 48 h. Excess NaH was decomposed with MeOH (10 cm^3), and the solvent was removed in vacuo. The residue was taken up in CH_2Cl_2 (50 cm^3) and washed with 1 N HCl (30 cm^3) then with water (2×30 cm^3). The organic layer was dried with $MgSO_4$ and evaporated to dryness to afford a solid that was purified by flash chromatography using CH_2Cl_2/MeOH (98:2, v/v) as eluent. Starting compound **1** eluted first, followed by L^6. The latter was obtained as an analytically pure white solid ($R_f = 0.55$, CH_2Cl_2/MeOH, 94:6, v/v) (0.205 g, 25%), m.p. 255°C (Found: C, 78.20; H, 7.21. $C_{70}H_{78}O_6P_2$ requires C, 78.04; H, 7.30%; M_r = 1077.35); ν_{max} cm^{-1} (KBr) 1192s (P=O, tentative assignment). NMR: ^1H ($CDCl_3$), δ 8.64 (2H, s, O*H*), 7.91–7.82 and 7.56–7.30 [20H, P(O)Ph_2], 6.89 (4H, 2s, *m*-C_6H_2), 6.71 and 6.61 [4H, AB system, ^4J(AB) 2 Hz, *m*-C_6H_2], 5.11 and 4.99 [4H, ABX system with X = P, ^2J(AB) 14 Hz, ^3J(AX) 4 Hz, ^3J(BX) 0 Hz, $OCH_2P(O)$], 4.82 and 3.25 [2H, AB system, ^2J(AB) 13 Hz, $C_6H_2CH_2C_6H_2$], 4.67 and 3.13 [4H, AB system, ^2J(AB) 13 Hz, $C_6H_2CH_2C_6H_2$], 4.29 and 3.27 [2H, AB system, ^2J(AB) 14 Hz, $C_6H_2CH_2C_6H_2$], 1.19 and 1.00 (18H + 18H, 2s, Bu^t); $^{13}C\{^1H\}$ ($CDCl_3$), δ 153.5–127.0 (aromatic C_{quat}), 132.3–124.9 (aromatic *C*H's), 72.9 [d, *J*(PC) 80 Hz, $OCH_2P(O)$], 33.8 and 33.7 [2s, $C(CH_3)_3$], 32.1, 31.9 and 29.7 (3s, $C_6H_2CH_2C_6H_2$), 31.5 and 31.1 [2s, $C(CH_3)_3$]; $^{31}P\{^1H\}$ (CH_2Cl_2/C_6D_6), δ 26.6 [s, P(O)Ph_2].

3.2.8. Synthesis of 5,11,17,23-tetra-tert-butyl-25,27-bis(diphenylphosphinoylmethoxy)-26,28-dihydroxycalix[4]arene (L^7)

This compound has been synthesised in two ways, either by direct alkylation of *p-tert*-butylcalix[4]arene (**1**) (method A) or *via* a protection–deprotection procedure starting from **5** or **6** (method B).

3.2.8.1. Method A. A suspension of *p-tert*-butylcalix[4]arene (**1**) (1.000 g, 1.54 mmol) and NaH (0.185 g, 7.70 mmol) in toluene (30 cm^3) was stirred at 80°C for 4 h. Then $Ph_2P(O)CH_2I$ (1.160 g, 3.40 mmol) was added and the resultant solution was maintained at 80°C for a further 6 d. Excess NaH was decomposed with MeOH (20 cm^3), and the solvent was removed in vacuo. The residue was taken up in CH_2Cl_2 (100 cm^3). The solution was washed with a saturated $Na_2S_2O_3$ solution (50 cm^3) then with water (2×50 cm^3). The resulting colourless organic solution was dried with $MgSO_4$, concentrated to ca. 10 cm^3 in vacuo. Addition of hexane yielded the product as a white powder (R_f = 0.37, CH_2Cl_2/MeOH, 95:5, v/v) (1.294 g, 78%) (characteristic NMR data are given below).

3.2.8.2. Method B. Compound L^7 was obtained from L^8 or L^9 (2.00 mmol) using a procedure similar to that given for L^4 but employing two equivalents of TMSI. The solid residue was recrystallised from CH_2Cl_2/hexane yielding L^7 as a white powder (80%

from $\mathbf{L}^8$, 85% from $\mathbf{L}^9$), m.p. > 270°C (Found: C, 77.87; H, 7.11. $C_{70}H_{78}O_6P_2$ requires C, 78.04; H, 7.30%; $M_r = 1077.35$). FAB mass spectrum: m/z 1077 (74%) $[(M+H)^+]$; ν_{max} cm^{-1} (KBr) 3470m br (OH), 1186s (P=O, tentative assignment). NMR: ^1H ($CDCl_3$), δ 8.08–7.99 and 7.44–7.43 [20H, $P(O)Ph_2$], 7.03 and 6.58 (4H + 4H, 2s, *m*-C_6H_2), 5.73 (2H, s, O*H* exchanges with D_2O), 4.64 [4H, d, $^2J(PH)$ 6 Hz, $OCH_2P(O)$], 4.15 and 3.18 [8H, AB system, $^2J(AB)$ 13 Hz, $C_6H_2CH_2C_6H_2$], 1.32 and 0.83 (18H + 18H, 2s, Bu^t); $^{13}C\{^1H\}$ ($CDCl_3$), δ 151.4, 151.2, 150.2, 147.1, 141.5, 131.1, 129.5 and 127.9 (aromatic C_{quat}), 132.3, 131.6, 131.4, 128.9, 128.7, 125.6 and 124.95 (aromatic *C*H's), 74.6 [d, $J(PC)$ 81 Hz, $OCH_2P(O)$], 33.7 and 33.7 [2 s, $C(CH_3)_3$], 31.6 and 30.8 [2s, $C(CH_3)_3$]; $^{31}P\{^1H\}$ ($CDCl_3$), δ 25.6 [s, $P(O)Ph_2$].

3.2.9. *General procedure for the synthesis of 5,11,17,23-tetra-tert-butyl-25,27-dialkoxy-26,28-bis(diphenylphosphinoylmethoxy)calix[4]arenes [alkoxy = OCH_2Ph (L^8), OMe (L^9)]*

A solution of 5,11,17,23-tetra-*tert*-butyl-25,27-dialkoxy-26,28-dihydroxycalix[4]arene (alkoxy = OCH_2Ph, **5**; alkoxy = OMe, **6**) (3.48 mmol) in a refluxing THF/DMF mixture (9:1, v/v, 200 cm^3) was treated with the adequate base (7.66 mmol, Bu^tONa for the benzyloxy calixarene, NaH for the methoxy compound) for 2 h. Then $Ph_2P(O)CH_2OTs$ (7.66 mmol) was added and the resultant solution was further refluxed for 3 d (2 d in the case of **6**). If NaH was used for deprotonation, MeOH (20 cm^3) was added at this stage; no quenching was necessary for the reaction with Bu^tONa. After filtration, the solvent was evaporated in vacuo. The residue was taken up in CH_2Cl_2 (100 cm^3) and washed with 1 N HCl (50 cm^3) then with water (2 × 50 cm^3). The organic layer was dried with $MgSO_4$ and the solvent was evaporated in vacuo. Compounds $\mathbf{L}^8$ and $\mathbf{L}^9$ (white solids) were recrystallized from CH_2Cl_2/acetone at −20°C (yield: $\mathbf{L}^8$, 80%; $\mathbf{L}^9$, 90%).

3.2.10. *5,11,17,23-tetra-tert-butyl-25,27-dibenzyloxy-26,28-bis(diphenylphosphinoyl-methoxy)calix[4]arene (L^8)*

($R_f = 0.28$, CH_2Cl_2/MeOH, 95:5, v/v), m.p. > 270°C (Found: C, 80.39; H, 7.09. $C_{84}H_{90}O_6P_2$ requires C, 80.23; H, 7.21%; $M_r = 1257.60$). FAB mass spectrum: m/z 1257 (58%) $[(M+H)^+]$; ν_{max} cm^{-1} (KBr) 1208s (P=O, tentative assignment). NMR: ^1H ($CDCl_3$), δ 7.70–6.96 (30H, aromatic H's), 6.66 and 6.42 (4H + 4H, 2s, *m*-C_6H_2), 5.09 [4H, s, OCH_2Ph or $OCH_2P(O)$], 4.75 [4H, s, $OCH_2P(O)$ or OCH_2Ph], 4.48 and 2.90 [8H, AB system, $^2J(AB)$ 13 Hz, $C_6H_2CH_2C_6H_2$], 1.22 and 0.85 (18H + 18H, 2s, Bu^t); $^{13}C\{^1H\}$ ($CDCl_3$), δ 153.0 (s, O–C_{quat}), 151.5 [d, $^3J(PC)$ 5 Hz, O–C_{quat}], 145.6, 144.2, 138.2, 135.6, 133.4, 132.2 and 131.5 (aromatic C_{quat}), 130.7–124.5 (aromatic *C*H's), 77.7 (s, OCH_2Ph), 69.0 [d, $J(PC)$ 72 Hz, $OCH_2P(O)$], 33.7 and 33.4 [2s, $C(CH_3)_3$], 32.0 (s, $C_6H_2CH_2C_6H_2$), 31.4 and 30.9 [2s, $C(CH_3)_3$]; $^{31}P\{^1H\}$ ($CDCl_3$), δ 22.2 [s, $P(O)Ph_2$].

3.2.11. *5,11,17,23-tetra-tert-butyl-25,27-dimethoxy-26,28-bis(diphenylphosphinoyl-methoxy)calix[4]arene (L^9)*

($R_f = 0.50$, CH_2Cl_2/MeOH, 96:4, v/v), m.p. 235–240°C (Found: C, 77.94; H, 7.64. $C_{72}H_{82}O_6P_2$ requires C, 78.23; H, 7.48%; $M_r = 1105.39$). FAB mass spectrum: m/z 1105 (52%) (M^+); ν_{max} cm^{-1} (KBr) 1193s (P=O, tentative assignment). NMR: ^1H ($CDCl_3$), δ 7.91–7.82 and 7.53–7.40 [20H, $P(O)Ph_2$], 7.02 and 6.29 (4H + 4H, 2br s, *m*-C_6H_2), 4.51 [4H, d, $^2J(PH)$ 4 Hz, $OCH_2P(O)$], 4.17 and 3.01 [8H, AB system, $^2J(AB)$ 12 Hz, $C_6H_2CH_2C_6H_2$], 3.28 (6H, br s, OCH_3), 1.29 and 0.74 (18H + 18H, 2s, Bu^t); $^{13}C\{^1H\}$ ($CDCl_3$), δ 155.6–124.5 (aromatic *C*), 71.8 [d, $J(PC)$ 84 Hz, $OCH_2P(O)$], 60.3 (s, OCH_3), 34.1 and 33.5 [2s, $C(CH_3)_3$], 31.7 and 31.0 [2s, $C(CH_3)_3$], 31.5 (s, $C_6H_2CH_2C_6H_2$); $^{31}P\{^1H\}$ (CH_2Cl_2/C_6D_6), δ 24.1 [s, $P(O)Ph_2$].

3.2.12. *25,27-bis(diphenylphosphinoylmethoxy)calix[4]-arene-crown-6 (L^{10})*

A solution of 25,27-dihydroxycalix[4]arene-crown-6 (**7**) (4.000 g, 6.38 mmol) and NaH (0.367 g, 15.31 mmol) in DMF (150 cm^3) was heated for 2 h at 60°C. Then $Ph_2P(O)CH_2OTs$ (5.911 g, 15.31 mmol) was added and the resultant solution was further heated for 4 d. Excess NaH was decomposed with MeOH (20 cm^3), and the solvent was evaporated in vacuo. The residue was taken up in CH_2Cl_2 (100 cm^3) and washed with 1 N HCl (50 cm^3) then with water (2 × 50 cm^3). The organic layer was dried with $MgSO_4$ and evaporated to afford a solid which was purified by flash chromatography using CH_2Cl_2/MeOH (93:7, v/v) as eluent (other, non-identified products elute first). Evaporation in vacuo of the solvent yielded a white solid ($R_f = 0.38$, CH_2Cl_2/MeOH, 93:7, v/v) (1.750 g, 26%), m.p. 175–177°C (Found: C, 73.14; H, 6.24. $C_{64}H_{64}O_{10}P_2$ requires C, 72.85; H, 6.11%; $M_r = 1055.16$). FAB mass spectrum: m/z 1055 (31%) $[(M+H)^+]$; ν_{max} cm^{-1} (KBr) 1185s (P=O, tentative assignment). NMR: ^1H ($CDCl_3$), δ 7.92–7.81 and 7.55–7.48 [20H, $P(O)Ph_2$], 7.04 and 6.89 [A_2B spin system constituted by a doublet (δ 7.04, 4H) and four lines (2H) centred at 6.89, *m*- and *p*-ArH of calix], 6.13 and 5.86 [AB_2 spin system, t(2H) + d(4H), *m*- and *p*-ArH of calix], 4.56 [4H, d, $^2J(PH)$ 4 Hz, $OCH_2P(O)$], 4.16 and 3.00 [8H, AB system, $^2J(AB)$ 14 Hz, $C_6H_2CH_2C_6H_2$], 3.86–3.66 (12H, m, CH_2's of crown), 3.72 (8H, s, $ArOCH_2CH_2OCH_2CH_2$, tent. assignment); $^{13}C\{^1H\}$ ($CDCl_3$), δ 158.1 (O–C_{quat}), 156.1 [d, O–C_{quat}, $^3J(PC)$

9 Hz], 136.7–122.0 (aromatic *C*'s), 73.5 [d, *J*(PC) 83 Hz, $OCH_2P(O)$, tent. assignment], 72.55, 71.15, 71.0, 70.4, and 69.3 (5s, CH_2's of crown), 30.9 (s, $C_6H_2CH_2C_6H_2$); $^{31}P\{^1H\}$ (CH_2Cl_2/C_6D_6), δ 24.1 [s, $P(O)Ph_2$].

3.2.13. Addition of KSCN to a solution of L^{10}

Excess KSCN was added to a dichloromethane solution of L^{10}. After filtration, pentane was added to the solution affording a white precipitate. FAB mass spectrum: *m/z* 1093 (100%) (expected mass of $L^{10} \subset K^+$: 1093). ^1H ($CDCl_3$), δ 7.88–7.77 and 7.59–7.45 [20H, $P(O)Ph_2$], 7.03 and 6.88 [A_2B spin system constituted by a doublet (δ 7.03, 4H) and four lines (2H) centered at 6.88, *m*- and *p*-ArH of calix], 6.23 and 6.05 [AB_2 spin system constituted by four lines (2H) centered at 6.23 and a doublet (4H) at 6.05, *m*- and *p*-ArH of calix], 4.69 [4H, d, ^2J(PH) 3 Hz, $OCH_2P(O)$], 4.17 and 2.95 [8H, AB system, ^2J(AB) 12 Hz, $C_6H_2CH_2C_6H_2$], 4.03 (4H, pseudo t, CH_2's of crown), 3.82 (8H, s, $ArOCH_2CH_2OCH_2CH_2$), 3.85–3.75 (m, 4H, CH_2's of crown), 3.64 (d, 4H, CH_2's of crown). $^{31}P\{^1H\}$ ($CDCl_3$), δ 25.3 [s, $P(O)Ph_2$].

3.2.14. 5,11,17,23-tetra-tert-butyl-25-(diphenylphosphinoylmethoxy)-26,27,28-trihydroxycalix[4]arene (L^{11})

A suspension of *p-tert*-butylcalix[4]arene (1) (1.000 g, 1.54 mmol) and NaH (0.111 g, 4.62 mmol) in THF (45 cm^3) was stirred under reflux for 4 h. Then $Ph_2P(O)CH_2I$ (1.160 g, 3.40 mmol) was added and the resultant solution was further refluxed for 5 d. Excess NaH was decomposed with MeOH (20 cm^3), then the solvent was evaporated in vacuo. The residue was taken up in CH_2Cl_2 (100 cm^3) and washed with 1 N HCl (50 cm^3) then with water (2 × 50 cm^3). The organic layer was dried with $MgSO_4$ and evaporated to afford a yellow solid that was purified by flash chromatography (CH_2Cl_2/MeOH, 98:2, v/v). Compound **1** eluted first, followed by L^{11} (R_f = 0.83, CH_2Cl_2/MeOH, 95:5, v/v) (0.571 g, 43%), m.p. > 270°C (Found: C, 79.39; H, 8.00. $C_{57}H_{67}O_5P$ requires C, 79.32; H, 7.82%; M_r = 863.13). FAB mass spectrum: *m/z* 863 (100%) [$(M + H)^+$]; ν_{max} cm^{-1} (KBr) 3370m and 3178m sh (OH), 1202ms (P=O, tentative assignment). NMR: ^1H ($CDCl_3$), δ 9.76 (1H, s, O*H* exchanges with D_2O), 8.87 (2H, s, O*H* exchanges with D_2O), 8.11–8.01 and 7.66–7.60 [10H, $P(O)Ph_2$], 7.05 and 6.95 [4H, AB system, ^4J(AB) 2 Hz, *m*-C_6H_2], 7.04 (4H, s, 2 × *m*-C_6H_2), 5.01 [2H, d, ^2J(PH) 3 Hz, $OCH_2P(O)$], 4.64 and 3.39 [4H, AB system, ^2J(AB) 13 Hz, $C_6H_2CH_2C_6H_2$], 4.14 and 3.39 [4H, AB system, ^2J(AB) 13 Hz, $C_6H_2CH_2C_6H_2$], 1.23, 1.21 and 1.17 (9H + 18H + 9H, 3s, Bu^t); $^{13}C\{^1H\}$ ($CDCl_3$), δ 151.6 [d, ^3J(PC) 7 Hz, O–C_{quat}], 148.3–127.0 (aromatic C_{quat}), 132.65–125.4 (aromatic *C*H's), 74.0 [d, *J*(PC) 81 Hz, $OCH_2P(O)$], 34.1, 33.9 and 33.8 [3s, $C(CH_3)_3$], 32.8 and 32.2 (2s, $C_6H_2CH_2C_6H_2$), 31.5 [br s, $C(CH_3)_3$], 31.1 [s, $C(CH_3)_3$]; $^{31}P\{^1H\}$ ($CDCl_3$), δ 27.9 [s, $P(O)Ph_2$].

3.2.15. X-ray structure analysis of L^5

Single crystals of L^5 were obtained by slow diffusion of hexane into a chlorobenzene solution of the compound. *Crystal data*: $L^5 \cdot 2C_6H_5Cl \cdot 0.5C_6H_{14}$, $C_{105}H_{112}Cl_2O_7P_2$, M_r = 1649.76, triclinic, space group *P*1-, *a* = 13.934(2), *b* = 14.854(2), *c* = 23.798(3) Å, α = 106.242(10), ß = 99.974(10), γ = 93.949(8)°, *V* = 4621.5 Å^3, *Z* = 2, D_x = 1.186 Mg m^{-3}, λ (Mo K_α) = 0.71073 Å, μ = 0.18 mm^{-1}, T = −100°C. *Data collection and reduction* : A colourless block 0.9 × 0.4 × 0.4 mm was mounted in inert oil. Data were collected to $2\theta_{max}$ 50° on a Siemens P4 diffractometer (scan type ϖ). Monochromated Mo K_α radiation was employed. Of 16344 measured data, 15926 were unique (R_{int} 0.020). Structure solution and refinement: the structure was solved by direct methods and refined anisotropically on F^2 using all reflections (program: SHELXL-93, G.M. Sheldrick, University of Göttingen). Hydrogen atoms were included using a riding model or rigid methyl groups. The hexane molecule was badly resolved. The final $wR(F^2)$ was 0.158 for 1039 parameters, conventional $R(F)$ 0.055 for $F > 4\sigma(F)$. *S* = 0.97; max. $\Delta\rho$ 1.1 e Å^{-3}.

4. Supplementary material available

Full details of the structure determination have been deposited at the Fachinformationszentrum Karlsruhe, Gesellschaft für Wissenschaftlich-technische Information mbH, D-76344 Eggenstein-Leopoldshafen, Germany. Any request for this material should quote the full literature citation and the reference number CSD 406836.

5. Note added in proof

Since submission of this paper, an improved synthesis was found for compound L^3. Thus, treatment of **3** with NaH (3.2 equivalents) and $Ph_2P(O)CH_2OTs$ (3.2 equivalent) in toluene at 90°C for 3d gave L^3 in 65% yield. Same work-up as for L^1, recrystallisation from CH_2Cl_2/methanol (1:5 , vol/vol).

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