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Phosphorus-containing calixarenes

I S Antipin, E Kh Kazakova, W D Habicher, A I Konovalov

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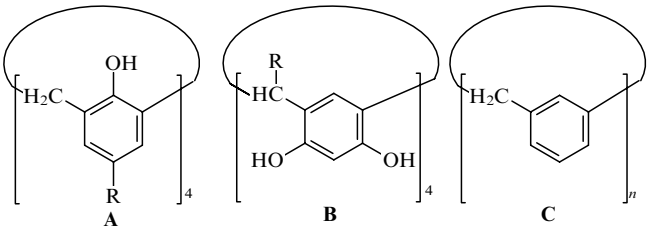
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Abstract. Data on the synthesis, conformational behaviour and complexing properties of calix[4]resorcinolarene and calix[*n*]arene derivatives modified by phosphorus-containing fragments are surveyed. The bibliography includes 123 references.

I. Introduction

The chemistry of calixarenes — cyclic products of condensation of phenols with aldehydes — has vigorously developed during the last 20 years. Calixarenes are readily accessible compounds (many of them can be easily obtained by a one-stage synthesis); they contain reactive sites permitting modification of the structure. In addition, they are capable of forming inclusion complexes of the 'host–guest' type both with charged and non-polar molecules.

The first mention of the interaction of phenols with aldehydes [1] dates back to 1872 (A Bayer); however the structure of the reaction products has remained barely known for almost 70 more years. It was not until the 1940s that tetrameric cyclic structures **A** and **B** were ascribed to the products of condensation of *p*-alkylphenols with formaldehyde in an alkaline medium [2] and to the products of acid-catalysed reaction of resorcinol with aldehydes.[3]



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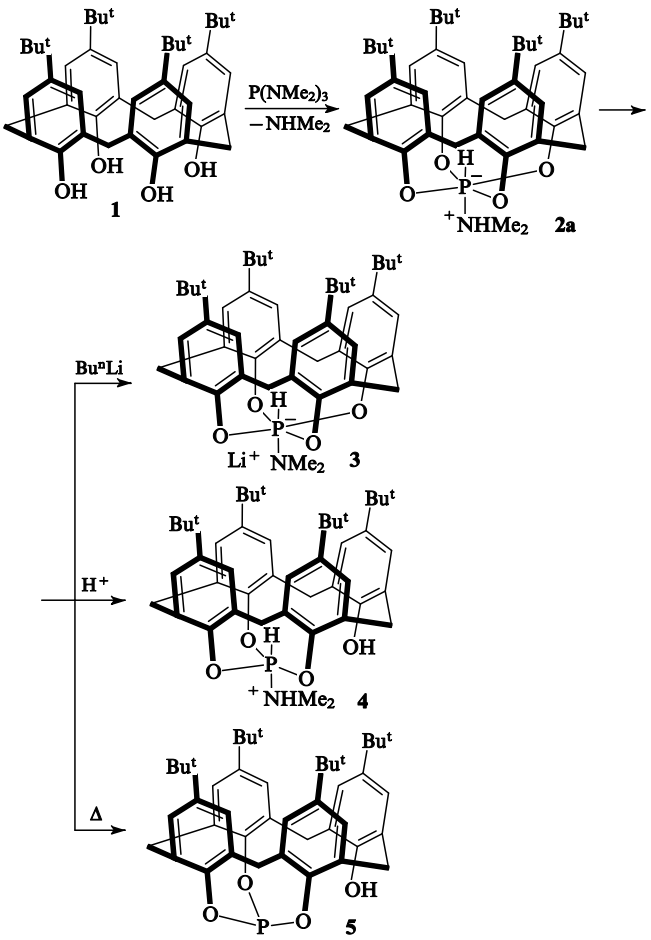
The term 'calixarene' was brought into use by Gutsche *et al.*[4] to characterise the shape of these cyclic tetramers, which resembles a bowl ('calix' is the Greek for bowl or cup). Although later it was found [5–7] that these macrocycles can also exist in other conformations, this term has been adopted to denote the whole class of [1$_n$]-metacyclophanes (including compounds **C**).

Calixarenes are widely used as molecular platforms for the development of pre-organised three-dimensional receptors.[5–8] Upon functionalisation of the phenolic groups, the aromatic rings and the bridging fragments in the initial macrocycles by appropriate organic or organoelement reagents, the receptor capacity can be increased by a large factor. The number of publications dealing with calixarene derivatives doubles every three years.[8] The number of patents also swiftly increases, indicating that these compounds are important not only for theoretical studies but also for practical purposes and for industry. The latest achievements in the studies of organic derivatives of calixarenes were summarised in a special issue of the journal *Gazzetta Chimica Italiana* (No. 11 in 1997), which was based on the contributions to the 4th International Conference on Calixarenes held in Parma (Italy) from August 31 to September 4, 1997.

Organic derivatives of phosphorus are of special interest for functionalisation of calixarenes, because phosphorus compounds play an important role in many biological and catalytic properties. The complex-forming ability of organophosphorus groups, the strictly definite size of the molecular cavity in the initial calixarene and the possibility of introducing fragments with a specified spatial orientation open up the way to the synthesis of a new generation of receptors capable of recognising complex molecular images. However, the size and the vicinity of functional groups in the supramolecular systems impart some specific features to their chemical behaviour. This makes development of an efficient methodology for selective functionalisation of calix[*n*]arenes a fundamentally important task. Studies on phosphorylation of calixarenes were started in the late 80s – early 90s. This review is the first attempt to describe systematically experimental data now accumulated along this line.

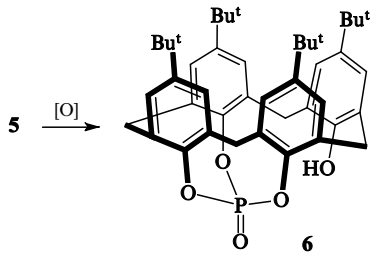
II. O-Phosphorylation of calixarenes by P(III) compounds

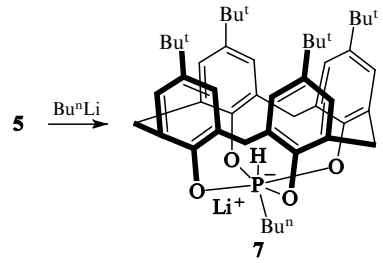
The pioneering investigations dealing with the reactions of P(III) compounds with calixarenes were published by a group of American scientists,[9–13] who accomplished a series of studies dealing with functionalisation of the hydroxy groups in *p-tert*-butylcalix[4]arene (**1**).



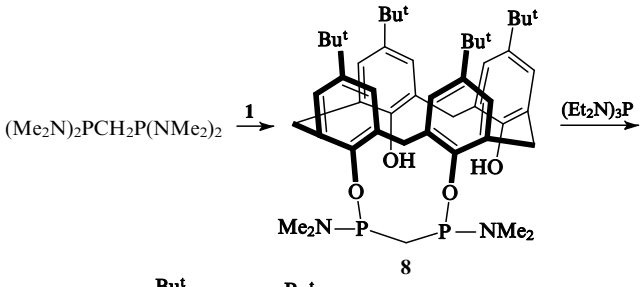
It was shown that the inner cavity of calix[4]arene can stabilise the 'hypervalent' hexacoordinated state of the phosphorus atom. The reaction of the compound **1** with tris(dimethylamino)-phosphine [10] is accompanied by elimination of two dimethylamine molecules and gives spirocyclic zwitter-ionic product **2a** ($\delta_P = -120$ ppm, $J_{P-H} = 737$ Hz).

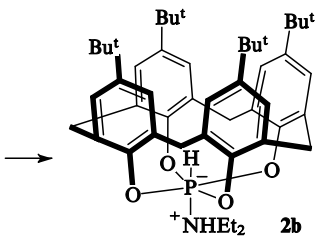
The two apical positions are occupied by an N^+HMe_2 group and a hydrogen atom, the bond of the latter with phosphorus being directed inside the aromatic cavity; this was confirmed by NMR spectroscopy and X-ray diffraction analysis.[12, 13] On treatment of the compound **2** with one equivalent of butyllithium, the dimethylammonium group is deprotonated, which results in the formation of salt **3**. When the zwitter-ion **2** is thermolysed at 200 °C or treated with strong acids (CF_3CO_2H or HBF_4), dimethylamine is eliminated and cage phosphite **5** is produced. Spectral studies (^1H and ^{31}P NMR) showed that the reaction with HBF_4 occurs *via* the formation of pentacoordinated phosphorane intermediate **4** ($\delta_P = -22$ ppm). Oxidation of phosphite **5** with *tert*-butyl hydroperoxide affords the corresponding phosphate **6**; according to X-ray diffraction analysis, this product occurs in a conformation intermediate between *1,2-alternate* and *partial cone*. The reaction of the phosphite **5** with one equivalent of n-butyllithium gives product **7** with a hexacoordinated phosphorus atom.

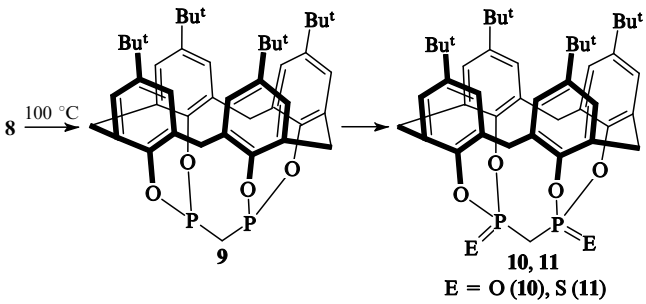




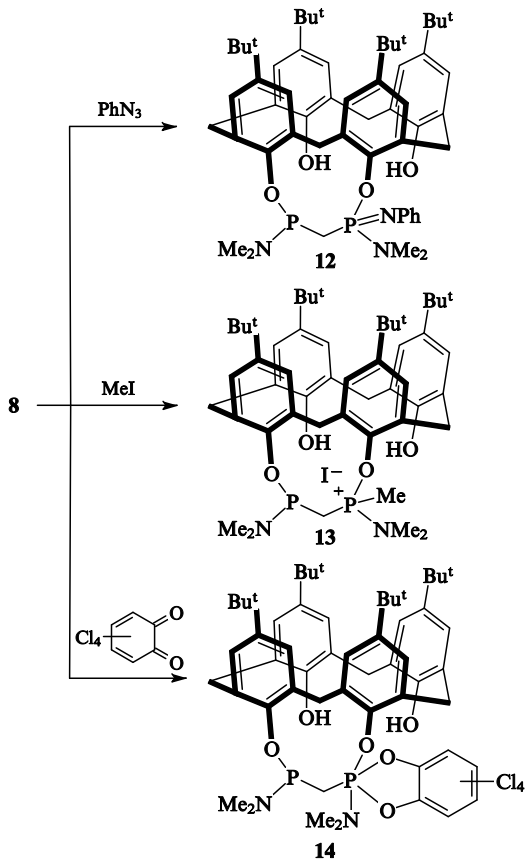
The same group of researchers [14] succeeded in the introduction of more than one phosphorus atom in the calixarene platform. Treatment of the compound **1** with di[bis(*N*,*N*-dimethylamino)phosphino]methane in dichloromethane at room temperature gives rise to disubstituted product **8**.





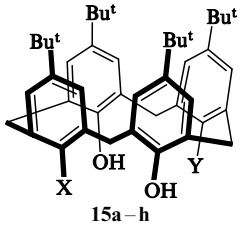


An X-ray diffraction study showed that the compound **8** is the (*R*,*S*) isomer in relation to the phosphorus atoms. Binding of the remaining hydroxyl groups upon the reaction with tris(diethylamino)phosphine gave the product **2b** and diphosphine. Keeping compound **8** in toluene for 14 h at 100°C resulted in the evolution of two moles of diethylamine and the formation of product **9** containing no free hydroxyl groups. Subsequently this product can be converted into bisphosphonate **10** or bis(phosphonothioate) **11**. NMR monitoring of the formation of the bis(phosphonothioate) **11** showed that reaction consists of two stages. The monothio-derivative formed initially is responsible for two ^{31}P NMR signals, with $\delta_P = 84$ and 179 ppm ($J_{P-P} = 29$ Hz). To convert this compound into the bisthio-derivative, an additional heating for 24 h is required. When the compound **8** is made to react with electrophilic reagents such as phenyl azide, methyl iodide and tetrachloro-1,2-benzoquinone, compounds **12**–**14** are formed in which only one phosphorus atom of the diphosphinomethylene bridge has changed its coordination. The products **12** and **14** are unstable and rapidly decompose.

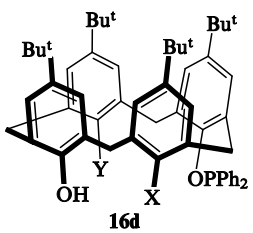


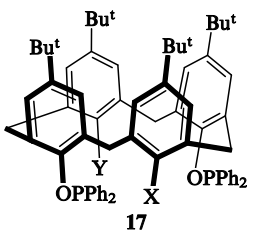
Synthesis of polyfunctional phosphinite derivatives has been reported in several studies.[15–17] Both *p-tert*-butylcalix[4]arene **1** itself and its 1,3-diethers **15** have been subjected to phosphorylation by chloro(diphenyl)phosphine. Treatment of these substrates with lithium diisopropylamide or butyllithium at a temperature below 50 °C followed by reaction with Ph_2PCl results in the selective formation of bis(phosphinites) **17**. These products exist in a *cone* conformation, except for the compound **17a** in which fast interconversion of the *cone* and *partial cone* conformations occurs. When Et_3N is used as the base in boiling THF, the compound **15d** can be converted only into the monophosphinite **16d** having a *cone* conformation. Under the same conditions, the calixarene **1** is converted into 1,3-bisphosphinite as a mixture of two conformers, the *cone* and the *1,2-alternate*.

The structures of the 1 : 1 complexes formed by **16d** with Au(I) cations and the 2 : 1 complexes with Pd(II) and Pt(II) cations have been studied by X-ray diffraction analysis.[18]

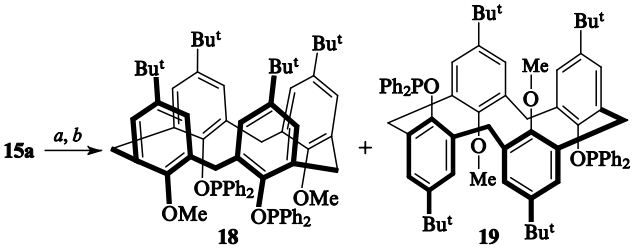


X = Y = OMe (**a**), OEt (**b**), OPr^n (**c**), OCH_2COOEt (**d**), $OCH_2COOC_{10}H_{19}$ (**e**); X = OEt: Y = OCH_2COOEt (**f**), $OCH_2COOC_{10}H_{19}$ (**g**), OCH_2COO[(−)-menthyl)] (**h**).



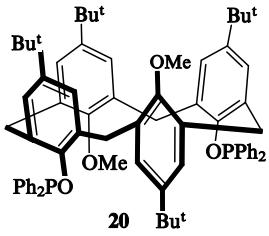


Deprotonation of the dimethyl ether **15a** by Bu^nLi in THF followed by the reaction with Ph_2PCl at room temperature also gives a mixture of conformers, *cone* **18** (25%) and 1,2-*alternate* **19** (60%). At lower temperatures (−78 °C), the content of the conformer **19** increases to 82%; the two possible *1,2-alternate* structures of this compound undergo fast interconversion.[15]



(*a*) Bu^nLi, THF; (*b*) Ph_2PCl.

It has been noted [19] that treatment of the calixarene **15a** with two equivalents of KH followed by reaction with Ph_2PCl results in the selective formation of diphosphorylated product **20** in a *partial cone* conformation.



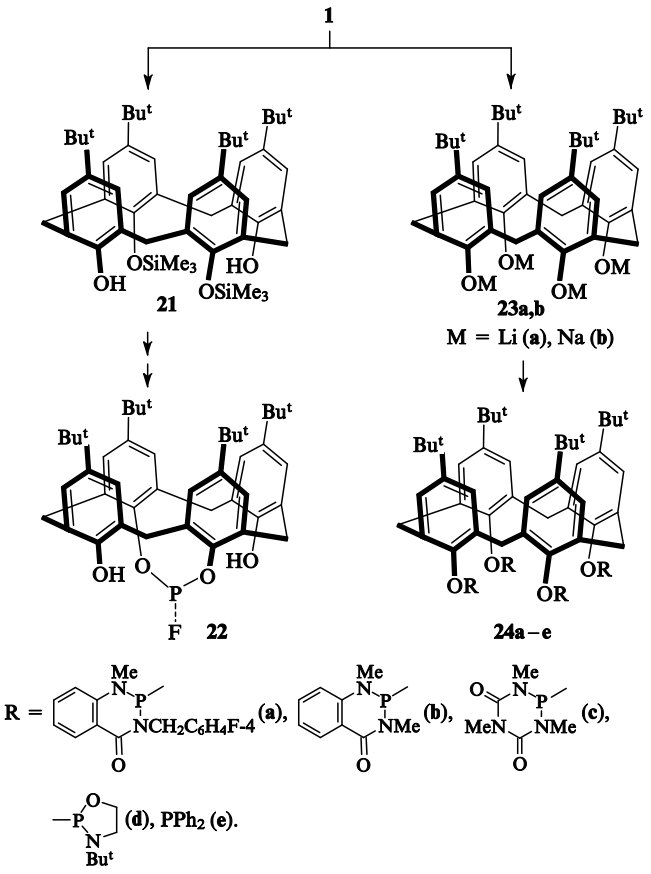
The data of dynamic ^1H NMR in solution point to the occurrence of a dynamic equilibrium between the *cone* **18** and *partial cone* **20** conformations, the former conformer predominating (the ratio **18** : **20** = 2.7 : 1).[16] The number of introduced diphenylphosphinite fragments can be controlled by preliminary methylation of the phenolic hydroxy groups by methyl tosylate in the presence of potassium carbonate.[19]

The complex-forming ability of the phosphinite ligands **16d** and **17** in relation to transition metal cations [Pt(II), Pd(II) and Rh(I)] has been studied.[16, 17]

The introduction of P(III) atoms into the lower rim of calix[4]arene by preliminary silylation of hydroxy groups has been described by Schmutzler *et al.*[20, 21] Treatment of the calixarene **1** with hexamethyldisilazane gives rise to 1,3-disubstituted derivative **21**.

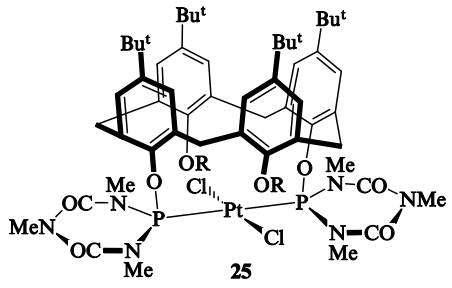
The reaction of this product with PF_2Cl affords mono- and bis-difluorophosphites, which are converted into monofluorophosphite **22** upon elimination of Me_3SiF or PF_3. The macrocycles **21** and **22** occur in a *cone* conformation.

In order to synthesise completely *O*-phosphorylated calix[4]arenes, the compound **1** is first converted into the corresponding tetraanion by treatment with a strong base (Bu^nLi or KH). The highly nucleophilic tetraanion is made to react with phosphorus-containing electrophiles with P–Cl bonds. Thus the reaction of the lithium derivative **23a** with *N*-substituted 2-chloro-4-oxobenzo-1,3,2-diazaphosphorinanes or 2-chloro-4,6-dioxobenzo-1,3,5,2-triazaphosphorinane yields calixarenes **24a–c**. The macrocycles **24d,e** were synthesised by similar reactions of the sodium derivative **23b** with 3-*tert*-butyl-2-chloro-1,3,2-oxaazaphospholidine and chloro(diphenyl)phosphine.[22–24] The stereochemical outcome of the above reactions is determined by the nature of the organophosphorus group entering the molecule. The compounds **24a, d, e** exist exclusively in a *cone* conformation,[23] whereas for compounds **24b, c** all of the four possible conformers are formed.[21] Under similar conditions, calix[6]arene is converted into hexakis(diphenylphosphinite),[24] while calix[8]-

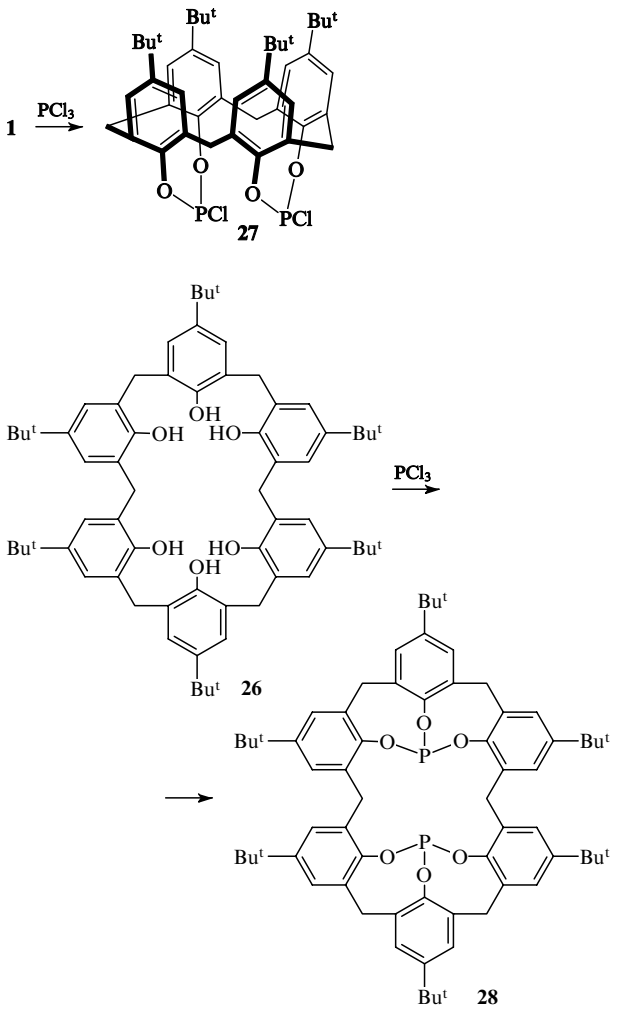


arene gives octaphosphorylated derivatives with diphenylphosphine and 1,3,2-oxaazaphospholane fragments.[22]

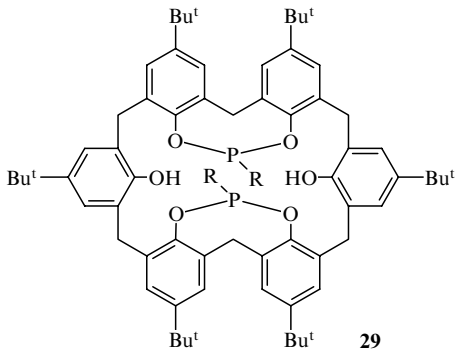
The cyclophane **24c** in a *cone* conformation reacts with dichloro(cycloocta-1,5-diene)platinum(II) giving 1 : 1 *trans*-complex **25**, in which two phosphorus atoms are coordinated to the Pt(II) cation.[20] The tetrakis(phosphinites) **24e** and **24d** also form stable complexes. For example, homodimetal complexes of **24e** with $Fe(CO)_3$,[23] $[Pd(COD)Cl_2]$ and $Pt[COD]Cl_2$ (COD is cycloocta-1,5-diene)[25] and a polymeric 1 : 1 complex of **24d** with copper(I) chloride[23] have been obtained. The tetradentate ligand **24e** is capable of forming both dimeric complexes, for example, $\{$(**24e**)$[Rh(CO)Cl]_2\}$, and binuclear heterometal complexes, for example, $[$(**24e**)$\{NiCl_2\}\{Mo(CO)_4\}]$.[25]

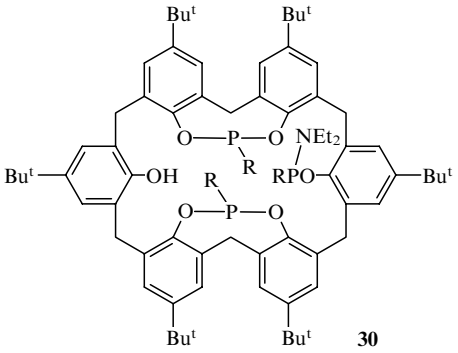


Phosphorylation of the calix[4]arene **1**[26] and the calix[6]arene **26**[27] with phosphorus(III) chloride (in some cases, in the presence of Et_3N as a base) yields cyclic bisphosphites **27** and **28**.

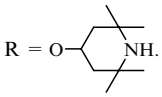


The product **27** is hydrolytically unstable; an attempt to recrystallise it from methanol resulted in the isolation of the initial calixarene **1**. According to X-ray diffraction data, the lone electron pairs of the phosphorus atoms in the compounds **27** and **28** point in the same direction; this makes them promising bidentate ligands for complexation with many *d*- and *f*-metal cations. Thus the compound **28** forms *cis*-complexes with Pd(II), Pt(II) and Re(I). In the complex $[PdCl_2L]$, the metal coordinates the bisphosphite fragments at an angle of 90 °C. Calix[6]arene derivatives containing cyclic (**29**) and acyclic (**30**) phosphorus fragments were synthesised by the reaction of calixarene **26** with phosphorous diethylamide.[28] These compounds were found[22] to exhibit antioxidant properties.

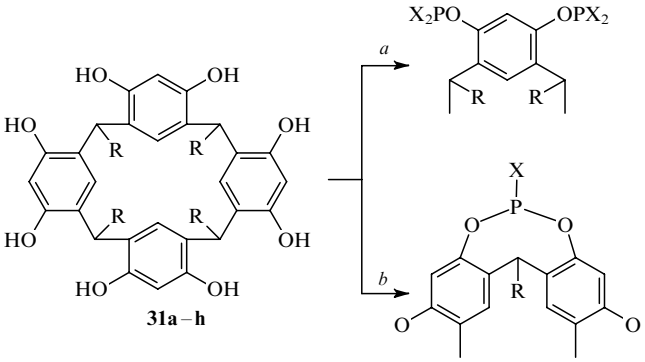




30



Due to the conformational flexibility of calix[4]resorcinolarenes **31**,[29,30] their phosphorylation can follow two major pathways: (*a*) functionalisation of separate hydroxy groups or (*b*) cyclophosphorylation of two neighbouring hydroxy groups.



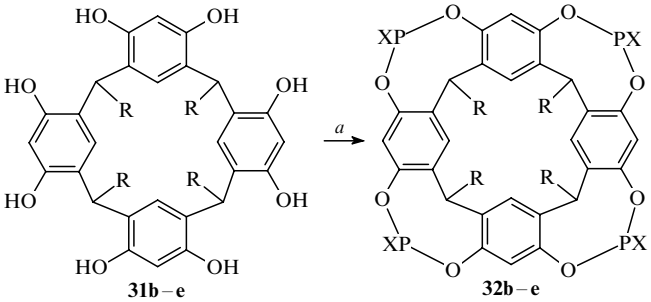
31a–h

R = Ph (**a**), Me (**b**), Bu^n (**c**), C_6H_{13} (**d**), C_7H_{15} (**e**), C_9H_{19} (**f**), $C_{11}H_{23}$ (**g**), $(CH_2)_2Ph$ (**h**).

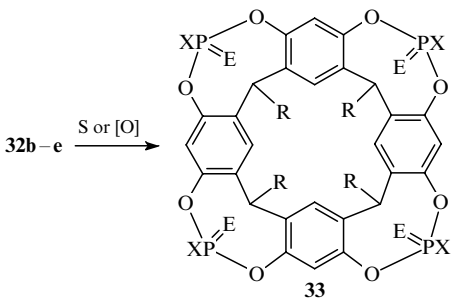
It is obvious that the reaction route depends both on the nature of the phosphorylating reagent (most of all, the number of reaction sites) and on the conformation of the macrocycle. The most favourable conformation of octol **31** for cyclophosphorylation is the *crown* conformation (C_{4v} symmetry). In this conformation, the aromatic rings are directed upwards and form a bowl-like cavity, stabilised by a system of intramolecular hydrogen bonds.[29,30] Monochlorophosphines, monochlorophosphites, dichlorophosphines and aminophosphines are usually employed as phosphorylation agents.

Phosphorylation using aminophosphines is distinguished by experimental simplicity and mild reaction conditions (room temperature).[31]

A series of P(III)-containing cavitands **32** have been prepared by the reactions of calixarenes **31b–e** with a number of aminophosphines (the reactants were taken in 1 : 4 molar ratio).[32–37]



31b–e **32b–e**



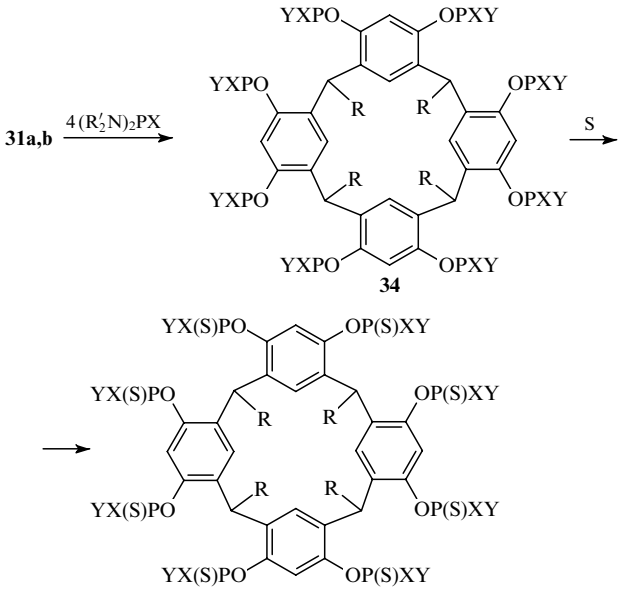
33

(*a*) 4 equiv. $(R'_2N)_2PX$; R′ = Me, Et; X = NMe_2, NEt_2; E = O, S.

The influence of the nature of the substituent R in the bridging fragment on the reaction route has been studied.[36] It was found that the reaction of tris(diethylamino)phosphine with tetraphenyloctol **31a** mainly follows pathway (*a*). Even when the ratio of the reactants is 1 : 2, the proportion of the cyclophosphorylation product is only 23%. In the case of tetramethyloctol **31b**, product mixtures containing both cyclic and acyclic phosphorus-containing fragments are formed at various ratios of the reactants. For tetrabutyloctol, cyclophosphorylation becomes the prevailing process; when the reactant ratio is 1 : 4, only pathway (*b*) is realised. It was suggested [36] that the dependence of the phosphorylation route on the nature of the substituent R is a consequence of the calix[4]resorcinolarene preorganisation (*i.e.* the position of the conformation equilibrium in the given solvent). Bulky alkyl radicals stabilise the *crown* conformation, due to lipophilic interactions with one another, and thus they promote cyclophosphorylation. The reactions of aminomethylated calix[4]resorcinol-arenes at a 1 : 4 reactant ratio also follow pathway (*b*).

Recently triaminophosphines were used to phosphorylate *p-tert*-butylcalix[5]arene. This substrate reacts with $P(NMe_2)_3$ to afford monocylic aminophosphine, *O*,*O*′-(dimethylaminophosphinediyl)calix[5]arene.[38]

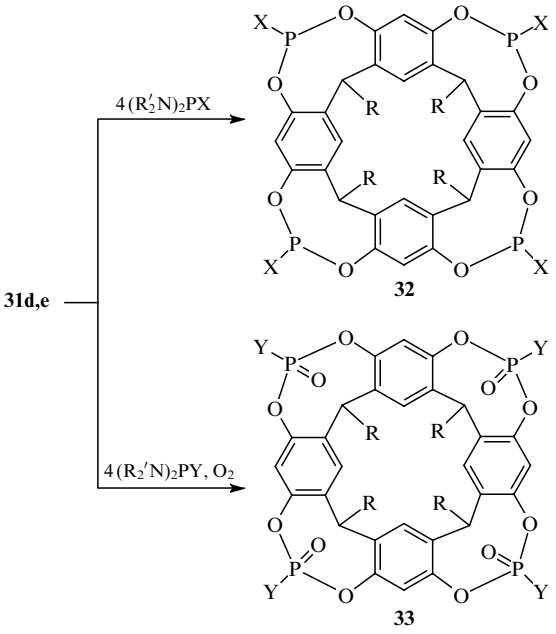
It is noteworthy that, unlike ordinary aminophosphines, aminophosphine cavitands **32** are stable against alcohols, water and oxygen and add sulfur only under rigorous conditions. Oxidation of these compounds or addition of sulfur gives macrocyclic phosphoroamidates or phosphorothioamidates **33**. Octaphosphorylated macrocycles **34** react with sulfur in a similar way.



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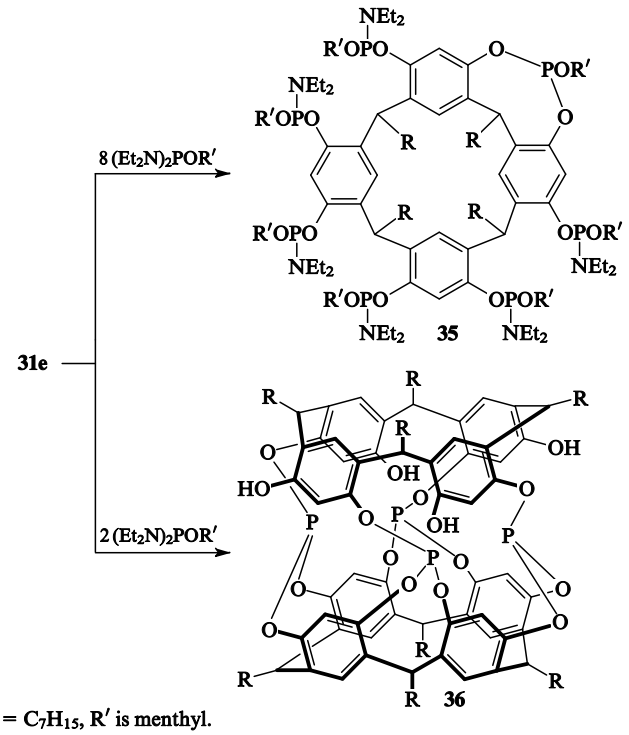
R = Ph, Me; X = NEt_2, OMe; Y = NEt_2.

When calixarenes **31d,e** were made to react with methyl and ethyl phosphorous diamides, the phosphates **33** were isolated from the reaction mixture instead of the expected macrocyclic phosphites **32**; the latter proved to be extremely unstable and were easily oxidised to phosphates by atmospheric oxygen. The macrocyclic phosphites **32** were detected only in the reactions of **31d,e** with heptyl and octyl phosphorous diamides.[39]



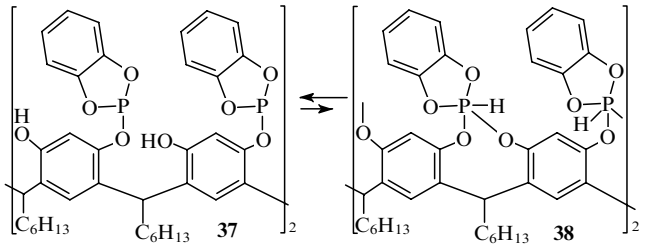
R′ = Me, Et; X = OC_7H_{15}, OC_8H_{17}; Y = OMe, OEt.

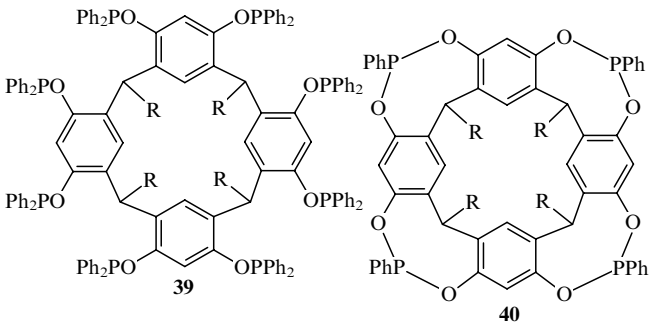
Phosphorylation of the calixarene **31e** with (−)-menthyl tetraethylphosphorous diamide under mild conditions with different ratios of the reactants affords completely and partially phosphorylated optically active derivatives containing both cyclic phosphite groups and acyclic menthyl phosphorous amide fragments (for example, compound **35**). When the ratio of the reactants is 1 : 2 and the reaction conditions are more drastic the 'ball' structure **36** is formed.[40]

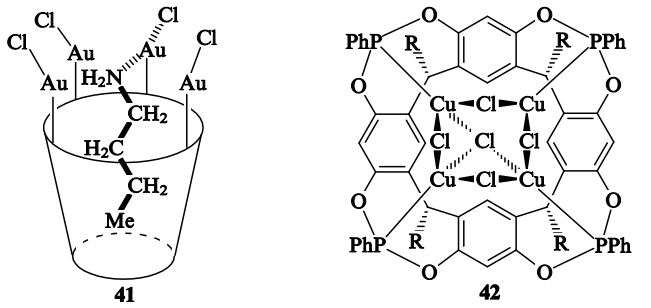


R = C_7H_{15}, R′ is menthyl.

The reaction of the calixarene **31d** with 2-chloro-1,3,2-benzodioxaphospholene at any ratio of the reactants gives phosphite **37**, occurring in an equilibrium with a slight amount of spirophosphorane **38**.[41]







R = CH_2CH_2Ph

Cavitands containing acyclic phosphinite (**39**) and cyclic phosphonite (**40**) fragments have been prepared by the reaction of the calixarene **31h** with chloro(diphenyl)phosphine and dichloro(phenyl)phosphine, respectively, in the presence of pyridine.[42] The high complexation capacity of these calixarenes was confirmed by introducing them into reactions with Pt(II) and Au(I) salts. The structures of the resulting complexes (their composition is 1 : 4 or 1 : 8) depend on the nature of the metal (its coordination number). For the 1 : 4 complex, an unusual arrangement of the AuCl groups was established. Three of these groups are located at the upper rim of the calixresorcinolarene due to coordination to the phosphorus atom, while the fourth AuCl group resides in the macrocycle cavity; as a result, solvent molecules are arranged in the intermolecular space rather than inside the cavity. Only in the presence of amines, does the inclusion *endo*-complex **41** form. This property of the complex was used for extraction of alkali metal picrates.[42]

An unusual μ_3- and μ_4-bridging position of halide anions has been established by X-ray diffraction analysis for inclusion complexes **42** and for the complexes [Py][**40** · $Ag_4(\mu\text{-}Cl)_4 \cdot (\mu_4\text{-}Cl)$] and [Py][**40** · $Cu_4(\mu\text{-}Cl)_4 \cdot (\mu_3\text{-}Cl)$], in which one of the Cl^- anions is located in the cavity formed by the four cationic centres.[43,44] However, the bridging anion is only weakly fixed in the complex and can be easily replaced by other halide anions.

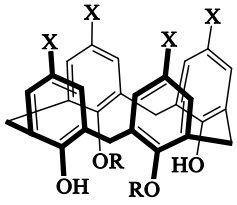
The use of phosphorus(III) halides for phosphorylation of calix[4]resorcinolarenes has been described.[45,46] The reaction of the macrocyclic compound **31b** with excess PCl_3 affords cyclic phosphorochloridites, similar to compounds **32** (X = Cl), rather than octakis(phosphorodichloridites) **34** (X = Y = Cl).[45] The structure of the reaction products was confirmed by the data of IR

spectroscopy, mass spectrometry and elemental analysis. The halogen atom in these compounds can be readily replaced by a methyl or dimethylamino group upon the reaction with MeMgI or Me_3SiNMe_2, respectively. The latter reaction gives the cyclic phosphorous amide **32b**, which reacts with tetrachloro-*o*-benzoquinone or hexafluoroacetone yielding spirophosphorane structures containing four $\sigma^5\lambda^5$ phosphorus atoms.

The octakis(phosphorodifluoridite) **34** (X = Y = F) was formed in the reaction with PF_2Cl[46] only when the calix[4]resorcinolarene **31g** had been first treated with excess Bu^nLi. This product was relatively unstable and decomposed over a period of 24 h at −35 °C to give PF_3 and a mixture of various compounds containing P(=O)F(O) and $P(=O)F_2$ fragments.

III. O-Phosphorylation of calixarenes by P(V) compounds

Phosphorylation of the tetrahydroxy-derivative **1** with diethyl phosphorochloridate was carried out in the presence of sodium hydride,[22] potassium carbonate in THF[47] or triethylamine in chloroform.[48,49] In all cases, the reaction gave bisphosphate **43a**, which exists in a *cone* conformation.



43a,b

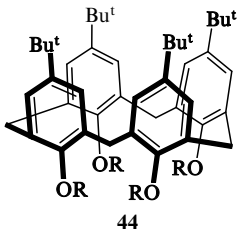
R = P(O)(OEt)$_2$, X = Bu^t (**a**), H (**b**).

Synthesis of the compound **43a** by the Atherton–Todd reaction (diethyl phosphite–triethylamine–tetrachloromethane, 0 °C) has been reported.[50–53] The phosphorylation of 25,27-dihydroxy-26,28-dimethoxy-*p*-*tert*-butylcalix[4]arene with diethyl phosphorochloridate in the presence of NaH[47] gives bisphosphate in the *1,2-alternate* conformation in which the methoxy groups are oppositely directed with respect to the main plane of the macrocycle.

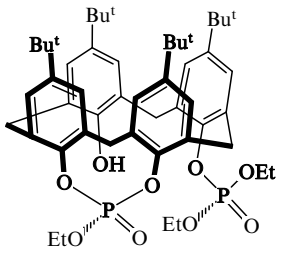
A detailed study[49] of the reaction of the compound **1** with diethyl chlorophosphate in the presence of triethylamine in chloroform has shown that under these conditions, in addition to the previously described bisphosphate **43a**, occurring in a *cone* conformation, a *1,2-alternate* with *anti*-orientation of the diethoxyphosphoryl groups with respect to the main plane of the macrocycle is also formed (its structure in the crystal was determined in another study[54]). The content of this compound in the reaction mixture changes from 9% to 15% following an increase in the excess of triethylamine. Phosphorylation of unsubstituted calix[4]arene under the same conditions gives the bisphosphate **43b** exclusively in a *cone* conformation. Alkylation of the phenolic hydroxy groups in the phosphate **43a** with ethyl iodide in the presence of NaH (THF : DMF = 4 : 1) gives rise to 5,11,17,23-tetra-*tert*-butyl-25,27-diethoxy-26,28-bis(diethoxyphos-phoryloxy)calix[4]arene in a *partial cone* conformation.[49]

Phosphorylation of the calixarene **1** with excess diethyl phosphorochloridate[50] or diethyl phosphite[55] under phase transfer catalysis conditions (CCl_4–H_2O, 50% NaOH, tetrabutylammonium bromide) yields tetraphosphorylated derivative **44**.

When a less lipophilic catalyst (tetraethylammonium bromide) is used, the reaction affords a mixture of the tetrakis(phosphate) **44** in a *partial cone* conformation and bis(phosphate) **45**, which contains both cyclic and acyclic phosphate fragments.[56] Complex-forming properties of a number of phosphates based on calix[4]arene have been studied by extraction.[57] It was found that the introduction of these compounds in the organic phase markedly increases the extraction of lanthanide picrates; however, no pronounced selectivity was observed.



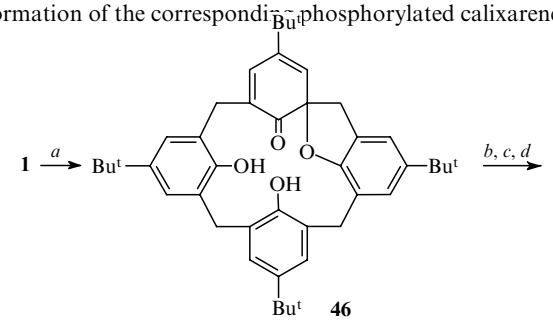
44



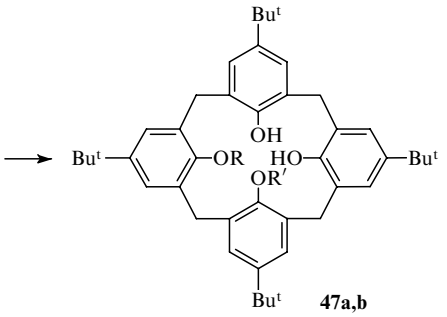
45

R = P(O)(OEt)$_2$

Mild oxidation of the compound **1** gives rise to spirodienone **46**, which can be used as the starting compound in the synthesis of mono- and 1,2-di-substituted calixarenes.[58,59] In particular, treatment of this compound with lithium diisopropylamide (THF, −78 °C) followed by the reaction of the resulting mono- or dilithium salt with excess diisopropyl phosphorochloridate and subsequent reduction of the spirodienone fragment result in the formation of the corresponding phosphorylated calixarenes **47**.



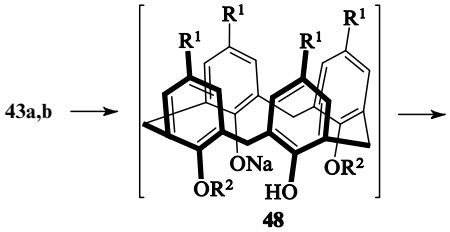
46



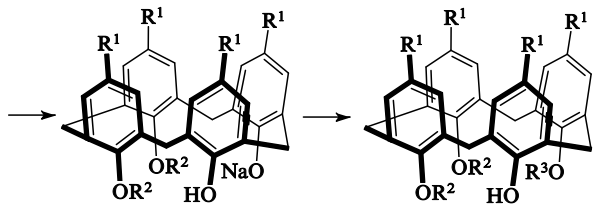
47a,b

R = P(O)(OPr^i)$_2$, R′ = H (**a**); R = R′ = P(O)(OPr^i)$_2$ (**b**);
(*a*) $Me_3PhN^+Br_3^-$, CH_2Cl_2, 0 °C; (*b*) $LiNPr^i_2$, THF, −78 °C;
(*c*) ClP(O)(OPr^i)$_2$; (*d*) EtOH, HBr.

Synthesis of asymmetrically substituted phosphorylated calix[4]arenes **50** has been described by Markovskii *et al.*[60] The treatment of 1,3-bis(diethoxyphosphoryl)calix[4]arenes **43a**,**b** with sodium hydride in boiling benzene followed by interaction with electrophilic reagents, such as benzoyl chloride or methyl bromoacetate, affords asymmetrically substituted calix[4]arenes **50a–c** of the AABH type. The use of diethyl phosphorochloridate as an electrophilic reagent gives rise to triphosphorylated calixarenes **50c**.



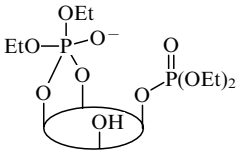
48



49 **50a–c**

R^1 = H or Bu^t, R^2 = P(O)(OEt)$_2$; R^3 = $CH_2C(O)OMe$ (**50a**), PhCO (**50b**), P(O)(OEt)$_2$ (**50c**).

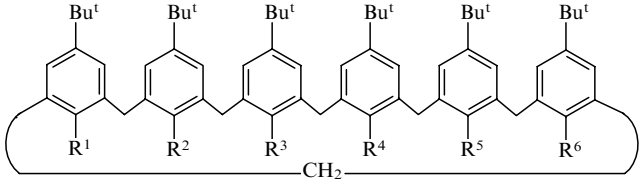
The key stage in the synthesis is the formation of the unstable monoanion of **48** and its *O*,*O*-phosphorotropic rearrangement to the 1,2-bis(diethoxyphosphoryl)calix[4]arene monoanion of **49**; the rearrangement occurs *via* phosphorane **51**, which was detected by ^{31}P NMR spectroscopy.



51

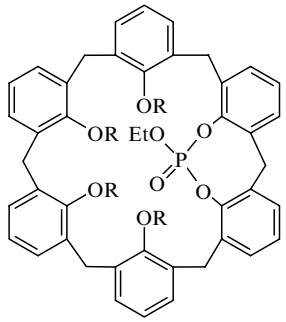
All these products exist in a *cone* conformation, while the asymmetrically substituted calix[4]arenes **50a**,**b** have C_1 symmetry and are formed as racemic mixtures, which is indicated by doubling ($\Delta\delta$ = 0.01 ppm) of the phosphorus signals in the ^{31}P NMR spectra recorded in a chiral solvent.

O-Phosphorylation of calix[5]-, -[6]- and -[8]arenes is less studied. Data on selective phosphorylation are available only for calix[6]arene. Selective functionalisation of the hexahydroxy-derivative **26** by diethyl phosphorochloridate and *O*,*O*-diethyl phosphorothiochloridate has been performed and the conformational behavior of the products synthesised has been studied.[61,62] In the case of diethyl phosphorochloridate, the reaction was carried out with various amounts of triethylamine in boiling chloroform. In all cases, the obtained product mixtures were analysed by HPLC and separated by column flash chromatography. This gave mono-, 1,3-bis-, 1,4-bis-, and 1,2,4-tris(phosphorylated) derivatives **52a–d**.



52a–l

R^1 = OP(O)(OEt)$_2$, R^2 = R^3 = R^4 = R^5 = R^6 = OH (**a**);
R^1 = R^3 = OP(O)(OEt)$_2$, R^2 = R^4 = R^5 = R^6 = OH (**b**);
R^1 = R^4 = OP(O)(OEt)$_2$, R^2 = R^3 = R^5 = R^6 = OH (**c**);
R^1 = R^2 = R^4 = OP(O)(OEt)$_2$, R^3 = R^5 = R^6 = OH (**d**);
R^1 = R^2 = R^3 = R^4 = R^5 = R^6 = OP(O)(OEt)$_2$ (**e**);
R^1 = R^4 = OP(S)(OEt)$_2$, R^2 = R^3 = R^5 = R^6 = OH (**f**);
R^1 = OP(S)(OEt)$_2$, R^2 = R^3 = R^4 = R^5 = R^6 = OH (**g**);
R^1 = R^3 = OP(S)(OEt)$_2$, R^2 = R^4 = R^5 = R^6 = OH (**h**);
R^1 = R^2 = R^3 = R^4 = R^5 = OP(S)(OEt)$_2$, R^6 = OH (**i**);
R^1 = R^3 = R^5 = OMe, R^2 = R^4 = R^6 = OP(O)(OEt)$_2$ (**j**);
R^1 = R^3 = R^5 = OMe, R^2 = R^4 = R^6 = OP(S)(OEt)$_2$ (**k**);
R^1 = R^2 = OMe, R^3 = R^4 = R^5 = R^6 = OP(S)(OEt)$_2$ (**l**).

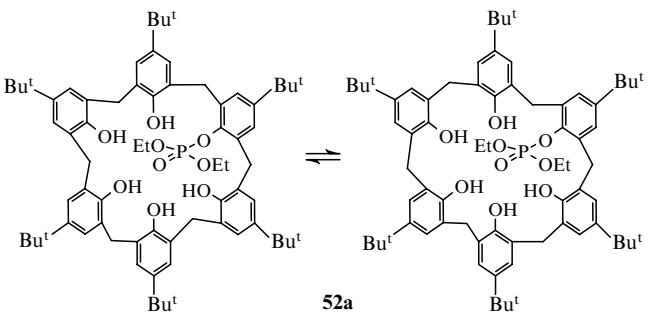


52m (R = P(O)(OEt)$_2$)

Depending on the reaction conditions, the optimum yields of these compounds vary from 28% to 56%. It is of interest that in another study,[48] 1,3,5-tris(phosphorylated) product was obtained in 60% yield under the same conditions.

The fully substituted derivative **52e** was synthesised in 20% yield under conditions of phase transfer catalysis in the CH_2Cl_2–50% NaOH system in an excess of diethyl phosphorochloridate. The use of anhydrous solvent and solid alkali permitted the yield to be increased to 37%.[61] Under the same conditions, pentakis(-diisopropoxyphosphoryloxy)calix[5]arene[26] (in a *cone* conformation) and octakis(diethoxyphosphoryloxy)calix[8]-arene[63] have been obtained. It was also noted[63] that phosphorylation of the compound **26** with diethyl phosphorochloridate can give not only the product **52e** but also the pentaphosphorylated derivative **52m** with one cyclic phosphate fragment. The use of sodium hydride as a base in a THF–DMF mixture (10 : 1) affords the compound **52e** as a *flattened 1,2,3-alternate* conformation in 75% yield.[64]

When the calixarene **26** is made to react with a large excess of less reactive *O*,*O*-diethyl phosphorothiochloridate in the CH_2Cl_2–50% aqueous NaOH system, the 1,4-bis(thiophosphorylated) product **52f** is formed selectively in 60%–70% yield. Variation of the conditions of phase transfer catalysis makes it possible to synthesise also mono-, 1,3-bis-, and pentakis-thiophosphorylated derivatives **52g–i**.[65] The phosphates **52j–l** were prepared by phosphorylation of partially methylated calix[6]arenes under similar conditions.[66] Study of the mono-(**52g**)[62] and 1,4-bis(thiophosphorylated) (**52f**)[61] products by X-ray diffraction analysis and ^{1}H NMR spectroscopy (solution in $CDCl_3$) showed that they exist in a *pinched cone* conformation (C_{2v} symmetry), in which the two opposite methylene bridges are directed towards the centre of the macrocycle. It is notable that 1,4-diphosphorylated compound **52c** exists in a *1,2,3-alternate* conformation. According to NMR spectroscopy, the macrocycle **52j** in $CDCl_3$ solutions exists as an equilibrium of two conformers, *cone* (C_{3v} symmetry) and *1,2,3-alternate* (C_s symmetry), the former conformation being 4 kJ mol^{-1} more stable.[66] The researchers believe[66] that the *cone* conformation is stabilised due to the weak CH–π interactions of the methyl groups, which, according to X-ray diffraction analysis, are directed inside the ring.

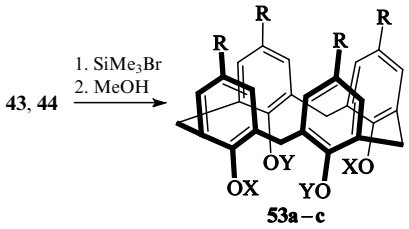


52a

Study of partially phosphorylated and thiophosphorylated *p-tert*-butylcalix[6]arenes, for example **52a**, by dynamic NMR has shown [62] that these macrocycles participate in, at least, three dynamic processes: (a) interconversion of the macrocyclic ring; (b) redistribution of hydrogen bonds; (c) interconversion of two *pinched cone* conformations.

Monosubstituted derivatives proved to be conformationally more rigid than 1,3- and 1,4-disubstituted derivatives. This is due to the fact that the activation energy of conformation transitions depends on the number of hydrogen bonds, which can be formed by the hydroxy groups that remain free. The contributions of hydrogen bonding to $\Delta G^{\neq}$ are 45 and 31 kJ mol^{-1} for the mono- and di-substitiuted derivatives, respectively.

The calix[4]arenes **53**, containing two or four dihydroxyphosphoryl groups on the 'lower' rim of the macrocycle, were prepared in high yields [67] from readily acessible bis- and tetrakis-diethoxyphosphoryl derivatives of calixarenes **43** and **44**.

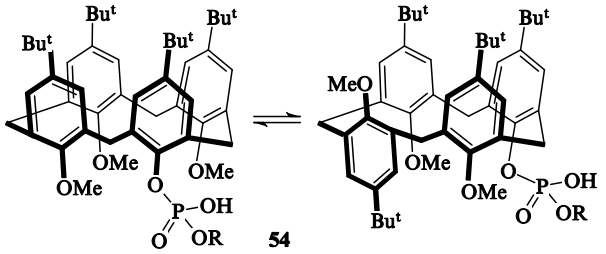


53a–c

R = H, X = H, Y = $(HO)_2PO$ (**a**);
R = Bu^t: X = H, Y = $(HO)_2PO$ (**b**); X = Y = $(HO)_2PO$ (**c**).

When these products are treated with excess bromotrimethylsilane in a solution in anhydrous chloroform, the corresponding silyl esters are prepared in quantitative yields. On treatment of these compounds with methanol, the labile P–O–Si bond ruptures; this gives the acids **53** as colorless crystalline compounds, readily soluble in polar organic solvents (alcohols, DMSO, DMF) and in aqueous solutions of alkali; they are stable in aqueous alcohols and in amine–alcohol mixtures for several days. The compounds **53a–c** are relatively strong acids [pK_a 2.85, 3.10 and 2.90 (aqueous methanol)]. They form 1 : 1 and 1 : 2 *exo*-complexes with *tert*-butylamine, α-phenylethylamine and ephedrine; the complexes exist in a solution in deuterated methanol as contact ion pairs.[67]

In order to develop selective agents for the transfer of lithium cations through liquid membranes, the phosphates **54** were synthesised by the reaction of 25,26,27-trimethoxy-28-hydroxy-*p-tert*-butylcalix[4]arene with alkyl phosphorodichloridates followed by hydrolysis.[68] Spectral data indicate that the compounds **54a–c** occur in solution as mixtures of two conformers, a *cone* and a *partial cone*, the equilibrium being sensitive to the influence of the medium.

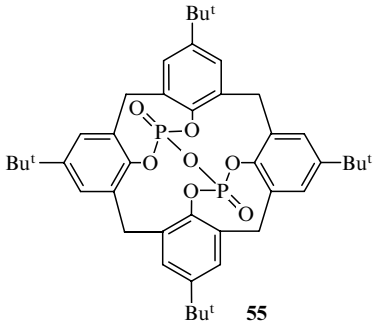


54

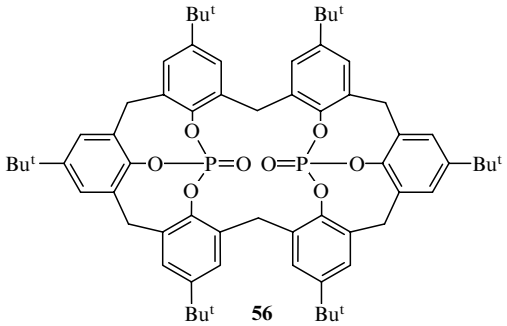
R = Me (**a**), Et (**b**), Pr^n (**c**).

The fraction of the *cone* conformation in which all the four dipoles point in the same direction increases with increase in the solvent polarity. It is noteworthy that the complexation of the compounds **54** with Li^+ and Na^+ cations occurs more readily for the *cone* conformation of the calixarenes; therefore, no macrocycles in the *partial cone* conformation were found in the complexes.

Pyrolysis *in vacuo* (230–240 °C) of mono-, bis-, and tetrakisphosphates **43**, **44** and **47**, irrespective of the number of phosphorus-containing groups, gives the same product, pyrophosphate **55**, in which all the hydroxy groups are bound intramolecularly.[26, 69] This means that the formation of the compound **55** involves stages of fragmentation and intermolecular migration of the phosphate groups. Study of the crystal structure of the pyrophosphate **55** showed that the two terminal oxygen atoms and the oxygen atom of the P–O–P bridge are directed away from the plane of the molecule. The conformation of the pyrophosphate can be defined as a *pinched* or *flattened cone*. Pyrolysis of a mixture of regioisomers of phosphorylated *p-tert*-butylcalix[6]arenes yields isomeric bridged bis(phosphates) **56**, which differ in the arrangement of the phosphoryl oxygen atoms (either *syn*- or *anti*-).

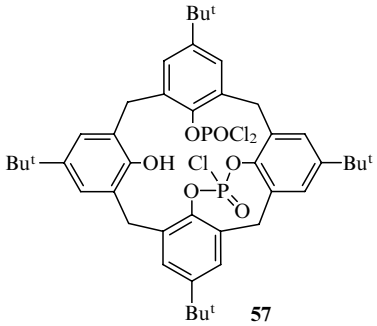


55

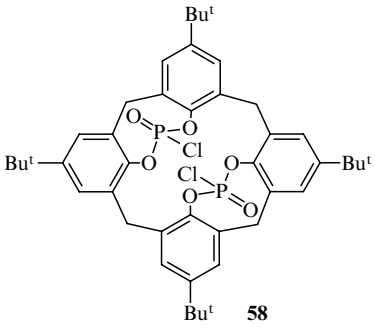


56

Yet another pathway to phosphorus-containing bridged macrocyclic structures is reaction of the compound **1** with phosphorus halides. Thus refluxing of **1** with $POCl_3$ in chloroform in the presence of Et_3N gives rise to the mono-bridged system **57**. At higher temperatures (xylene, 85 °C), the reaction affords structure **58** with two bridges, which might be a mixture of stereoisomers with different spatial arrangements of the P–Cl and P=O bonds.[23]

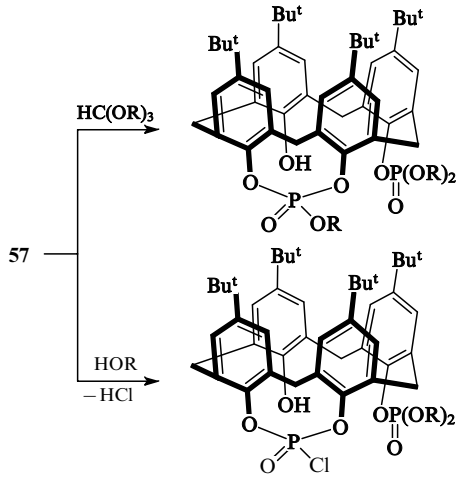


57



58

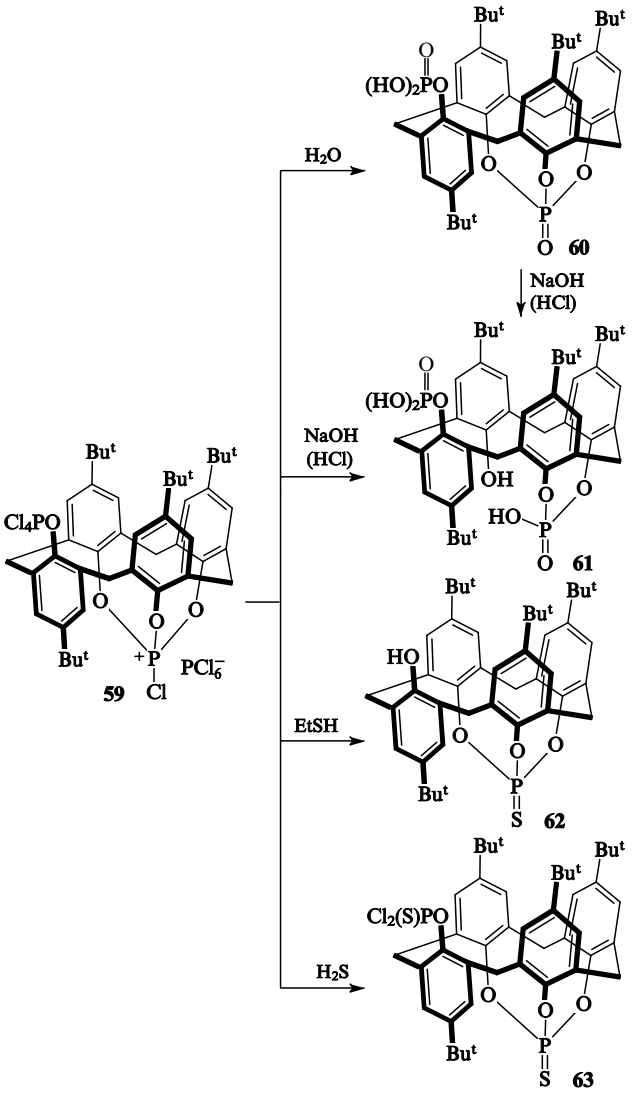
Interestingly, pyrolysis of the compound **57** also gives the pyrophosphate **55**. Glode *et al.*[70] have studied the reactivity of the compound **57** towards nucleophilic reagents such as water, alcohols and orthoformates. It was found that the halogen atoms can be successfully substituted by hydroxy or alkoxy groups to give the corresponding acids or esters; these reactions do not involve the P–O–C bonds.[70]



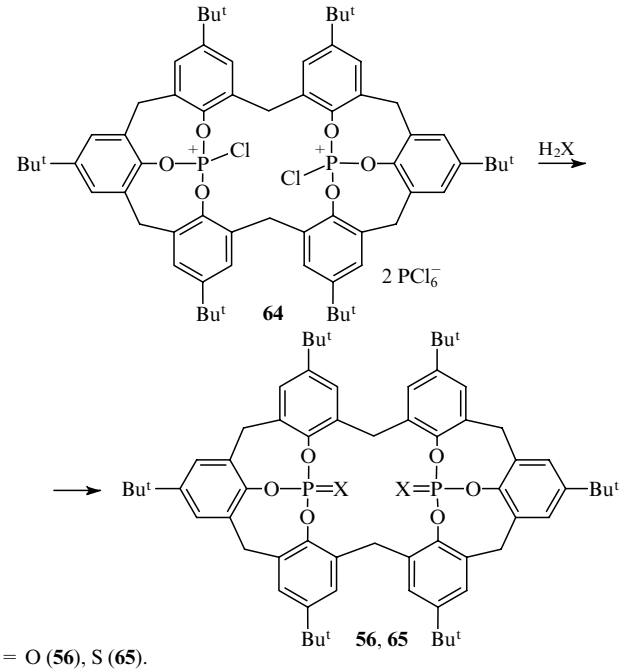
R = H, Me, Et.

When the calixarene **1** is treated with three equivalents of PCl_5, the macrocyclic compound **59**, containing three phosphorus atoms, is formed.[71,72] According to ^{31}P NMR spectroscopy, one of these atoms forms a phosphonium cation upon linking to the three phenolic groups, a second phosphorus atom forms the quasiphosphonium group $OPCl_4$, while the third atom occurs as the PCl_6^- anion (δ_P = 8.1, −66.0 and −296 ppm, respectively). The X-ray diffraction analysis of the compound **59** confirmed the presence of tetra-, penta- and hexa-coordinated phosphorus atoms. The macrocycle conformation is intermediate between a *partial cone* and *1,2-alternate*.[73] All the three phosphorus atoms in the compound **59** are reactive. On treatment with $SbCl_5$, the PCl_6^- anion is replaced by $SbCl_6^-$; reactions with nucleophiles occur as substitution at the P–Cl bond and, under more rigorous conditions, also at the P–O bond.

For example, the reaction of **59** with water gives phosphate **60** in which the P–O–C bonds remain intact. However, upon prolonged action of acids or alkali, the 1,2,3-linked phosphate is converted into 1,2-phosphate **61** as a result of hydrolysis of one P–O–C bond. The compounds **60** and **61** contain free hydroxy groups and can be easily converted into the corresponding esters on treatment with diazomethane or orthoformates. Reactions with sulfur-containing nucleophiles give phosphorothioates **62** and **63**, the character of binding in the lower rim of calix[4]arene remaining invariable; this points to high stability of phosphates and phosphorothioates bound to the 1,2,3-positions of the calixarene system. According to ^1H and ^{13}C NMR spectroscopy and X-ray diffraction analysis, the compounds **60**–**63** occur in a *partial cone* conformation.[71,72,74,75]



The reaction of the calix[6]arene **26** with four equivalents of PCl_5 yields hexakis(chlorophosphate) **64**, which, like **59**, is capable of exchanging the PCl_6^- anion for the $SbCl_6^-$.[72]



X = O (**56**), S (**65**).

The reactions with water and hydrogen sulfide afford the phosphate **56** and phosphothioate **65**. The phosphoryl oxygen and sulfur atoms point in the same direction in relation to the main plane of the macrocycle. This makes these compounds promising chelating agents for cations of many *d*- and *f*-elements.

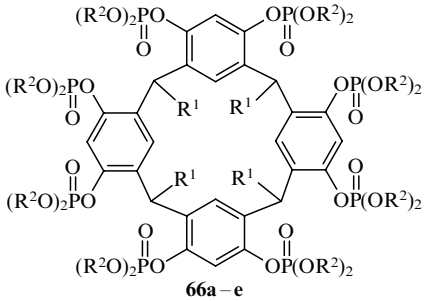
The reaction of the compound **26** with ethyl phosphorodichloridate gives rise to cyclic mono- and bis-phosphates.[76] The reaction route depends on the nature of the base used. In the presence of CsF, monophosphate is formed, while the use of calcium hydride results in the formation of the diphosphorylated product.[76] The spatial structure of the macrocycles obtained was not determined.

The calix[4]resorcinolarenes **31** are readily phosphorylated by traditional reagents, chlorides of acids of tetracoordinated phosphorus and the $(RO)_2PHO-CCl_4-Et_3N$ ternary system. The reactions of the octahydroxy-derivative **31** with excess diorganyl phosphorochloridates and triethylamine (20 °C, THF) afford octaphosphorylated cyclophanes **66**.[77–79]

The reaction outcome depends on the nature of the radical in the diorganyl phosphorochloridate. Even when excess phosphorylating reagent is used, the reactions with diethyl and dipropyl phosphorochloridates give tetraphosphorylated products **67** together with octasubstituted derivatives. In the case where diisopropyl phosphorochloridate is employed, the reaction stops at the stage of formation of the tetraphosphorylated product, due to the steric hindrance during the process and the low solubility of the corresponding tetrasubstituted products, resulting in their removal from the reaction area.[79] The tetrakis(phosphates) **67** were obtained by using a large excess of the reagent (**31** : phosphorochloridate : triethylamine = 1 : 5 : 5) and by treating the compound **31** with the $(RO)_2PHO-CCl_4-Et_3N$ ternary system (**31** : reagent = 1 : 10). It should be noted that in early studies,[77,78] the structure with alternating positions of the phosphoryl groups along the macrocycle rim had been assigned to the tetrakis(phosphates) formed in these reactions; however, later it was found[79] that a structure of the type **67** in which the phosphoryl groups occupy the opposing positions is more probable. The tetrakis(phosphates) **67** were further modified. Thus hydrolysis of the phosphate groups in **67**, *via* the intermediate synthesis of the corresponding trimethylsilyl ester, gave tetrakis(dihydroxyphosphoryloxy)tetrahydroxycalix[4]resorcinolarene **67g**.[81] Reaction of the free hydroxy groups in **67** with 4-chlorosulfonylbenzo-15-crown-5 in the presence of triethylamine gave the derivative **67h**.[82]

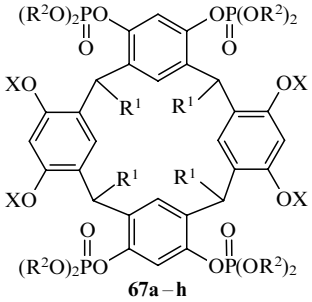
A study of the conformational behaviour of the tetrakis(phosphates) **67** by dynamic NMR spectroscopy has shown that at room temperature, fast pseudo-rotation of the *boat–boat* type occurs, which consists in the mutual transition of the two pairs of opposing benzene rings between the perpendicular and coplanar arrangements with respect to the main macrocycle plane.[79]

Estimation of the complex-forming properties of the cyclophanes synthesized showed that they can form stable complexes both with some metal cations and with neutral aromatic molecules. The phosphoryl groups present in the molecule impart pronounced ionophoric properties to it. When the octakis(phosphate) **66d** is used as an ion transferring agent, the rate of transfer of alkali and alkaline earth metal picrates through a liquid membrane increases 1.3–9.0-fold compared to that attained with 15-crown-5; however, the transfer is almost nonselective.[79] The compound **67h** has demonstrated selectivity towards potassium cations.[82] The octakis(phosphates) **66c**,**d**, owing to their lipophilic cavity, form crystalline 'host–guest' complexes with aromatic compounds, toluene and *m*-cresol.[79] Later,[80] the structures of several complexes of this type in solution and in the solid state were studied by X-ray diffraction analysis and NMR spectroscopy. The cyclophane **67g** forms 'host–guest' complexes with benzene, toluene, anisole, xylenes, phenol and 1-phenylalanine in aqueous solutions. The complexes result from inclusion of a 'guest' molecule into the cavity formed by the preorganised pentyl radicals.[81]



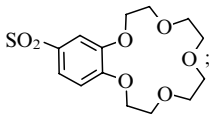
66a–e

R^1 = Me: R^2 = Et (**a**), Pr^n (**b**), Ph (**c**), *p*-MeC_6H_4 (**d**);
R^1 = n-C_5H_{11}, R^2 = Ph (**e**).



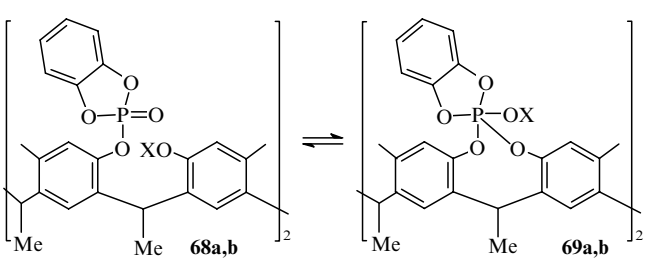
67a–h

X = H, R^1 = Me: R^2 = Et (**a**), Pr^n (**b**), Pr^i (**c**), Bu^i (**d**);
X = H, R^1 = n-C_5H_{11}: R^2 = Et (**e**), Pr^i (**f**), H (**g**);

X =  ; R^1 = n-C_5H_{11}, R^2 = Et (**h**).

Tetrakis(phenylenephosphoryloxy)[1.4]metacyclophane **68a** was synthesised by the reaction of the octahydroxy-derivatives **31b** with four equivalents of *o*-phenylene phosphorochloridate and triethylamine.[78,79]

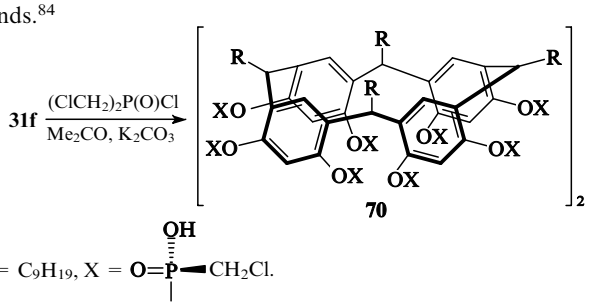
Since the phosphorus atoms are located closely to the hydroxy groups of the neighbouring aromatic rings, intramolecular nucleophilic addition of the hydroxy groups to the P=O bonds occurs to give spirophosphorane structure **69a**. The driving force of this process is formation of the energetically more favourable pentacoordinated phosphorus atom in the dioxaphospholane ring. This reaction is reversible; the position of the equilibrium depends on the temperature and the nature of the solvent. On treatment with triethylamine, the **68a** ⇌ **69a** equilibrium shifts towards the more acidic form, **68a**. A similar equilibrium is observed for the **68b** ⇌ **69b** system. In pyridine, which is capable of binding to a pentacoordinated phosphorus atom,[83] the equilibrium shifts towards the spirocyclic tautomer **69b**.



68a,b **69a,b**

X = H (**a**), $SiMe_3$ (**b**).

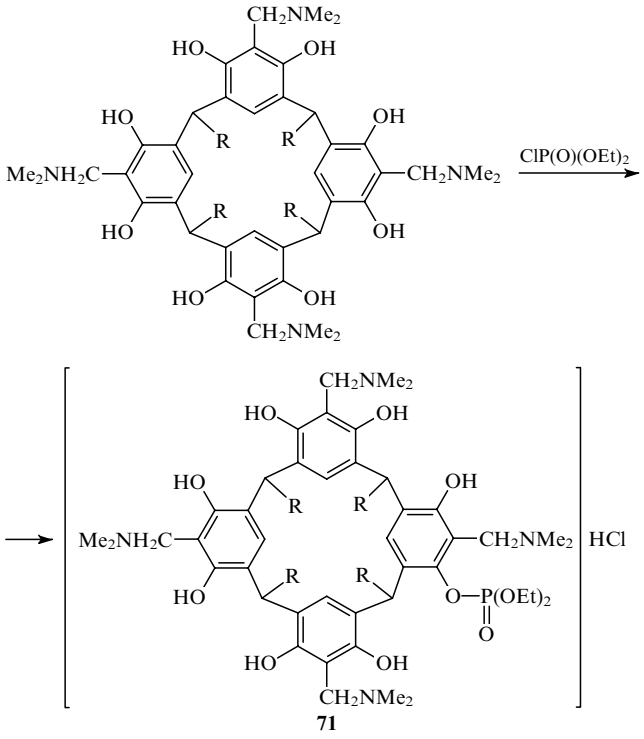
When the compound **31f** (R = C_9H_{19}) was made to react with excess bis(chloromethyl)phosphinic chloride (acetone, K_2CO_3), instead of the expected bis(chloromethyl)phosphinic acid derivatives, octakis(chloromethylphosphonate) was isolated, due to the extremely easy rupture of one of the P–C bonds in the phosphinate. The product exists in solution as dimer **70** formed according to the 'head-to-head' pattern due to intermolecular hydrogen bonds.[84]



70

R = C_9H_{19}, X =

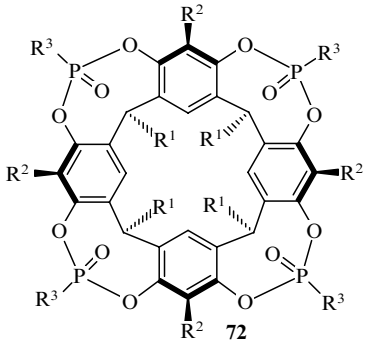
The first representatives of monophosphorylated cyclophanes **71** were prepared by refluxing in benzene of aminomethylated octahydroxy-derivatives with diethyl phosphorochloridate.[85]



71

R = Me, Hex^n.

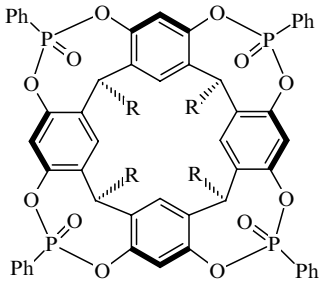
The use of organyl phosphorodichloridates or organylphosphonodichloridates for phosphorylation of the cyclophanes **31** has been reported.[84,86–88] The reaction with alkyl and aryl phosphorodichloridates in acetone in the presence of triethylamine results in the formation of diastereoisomeric cavitands **72**, which differ in the spatial arrangement of the P=O groups in the four phosphocine rings: *i* (the P=O group points to the centre of the upper rim) and *o* (the P=O group points outwards).[86,87] The reaction with ethyl phosphorodichloridate proceeds with a low yield (12%), owing to the competing intermolecular cross-linking of the calixarene fragments, resulting in the formation of polymers. The use of aryl phosphorodichloridates permits the yields of the target products to be increased to 50%–80%. The reaction gives all of the six possible stereoisomers, although three of them, *iiio*, *iioo* and *iooo*, proved to be more preferable (the proportion of each isomer was determined by HPLC). The proportions of the *iiii* (compound **72**) and *oooo* isomers in the reaction mixture are not higher than 10%; in some cases, they do not form at all. It is quite natural that as the substituent R^3 becomes larger, the content of the *iiio* isomer increases, whereas the content of the *iooo* isomer correspondingly decreases. It is clear that the receptor capacity of the macrocyclic compounds obtained depends on the spatial arrangement of the phosphoryl groups. The *iiii* and *iiio* isomers are the most promising complex-forming agents. Thus the *iiio* isomer forms a complex with cyclohexylammonium (K_a = 1370 litre mol^{-1}) as a result of three-point hydrogen binding, whereas the *iioo* and *iooo* isomers do not form complexes of this type.



72

R^1 = Ph, Alk; R^2 = H, Br; R^3 = OEt, OAr.

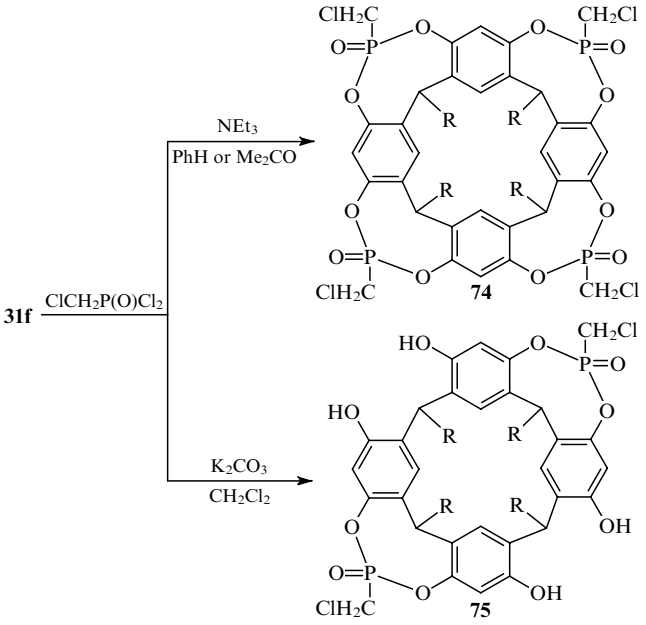
It has been reported[88] that the *iiii* stereoisomer of compound **73** is formed as the major product in the reaction of the octahydroxy-derivative **31a** with phenylphosphonic dichloride. The publication does not present the conditions of the synthesis. The product was identified as having the *iiii* configuration based on its C_{4v} symmetry (although the *oooo* isomer has the same symmetry). The strong complexing properties of the reaction product served as additional evidence for its *iiii* configuration. The compound **73** forms stoichiometric complexes with alkali metal and alkylammonium cations, characterised by association constants of 10^8–10^{10} litre mol^{-1}; the composition of the complexes is 1:1 (K^+, Rb^+, Cs^+, NH_4^+, $MeNH_3^+$, $Bu^tNH_3^+$) or 1:2 (Li^+, Na^+).



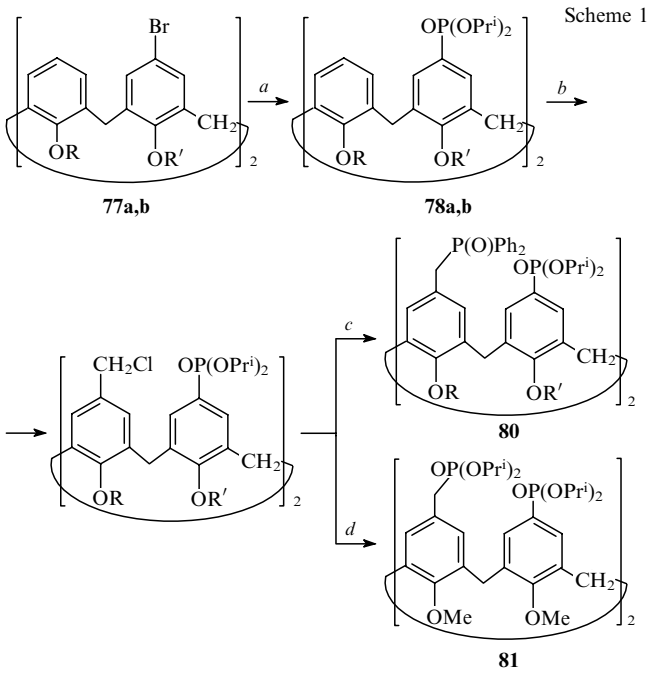
73 (R = Me)

The reaction of the long-chain calix[4]resorcinolarene **31f** with chloromethylphosphonic dichloride in the presence of triethylamine gives completely phosphorylated product **74**; when potassium carbonate is used as the base, partially phosphorylated product **75** is formed.[84]

The use of $POCl_3$ (in the presence of pyridine as the base) for introduction of phosphate groups has been reported.[89] In relation to *C*-undecylcalix[4]resorcinolarene, it was shown that at various ratios of the reactants (ranging from 1:1 to 1:39), complex mixtures of cyclic and acyclic phosphates with different numbers of phosphate fragments (from 1 to 6.3) are formed. Complete phosphorylation was not attained even with a large excess of $POCl_3$. These compounds exhibit surfactant properties and form stable complexes with UO_2^{2+}.



Scheme 1

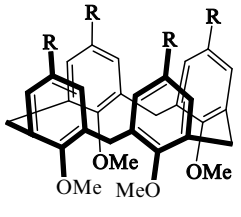


R = R′ = Me (**a**); R = Me, R′ = $C_{12}H_{25}$ (**b**).
(*a*) $P(OPr^i)_3$, $NiBr_2$; (*b*) $C_8H_{17}OCH_2Cl$, $SnCl_4$; (*c*) $AlkOPPh_2$; (*d*) $P(OPr^i)_3$, R = R′ = Me.

IV. Phosphorylation of the aromatic rings in calixarenes

Phosphorylation of the aromatic rings in calixarenes gives rise to a new type of receptors in which, unlike *O*-phosphorylated derivatives, the molecular cavity of the cyclophane can also be involved in the molecular binding of a substrate. The presence of organophosphorus compounds in the upper rim of the macrocycle permits the receptor to interact both with polar or ionic groups of a substrate and with non-polar fragments, the latter being included in the molecular cavity of the cavitand. Thus, multi-point 'host–guest' binding is attained, which is known to increase sharply the efficiency and selectivity of complex formation.[90,91] Moreover, P–C bonds are thermally and hydrolytically more stable than P–O bonds, which are formed upon phosphorylation of the lower rim of calix[*n*]arenes.

The first representative of this type of cyclophanes, tetrakis(diphenylphosphino)calixarene **76**, was synthesised by successive reactions of the tetramethyl ether of *p*-tetrabromo-calix[4]arene **76a** with butyllithium and chloro(diphe-nyl)phosphine.[92] Nevetheless, the Arbuzov reaction catalysed by nickel(II) salts is now the simplest and the most efficient method for direct phosphorylation of the upper rim of calix[4]arenes.[93]

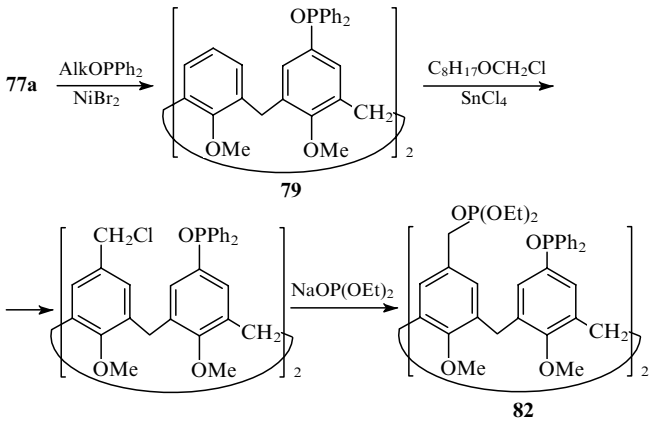


76a–d

R = Br (**a**), PPh_2 (**b**), $P(O)(OPr^i)_2$ (**c**), $P(O)Ph_2$ (**d**).

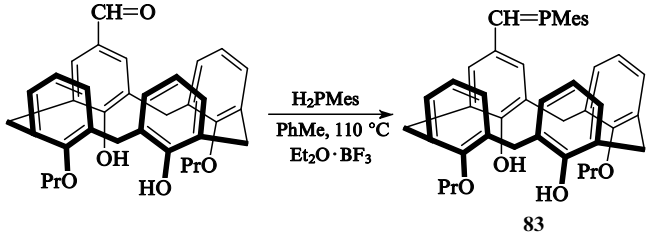
The reaction of the compound **76a** with triisopropyl phosphite or isopropyl diphenylphosphinite gives the corresponding tetraphosphorylated calix[4]arenes **76c**,**d** in high (75%–80%) yields.

The same approach was used in another study[94] in order to prepare bis- and ABAB-tetrakis-phosphorylated derivatives. The reactions of *O*-alkylated dibromides **77a**,**b** with triisopropyl phosphite or alkyl diphenylphosphinite in the presence of $NiBr_2$ gave bisphosphonates **78a**,**b** and bis(phosphine oxide) **79** (Scheme 1). Treatment of the compounds **78** and **79** with octyl chloromethyl ether in the presence of $SnCl_4$ resulted in the introduction of CH_2Cl groups into the free *p*-positions of the



aromatic rings. It is of interest that in the case of the methyl ethers **78a** and **79**, the chloromethyl derivatives are formed in high yields (60%–70%); when the dodecyl ether **77b** is used, the yield decreases to 26%. It has been reported that the size of the alkyl radical has a considerable influence on the kinetics of phosphorylation of calix[4]resorcinolarenes.[95,96] This was explained by assuming formation of different types of aggregates in the solution. The subsequent substitution of the chlorine atom by phosphorus-containing nucleophiles gave rise to ABAB-tetraphosphorylated cyclophanes **80**–**82**.

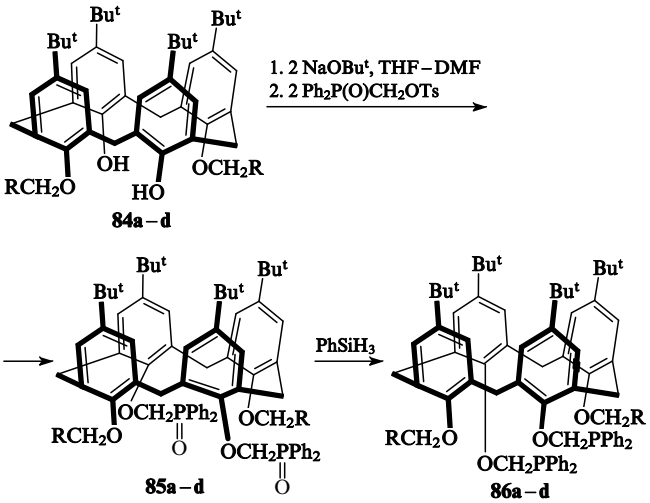
The first representative of calixarenes containing a low-coordinate phosphorus atom, phosphinylidenemethylcalixarene **83**, was synthesised as a mixture of stable *Z*- and *E*-stereoisomers capable of forming complexes with transition metals, by the following reaction:[97]



V. Introduction of phosphorus-containing fragments *via* a chain of atoms (spacer)

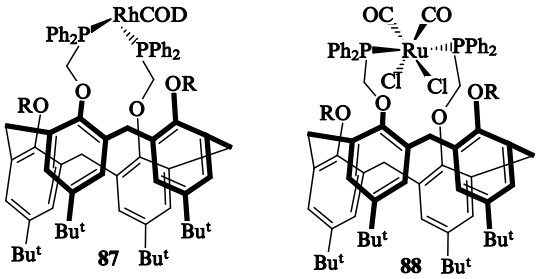
A vigorously developing route of the functionalisation of calix[*n*]arenes aimed at producing more efficient and selective complex-forming agents is introduction of organophosphorus groups in which phosphorus atoms are not attached directly to the lower or upper rim of the macrocycle but are linked to the calixarene platform *via* a chain of other atoms (spacer). This approach makes it possible to extend substantially the synthetic potential in the construction of new macrocyclic receptors.

Deprotonation of 1,3-bis(ethoxycarbonylmethyl) calix[4]-arene derivative **84a** with sodium *tert*-butoxide and subsequent alkylation of the resulting dianion with $Ph_2P(O)CH_2OTs$ gives rise to bis(phosphine oxide) cyclophane **85a** in a *cone* conformation.[98]



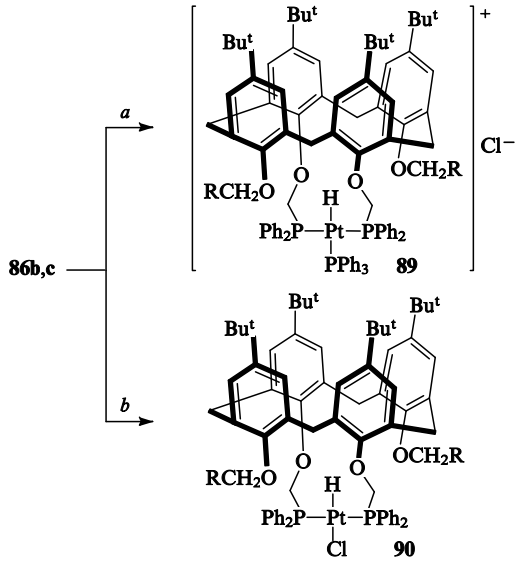
R = C(O)OEt (**a**), C(O)NEt$_2$ (**b**), CH_2OMe (**c**), C(O)NHCH(Me)Ph (**d**).

When potassium *tert*-butoxide is used as the base in this reaction, the product **85a** is formed in a *partial cone* conformation. The crucial influence of the nature of the cation on the stereochemical outcome of the reaction was explained by the difference in the energy of binding of potassium and sodium cations to the intermediate diphenoxide. The harder sodium cation interacts more strongly with phenoxide anions and thus it fixes the *cone* conformation of the calixarene platform. When the compounds **85** are refluxed with phenylsilane in toluene, the phosphine oxide group is quantitatively reduced to give the corresponding bis(phosphine) macrocycles **86**; according to X-ray diffraction and ^1H and ^{13}C NMR data, this product also occurs in a *cone* conformation.[98] The compounds **86** can act as both *cis*- and *trans*-chelating ligands. *cis*-Complexes are formed upon the reactions of the calixarene **86a** with $PtCl_2(PhCN)_2$ and $[Rh(COD)Cl]_2$ (**87**) in the presence of $AgBF_4$. The reaction of the compound **86a** with $RuCl_3$ and CO in boiling 2-ethoxyethanol affords the complex **88** with *trans*-P,P stereochemistry in a quantitative yield.[98]



R = CH_2CO_2Et; COD is cycloocta-1,5-diene.

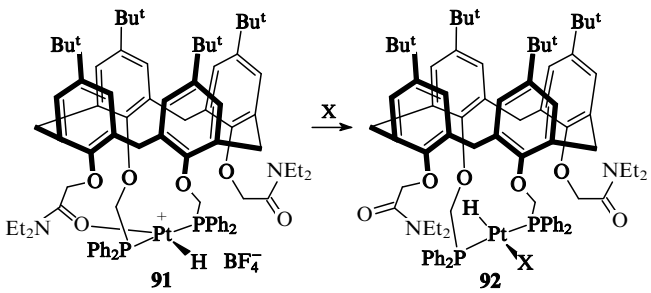
This method was used to prepare a series of metal-containing calixarenes[99–104] able to participate in catalytic processes. Based on the bis(phosphine) cyclophanes **86**, a number of new Pt(II), Pd(II), Rh(I) and Ru(II) complexes were prepared. The reaction of the compound **86c** with the platinum(II) bis(triphenylphosphine) complex in boiling THF is accompanied by displacement of a PPh_3 molecule and the chloride anion from the metal coordination sphere and yields the cationic complex **89**.



R = C(O)NEt$_2$ (86b, 90), CH_2OMe (86c, 89); (*a*) $(Ph_3P)_2PtHCl$, THF; (*b*) $(Ph_3P)_2PtHCl$, CH_2Cl_2.

The replacement of the ester side groups by amide groups, which interact more strongly with cations, crucially changes the reaction route. In this case, both triphenylphosphine ligands are replaced and neutral hydridochloride complex **90** is formed. Apparently, this outcome is due to the participation of two amide groups in the interaction with Pt(II); this accelerates the formation of intermediate species with pentacoordinated platinum and facilitates the ligand substitution.[101–103]

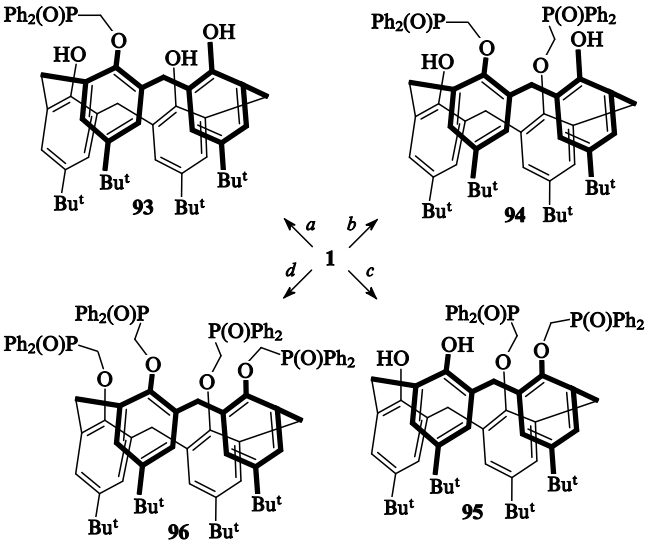
The structure of the complex **90** was studied. Two-dimensional (ROESY) NMR spectra and X-ray diffraction data attest convincingly that the hydride ion, responsible for the resonance signal at $\delta = -15.04$ ppm ($J_{H-Pt} = 1150$ Hz, $J_{P-H} = 15$ Hz), points to the centre of the calixarene cavity.[101, 103] The stereochemistry of the Pt–H bond can be changed by involving the amide groups in complex formation. Thus the reaction of the complex **90** with silver tetrafluoroborate yields hydrido complex **91** in which the Pt–H bond is directed outwards.[102, 103]



X is a donor.

In this environment, the hydride becomes much more reactive and can participate in various reactions. It is of interest that addition of a strong donor to the complex **91** results in displacement of the amide group from the coordination sphere yielding complex **92**, in which hydrogen is again directed inwards. This reaction makes it possible to change the reactivity of the hydride ion and creates conditions for the synthesis of bimetal hydrido complexes upon reactions with bidentate donors.[103]

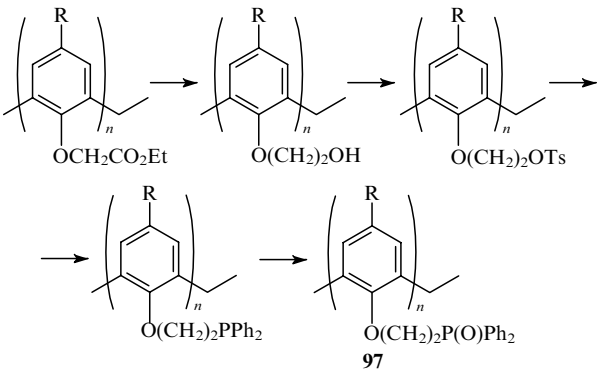
Selective introduction of one, two or four $CH_2P(O)Ph_2$ substituents into the lower rim of *tert*-butylcalix[4]arene **1** was attained by using NaH and an appropriate alkylating reagent.[105, 106]



(*a*) 3 equiv. NaH, 2.2 equiv. $Ph_2P(O)CH_2I$, THF, 50%;
(*b*) 5 equiv. NaH, 2.5 equiv. $Ph_2P(O)CH_2I$, PhMe, 80%;
(*c*) 2.5 equiv. NaH, 2.2 equiv. $Ph_2P(O)CH_2OTs$, THF–DMF, 25%;
(*d*) 6 equiv. NaH, 4.2 equiv. $Ph_2P(O)CH_2OTs$, THF–DMF, 70%.

When iodomethyl(diphenyl)phosphine oxide is employed as the alkylating reagent, the reaction gives, depending on the temperature and the amount of NaH used, either mono- (**93**) or 1,3-bis-(phosphine oxide) **94**. The reaction with more reactive hydroxymethyl(diphenyl)phosphine oxide tosylate allows the synthesis of the corresponding 1,2-di- (**95**) and tetra-substituted (**96**) derivatives. According to NMR and X-ray diffraction analysis, the cyclophanes **93**–**96** occur in a *cone* conformation; they are widely used as complexing reagents and membrane transferring agents for various metal cations.[107–109] The reduction of the compound **96** with phenylsilane gives a tetrakis(phosphine) ligand capable of forming polynuclear complexes.[105, 110]

A new series of polyfunctional phosphine oxide derivatives of calix[4]-, -[6]- and -[8]arenes **97**, containing $(CH_2)_2P(O)Ph_2$ fragments, have been modelled and synthesised for the extraction and complexation of actinide and lanthanide ions.[111] The synthetic strategy is presented in the scheme.



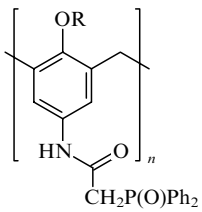
97

R = Bu^t, H; *n* = 4, 6, 8.

The properties of these compounds as extractants have been studied.[112–115]

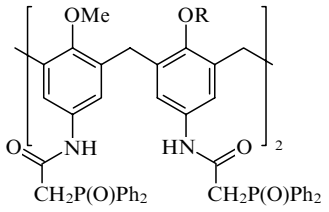
The further development of the methods for functionalisation of calixarenes followed the path of introduction of groups containing both an organophosphorus fragment and another binding site into the upper or lower rim of the macrocycle. Cavitands with the carbamoylmethylphosphine oxide $[NHC(O)CH_2P(O)Ph_2]$[116–118] and α-aminophosphonate $[NHCR_2P(O)(OR'_2)_2]$[119] groups have now been obtained.

It has been shown[116] that the extraction properties of the traditional extractant for actinides, (*N*,*N*-diisopropylcarbamoylmethyl)octylphenylphosphine oxide (CMPO), can be markedly improved by grafting four or five carbamoylphosphine oxide groups to the upper rim of calix[4]- or -[5]arenes **98** and **99**.



98a–h

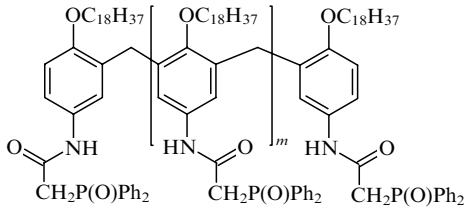
n = 4: R = C_5H_{11} (**a**), CH_2CHBu_2 (**b**), $C_{10}H_{21}$ (**c**), $C_{12}H_{25}$ (**d**), $C_{14}H_{29}$ (**e**), $C_{16}H_{33}$ (**f**), $C_{18}H_{37}$ (**g**); *n* = 5, R = $C_{14}H_{29}$ (**h**).



99a–c

R = CH_2CHBu_2 (**a**), $C_{10}H_{21}$ (**b**), $C_{18}H_{37}$ (**c**).

It is worth noting that the extraction capacity of the specially synthesised[116] linear analogues of receptors **98** and **99** — the dimer and the trimer **100a**,**b** — was equal to that of the initial CMPO.

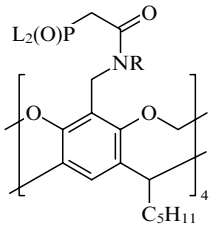


100a,b

m = 0 (**a**), 1 (**b**).

These results demonstrate the synergistic effect of combining carabamoylphosphine oxide fragments with the calixarene platform within the same molecule. The compounds **98** and **99** were prepared by aminolysis of *p*-nitrophenyl diphenylphosphorylacetate with *O*-tetra- or *O*-pentaalkyl ethers of *p*-aminocalix[4]- or -[5]arenes. The calixarenes **98** occur in a *cone* conformation, whereas **99** can be a mixture of *cone*, *partial cone* and *1,3-alternate*, because for mixed ethers with two methoxy groups, inversion of the macrocycle is possible.

Several studies have been devoted to the introduction of carbamoylmethylphosphonate fragments into the calix[4]resorcinolarenes **31** and to the extraction properties of the products towards a number of metal cations.[117, 118] Mono-, 1,2-bis-, 1,3-bis, tris- and tetrakis(carbamoylmethyl)phosphonates and -phosphine oxides **101** were synthesised starting from tetrakis(bromo-methyl)calix[4]resorcinolarene. The conditions for partial functionalisation were created at the stage of formation of the aminomethyl derivatives. The amino group was introduced *via* phthalimide derivatives, by their hydrazinolysis. The transition to the cyclophanes **101** was accomplished either by acylation of the amines with chloroacetyl chloride followed by Arbuzov introduction of the phosphorus-containing fragment or by aminolysis of *p*-nitrophenyl diphenylphosphorylacetate.

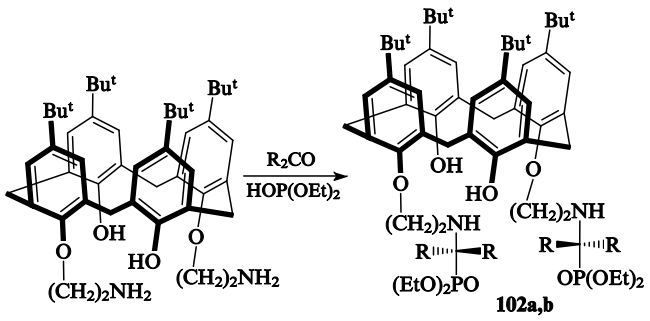


101a–d

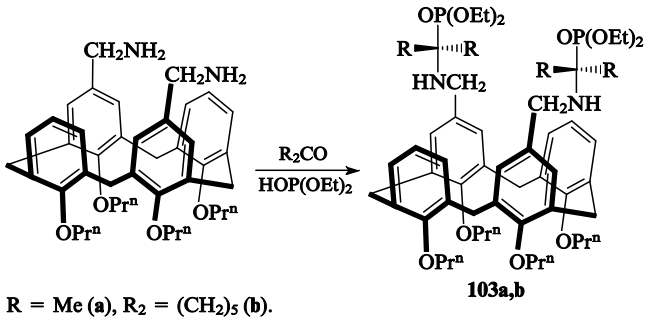
R = H: L = Ph (**a**), OEt (**b**); R = Pr^n: L = Ph (**c**), OEt (**d**).

Study of the extraction of Na^+, Cs^+, Sr^{2+}, UO_2^{2+}, Fe^{3+} and Eu^{3+} with the compounds **101** showed that Na^+ and Cs^+ are not extracted, while the degree of extraction of Sr^{2+} reaches 85%. The cavitands containing three or four carbamoylmethylphosphine oxide groups were found to be the most efficient extractants. As the number of these groups decreases, the efficiency of extraction and its selectivity with respect to Eu^{3+} decrease. Interestingly, 1,2-disubstituted cavitands are more efficient than the 1,3-isomers.

Calixarenes **102** and **103**, which contain α-amino phosphonate fragments in the lower and upper rims of the macrocycle, have been constructed as receptors and membrane transferring agents for α-amino acids occurring in the zwitter-ionic form.[119]



102a,b



103a,b

R = Me (a), R_2 = $(CH_2)_5$ (b).

These compounds were synthesised by the Kabachnik – Fields reaction from the corresponding 1,3-bis(aminoalkyl)-derivatives, diethyl phosphite and a carbonyl compound (yields 50% – 65%). The calixarenes **102** and **103** occur in a *cone* conformation.

It should be noted that transfer of highly hydrophilic amino acid zwitter-ions through lipophilic organic membranes is a difficult task due to the very high energy of hydration of these species. Therefore, the receptor should interact efficiently with as many active sites in the substrate as possible. As applied to α-amino acids, this can be interaction with the carboxylate and ammonium groups and with the side chain, which normally does not contain any polar or charged substituents. The presence of α-amino phosphonate fragments, containing both proton-donor (NH bond) and proton-acceptor (P=O bond and the lone electron pairs of nitrogen) groups together with the calixarene molecular cavity in the receptor molecule ensures efficient transport of α-amino and α-hydroxy acids.[120, 121] The cavitands **102** and **103** exhibited high selectivity of transfer of α-amino acids, the compounds **102** being more efficient towards histidine, and **103**, towards *d,l*-phenylalanine.

A water-soluble receptor for the uranyl ion UO_2^{2+} was synthesised by introducing six phosphonic acid fragments $[CH_2P(O)(OH)_2]$ into the calix[6]arene upper rim. This was done by the Arbuzov reaction of the corresponding chloromethyl derivatives with triethyl phosphite and subsequent hydrolysis.[122, 123]

This review surveys the main routes of functionalisation of calix[4]resorcinolarenes and calix[*n*]arenes by organophosphorus compounds of various types and clearly demonstrates the great potential and the prospects for the use of these macrocycles for complex formation and molecular recognition (extraction, membrane transfer) of both charged and neutral substrates and for the assembly of novel supramolecular systems.

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