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ORIGINAL ARTICLE

Macrocycles and cavitands containing phosphorus

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Abstract Macrocycles and cavitands containing phosphorus represent two interesting and promising classes with special properties and applications as catalysts or in biology. In this paper we tried to review the progress in synthesis of macrocycles and cavitands containing phosphorus.

Keywords Phosphorus · Macrocycles · Cavitands

Introduction

Macrocycles and cavitands have developed into the most active and promising research areas of chemical science. Based on the pioneering and stimulating work of the 1987 Nobel Prize Winners [1], the field of macrocyclic chemistry encompasses fundamental aspects of molecular recognition and self organization [2]. Phosphorus macrocycles are attractive and interesting molecules with potential applications in supramolecular and synthetic organic chemistry. These macrocycles containing phosphorus have been much less studied than their aza analogs [3]. Crown ether analogs, phosphorous hydrazides, and cyclophosphazenes [4] or another P–N macrocycles [5] have the largest section in this field. Phosphorus macrobicycles with stable configurationally P bridgehead atoms has an interesting feature, *in*,*out*-isomerism, with respect to their exocyclic residues [6]. Because of their position inside the cavity, the *in*-isomers (directed inside the macrocycle cavity) are more attractive, as their micro environment can offer unusual properties. Only a small number of stable *in* isomers have been isolated. They are bicyclic compounds devoid of phosphorus. The head atoms are mostly amine or ammonium nitrogen atoms [7–9]. In some cases, these are methine C atoms [10] or phosphine and phosphine oxide P atoms [11]. The largest *in* substituent reported is the methyl group at the sp^3 bridgehead carbon atom [12–14]. A small *in*-fluorosilane has been reported [15]. The synthetic access to such *in*-functional groups with the aim of functionalization of macrobicyclic compounds has not been elaborated.

As originally defined by Cram [16], the cavitands are "synthetic organic compounds" with enforced cavities large enough to complex complementary organic compounds or ions. The two key words in this definition are "enforced" and "cavity." Cavitands are then generally macrocyclic compounds, comprising several aromatic rings covalently linked in a highly constrictive manner. Implicit in the word "cavity" is a range of topologies ranging from a concave or bowl-shaped feature, to a fully encapsulating molecular surface [17].

Phosphorous macrocycles

Phosphorous chloride method in synthesis of macrocycles

Macrocycles [18] are another type of macromolecules that have attracted the attention of researchers. Combination of both types of macromolecules is supposed to increase the level of preorganization [19].

The methods used for obtaining macrocyclic compounds have been classified by Lehn [20]. To obtain macrocycles

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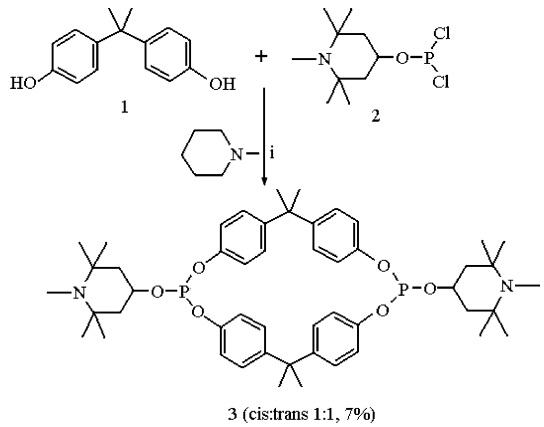


Fig. 1 The reaction of phosphodichloridite with bisphenol **1**

containing phosphorus, the condensation using bisphenols and phosphodichloridites give good results. The reaction of phosphodichloridite **2** with bisphenol **1** under moderate dilution conditions (2.5×10^{-3} M) produces macrocycle **3** in 7% yield (Fig. 1) [21, 22].

The reaction of phosphodichloridite **2** with the bisphenol **4** give a mixture of *cis* and *trans* diastereomers of the macrocycle phosphite **5** (Fig. 2) [21]. The yield of macrocycle **5** (25%) was higher than that the yield of macrocycle **3**.

Oxidation of macrocycle **5** with cumene hydroperoxide produces the corresponding phosphate **6** in a very good yield (Fig. 2).

The addition of sulfur to product **5** give a *cis*,*trans*-isomer mixture of macrocyclic thiophosphate **7** [21]. A comparative study of the synthesis of phosphorous macrocycles starting from the phosphodichloridite **8** and bisphenols showed that the structural information of the building blocks leads to macrocycles of different sizes, thus amplifying the structural differences in the starting materials [23]. The reaction was performed in toluene at room

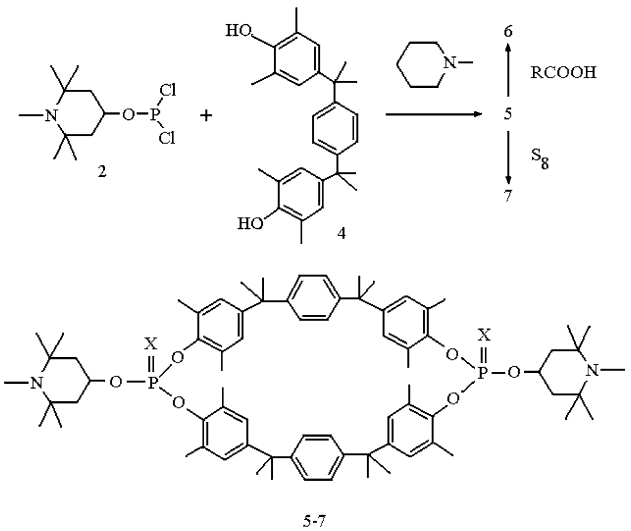


Fig. 2 The reaction of phosphodichloridite with bisphenol **4**

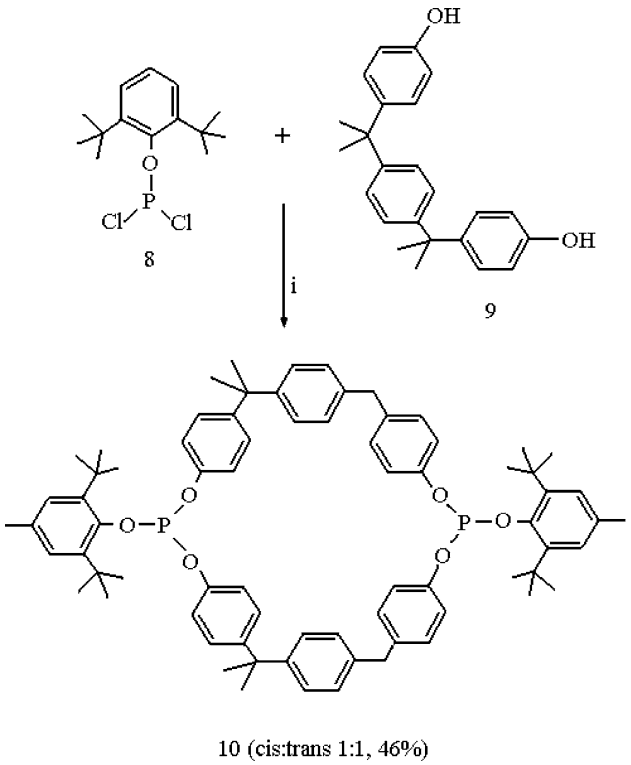


Fig. 3 The reaction of bisphenol **9** with phosphodichloridite

temperature for 24 h in the presence of Et_3N with a concentration of 4.5×10^{-3} M. The reaction of bisphenol **9** with phosphodichloridite **8** afforded the corresponding phosphorous macrocycle **10** in a yield of 46%, as a mixture of *cis* and *trans* isomers (Fig. 3) [23]. This proves that bisphenol **9** is well suited for this type of macrocyclocondensation, giving only low amounts of oligomeric side products. The two isomers of **10** from the mixture are formed in an equal ration (1:1).

The large size of the macrocycle is maybe responsible for the absence of any substrate induced diastereo-selectivity mediated by the first phosphite center appearance. Bisphenol **11** has been used for the synthesis of macrocycles [24]. In the reaction of **8** with **11**, it was obtained the dimeric compound **12** as a 1:1 mixture of *cis*- and *trans*-isomers (Fig. 4) [23].

However, the trimeric compound **13** it was isolated in nearly the same yield. In the case of **13**, two isomers (*cis*,*cis* and *cis*,*trans*) can be formed. The *cis*,*cis* isomer **13** is formed in very low amounts. According to its geometric features, the compound **14** it is not expected to form macrocyclic structures. One would expect the preferred formation of oligomers. However, even in this case, in the reaction with phosphorous dichloride **8**, it was possible to isolate the tetrameric macrocycle **15** (Fig. 5). The finally isolated product **15** shows only one signal at 138.4 ppm of ^{31}P NMR spectra [25].

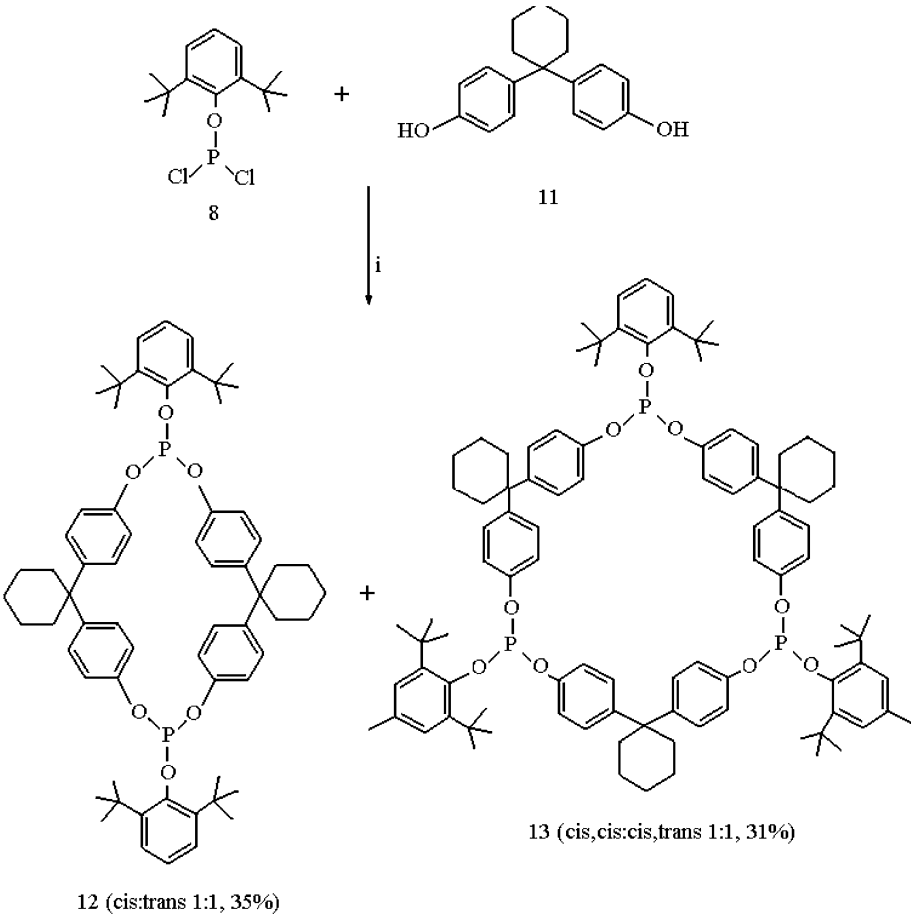


Fig. 4 Obtaining of mixture of *cis*- and *trans*-phosphorous macrocycles isomers

Phosphites can be synthesized not only from phosphorous chlorides reacting with alcohols or phenols, but also using phosphorous amides [26]. The reaction of bisphenol with the phosphorous amide from the same bisphenol gave only open chain and oligomeric products [27, 28]. The cyclization reaction was successful only for bisphenols with phosphonous acid diamides, to obtain finally macrocyclic phosphonites [29–31].

Synthesis and structure elucidation of large phosphorus macrocycles

Very large phosphorous macrocycles and oligomers with cycles are very interesting for investigating recognition phenomena. Their synthesis provides useful information for the development of original supramolecular structures. They can afford new hosts with molecular cavity of unusual functionality and unusual size, to produce original multicomponent assemblies of high complexity. The monomer-oligomer rearrangement is well documented [32]. This equilibrium has been used to design macromolecules and supramolecular structures [33]. The rational design of large macrocycles proved to be attained in the synthesis of the crown-like phosphoramide macrorings [34]. There has been particularly interested in the complexation behavior of phosphorus macrocyclic ligands because phosphorus groups are efficient binding sites particularly when they are introduced in reorganized systems [35–37]. Small size cyclic compounds containing N–P–N groups have been available for a long time. Moreover, cyclic oligomeric derivatives of the parent macrocyclic monomeric compounds can be obtained and isolated [38, 39].

The short route to phosphorus macrocycles **21**–**29** was devised by application of the straightforward phosphorylation (Fig. 6). In this method the cyclization reaction takes place in refluxing toluene under dilution conditions and without any templating partner to give the P(III) derivatives, which are easily oxidized with sulfur, which in turn can give the P(O) compounds by reaction with *m*-chloroperoxybenzoic acid (MCPBA) [32]. The starting diamines **16**–**20** were prepared from 1,x-oligoethyleneglycol-ditosylates by reaction with *o*-nitro-phenol, 3-aminobenzyl alcohol or 2-aminobenzyl alcohol. The reduction of the nitro groups was performed with hydrazine. The ring closure reaction with $CH_3P[N(CH_3)_2]_2$ or $C_6H_5P[N(CH_3)_2]_2$ yielded the macrocyclic three-coordinated phosphorus derivatives, which were allowed to react with sulfur to give the P(V) macrocycles in good yields.

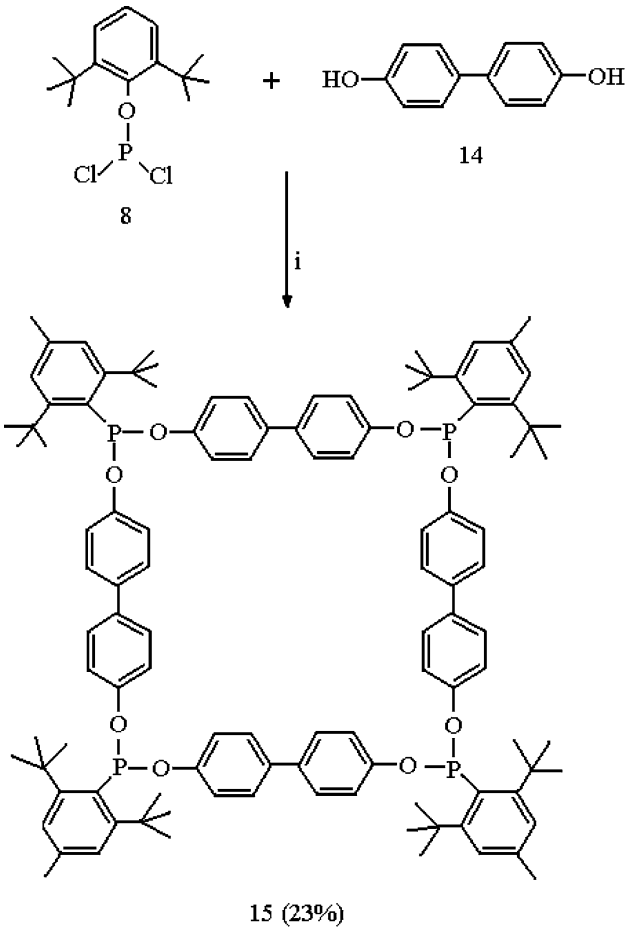


Fig. 5 The isolation of the tetrameric macrocycle **15**

To isolate the pure monomeric compounds, a chromatographic separation was performed. Further elution during the separation often allowed the separation of the higher cyclic oligomers. The cyclic dimers of **23** and the cyclic forms of **25** were unambiguously characterized. The compounds are stable and crystalline or oily materials. In the case of **23**, the two expected 40-membered cyclic dimers were isolated by column chromatography. Both compounds, **23** and **25**, are crystalline materials with different melting points. Mass spectrometry revealed very clear the corresponding mass 1029.1 without difference between both isomers. Only an X-ray analysis would provide the complete assignment of the *cis* and *trans* compounds.

The reaction of diamine **18** with $C_6H_5P[N(CH_3)_2]_2$ and the addition of sulfur, produce the compound **25**, as a solid (39% yield). Macrocyclic dimer and trimer of **25** were isolated and characterized. Only ^{31}P NMR spectra can make the difference between **25D** and **25T**. The mass spectrometry was very important to characterize unambiguously these molecules. MS showed the main peak (100%) at m/z 603.1, 1205.3 and 1807.5 for **25**, **25D** and **25T**, respectively.

The meta aminobenzyl precursor revealed to be a good candidate for the design of cyclic phosphoramide molecular receptors [33] or hemispherand like structures containing one phosphoryl group and ether oxygen atoms [35, 36]. For instance, 18- and 21-membered compounds have been previously described and were synthesized according to this procedure (44 and 38% yields, respectively) [40]. The 27-membered of compound **26** were produced in 31% yield. The ortho-substituted bisbenzylamine (Fig. 6c) was synthesized as well. 25-membered of the macrocycles **27** and **28,** in 30 and 49% yield, were also prepared.

In view of the complexation potential of these macrocyclic structures, it was interesting to produce derivatives bearing a strong polar P(O) group to bind hard cationic species. The conversion of P(S) to P(O) compounds was easily achieved using *m*-chloroperoxybenzoic acid (MCPBA) as oxidizing agent. This procedure has been already used and was applied with good yields to obtain macrocyclic compounds [36, 41].

All possibilities were not explored for the obtaining of oligomeric species, and it was only report the cases of compounds **23** and **25**, for which dimeric and trimeric compounds were characterized. An interesting point that should be highlighted is the reversibility of the formation of oligomeric species during the ring closure reaction with the three-coordinated phosphorus species. According to previous observation, monomeric and oligomeric species are in equilibrium when phosphorus is not oxidized (P(III) species). This has been investigated for cyclic phosphonite derivatives [42–47].

A new family of macrocyclic phosphorus compounds

Di- and tri-amidophosphites are as well very used in the design of organophosphorus compounds, including cyclic systems [48]. This is because of the presence of several P–N bonds. The structure of resulting products from the phosphorylation it depends on the reactivity of nucleophilic groups in the substrate. For example, the cyclophosphorylation reaction of dihydroxyaromatic compounds with remote hydroxy groups leads to phosphorus containing ethers and cyclophanes [49]. In the same time, the cyclophosphorylation of polyhydroxyaromatic compounds containing hydroxyl groups give polycyclic cage phosphocavitand molecules [49–52]. The design of previously macrocyclic containing phosphorus based on 2,2′,7,7′-tetrahydroxydinaphthylmethane show diverse reactivity (Fig. 7). The hydroxy groups in the 2,2′-positions are spaced, which facilitates intramolecular interactions, whereas the remote arrangement of the hydroxy groups in the 7,7′-positions excludes intramolecular interactions but does not prevent intermolecular interactions. Such a

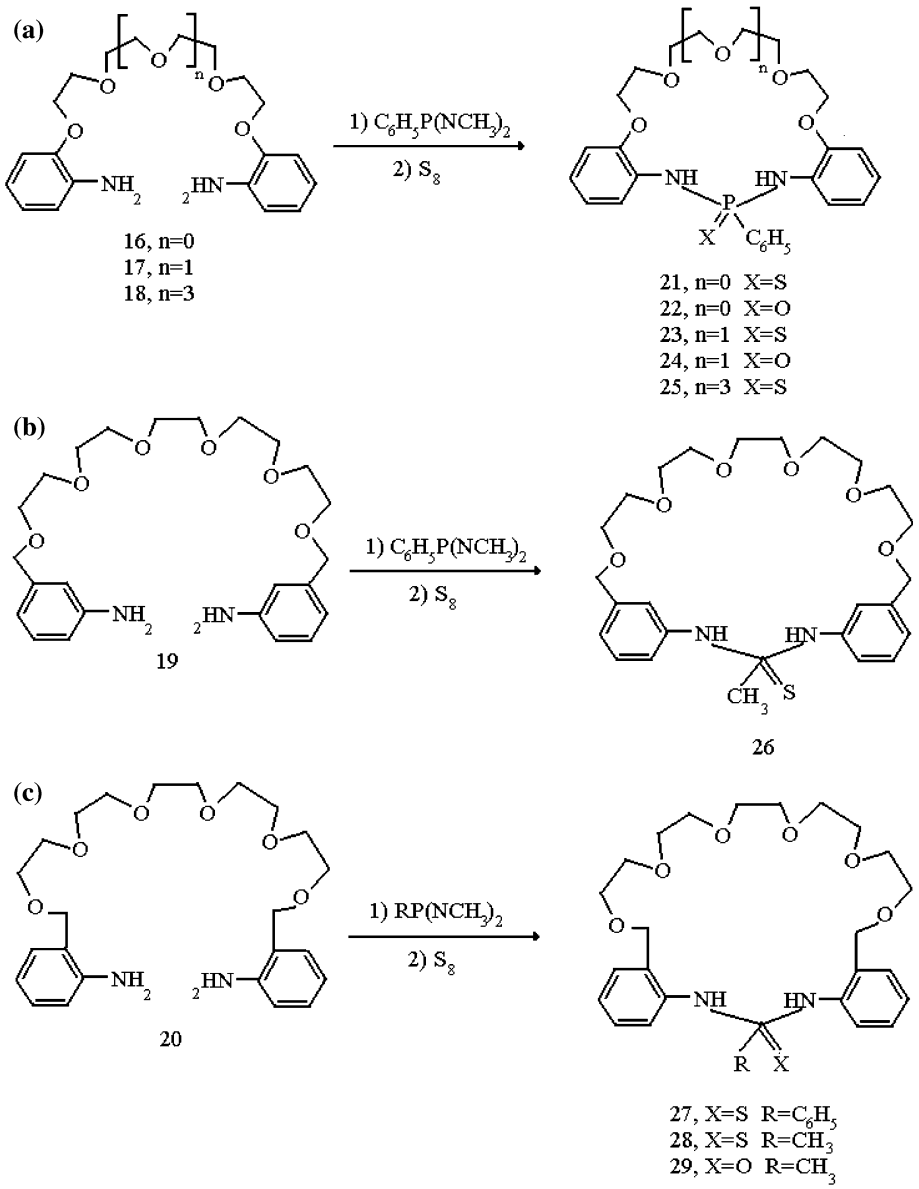


Fig. 6 Synthesis of phosphorous macrocycles by straightforward phosphorylation

molecular geometry makes it possible to provide the regiocontrol of its phosphorylation. It favors the formation of macrocyclic compounds, as phosphacyclophanes and phosphocavitands. The reactions of **30** with triamidophosphites **31** were accomplished in dioxane or acetonitrile and produce the compound **33** which is a macrocycle phosphorous containing.

Phosphorous cavitands

Phosphorus-bridged cavitands

In the study of phosphorus-bridged cavitands, the X-ray crystal structure determination of **34b** (Fig. 8) was made [53]. Cavitands **35a,b** (Fig. 9) have been synthesized from appropriate resorcin arenes by treatment with hexaethylphosphorous triamide [54, 55].

It was observed that **35b** forms complexes with amines in 1:2 ratio, such as Et_2NH, Et_3N, and $H_2NCH_2CH_2OH$ [56]. The cleavage of endocyclic P–O bonds of cavitand **36** in aqueous solution affords compound **37** (Fig. 10). By heating the compound **37** in benzene with azeotropic distillation of water produce back the compound **36** [49]. Chiral phosphorus-bridged cavitand **38** (Fig. 11) has been used for the pH-dependent enantioselection of amino acids in Langmuir monolayers [57–61].

The bridging reactions of resorcinarenes **39a–d** produce cavitands **40a–d** (Fig. 12). The reaction of resorcinarene **39a** with phenylphosphonyl dichloride affords two

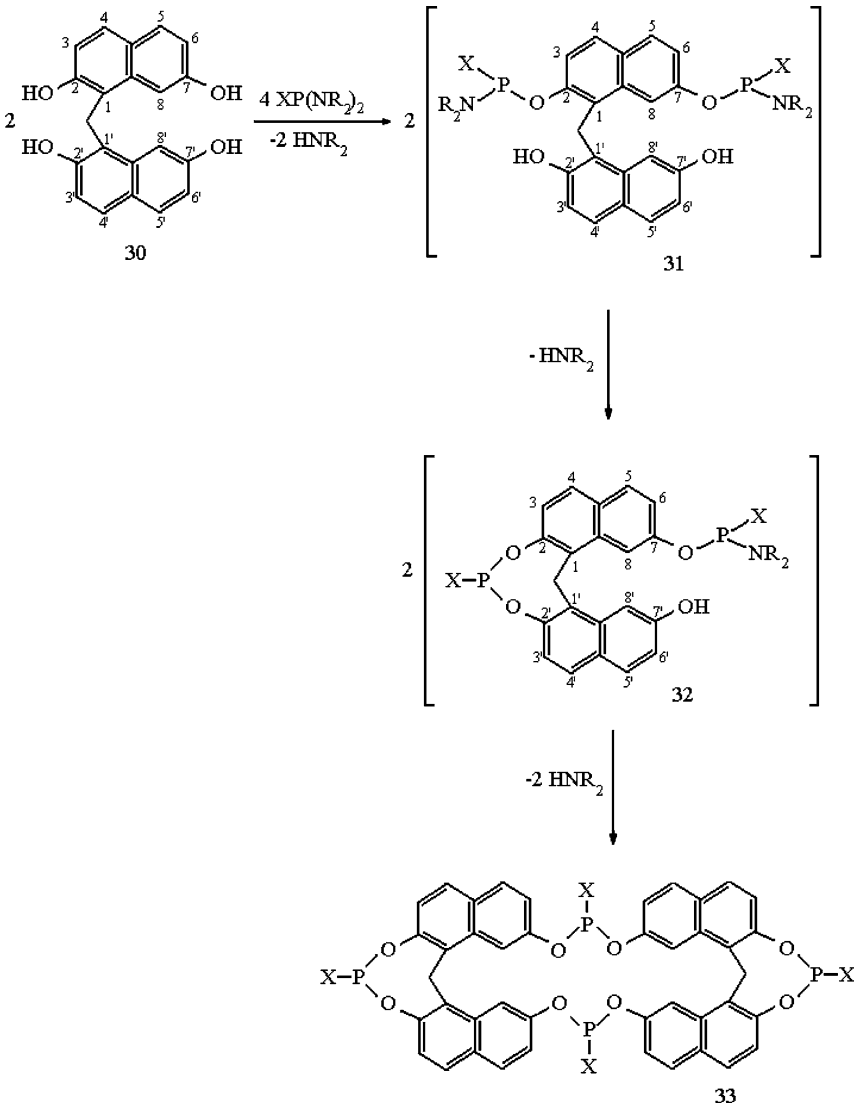


Fig. 7 The design of macrocyclic containing phosphorus based on tetrahydroxydinaphthylmethane showing diverse reactivity [52]

diastereomers **40a′** and **40a″** (Fig. 13) out of the six possible ones [62, 63].

Here are presented only a few examples of cavitands. The fast development of the synthesis chemistry of these compounds [64–71] is a good prove of their importance in practical applications.

Cyclic phosphorochloridites, phosphorochloridates and phosphorochloridothioates based on calix-4-resorcinolarenes

Recently has been a great deal of interest in calixarenes and their organophosphorus derivatives [72–74]. The use of complexing compounds, such as calixarenes [75], in artificial membranes is one of the general trends of molecular electronics and microsensorics. It is known that calixarenes

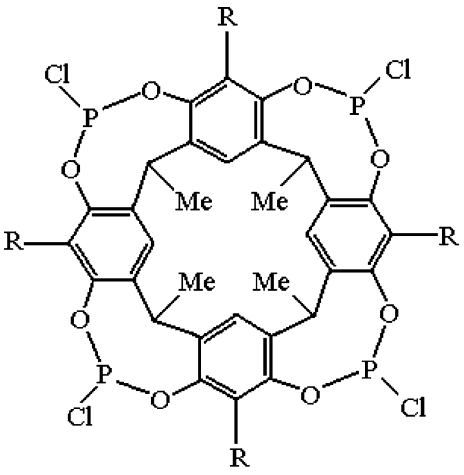
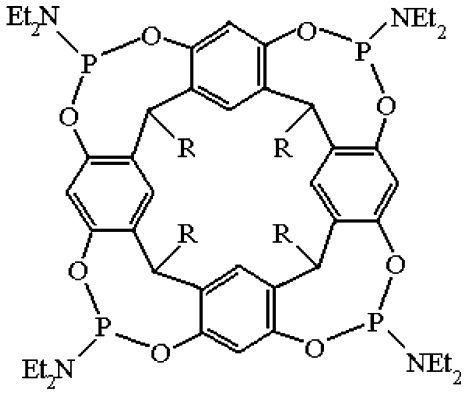


Fig. 8 Structure of phosphorus-bridged cavitands **34**



35a,b a) R = n-Pr
b) R = n-C6H13

Fig. 9 Structure of phosphorus-bridged cavitands **35** synthesized from appropriate resorcin arenes by treatment with hexaethylphosphorous triamide

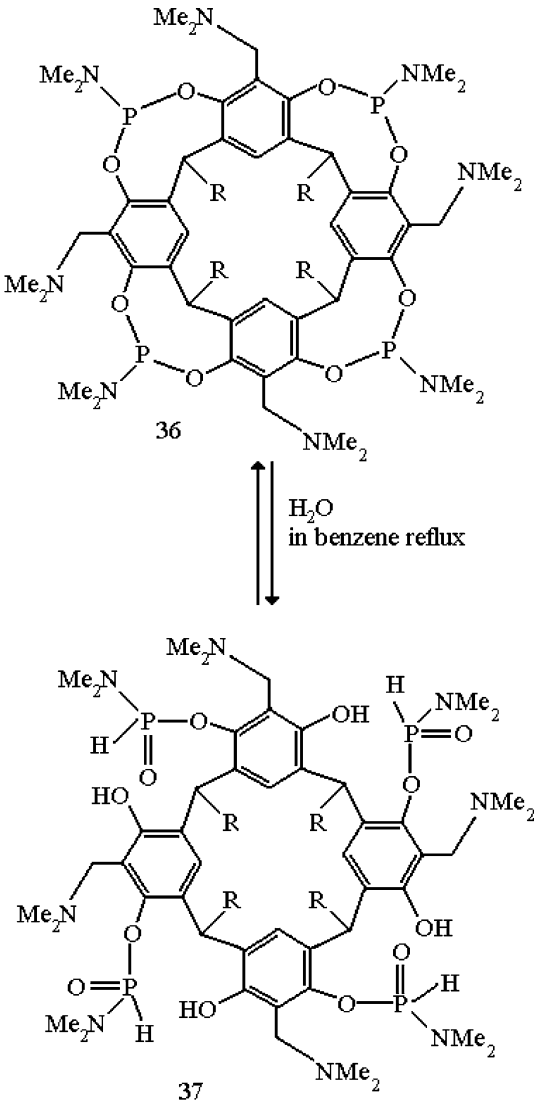
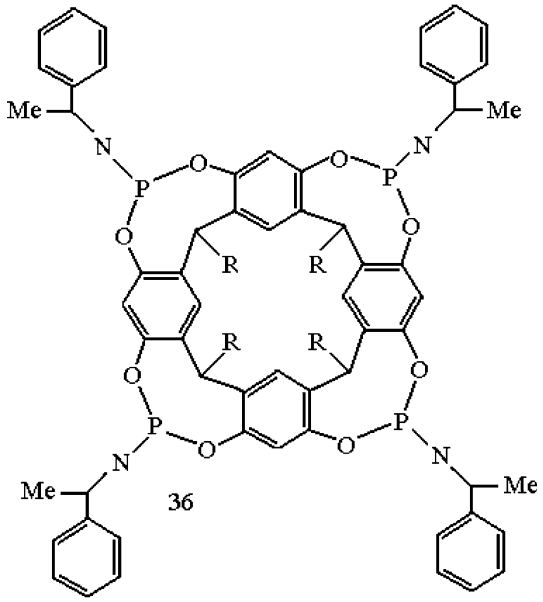


Fig. 10 The cleavage of endocyclic P–O bonds affords compound **37**



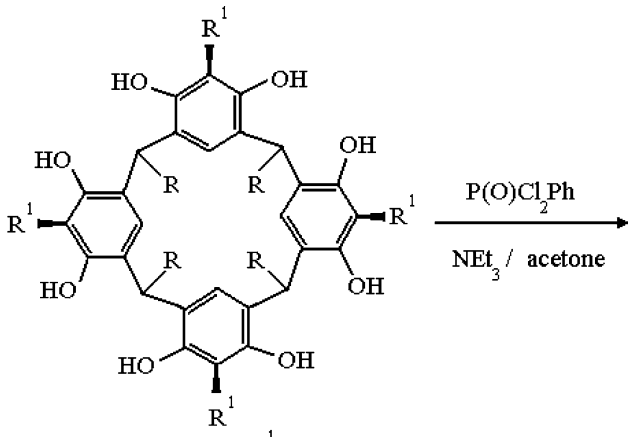
38 R = $C_{11}H_{23}$

Fig. 11 The structure of a chiral phosphorus-bridged cavitand

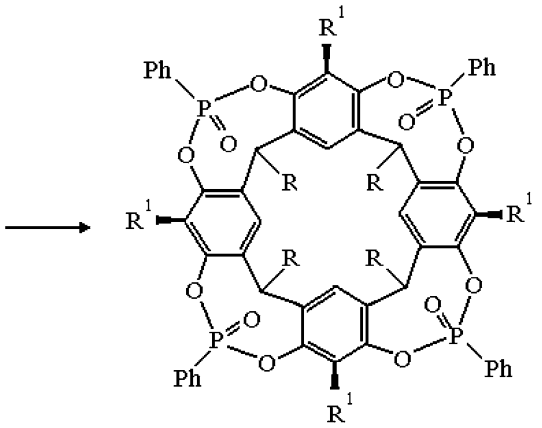
and their organophosphorus derivatives are able of fixing metal cations [75, 76] and neutral molecules (especially arenes) [77]. Of particular interest are cavitands containing reactive groups, e.g. P(IV)Cl fragments, on the upper rim of the calixarene matrix.

These cavitands can be precursors of carceplexes, hemicarceplexes and novel organophosphorus compounds. Published data show that calix resorcinolarenes are readily phosphorylated with organyl phosphorochloridates or phosphonic chlorides to form cavitands [78–81]. Koide et al. [82] studied phosphorylation of C-undecylcalix resorcinolarene with $POCl_3$ in the presence of pyridine and obtained mixtures of complex cyclic and acyclic phosphates, with different content of phosphate fragments (from 1 to 6.3). Phosphorylation was incomplete even at a large excess of $POCl_3$.

Cavitands with cyclic phosphorochloridate fragments on the upper rim by phosphorylation of calyx resorcinolarenes **41a–c** (Fig. 14) with $POCl_3$ and $PSCl_3$ at various molar ratios (from 1:1 to 1:8) in the absence of a base were obtained. These reactions also failed to give cyclic phosphorochloridates or chloridothioates. At a molar ratio of calixarene to $POCl_3$ of 1:4, according to MS, the reaction product acyclic cavitands containing three (M = 1,175) and four (M = 1,292) phosphorodichloridate groups in 3:4 ratio. Phosphorylation of calyx resorcinolarenes with $PSCl_3$, according to the ^{31}P NMR spectra, yields a mixture of products containing cyclic and acyclic phosphorus structures. This result it is unexpected, as linear and aromatic diols and triols are smoothly phosphorylated with



39 a) R = Me, R^1 = H
b) R = R^1 = Me
c) R = Me, R^1 = Br
d) R = C_6H_{13}, R^1 = Br

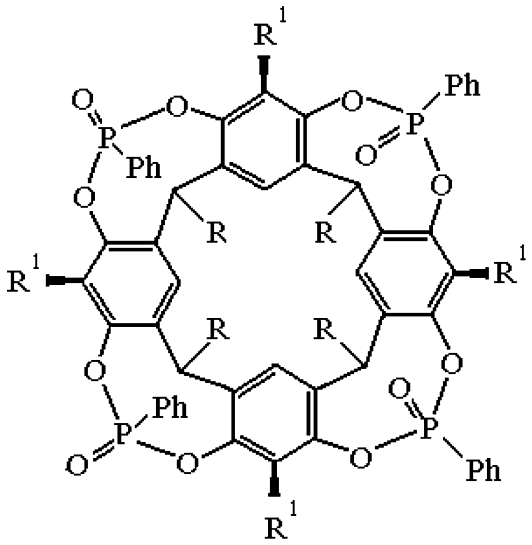


40 a) R = Me, R^1 = H
b) R = R^1 = Me
c) R = Me, R^1 = Br
d) R = C_6H_{13}, R^1 = Br

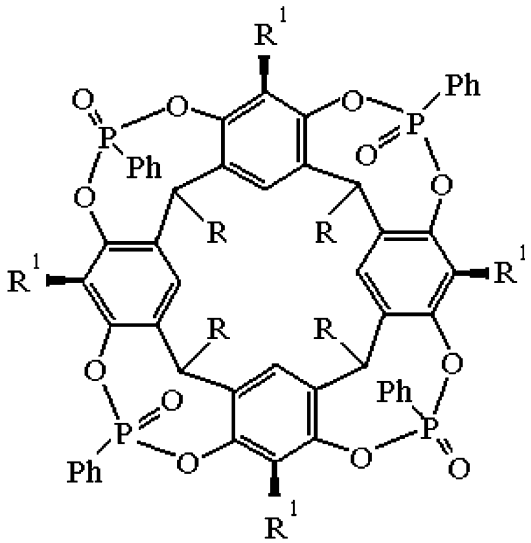
Fig. 12 The bridging reactions of resorcinarenes produce cavitands

both $PSCl_3$ and $POCl_3$ to give the corresponding dioxaphosphacyclanes.

The only one example of phosphorylation of calix resorcinolarene (with methyl substituents on the lower rim) with PCl_3, which gives the cyclic phosphorochloridite, was reported by Vollbrecht et al. [53]. The reactions of PCl_3 with calixarenes **41a–c** were performed in refluxing toluene for 3–4 h, and produced the cavitands **42a–c** in a high yield. Phosphorochloridites **42a–c** were oxidized with dimethyl sulfoxide, molecular oxygen, hydrogen peroxide and sulfuryl chloride. In the first three cases, according to the ^{31}P NMR spectra, the reaction pathway was not unequivocal, and mixtures of products were obtained. Oxidation with SO_2Cl_2 occurred smoothly, and cavitands **43a–c** was obtained in a very good yields.



40′ a) R = Me, R^1 = H
b) R = R^1 = Me
c) R = Me, R^1 = Br
d) R = C_6H_{13}, R^1 = Br



40″ a) R = Me, R^1 = H
b) R = R^1 = Me
c) R = Me, R^1 = Br
d) R = C_6H_{13}, R^1 = Br

Fig. 13 The reaction of resorcinarene with phenylphosphonyl dichloride

It is known that the addition of sulfur to cyclic chlorides of P(III) acids it is performed by their heating with $PSCl_3$ and distillation of the resulted PCl_3 [83]. With **42b** as it was showed that the cavitands which contain cyclic

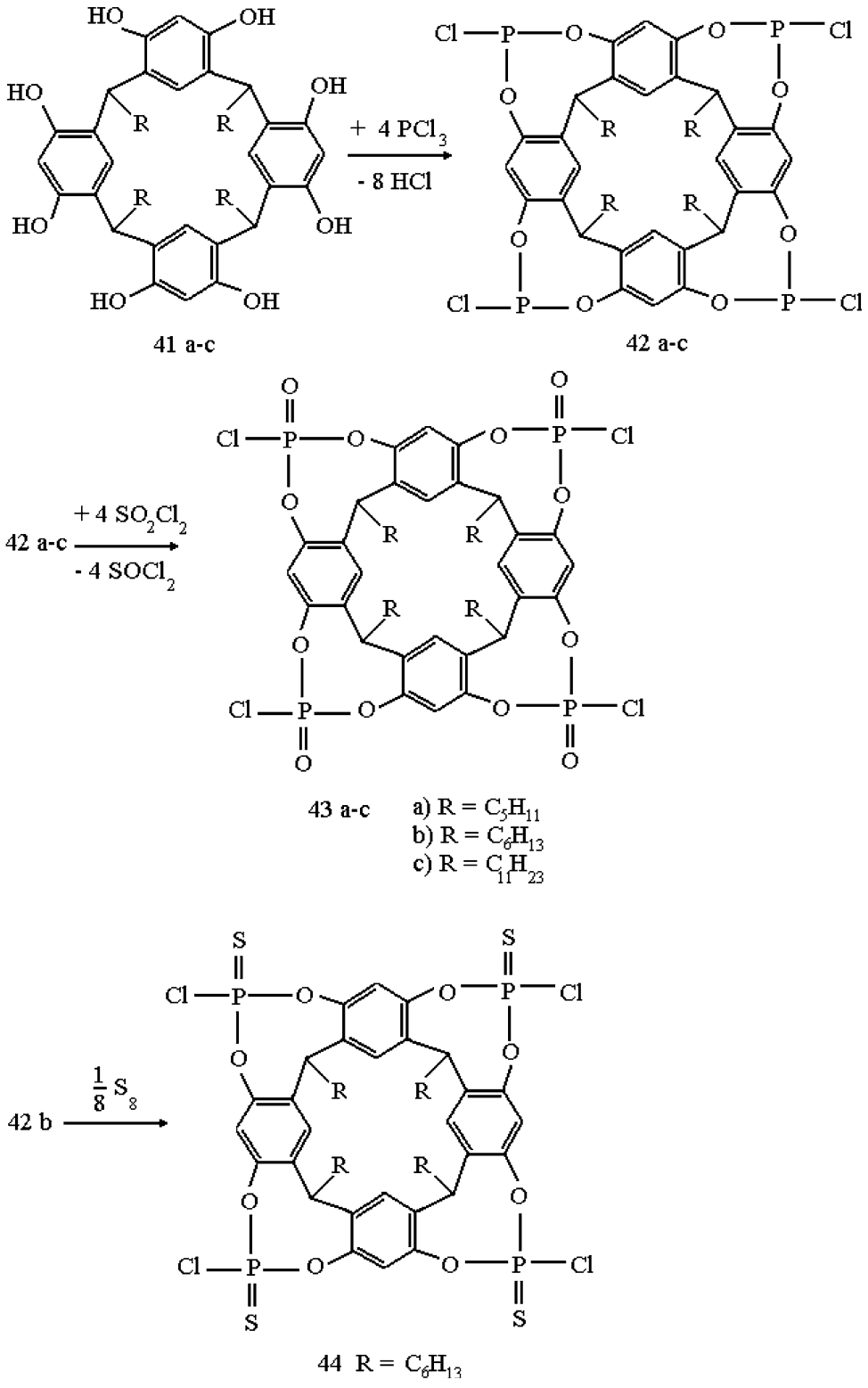


Fig. 14 Phosphorylation of calyx resorcinolarenes

phosphorochloridite fragments on the upper rim take up four equivalents of sulfur on heating to give cavitands **44**. The structures and the compositions of the compounds obtained were proved by ^{1}H NMR, ^{31}P NMR and IR spectroscopy [84].

Conclusions

The very fast development of the chemistry of these compounds containing macrocyclic structures is a reflection of their practical importance. All of these compounds

presented in this review continue to attract interest. It was shown that molecular design has allowed the synthesis of such a compounds containing macrocycles. Most of these compounds are obtainable only by using the phosphorus chemistry.

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