Russian Chemical Reviews **82** (2) 150 – 186 (2013) © 2013 Russian Academy of Sciences and Turpion Ltd

DOI 10.1070/RC2013v082n02ABEH004296

Phosphorus-containing macrocyclic compounds: synthesis and properties

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Abstract. Main trends in the development of methods for the synthesis of phosphorus-containing macrocyclic compounds in the past 15 years are considered. Emphasis is given to reactions producing macrocyclic structures with the participation of a phosphorus atom and other functional groups involved in organophosphorus molecules and to modifications of macrocycles by phosphorus compounds in different valence states. Possibilities of the practical application of phosphorus-containing macrocyclic compounds in difference areas of science and engineering are discussed. The bibliography includes 205 references.

I. Introduction

The past decades have witnessed the extensive development of methods for the synthesis and investigation of intricate organic compounds, with particular attention given to macrocyclic compounds. Various structures, which differ in the size and properties of molecular cavities, can be constructed by varying functional substituents and heteroatoms in the ring.

The design of phosphorus-containing macrocycles is a priority direction of the development of modern heteroorganic chemistry. These compounds attract interest due to their reactivity, the possibilities to investigate molecular recognition features and competitive interactions in systems containing several organophosphorus groups and the opportunity to design new supramolecular and coordination ensembles possessing unique properties. The enhancement of the efficiency of macrocyclic ligands is achieved by introducing a three-coordinate phosphorus atom, phosphoryl of thiophosphoryl groups, which have strong complexing ability, into the ring. It should be noted that macrocycles containing P—C bonds are most promising compounds due to their resistance to hydrolysis, which substantially extends the scope of their practical application.

Phosphorus-containing macrocyclic compounds can find use in various areas of science and engineering. For example, chemically stable macrocycles bearing aromatic moieties and phosphorus-containing substituents, which can form complexes with cations (in particular, with lanthanides), are of interest as luminescence sensors for diagnostics and modern efficient technologies of visualization in medicine.

Several reviews devoted to methods for the synthesis of phosphorus-containing macrocycles were published more than a decade ago. The review [1] describes the strategy of the design of phosphorus-containing macrocycles and cryptands and covers a wide range of investigations. Reviews [2–6] were confined to main methods for modifications of calix[*n*]arenes by organophosphorus moieties and possibilities of their practical application. This issue is also covered in the recent review;[7] however, the chemistry of phosphorus-containing calix[*n*]resorcinols and cavitands was beyond the scope of the latter review.

Currently, phosphorus-containing macrocyclic compounds still attract interest, as evidenced by a large number of publications. In the present review, new data on the synthesis and properties of various phosphorus-containing macrocycles obtained in the last 10 – 15 years are considered systematically and summarized. Particular attention is given to the following three aspects:

1) methods for the formation of phosphorus-containing macrocyclic structures with the participation of a phosphorus atom resulting in the formation of P—O or P—C covalent bonds;

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Received 23 December 2011
Uspekhi Khimii **82** (2) 150 – 186 (2013); translated by T N Safonova

2) modifications of macrocyclic compounds by phosphorus-containing functional groups;

3) synthesis of phosphorus-containing macrocycles with the participation of functional groups involved in organophosphorus molecules.

It should be noted that reviews concerning the abovementioned second area, which summarize mainly modifications of calixarenes, are available in the literature, whereas publications in the other two areas have not yet been considered systematically. Since it is impossible to cover all known classes of macrocyclic compounds in a single review, we restrict ourselves to the consideration of only some classes, such as crown ethers, cryptands, macrocyclic polyphosphines, calixarenes, cavitands and other cyclophanes.

II. Formation of phosphorus-containing macrocycles with the participation of a phosphorus atom

Although first representatives of inorganic phosphorus-containing macrocycles $(PNCl_2)_n$ (n = 5, 6, 7) were synthesized by Stoke in 1897, extensive studies in this area were started in the mid-1970s, a few years after the discovery of complex-forming properties of crown ethers by Pedersen (the citation from the publication [1]). The lack of interest in these compounds during a long period of time is explained by experimental difficulties encountered in the synthesis, such as many steps, low yields, instability of reaction products and so on.

The most complete review [1] devoted to the synthesis of phosphorus-containing macrocycles and cryptands was published in 1994. This summarizing paper exerted substantial influence on subsequent research. It considers methods based on the intramolecular cyclocondensation, the cleavage of small phosphorus-containing rings and the template synthesis giving nine-membered and larger macrocycles containing P–C, P–O, P–S, P–N, P–N–N, P–Si, *etc*. bonds and phosphorus atoms in different valence states.

The research in this area was continued by several groups, who developed approaches to the synthesis of macrocycles containing phosphorus atoms or phosphorus-containing groups as linkages. Below we consider methods for the synthesis of representatives of these compounds, such as phosphorus-containing crown ethers, cryptands and macrocyclic polyphosphines.

1. Synthesis of phosphorus-containing crown ethers

Compounds with a regular combination of phosphorus-containing functional groups and other structural blocks are the most promising new phosphorus-containing macrocycles. For example, the benzene rings located so that their p_z orbitals are directed inside the molecular cavity can serve as such blocks.

Various crown ethers containing arylene (often *o*-phenylene) and heteroatomic groups as repeating units were synthesized in different research centres. However, stable phosphorus-containing crown ethers containing regularly alternating symmetrical arylene bridges and phosphoric acid moieties were synthesized for the first time only by Nifantyev *et al*.[8] Resorcinol (**1**) was used as the starting compound, and hexaalkyltriamides of phosphorous acid **2a**,**b** were used as phosphorylating agents. Resorcinol was chosen for two reasons: first, the impossibility of cyclophosphorylation of this diol by phosphamides and, consequently, the creation of conditions for the formation of macroheterocycles and, second, the prospects of the synthesis of crown ethers, in which the aromatic rings are not in the common plane of the macroheterocycle. Phosphoramidites were chosen because of their high phosphorylating ability.[9]

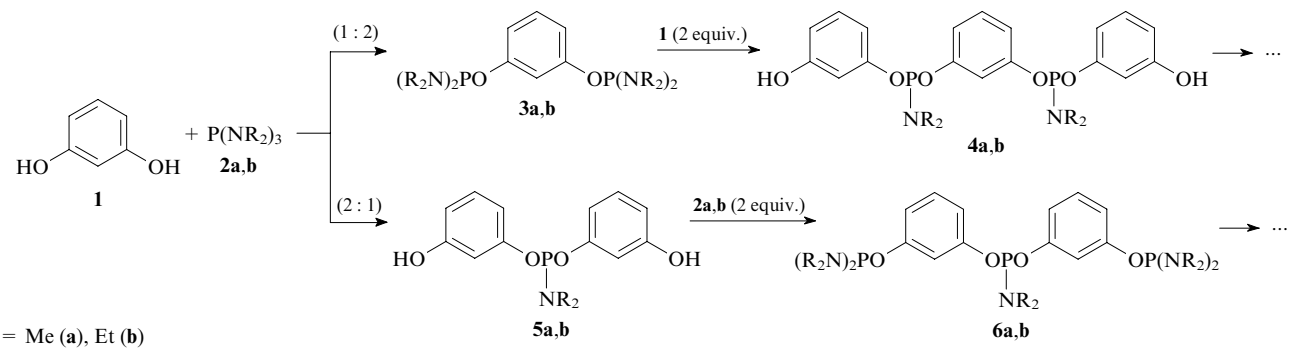
Nifantyev and co-workers developed [8] a strategy for the synthesis of macroheterocycles based on the molecular assembly, where reactions with the participation of resorcinol and phosphoramidites are combined. Initially, this strategy was intended to produce linear oligonuclear intermediate systems with active peripheral groups, which are then involved in the condensation reaction. This method was used to synthesize compounds **3**–**6** containing from one to four resorcinol moieties (Scheme 1).[8,10]

The reaction of equimolar amounts of diol **1** and phosphoramidites **3a**,**b** produces macrocyclic systems **7a**,**b**.[10–12] It was noted that the reaction proceeds ambiguously and gives cyclotris(resorcinophosphoramidites) **8a**,**b** as by-products (Scheme 2).

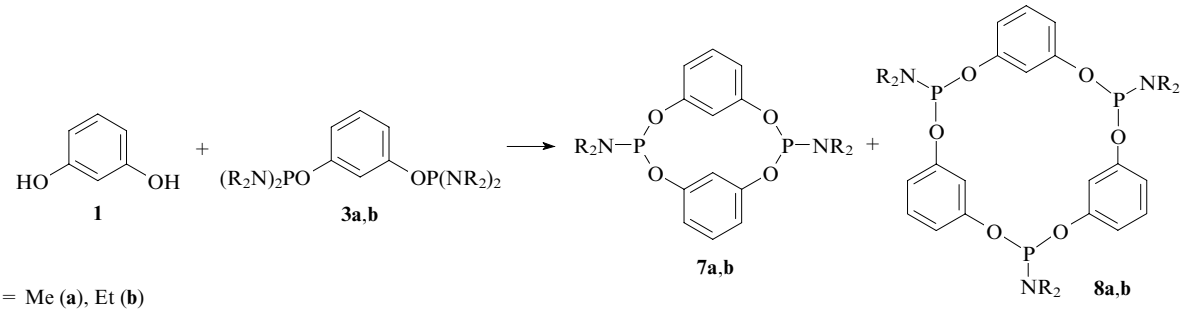
Higher representatives of such crown ethers, whose molecules contain larger inner cavities, such as cyclotetrakis-, cyclopentakis- or cyclohexakis(resorcinophosphoramidites), for example, macrocycle **9**, were also synthesized (Scheme 3).[11]

To prepare more stable compounds suitable for structural and spectroscopic studies, the synthesized compounds were subjected to sulfination and oxidation.[8,9,11,12] The oxidative imination of these products was studied.[13] It was shown that the reaction yields relatively stable phosphatri-

Scheme 1

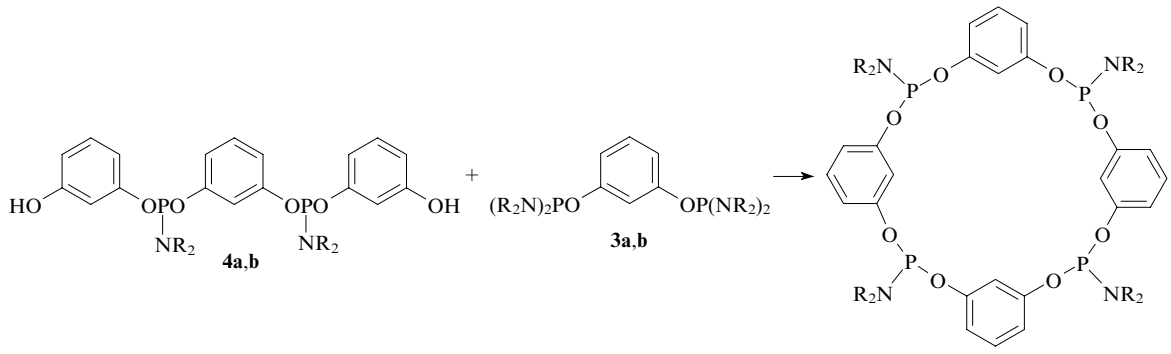


Scheme 2



R = Me (**a**), Et (**b**)

Scheme 3

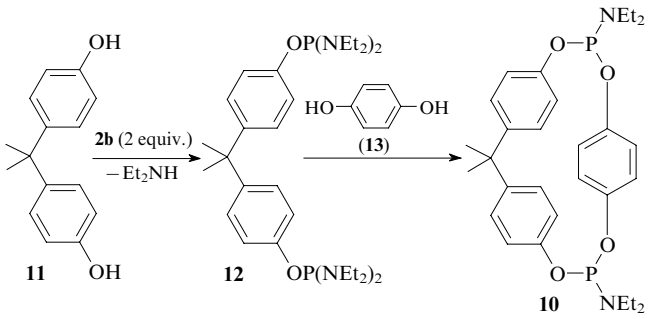


R = Me (**a**), Et (**b**)

azenes and they are transformed into macrocyclic iminophosphoryl compounds.

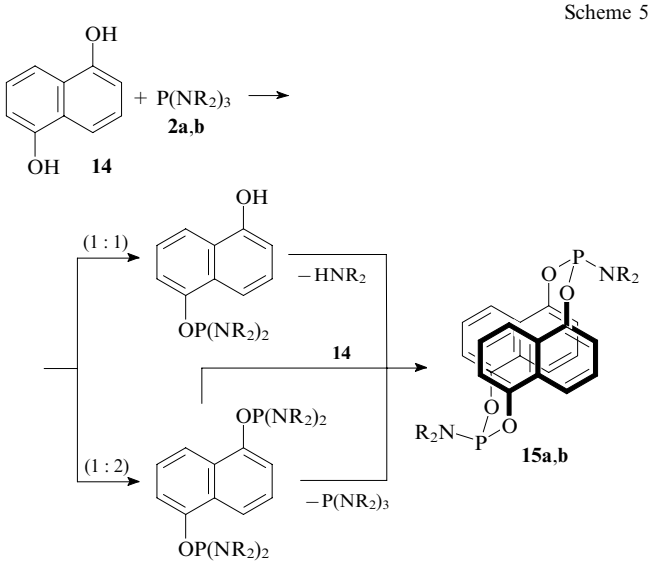
Based on bisphosphorylated products generated from aromatic diols, unsymmetrical phosphorus(III)-containing arene macrocycles bearing simultaneously two different diol moieties, such as hydroquinone, di(*p*-hydroxyphenyl)propane, resorcinol or pyrocatechol, were synthesized by the variative molecular assembly technique.[14, 15] For example, compound **10** can be prepared by bisphosphorylation of diol **11** with an excess of phosphorous acid hexaethyltriamide (**2b**) followed by the reaction of bisphosphorylated product **12** with hydroquinone (**13**) (Scheme 4). Another sequence of the molecular assembly giving the same product proved to be more efficient. It involves the initial bisphosphorylation of hydroquinone followed by the reaction with diol **11**. Apparently, the first step of this process proceeds more rapidly.

Scheme 4



Naphthalene-1,5-diol (**14**) served as the starting arylenediol in the studies.[8, 12, 16] This compound was used to synthesize bulky molecular systems **15a**,**b**, in which two naphthalene rings located one above another are linked by two phosphite moieties (Scheme 5).

Scheme 5



R = Me (**a**), Et (**b**)

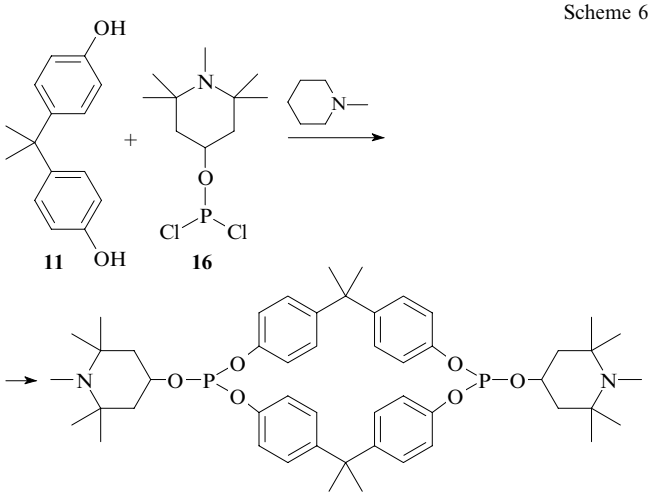
In the presence of a twofold excess of phosphoramide **2**, bisphosphorylated diol undergoes disproportionation accompanied by the elimination of phosphorous triamide. If the reagents are taken in a ratio of 1 : 1, monophosphorylated naphthalene that is formed undergoes rapid cyclization. Apparently, the formation of such dimeric systems is energetically favourable because both reactions give the same result. Bisphosphorylated naphthalene can react with 1 mole of the starting diol **14**, also resulting in the formation of cyclophanes **15**. The compounds thus synthesized are easily oxidized and bind sulfur at room temperature to form the corresponding phosphates and thiophosphates.[16]

As a continuation of this research, the reactions of phosphorous triamides were performed with other sym-

metrical (2,6 and 2,7) and unsymmetrical (1,3, 1,6 and 1,7) dihydroxynaphthalenes, 2,2′7,7′-tetrahydroxy-1,1′-dinaphthylmethane and dihydroxyanthracenes.[10, 17 – 26]

The [2 + 2]-cyclocondensation with the participation of various bisphenols and dichlorophosphites or phosphoramidites as building blocks was used for the construction of phosphorus-containing aromatic crown ethers.[27 – 29] Thus, the reaction of bisphenol **11** with dichlorophosphite **16** in moderately dilute solution affords macrocyclic compound **17** as a mixture of *cis* and *trans* stereoisomers in a ratio of 1 : 1 (Scheme 6).

Scheme 6



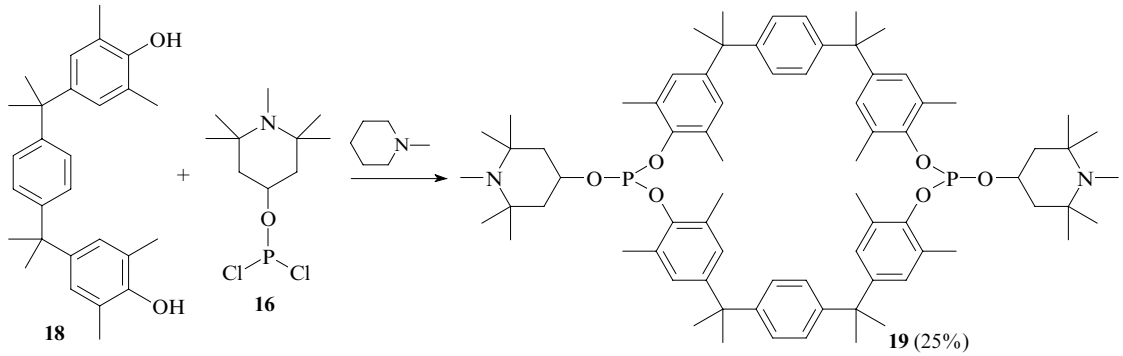
The reaction of dichlorophosphite **16** with bisphenol **18** gives phosphite-containing macrocyclic compound **19** as a mixture of *cis* and *trans* stereoisomers. However, the yield of compound **19** was higher than that of **17**. This suggests that the preorganization of functional groups favours the ring closure (Scheme 7).[27, 30]

It should be noted that in accordance with the structure of biphenyl-4,4′-diol (**20**), the formation of macrocyclic compounds should not be typical of this compound; instead, oligomeric organophosphorus compounds would be expected to be formed as the major products. However, the reaction of dichlorophosphite **21** with diol **20** produced tetrameric macrocycle **22** as a mixture of stereoisomers (Scheme 8).[27, 30]

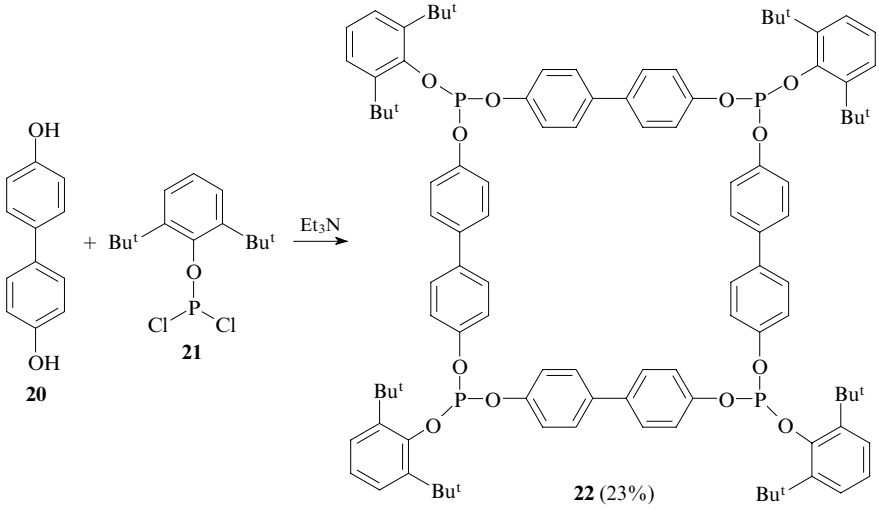
Attempts to synthesize the expected unsymmetrical macrocycle **24** by the reaction of bis(phosphorodiamidite) **23** with bisphenol **11** in boiling toluene failed (Scheme 9).[27, 31] In this reaction, symmetrical macrocycle **25** was isolated as a mixture of *cis* and *trans* isomers along with acyclic products. In this case, one diethylamino group remained intact after transesterification. Apparently, macrocycle **24** is formed as an intermediate, which reacts with bisphenol **11**. If this attack takes place from both sides of the molecule, both bisphenol **18** and symmetrical macrocycle **25** are produced (path *a*). If one phosphorus atom is involved in the reaction, macrocycle **24** is cleaved to form open-chain compounds **26** and **27** and other products (path *b*).

The possibilities of the use of di- and tripentaerythritol derivatives in the synthesis of original macroheterocycles

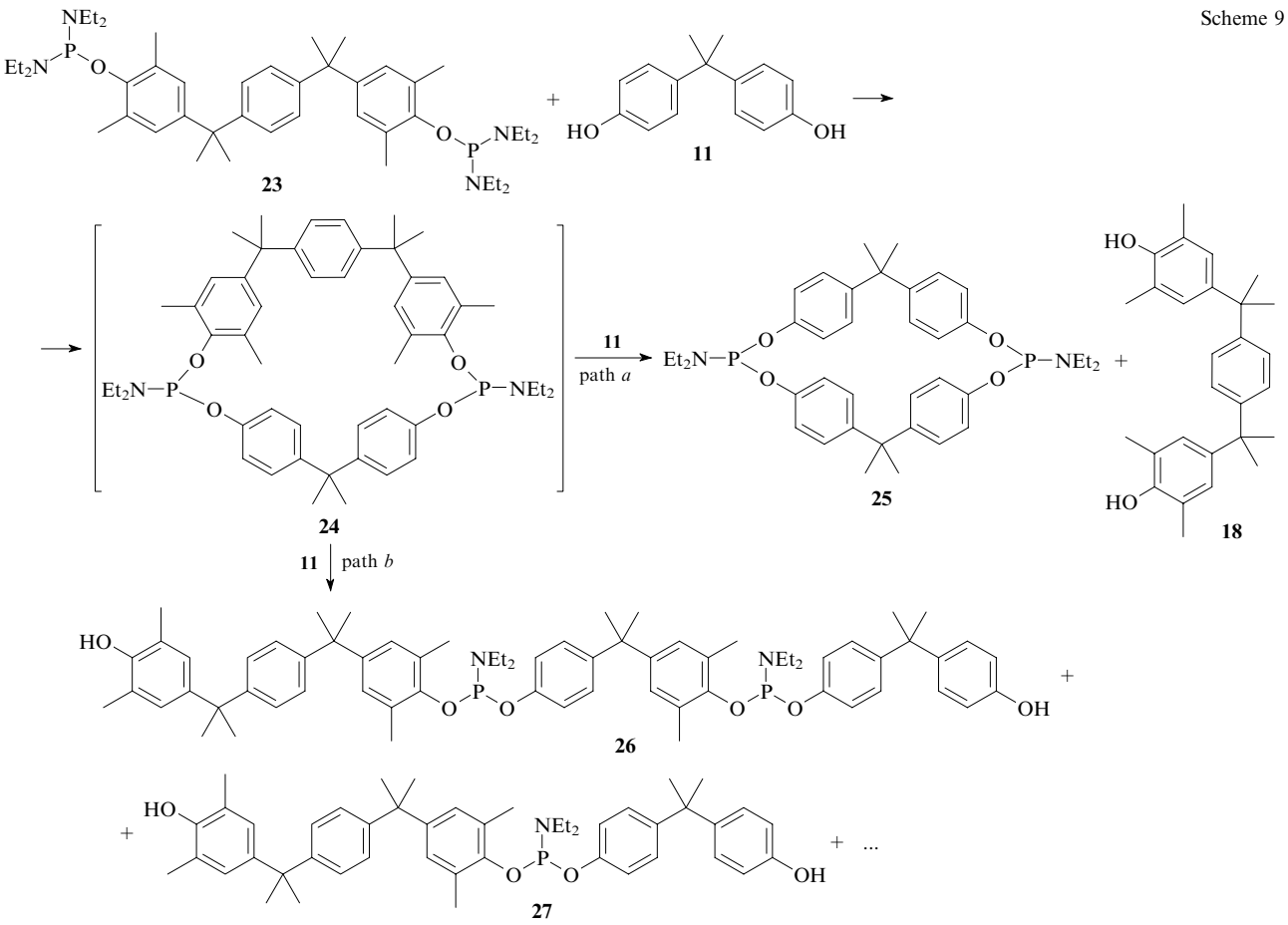
Scheme 7



Scheme 8

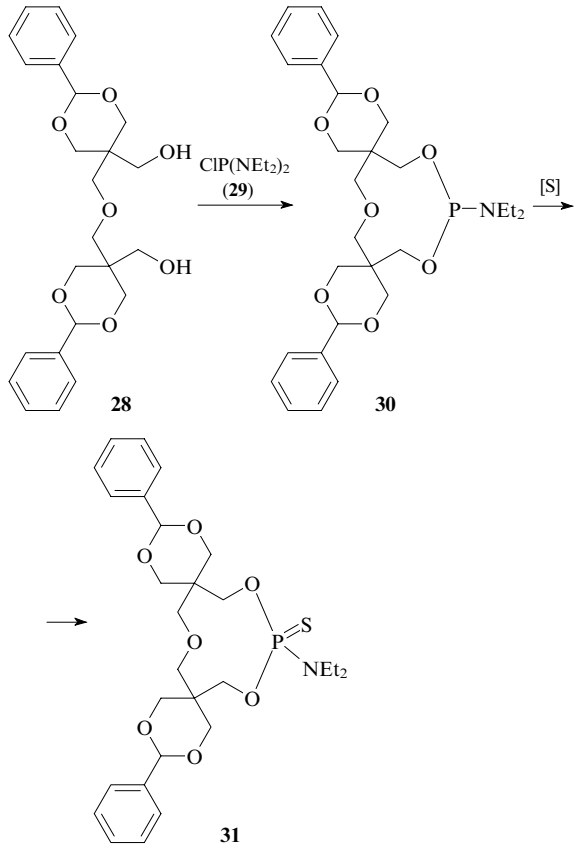


Scheme 9



were examined.[32 – 34] These compounds contain two quaternary carbon atoms, which can impart molecular recognition properties to macroheterocycles based on these compounds, thus enabling the recognition of organic and inorganic substrates. It was found that variations of the phosphorylating agent and the conditions of cyclophosphorylation allow one to synthesize different types of cyclic systems. For example, the reaction of equimolar amounts of dibenzylidene pentaerythritol **28** with tetraethylphosphorodiamidic chloride (**29**) in dioxane in the presence of pyridine at 5 °C for 2 h results in cyclophosphorylation of the starting diol to form macrocycle **30**. The bisphosphorylation also does not take place in the presence of a twofold excess of a phosphorylating agent. Cyclophosphoramidite **30** was subjected to *in situ* sulfurization to form more stable ten-membered cyclothiophosphoramidate **31** in a total yield of 65% (Scheme 10).[32]

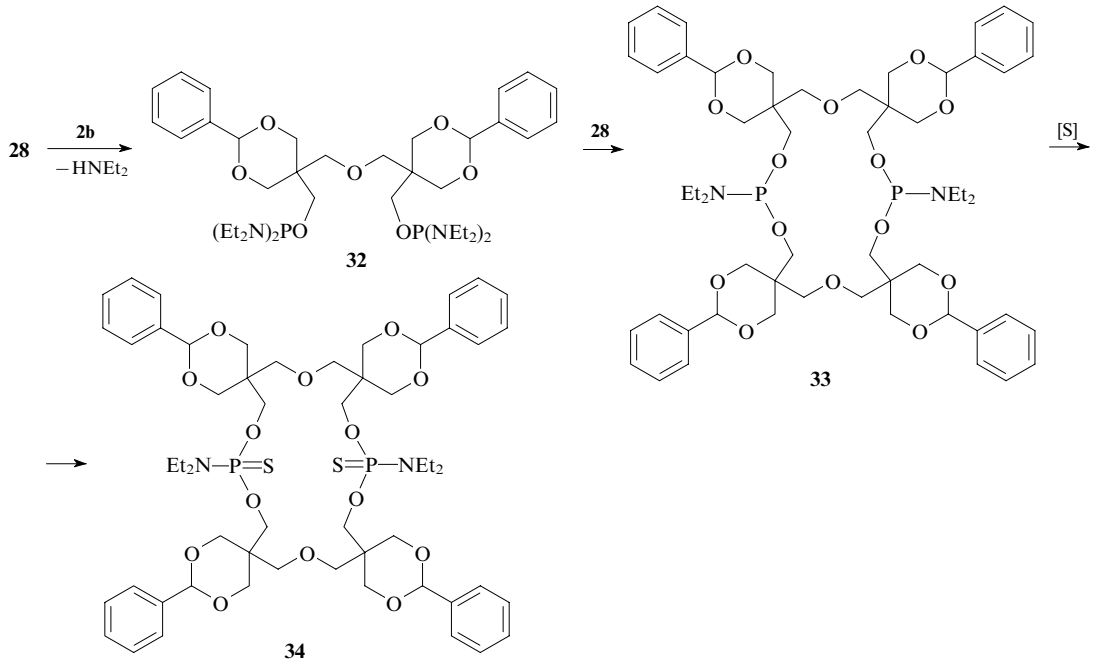
Scheme 10



Another unusual 20-membered bis(thiophosphoramidate) was synthesized based on diol **28** by means of molecular assembly.[32] The reaction of diol **28** with phosphorous triamide **2b** taken in a molar ratio of 1 : 2 in dioxane at 25 °C for 10 h produces bisphosphorylated diol **32**, which reacts with the starting diol **28** followed by sulfurization of cyclodiphosphite **33** to give dimeric phosphacyclane **34** (Scheme 11).

An important difference in the spatial structure of ten-membered thiophosphocyclane **31** and 20-membered dithiophosphocyclane **34** is that the former lacks the free inner cavity. According to the results of molecular simulation, the distance between the quaternary carbon atoms in molecule

Scheme 11

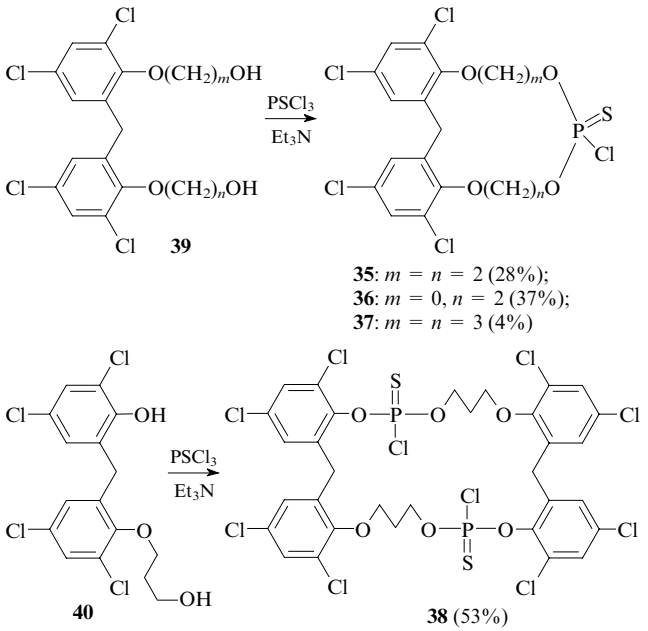


31 is as short as 4.69 Å, whereas the distance between the opposite phosphorus atoms in **34** is 7.39 Å. These data account for the possibility of the location of a water molecule found by spectroscopic methods in the inner cavity of macrocycle **34**.[32]

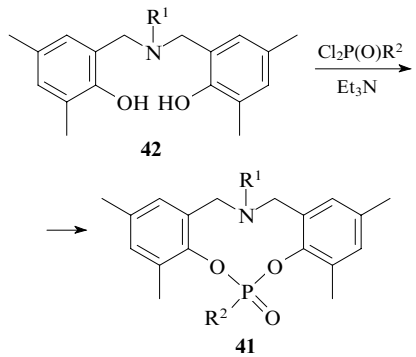
Polyoxamacrocycles **35**–**38** containing reactive thiophosphoryl groups were synthesized by the reactions of diols **39** and **40** with $PSCl_3$ (Scheme 12).[35] Low yields of two-component cyclization products **35**–**37** are apparently attributed to the fact that the bisphosphorylation is more favourable and gives finally linear polymers. The formation of macrocycle **38** occurs apparently *via* the reaction of $PSCl_3$ with the aliphatic hydroxy group of compound **40** and then with the phenolic hydroxy group, thus providing the high yield of the target product.[35]

New phosphorus-containing macrocyclic compounds **41** were synthesized in ~70% yield by the reaction of tertiary bis(hydroxybenzyl)amines **42** with phosphorus(V) dichlorides in the presence of triethylamine (Scheme 13). Diols **42** are easily produced by the condensation of 2,4-dimethylphenol, formaldehyde and the corresponding amines.[36] All synthesized compounds **41** exhibit moderate or high antibacterial and antifungal activities against gram-positive (*Staphylococcus aureus*) and gram-negative (*Escherichia coli*) bacteria and the fungi *Curvularia lunata* and *Fusarium oxysporium*.[36]

Scheme 12



Scheme 13

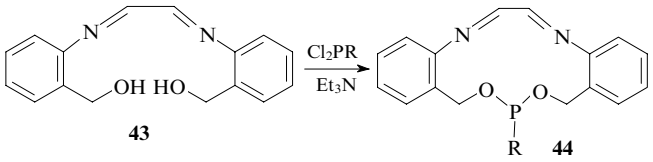


R^1 = Ph, 4-MeC_6H_4, 4-$MeOC_6H_4$, 2-$MeOC_6H_4$, 2-Py, 4-Py;
R^2 = Pr^n, Bu^n; Py is pyridyl

The condensation of diimine **43** with dichlorophenylphosphine or dichloroethylphosphite in the presence of triethylamine affords new 13-membered macrocycles **44** containing nitrogen, oxygen and phosphorus atoms in the ring.[37] The corresponding P-oxides, -sulfides and -selenides, which can be synthesized by oxidation of compounds **44** or by direct phosphorylation of precursor **43** with dichlor-

oxa(thioxa,selenoxa)phosphonates, exhibit antioxidant properties (Scheme 14).[37]

Scheme 14



R = Ph, OEt

2. Synthesis of phosphorus-containing cryptands

Phosphorus-containing cryptands (P-cryptands) are macroheterocyclic compounds consisting of two or more rings, which contain heteroatoms (in particular, phosphorus atoms) and are linked together by aliphatic or aromatic bridges. These compounds attract interest due to their strong complexing ability. They are not only suitable for the extraction of different metal ions from aqueous solutions but also can serve as ligands in the construction of transition metal complexes acting as catalysts for different reactions, such as hydroformylation and metathesis of alkenes, hydrogenation, Sonogashira and Suzuki reactions and so on.

Phosphite cryptands were synthesized by the one-step method, the so-called double-capping reaction.[27, 38, 39] The reaction of sterically unhindered bisphenol **45** with PCl_3 in the presence of triethylamine in toluene at 20 °C in moderately dilute solution affords three possible homeomorphic isomers **46** (*out*,*out*), **47** (*in*,*in*) and **48** (*in*,*out*) in a ratio of 2 : 1 : 2 in a total yield of 15% (Scheme 15)† Low yields of the products in this reaction were quite expected because the formation of the cage structure involves the formation of six new bonds. This explains why only a few examples of the double-capping synthesis are known.[40 – 42]

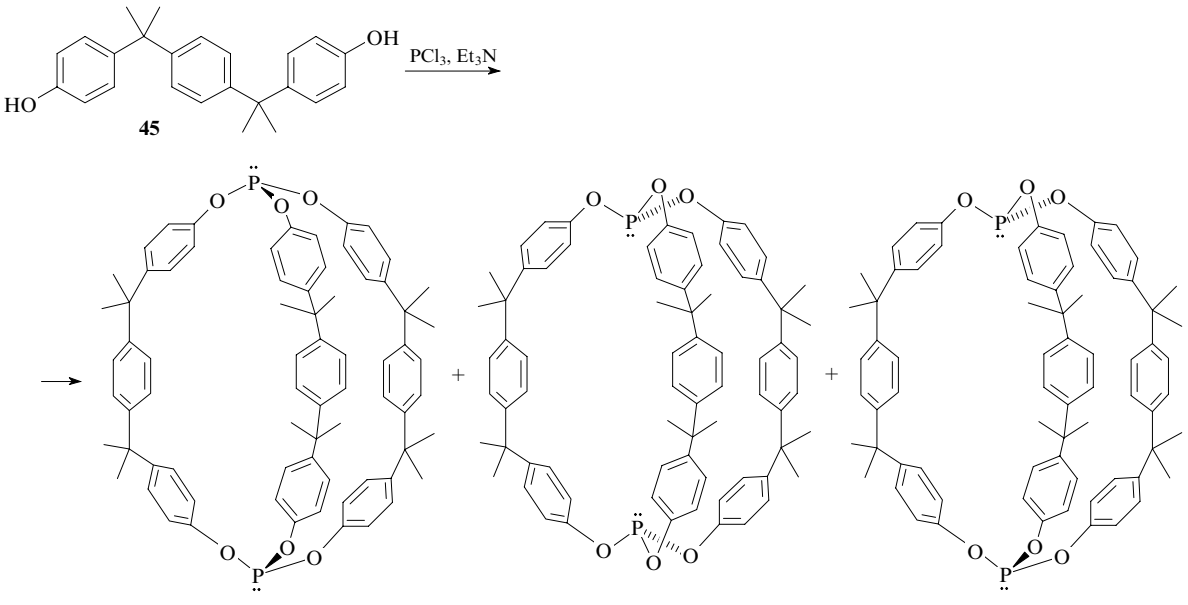
It should be noted that the use of $P(O)Cl_3$ instead of PCl_3 in the reaction with bisphenol **45** results in a higher content of the *out*,*out* isomer (14%) compared to the *in*,*out* (5.6%) and *in*,*in* isomers (1.6%) of the phosphate cryptand.[39] Apparently, this ratio of the products is associated with their thermodynamic stability.

The reaction of *in*,*in* isomer **47** with an excess of thiophosphoryl azide **49** (1 : 3 ratio) in boiling THF produced cage derivatives **50** – **52** bearing bulky P═N–P═S-containing moieties in the *in* orientation (Scheme 16).[27, 42]

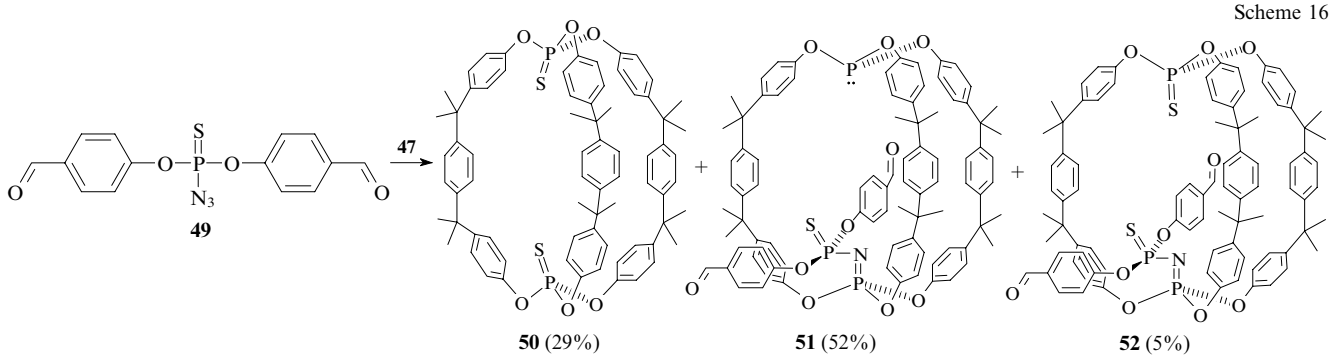
The cavity in *in*,*in*-phosphite **47** is apparently too small for the reaction of thiophosphoryl azide **49** to proceed at both *in* positions, due to which monosubstituted cryptand

† Convex-concave isomers, which differ in the position of the phosphorus bridgehead atoms with respect to the macrocyclic system, are referred to as *in* (inward) and *out* (outward) isomers.

Scheme 15



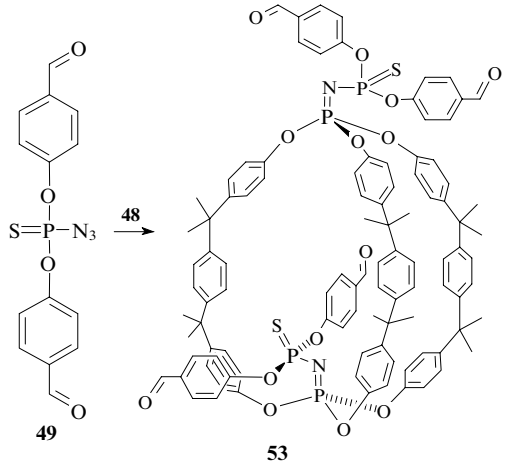
Scheme 16



51 is formed as the major product. In this case, the partial thionation of the starting phosphite and the product to form compounds **50** and **52**, respectively, are side reactions.

in,out-Phosphite **48** reacts with thiophosphoryl azide **49** much faster than *in,in*-phosphite **47**. The *in* position in cryptand **48** is more accessible due to a larger volume of the cavity in this compound. The doubly substituted *in,out* isomer **53** was isolated in 55% yield (Scheme 17).[27, 42]

Scheme 17



49 **53**

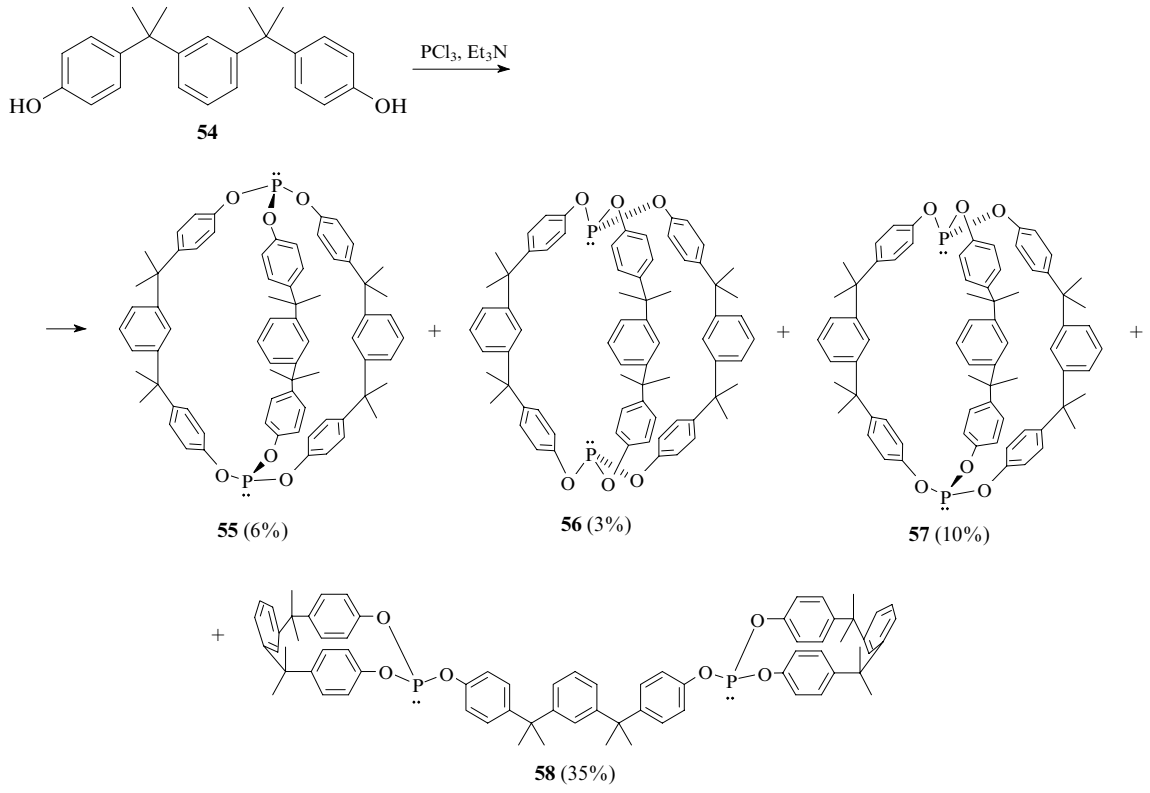
The synthesis of compounds **51** – **53** is the first example of the successful functionalization of the *in*-bridgehead positions in bicyclic cryptands. This modification can be used for the specific adaptation of host molecules to particular substrates for the molecular recognition or in the design of ligands for transition metal complex-catalyzed reactions.

The double-capping reaction was also performed with the participation of trinuclear bisphenol **54**.[27, 41] According to the ^{31}P NMR spectroscopic data, the mixture of reaction products contains three homeomorphic P-cryptands **55** – **57** and compound **58** as the major product (Scheme 18). Apparently, the spatial structure of the bisphenol component allows the intramolecular cyclization of intermediate chlorophosphite giving product **58** to take place as the competitive reaction. The latter reaction is much more favourable. Hence compound **58** is formed as the major product despite the fact that P-heterocycles in this structure are strained. The corresponding reaction with bisphenol **45** does not proceed.

An alternative approach to the construction of P-cryptands is based on the multistep method,[27, 38] by the so-called single-capping reaction. In the first step of the reaction, one hydroxy group of bisphenol **45** was protected by the *tert*-butyldimethylsilyl group. Then the reaction of compound **59** with PCl_3 was performed. As opposed the Me_3Si protecting group, which is easily eliminated by the action of PCl_3 to form phosphorus esters, the Bu^tMe_2SiO group is stable under these conditions. Phosphite, which was generated by the reaction of PCl_3 with bisphenol **59** at the hydroxy group, was oxidized by cumene hydroperoxide to the corresponding silicon-containing phosphate. The subsequent silyl deprotection afforded phosphate **60** (Scheme 19).

Phosphate **60** undergoes cyclization in the presence of PCl_3 to give P-bridged cage compounds. In this case, four homeomorphic isomers **61** – **64** bearing a lone pair on the phosphorus atom and the phosphate oxygen atom in the *in* or *out* position can exist (Scheme 20). All four isomers were detected in the crude product by ^{31}P NMR spectroscopy

Scheme 18

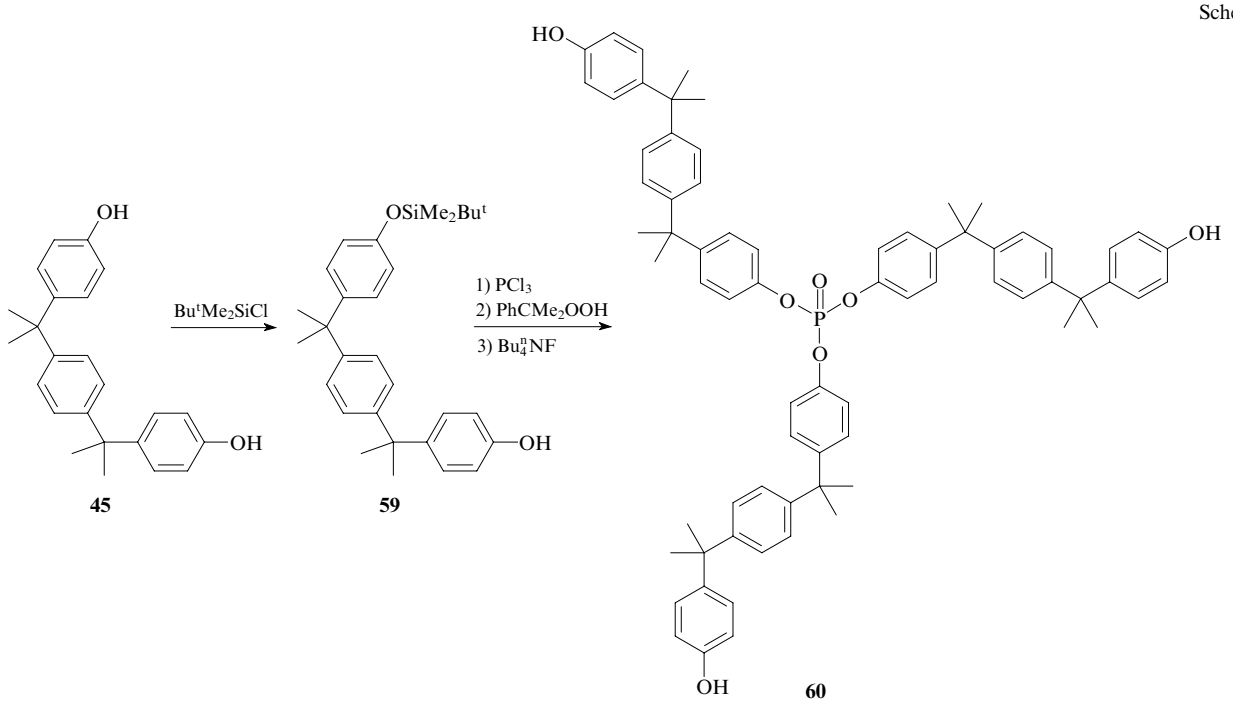


54

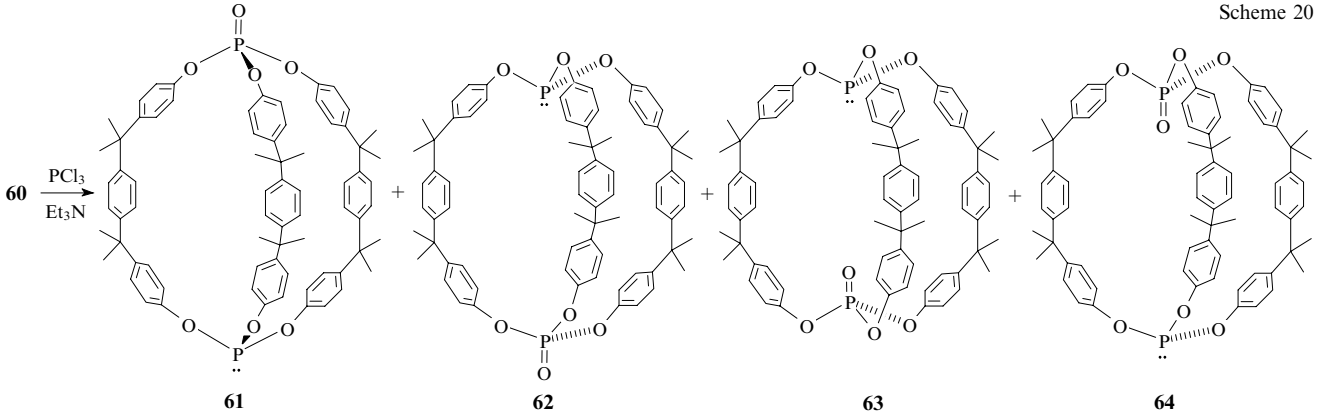
55 (6%) **56** (3%) **57** (10%)

58 (35%)

Scheme 19



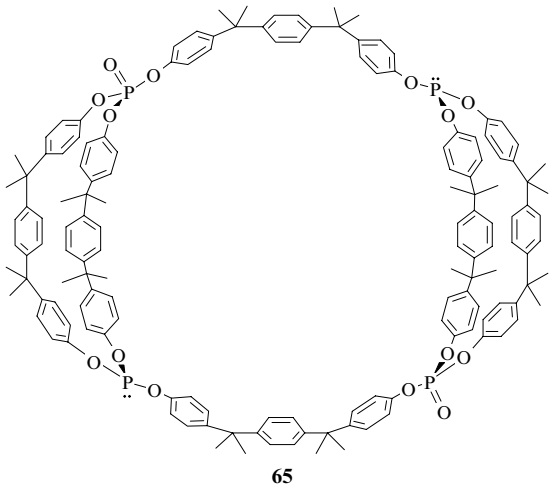
Scheme 20



(total yield was 12%). In the reaction mixture, compounds **61** and **62** were the major products, whereas cryptands **63** and **64** were present in trace amounts. Isomers **61** and **62** were isolated as a mixture by chromatography of the reaction mixture. Based on the results of matrix-assisted laser desorption/ionization time-of-flight (MALDI-TOF) mass spectrometry, one of the fractions was determined as a mixture of isomers of macrobicycle **65** having a cylindrical structure (yield was 8% of the total amount of the macrocycles).[27, 38]

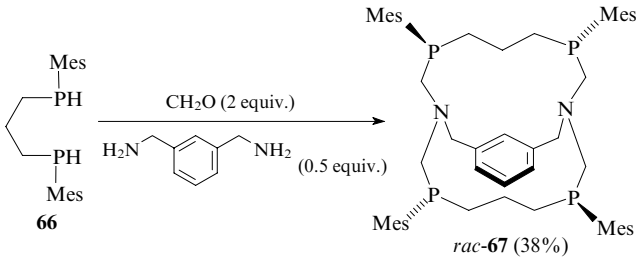
The single-capping strategy was further developed in the studies,[43, 44] where the synthesis of phosphine oxide derivatives of bicyclic cryptands containing ever larger cavities was documented.

The Mannich condensation was proposed for the stereoselective synthesis of a phosphorus-containing cryptand of a new type.[45, 46] The reaction of a mixture of diastereomers of 1,3-bis(mesitylphosphino)propane (**66**) with *m*-xylylenediamine and formaldehyde produced compound **67** in moderate yield as a racemic mixture of *S*,*S*,*S*,*S* and *R*,*R*,*R*,*R* isomers. The main 16-membered ring of **67** contains four chiral phosphorus atoms and two nitrogen atoms, which



hold the *m*-xylylene bridge. Apparently, the high stereoselectivity of the reaction is attributed to the fact that it proceeds under termodynamic control (Scheme 21).

Scheme 21

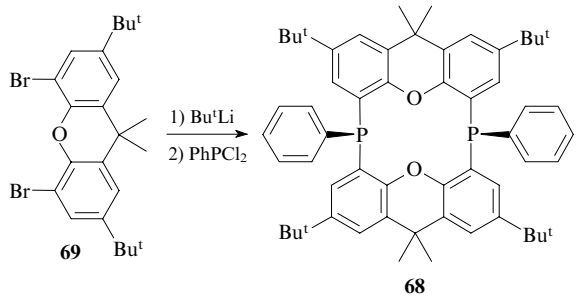


3. Construction of macrocyclic polyphosphines

Two main strategies are used for the formation of macrocyclic polyphosphines by reactions with the participation of phosphorus atoms: cyclocondensation and template synthesis.[47, 48]

Generally, a high dilution of the reaction medium and a long reaction time are required for the cyclocondensation reactions to proceed. However, even under these conditions, the reactions can produce the target macrocycles in low yields and be accompanied by the formation of oligomeric and other by-products. For instance, the stereoselective synthesis of diphosphine ligand **68** containing two xanthene moieties was documented.[49] The lithiation of 4,5-dibromo-2,7-di-*tert*-butyl-9,9-dimethylxanthene (**69**) with Bu^{t}Li followed by cyclocondensation with dichlorophenylphosphine afforded cyclic double-bridged diphosphine **68** in 10% yield as the *syn*,*syn* isomer. In addition to the target macrocycle, the reaction also produced a monophosphine derivative and oligomeric products (Scheme 22).

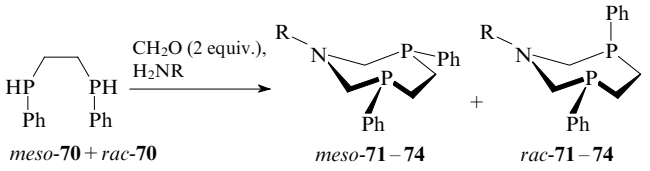
Scheme 22



Macrocyclic diphosphine **68**, in which both lone pairs on the phosphorus atoms are oriented in the same direction with respect to the macrocycle, is a promising chelating ligand for transition metal complex-catalyzed reactions. However, the rhodium complex with compound **68** exhibited very low catalytic activity and selectivity in the hydroformylation of oct-1-ene.[49]

A highly efficient method was developed for the synthesis of macrocyclic polyphosphine ligands, which is called the covalent self-assembly and is based on the Mannich condensation in the ternary system linear diphosphine – formaldehyde – primary amine.[46, 50 – 54] For example, the reactions of a mixture of diastereomers of 1,2-bis(phenylphosphino)ethane (**70**) with formaldehyde and primary amines (aniline, *p*-toluidine, benzylamine and 5-aminoisophthalic acid) give macroheterocyclic diphosphines **71** – **74**. They exist as mixtures of a racemate and a *meso* stereoisomer, which have substantially different properties and can act as different types of ligands. Thus, the *meso* isomers are chelating P,P-ligands, whereas the racemates are bridging ligands that form oligomeric metal complexes (Scheme 23).[46, 50]

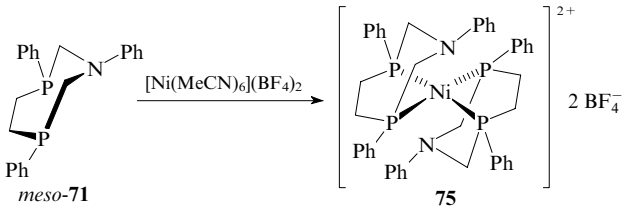
Scheme 23



R = Ph (**71**), 4-MeC$_6$H$_4$ (**72**), Bn (**73**), 3,5-(HO$_2$C)$_2$C$_6$H$_3$ (**74**)

Macrocyclic diphosphine ligand *meso*-**71** was used to synthesize mononuclear nickel complex **75** in 75% yield. The catalytic properties of **75** were studied in the electrochemical reduction of organic acids accompanied by the molecular hydrogen elimination (Scheme 24).[55]

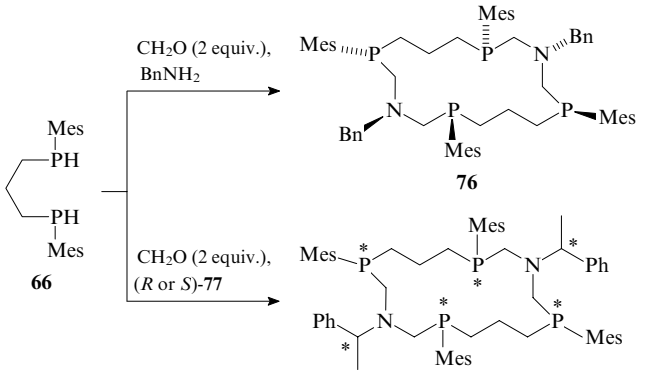
Scheme 24



Complex **75** efficiently catalyzes the hydrogen generation from protonated DMF or trifluoromethanesulfonic acid at a potential of -1.13 V. The turnover number of this catalyst is 33 000 s^{-1} in anhydrous acetonitrile, this number substantially increasing in the presence of small amounts of water (to 106 000 s^{-1}).[55] These values are substantially larger than the corresponding parameters of natural iron-containing hydrogenases, which are known as the most efficient catalysts for the hydrogen production from water in living organisms (the catalytic turnover number of these enzymes are not larger than 9000 s^{-1} at 30 °C).[56]

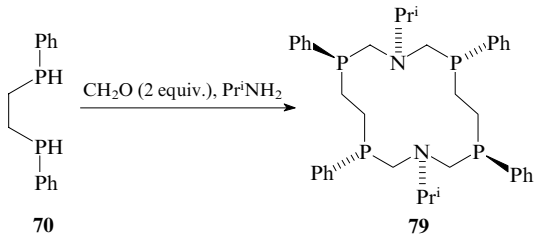
The covalent self-assembly was successfully used for the synthesis of macrocyclic tetraphosphines, including optically active compounds. Thus, the Mannich condensation of a mixture of diastereomers of 1,3-bis(mesitylphosphino)-propane (**66**) with formaldehyde and benzylamine in DMF resulted in the selective formation of the *R*,*S*,*S*,*R* diastereomer of new macrocyclic tetraphosphine **76** (yield 51%) instead of the expected 1-aza-3,7-diphosphacyclooctane.[46, 51] The corresponding reaction with the participation of (*S*)- or (*R*)-α-methylbenzylamine (**77**) results in the stereoselective formation of diastereomer **78** (the stereocentres have the *S* or *R* configuration, respectively) in moderate yield. The reaction monitoring by ^{31}P NMR spectroscopy showed that the concentration of product (*S*,*S*,*S*,*S*)-**78** is ~30% with respect to other products after 1 h and it reaches 47% after 24 h. Pure product (*S*,*S*,*S*,*S*)-**78** was obtained in 73% yield in 7 days, which is apparently attributed to fast equilibrium processes between intermediates and products in each step of the reactions (Scheme 25).[46, 52]

Scheme 25



The condensation in the 1,3-bis(phenylphosphino)-ethane (**70**) – formaldehyde – isopropylamine system leads to the stereoselective formation of new 14-membered diazatetraphosphine **79** in 57% yield.[54] The macrocycle is a *R*,*R*,*R*,*R*/*S*,*S*,*S*,*S* racemate with lone pairs on all phosphorus atoms in the *trans* orientation (Scheme 26).

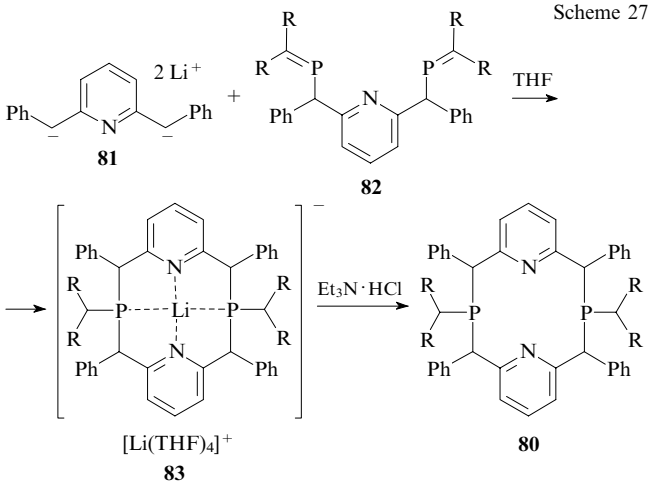
Scheme 26



The template synthesis is an alternative to the cyclocondensation. In this method, a metal ion (or another species) coordinates reactive synthons (building blocks), thus preparing them for the subsequent reaction resulting in the formation of a 'closed contour', a macrocyclic compound, which is difficult or even impossible to synthesize in the absence of a template. The macrocycle thus synthesized includes nine or more atoms, at least three of which are donor centres.

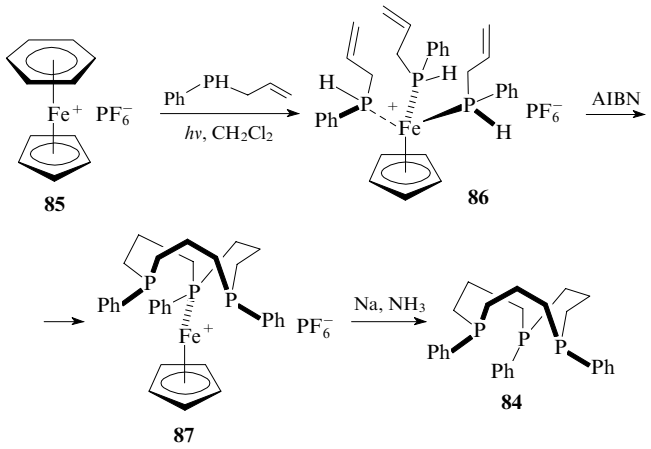
The template method was applied to the synthesis of diphosphine macrocycle **80** containing pyridine moieties.[57] Dilithium salt **81** generated from 2,6-dibenzylpyridine was used as the template. Its reaction with an equimolar amount of bisphosphinylene **82** produces metallomacrocycle **83**, and the treatment of the latter with triethylamine hydrochloride results in the release of neutral diphosphapyridinophane **80** (Scheme 27).

Scheme 27



The (η^5-cyclopentadienyl)iron(II) cation ($CpFe^{2+}$, Cp = η^5-C_5H_5) is a convenient template for the stereoselective synthesis of macrocyclic triphosphine ligands.[58 – 61] Thus, the synthesis of 1,5,9-triphosphacyclododecane **84** involves the photochemically induced replacement of the aryl group in compound **85** in the presence of allyl(phenyl)-phosphine as the first step giving rise to complex **86** in quantitative yield. The subsequent cyclization of this complex in the presence of azobisisobutyronitrile (AIBN) as the radical initiator is the first example of cyclotrimerization of secondary phosphines to form macrocycle **87** containing three tertiary phosphorus atoms. The template is then easily removed by the treatment with Na in liquid ammonia, resulting in the stereoselective elimination of ligand **84** as the *syn*,*syn* isomer (Scheme 28).[58]

Scheme 28

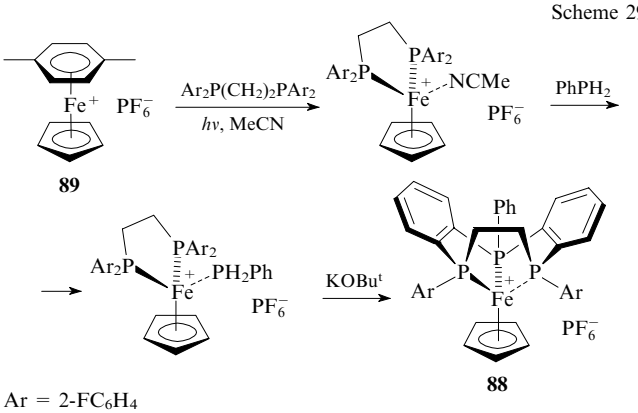


The macrocyclic triphosphine ligand containing ethyl groups at the phosphorus atoms, which was synthesized in a similar way,[58] forms relatively stable complexes with transition metal halides MCl_3 (M = Ti, V, Cr), the metal atom in the complexes being six-coordinate.[62] These complexes exhibit moderate catalytic activity in the homogeneous ethylene polymerization in the presence of alkylaluminium as the cocatalyst, which provides the formation of high-molecular-mass polymers.[63]

The same template was used for the synthesis of triphosphine macrocyclic ligands containing two[59] or three[61] *o*-phenylene groups. For example, compound **88** was synthesized in high yield (75%) in three steps starting from complex **89** (Scheme 29).[59] However, attempts to release the resulting macrocyclic triphosphines from the template failed.

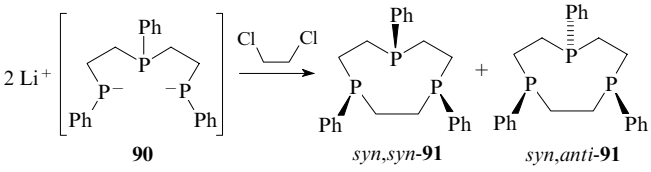
This first one-step synthesis of nine-membered macrocyclic triphosphine without the use of a template was performed by Lowry and Helm.[64] The method is based on the reaction of the dilithium salt of bis(2-phenylphosphidoethyl)phenylphosphine (**90**) with 1,2-dichloroethane (Scheme 30). The reaction affords macrocycle **91** as a mixture of two isomers (*syn*,*syn* and *syn*,*anti*) in a ratio of 3 : 7 (total yield 85%).

Scheme 29



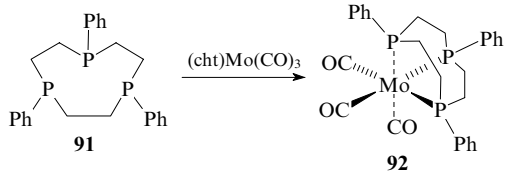
Ar = 2-FC_6H_4

Scheme 30



This method allows one to perform the synthesis without the use of a template, and the product is directly suitable for investigations of its coordination and catalytic properties. In particular, both isomers of macrocycle **91** react with cycloheptatriene molybdenum tricarbonyl [(cht)$Mo(CO)_3$] to form 1 : 1 complex **92** in 68% yield (Scheme 31).[64]

Scheme 31



III. Modifications of macrocyclic compounds by P^{III} and P^{V} derivatives

Approaches to the synthesis of phosphorus-containing macrocycles considered in the present section are based on modifications of macrocyclic structures by organic compounds of phosphorus(III or V). These approaches include the O- and C-phosphorylation of a calixarene template and the introduction of organophosphorus moieties into calixarene and other cyclophanes through different bridging groups.

1. Phosphorylation of calixarenes

Calixarenes (cyclic oligomers based on phenols) are polyfunctional macrocyclic compounds capable of forming host – guest inclusion complexes. Complexes of these macrocycles with biologically active guests,[65] as well as calixarenes chemically modified by biologically active (in particular, phosphorus-containing) groups,[66 – 71] are of great interest. Calixarenes containing phosphoryl groups at the upper or lower rim can undergo self-assembly to form dimeric associates through hydrogen bonding.[72] This makes it possible to prepare encapsulation complexes of these compounds with biologically active molecules. Such complexes can be transported across biological membranes.

It should be emphasized that macrocycles with P – C bonds resistant to hydrolysis are the most promising compounds for the practical application among a large number of diverse phosphorus-containing calixarenes.

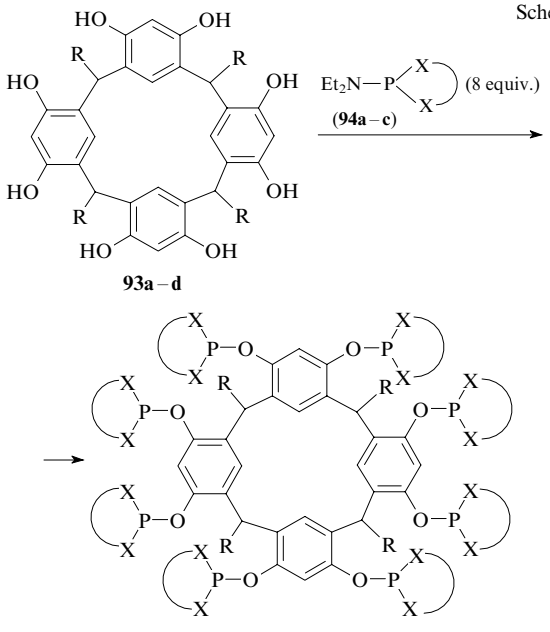
Currently, the following three approaches to the functionalization of calixarenes with organic compounds of phosphorus(III, V) are extensively developed: O-phosphorylation (introduction of phosphorus-containing moieties with the participation of hydroxy groups of calixarene), C-phosphorylation (with the participation of aromatic moieties of calixarene) and the introduction of organophosphorus groups through a spacer of a calixarene template. More recent studies in this area are summarized in reviews.[2 – 7] The most interesting publications devoted to this problem, including papers on the chemistry of phosphorus-containing calix[4]resorcinols and cavitands, are considered below.

a. O-Phosphorylation of calixarenes

Most of the studies concerned with the functionalization of calixarenes by phosphorus compounds are based on O-phosphorylation of hydroxy groups of calixarenes.[2] In these reactions, P^{III} and P^{V} halides, trialkyl phosphites, dialkyl phosphites, monochlorophosphites, mono- and dichlorophosphines, phosporamidites having different structures and so on are used as phosphorylating agents. In early investigations, only the possibility of the phosphorylation of phenol groups was examined, but more recently researchers have succeeded in controlling the number of the introduced phosphorus-containing groups, which allowed them to synthesize both unsymmetrical and chiral phosphorus-containing calixarenes.[2 – 7, 73 – 76]

Let us refer to the reaction of calix[4]resorcinols **93** with dioxaphosphorinane **94a** and its analogues **94b**,**c** as an example of these transformations.[77] The reaction proceeds slowly at room temperature even in the presence of a large

Scheme 32



95a – d; **96a**,**b**; **97a**,**b**

R = Me (**93a**, **95a**, **96a**, **97a**), Pr^n (**93b**, **95b**), n-C_6H_{13} (**93c**, **95c**), Ph (**93d**, **95d**, **96b**, **97b**);

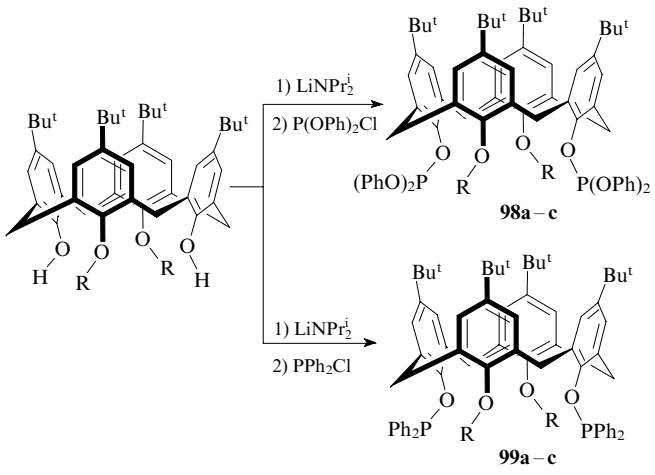


= $OCH_2CMe_2CH_2O$ (**94a**, **95**), $MeN(CH_2)_3NMe$ (**94b**, **96**), $Bu^tN(CH_2)_3NBu^t$ (**94c**, **97**)

excess of the phosphorylating agent to form a mixture of products with different degrees of phosphorylation. It was found that temperatures in the range of 90–95 °C are the optimal conditions for the production of perphosphorylated derivatives **95**–**97**. By contrast, the octaphosphorylation of compounds **93a**,**d** with diazophosphorinanes **94b**,**c** takes place at 20–25 °C, and an increase in the temperature leads to an increase in the reaction rate (Scheme 32).

The use of P^{III} compounds as phosphorylating agents made it possible to synthesize bisphosphite and bisphosphinite derivatives of *p-tert*-butylcalixarene, **98** and **99**, and investigate their coordination properties (Scheme 33).[78]

Scheme 33



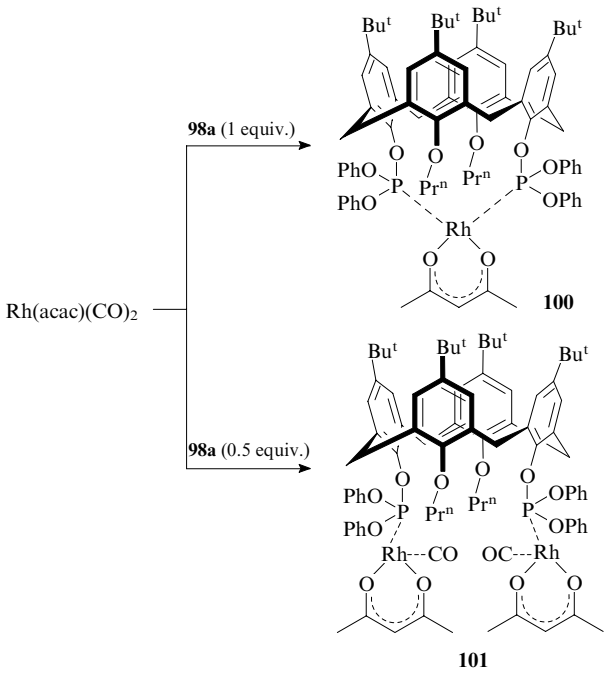
R = Pr^n (**a**), CH_2CO_2Et (**b**), CO_2chol (**c**);
chol is a cholesterol moiety

Ligands **98** and **99**, when mixed with [Rh(acac)$(CO)_2$] (acac is acetylacetonate), give complex compounds (for example, **100** and **101**), which efficiently catalyze the hydroformylation of alkenes, in particular, of octene and styrene (Scheme 34).[78]

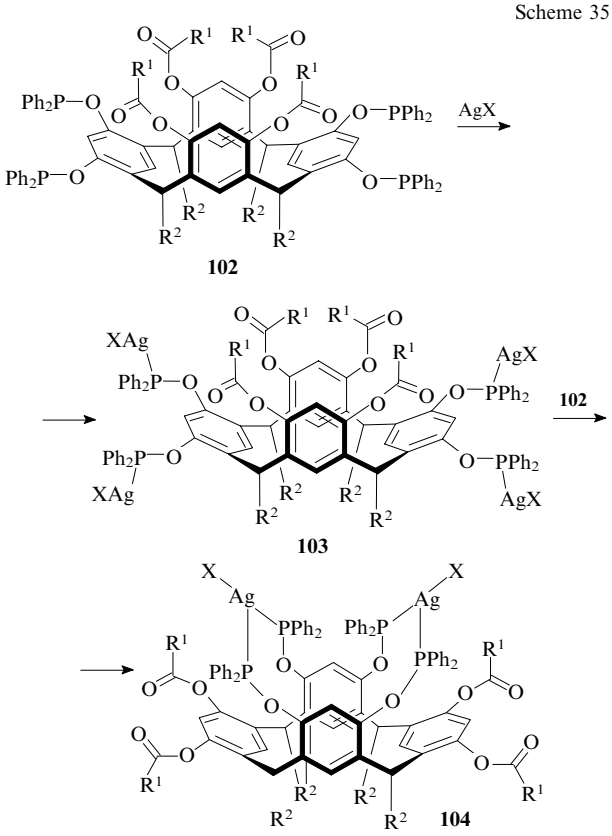
The partial O-acylation of unsubstituted calixarenes followed by O-phosphorylation of the four hydroxy groups that remained intact with chlorodiphenylphosphine diphenylphosphinite afforded diphenylphosphinite derivatives of calix[4]resorcinols **102** (Scheme 35).[79] These macrocycles can adopt two different boat conformations, which are in equilibrium in solution. Therefore, the aromatic rings containing phosphinite groups can be oriented either in a vertical or horizontal direction. The reactions of modified calix[4]resorcinols **102** with gold and silver salts produce complexes **103**, and the addition to the latter of 1 equiv. of the starting ligand results in the formation of binuclear chelate complexes **104**.[80, 81]

Ligands **105**, which were prepared by the sulfination of the diphenylphosphinite moieties in compounds **102**, show a radically different coordination behaviour. In the reactions giving cationic gold and silver complexes (for example, complex **106**), tetrakis(thiophosphinato)-substituted calix[4]resorcinols **105** act as bischelate ligands to form the linear S–M–S group (M = Ag or Au). In this case, pairs of thiophosphinate groups of the horizontally arranged aromatic rings of the calix[4]resorcinol template are involved in the complexation. The formation of chelate complexes for tetraphosphinite precursors **102** was observed only in the case of the vertically arranged aromatic rings of calixarene containing phosphinite moieties (Scheme 36).[82]

Scheme 34

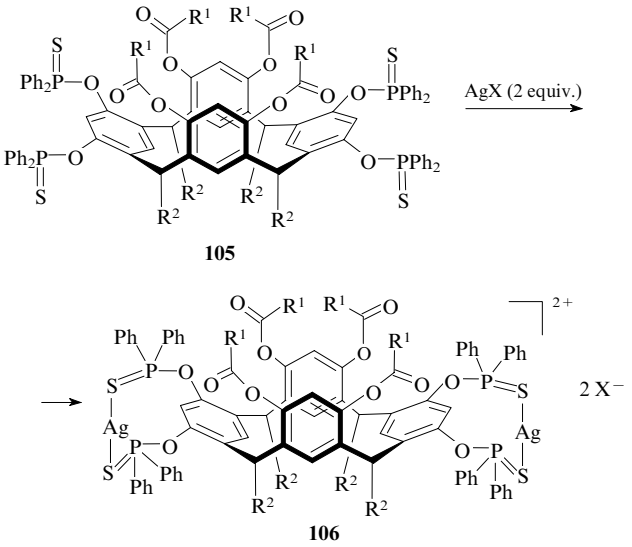


Scheme 35



R^1 = 4-MeC_6H_4, 2-Th, cyclo-C_6H_{11}, BnO;
R^2 = Ph$(CH_2)_2$; X = CF_3SO_3, CF_3CO_2; Th is thienyl

Scheme 36



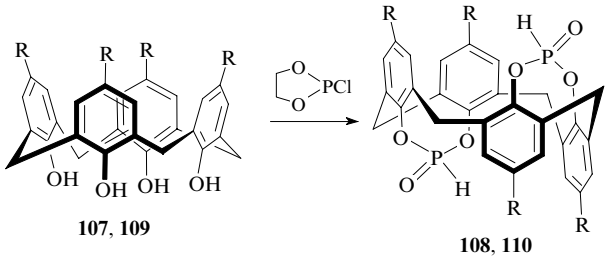
105

106

R^1 = BnO, CH≡CCH$_2$O, 4-MeC$_6$H$_4$, 2-Th; R^2 = Ph(CH$_2$)$_2$;
X = CF_3SO_3, PF_6

The use of ethylene chlorophosphite for the O-phosphorylation of *p-tert*-butyl(thia)calix[*n*]arenes (*n* = 4, 6) was documented.[83, 84] For example, the treatment of *p-tert*-butylcalix[4]arene **107** with this phosphorylating agent in a molar ratio of 1 : 2 (and even in the presence of a 10-fold excess) results in the formation of cyclic diphosphite **108** in the 1,2-alternate conformation in quantitative yield (Scheme 37). The corresponding reaction of calixarene **109** unsubstituted at the upper rim proceeds only in the presence of a fourfold excess of ethylene chlorophosphite to form diphosphite **110** in 62% yield. In this case, the moderate yield is apparently associated with higher conformational lability of the starting macrocycle **109** compared to calixarene **107**. Due to the presence of four bulky *tert*-butyl substituents, the latter has a conformationally more rigid structure, which is geometrically pre-organized to react with ethylene chlorophosphite. Apparently, cyclic products are formed *via* intramolecular transesterification accompanied by the elimination of a β-chloroethanol molecule. Evidently, the conformation of the reaction products (1,2-alternate) is determined by its high thermodynamic stability (the reaction temperature is 150 °C) and steric factors (see Scheme 37).[83]

Scheme 37



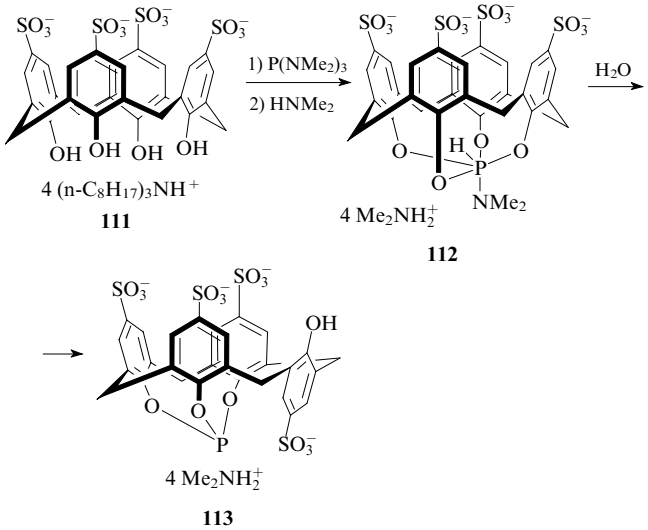
107, **109** **108**, **110**

R = Bu^t (**107**, **108**), H (**109**, **110**)

Noteworthy are the differences in the receptor ability of cyclic diphosphites **108** and **110** towards certain anions (used as tetrabutylammonium salts). Substantial changes in the ^{1}H and ^{31}P NMR and UV spectra of macrocycle **110** were observed only in the presence of F^-, AcO^- and $H_2PO_4^-$ anions. However, these anions did not cause changes in the spectroscopic characteristics of calixarene **108**. Evidently, the *tert*-butyl groups at the upper rim of the macromolecule shield the phosphoryl groups, thus hindering their binding to the anions.[83]

The reaction of tetrasulfonatocalix[4]arene **111** in the form of the tri-n-octylammonium salt with tris(dimethylamino)phosphine followed by the treatment with gaseous dimethylamine gave product **112** containing the six-coordinate phosphorus atom.[85] Since this compound is stable in the solid state even during prolonged storage, it serves as a convenient precursor in the synthesis of water-soluble ligand **113**, which is easily formed in one hour by the action of water on salt **112** (Scheme 38).

Scheme 38

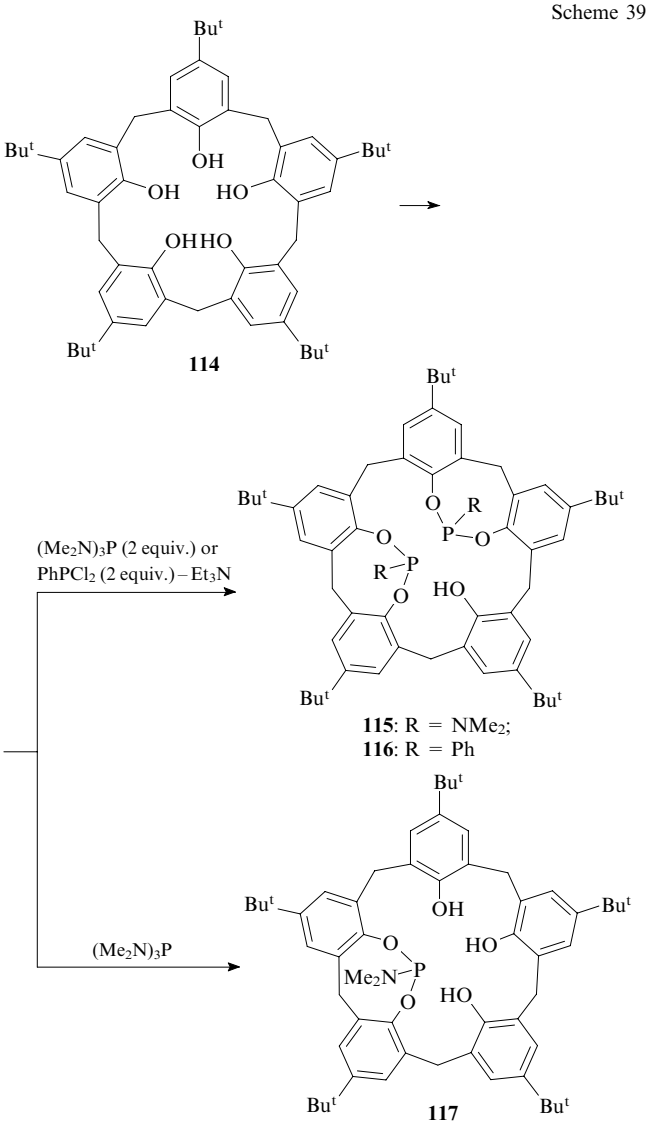


111 **112** **113**

This process is accompanied by the elimination of a dimethylamine molecule and a change in the conformation of the macrocycle. Phosphite **113** is hydrolytically unstable and decomposes in water during 24 h to form H_3PO_4 and the starting sulfonatocalixarene. However, the hydrolytic stability of water-soluble complexes of ligand **113** with Rh and Pt, which were prepared *in situ* from compound **112**, is a surprising fact. Thus, the complex [Rh(acac)(CO)(**113**)$_2$] remains intact in aqueous solutions at room temperature for more than six months. This complex also efficiently and selectively catalyzes the phase-transfer hydroformylation of 2-methyl pentanoate to form aldehydes having exclusively a branched structure.[85]

The reaction of *p-tert*-butylcalix[5]arene **114** with two equivalents of tris(dimethylamino)phosphine or dichlorophenylphosphine at room temperature is suitable for the introduction of two phosphorus-containing cyclic moieties into the calixarene cage giving rise to the corresponding derivatives **115** and **116**.[86] The use of one equivalent of the phosphorylating agent in this reaction results in the formation of monophosphorylated calix[5]arene **117**. It is interesting that attempts to synthesize mono-PPh-substituted calixarene failed. Thus, the reaction of dichlorophenylphosphine with calixarene taken in a ratio ⩾1 produced bisphoshporylation product **116** and unsubstituted calixarene **114** (Scheme 39).

Scheme 39



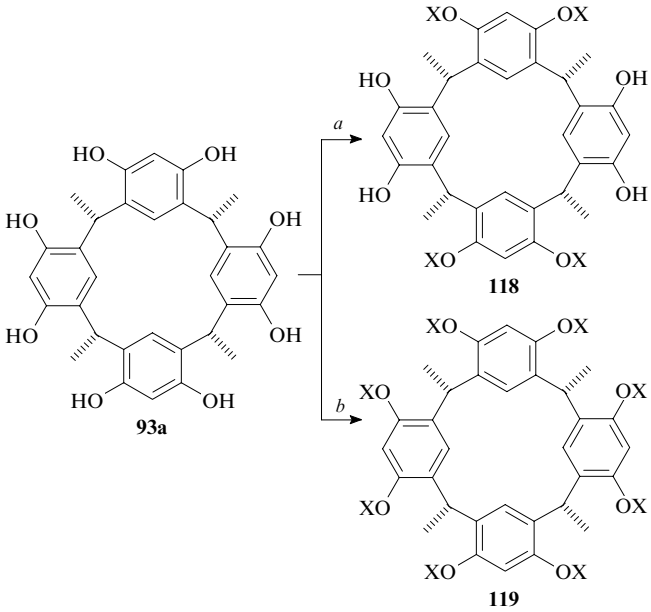
The heating of a solution of monophosphorylated calixarene **117** in toluene leads to the elimination of a dimethylamine molecule and the formation of the third P—O bond. The reaction proceeds mainly *via* an intramolecular mechanism to form cyclic monomeric phosphite (yield 50%); a dimeric tubular-like compound generated *via* an intermolecular reaction is the minor product (yield 10%).[86]

The reaction of ligand **117** with tetrakis(dimethylamino)titanium or tetrakis(diethylamino)zirconium is accompanied by the elimination of three dialkylamine molecules and the formation of three bonds between the metal and free oxygen atoms. The complexes thus produced can have both monomeric and dimeric structures.[87] In the latter case, they contain a planar four-membered M—O—M—O ring (M = Zr or Ti); the five-coordinate titanium atom does not form a bond with the phosphorus atom, as opposed to the six-coordinate zirconium atom involved in this bonding.

Representatives of cyclic di- and triphosphates were synthesized by phosphorylation of the hydroxy groups in *p-tert*-butyl-substituted calix[6]- (Ref. 88), calix[7]- (Ref. 89), calix[8]- (Refs 90 and 91) and calix[9]arenes[92] with phosphorus pentachloride followed by the hydrolysis with water.

The phosphorylation of calix[4]resorcinol **93a** with diethyl chlorophosphate affords partially (**118**) and completely (**119**) O-phosphorylated calix[4]resorcinols (Scheme 40).[93]

Scheme 40



(*a*) $(EtO)_2P(O)Cl$ (5 equiv.), Et_3N (5 equiv.), THF, 20 °C, 48 h;
(*b*) $(EtO)_2P(O)Cl$ (10 equiv.), Et_3N (10 equiv.), THF, 20 °C, 6 h;
X = $P(O)(OEt)_2$

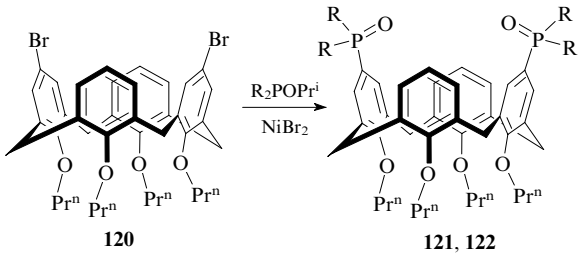
The fire-resistant properties of epoxy resins were studied with the use of the above-described antipyrene additives.[93] It was shown that the fire resistance of polymer samples containing additives of partially or completely phosphorylated calix[4]resorcinols increases with increasing phosphorus content (1.25% for macrocycle **118** and 2.5% for compound **119**). The rate of heat release decreases with increasing amount of the additive. For instance, the process slows down by 61% for a sample containing 2.5% of phosphorus (calix[4]resorcinol **119**). In addition, the amount of carbon dioxide that is eliminated decreases as the phosphorus content increases, which indicates that the rate of polymer combustion slows down.

b. C-Phosphorylation of calixarenes

The direct introduction of organophosphorus groups at the upper rim of calix[*n*]arenes is suitable for the synthesis of a new type of receptors, whose complexing ability is substantially higher due to the involvement of the macrocyclic cavity in the binding process. Methods for the direct phosphorylation of aromatic rings of calix[*n*]arenes are not very diverse. Thus, the Arbuzov reaction catalyzed by nickel(II) salts is commonly used for this purpose.

This approach was used to synthesize a family of new derivatives of dialkoxy- and tetraalkoxy-substituted calix[4]arenes containing from one to four phosphoryl groups at the upper rim of the macrocyclic molecule.[94] For example, the reaction of *p*-dibromocalix[4]arene tetrapropyl ether **120** with phosphorus(III) acid esters in the presence of catalytic amounts of $NiBr_2$ affords the corresponding diphosphorylated derivatives **121** and **122** in yields of up to 70% (Scheme 41).

Scheme 41

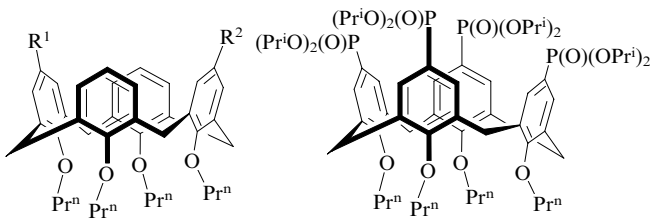


120 **121**, **122**

R = OEt (**121**), Ph (**122**)

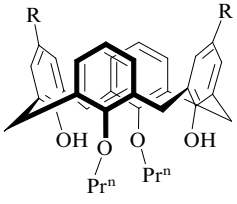
It was shown that amphiphilic phosphorylated calixarenes described by Solovyov *et al.*[94] can form inclusion complexes with various organic compounds (isobutyl alcohol, toluene, aniline and so on). These macrocycles were used to synthesize Langmuir – Blodgett films, which reversibly adsorb vapours of volatile organic substances from atmospheric air.

Tetra- (**123**) and dipropyl ethers (**124**) served as the starting compounds in the synthesis of calix[4]arenes **125** – **128** functionalized by hydrophilic diisopropoxyphosphoryl groups.[65] These compounds are efficient receptors of biologically active uracil derivatives in aqueous media. It should be noted that the introduction of each subsequent diisopropoxyphosphoryl group into the calixarene template decreases the complex-forming ability of calixarene tetrapropyl ethers **125** – **127** towards uracil derivatives but enhances this ability in the case of calixarene dipropyl ether **128** compared to its precursors **123** and **124**, respectively, unsubstituted at the upper rim.



123, **125**, **126** **127**

$R^1 = R^2$ = Br (**123**), $P(O)(OPr^i)_2$ (**126**);
R^1 = Br, $R^2 = P(O)(OPr^i)_2$ (**125**)



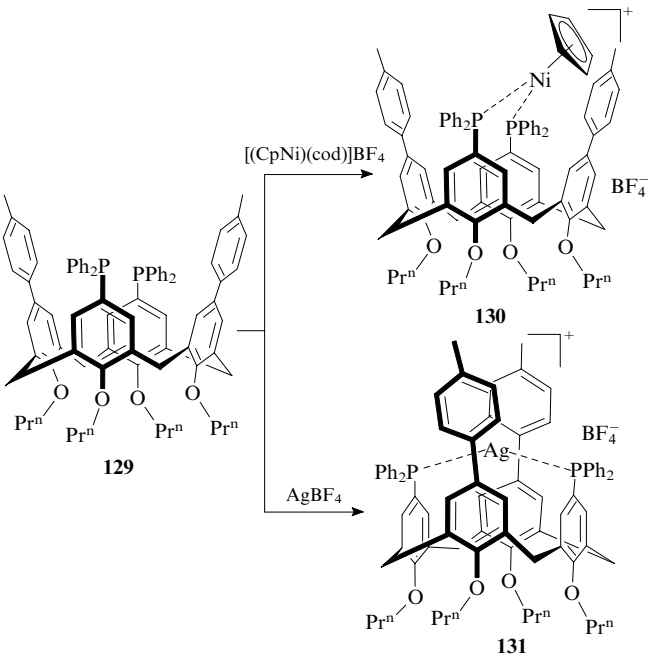
124, **128**

R = Br (**124**), $P(O)(OPr^i)_2$ (**128**)

Calix[*n*]arenes ($n = 4-6$, 8) containing four hydroxy substituents at the lower rim and their tetraalkyl or tetraacetyl ethers containing four dialkoxyphosphonate moieties at the upper rim were synthesized in a similar way by the Arbuzov reaction. These derivatives are easily hydrolyzed to form the corresponding phosphonic acid derivatives in quantitative yields. The synthesized compounds can undergo association through intermolecular hydrogen bonds involving phosphonic acid moieties to form nano-sized aggregates both in solution and in the gas phase.[95 – 98] In addition, tetrahydroxy-substituted calix[4]arene containing four phosphonic acid moieties at the upper rim with different degrees of deprotonation binds calcium ions in the solid state to give complexes with the calixarene : metal ion ratio of 2 : 5 or 1 : 1. These complexes are self-organized in the course of crystallization to form bilayered structures.[99]

Calix[4]resorcinol tetrapropyl ether **129** containing two phosphine groups and two tolyl groups at the upper rim were synthesized by the Arbuzov reaction of the corresponding bromo derivative with Ph_2POEt followed by reduction with phenylsilane. Ligand **129** reacts with $[(CpNi)(cod)]BF_4$ (cod is cycloocta-1,6-diene) or $AgBF_4$ to form chelate complex **130** or **131** in quantitative yield. In the solid state, the P – Ni – P angle in nickel complex **130** is 104.6° and it falls in the range expected for this type of complexes. In silver complex **131**, the P – Ag – P angle is larger (138.8°), which is indicative of the flexibility of the calixarene cage. It is noteworthy that the P – Ag – P fragment of complex **131** can reversibly change the geometry from linear to angular (Scheme 42).[100]

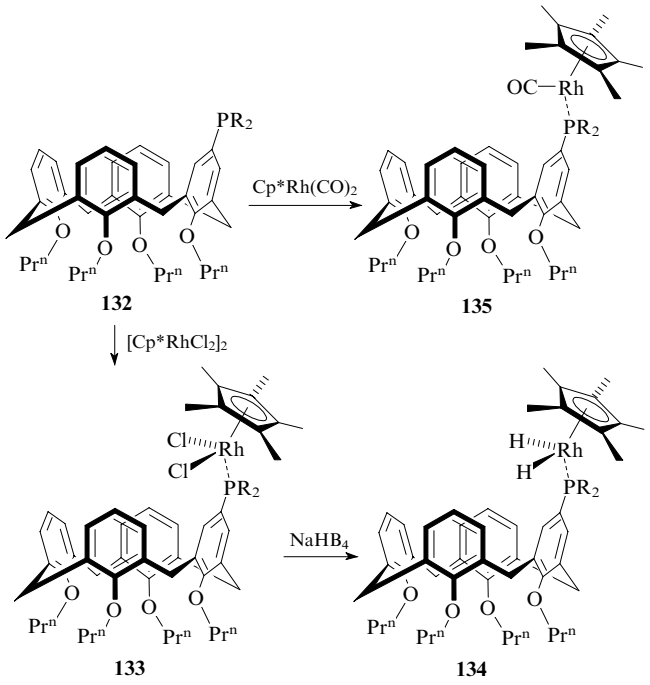
Scheme 42



129 **130** **131**

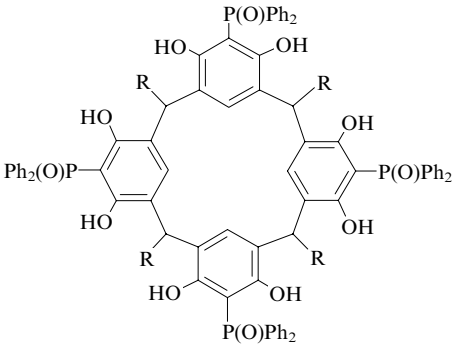
The regioselective method was developed [101 – 103] for the introduction of one to four diphenylphosphine groups at the upper rim of the calix[4]arene template. This method is based on the lithiation of *p*-bromo-substituted calix[4]arenes and the subsequent reaction of the intermediates with chlorodiphenylphosphine or chlorodiisopropylphosphine. Monofunctionalized calix[4]arenes **132** thus synthesized react with $[(\eta^5\text{-}C_5Me_5)Rh^{III}Cl_2]_2$ to form stable complexes **133** in high yields. The latter can be easily transformed into the corresponding dihydrides **134** unstable in the light and in air. The reaction of calixarenes **132** with $(\eta^5\text{-}C_5Me_5)Rh^{I}(CO)_2$ produces η^5-pentamethylcyclopentadienyl rhodium complexes **135**, which are decomposed under UV radiation (Scheme 43).[102, 103]

Scheme 43

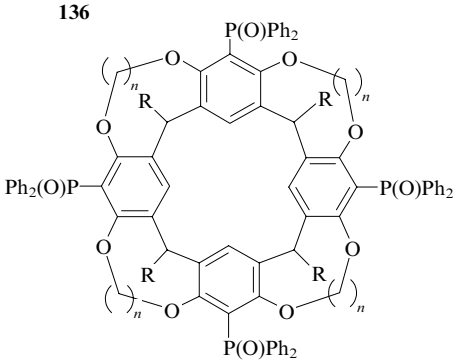


R = Ph, Pr^i; Cp* = η^5-C_5Me_5

The direct phosphorylation of the calix[4]resorcinol template was performed by means of the reaction of tetra(*p*-bromo)-substituted calixarenes and cavitands with potassium diphenylphosphide. The subsequent oxidation with hydrogen peroxides afforded new ligands **136** – **138**.[104]



136



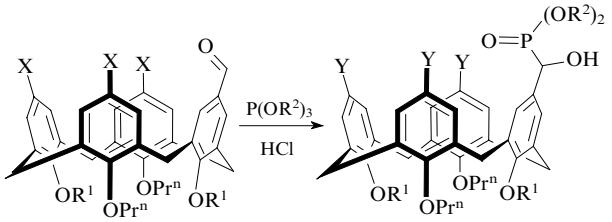
137, **138** [R = n-$C_{11}H_{23}$; *n* = 1 (**137**), 2 (**138**)]

c. Introduction of phosphorus-containing moieties into the calixarene template *via* a spacer

The most efficient and selective receptor systems based on calix[*n*]arenes are more often constructed based on the linking of phosphorus-containing moieties to the calixarene template *via* a spacer (a chain of other atoms) rather than by the direct attachment of organophosphorus groups at the upper or lower rim of the macrocycle.

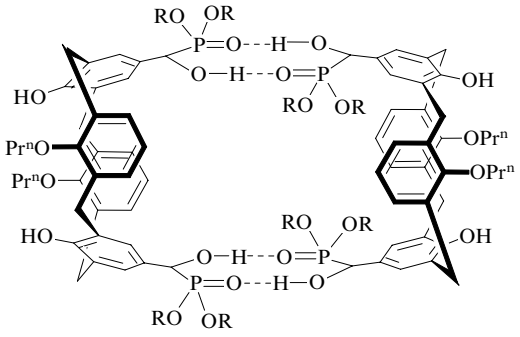
A facile synthetic approach to the introduction of hydroxymethylphosphonyl groups at the upper rim of the calixarene system was developed based on the reaction of *p*-formylcalix[4]arenes **139** with trialkyl phosphites.[72] The reaction proceeds in 1,4-dioxane saturated with dry hydrogen chloride at room temperature and produces α-hydroxyphosphonic acid derivatives **140** containing from one to four dialkoxyphosphorylhydroxymethyl moieties (Scheme 44).

Scheme 44



X = H, Br, CHO, CH(OH)P(O)$(OR^2)_2$; Y = H, CH(OH)P(O)$(OR^2)_2$; R^1 = H, Pr^n; R^2 = Me, Et, Pr^i

Calixarenes **140** existing in the stereochemically rigid cone conformation (with a large distance between the opposite phosphorus atoms equal to ~13 Å) can form dimeric associates through intermolecular hydrogen bonds CH—OH···O=P.[72]

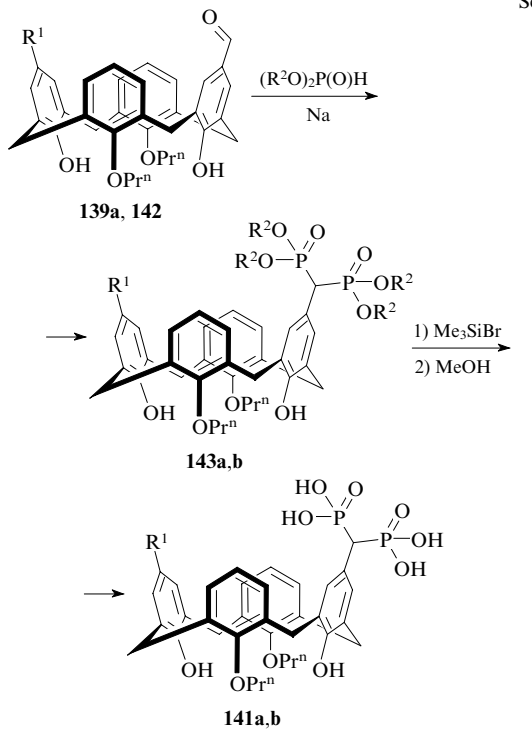


R = Me, Et, Pr^i

The hydrolysis of calix[4]arenes **140** with the participation of dialkoxyphosphorylhydroxymethyl groups affords the corresponding hydroxyphosphonic acids.[67] Mono- and bisphosphorylated calixarene derivatives, which can be prepared by this method, exhibit pronounced inhibitory properties for glutathione S-transferase. Thus, the concentrations yielding 50% inhibition of the enzyme (IC_{50}) are in the micromolar range.[70]

Calix[4]arenes **141a**,**b** modified by one or two methylenebisphosphonic acid moieties were synthesized by the reaction of the corresponding formylcalix[4]arenes **139a** (R^1 = X = H) and **142** with dialkyl phosphites followed by the treatment of intermediates **143a**,**b** with bromotrimethylsilane (Scheme 45).[68, 69]

Scheme 45



R^1 = H (**139a**, **141a**, **143a**), CHO (**142**), $CH[P(O)(OR^2)_2]_2$ (**143b**), $CH[P(O)(OH)_2]_2$ (**141b**); R^2 = Me, Et, Pr^n, Pr^i, Bu^n

Mono- (**141a**) and disubstituted (**141b**) calix[4]arenes synthesized by this method are more efficient inhibitors of alkaline phosphatase than their simplest analogues, such as methylenebisphosphonic and 4-hydroxyphenylmethylenebisphosphonic acids. Compound **141a** exhibits higher inhibitory activity than its disubstituted analogue. It should be noted that the use of calix[4]arene **143b** containing diethylphosphonate groups instead of phosphonic acid moieties resulted in a substantial decrease in the efficiency of inhibition of alkaline phosphatase.[68, 69]

Analogous tetrahydroxycalix[4]arene bearing four methylenebisphosphonic acid substituents at the upper rim proved to be a specific inhibitor of blood coagulation reactions, such as fibrin polymerization and blood plasma coagulation ($IC_{50} = 0.5 \times 10^{-6}$ mol litre^{-1}).[69]

Noteworthy is the use of calixarenes functionalized by methylenebisphosphonic acid moieties for the inhibition of protein tyrosine phosphatase from the bacterium *Yersinia*. Disubstituted calixarene **141b** showed the best results (the inhibition constant $K_i = 1.4$ μmol litre^{-1}) as compared with the mono- and tetrasubstituted derivatives ($K_i = 7.1$ and 40 μmol litre^{-1}, respectively). This compound is 400 times more efficient than its linear analogue, 4-hydroxyphenylmethylenebisphosphonic acid ($K_i = 570$ μmol litre^{-1}). However, calix[4]arene and thiacalix[4]arene tetrasubstituted at the upper rim by methylenephosphonic acid groups are the most efficient inhibitors in the series of compounds under study; their inhibition constants are 0.92 and 0.22 μmol litre^{-1}, respectively.[71]

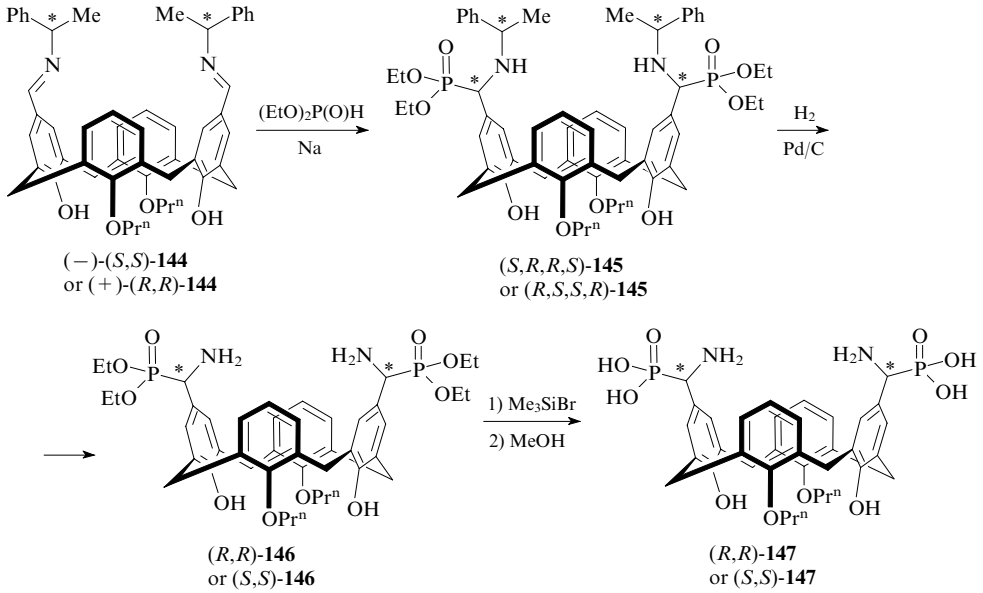
The diastereoselective addition (Pudovik reaction) of sodium diethyl phosphite to calix[4]arenes **144** containing imino groups afforded new chiral α-alkylaminophosphonic acid esters with the calix[4]arene cage, *viz*., compounds **145**.[66, 67, 105] The subsequent catalytic reduction giving amino derivatives **146** and the hydrolysis resulted in the formation of new chiral calixarenes **147** containing two α-aminophosphonic acid moieties at the upper rim (high yields) (Scheme 46).

The reaction products exhibit high inhibitory activity towards alkaline phosphatase, the activity being substantially dependent on the absolute configuration of the α-carbon atom. It was found that the *R*,*R* isomer of compound **147** is the best inhibitor of alkaline phosphatase.[66]

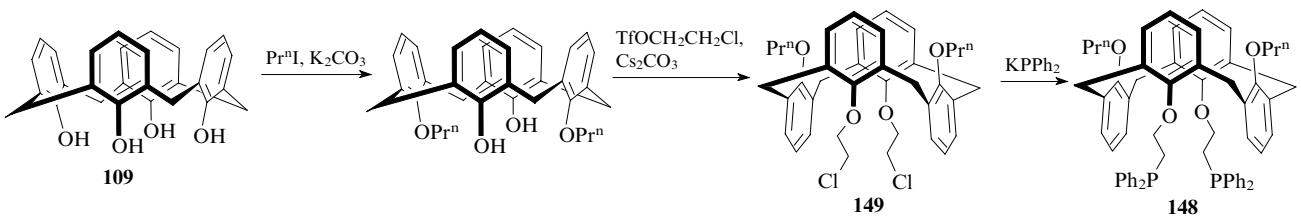
Successive modifications of unsubstituted calix[4]arene **109** afforded new phosphorus-containing ligand **148**.[106] All reactions proceed under mild conditions. The formation of compound **149** is accompanied by the change in the conformation of the calixarene cage. Final product **148** adopting ane 1,3-alternate conformation was isolated in a total yield of 64% (Scheme 47).

Ligand **148** containing two diphenylphosphine moieties is an interesting model for testing metal ion complexation properties. For example, the reaction of compound **148** with

Scheme 46

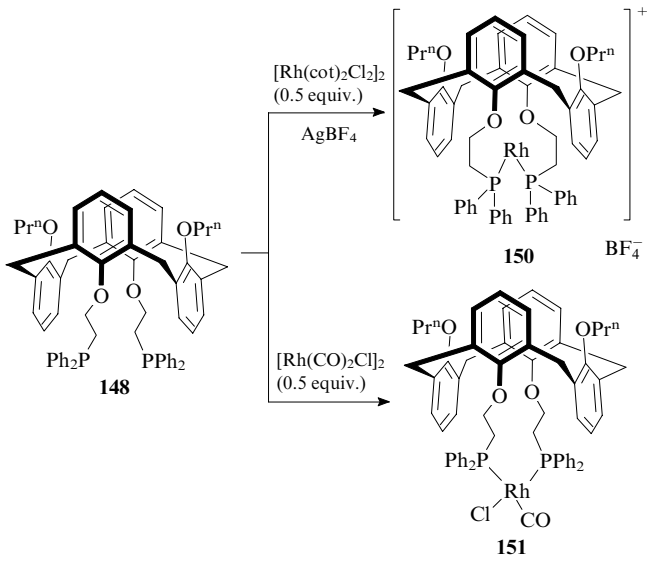


Scheme 47



$[Rh^{II}(cot)_2Cl_2]$ (cot is cyclooctatetraene) produces mononuclear complex **150** with an encapsulated Rh atom. The coordination of the metal centre by ligand **148** is characterized by a bent geometry with the P···Rh···P angle equal to 135.66°. The Rh atom does not coordinate oxygen atoms of the $Ph_2P(CH_2)_2O$ group (the Rh···O distance $\geqslant$ 3.3 Å); by contrast, the distances from the metal centre to two C atoms involved in the aromatic rings non-modified by diphenylphosphine groups is ~3.05 Å, which is indicative of the possibility of strong Rh···C interactions. The reaction of compound **148** with $[Rh^{II}(CO)_2Cl]_2$ proceeds in a different way. Thus, calixarene acts as a bidentate ligand, the metal centre is not encapsulated, and chelate *cis*-complex **151** is formed (Scheme 48).

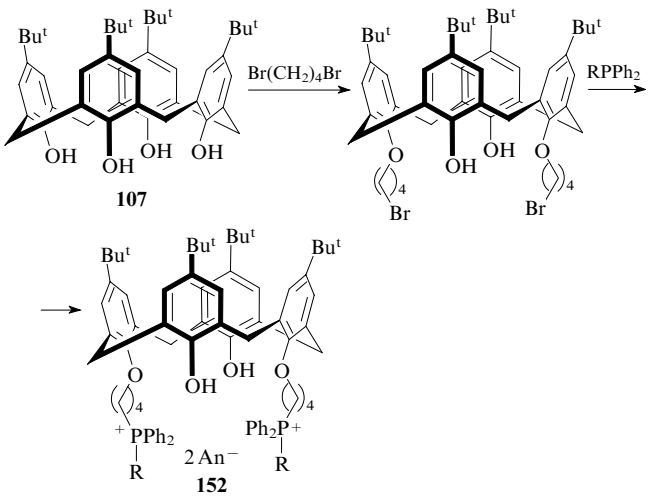
Scheme 48



p-tert-Butylcalix[4]arenes **152** in the cone conformation disubstituted at the lower rim by phosphonium moieties were synthesized by bromoalkylation of O-unsubstituted calixarene **107** followed by the reaction with triphenyl- or methyldiphenylphosphine (Scheme 49).[107–109] Tetraphosphonium derivatives were synthesized according to the same procedure.

An interesting feature of the synthesized receptor macromolecules containing either two or four phosphonium moieties is that they prefer to bind lipophilic anions, such as SCN^-, I^- and particularly ClO_4^-. When used as an active material of ion-selective membrane electrodes, these compounds exhibit selectivity towards ions that changes in the order reverse to the Hoffmeister series: $ClO_4^- > SCN^- > I^- > Cr_2O_7^- > NO_3^- > Br^- > HCO_3^- > HPO_4^{2-} > SO_4^{2-}$. It should be noted that tetraphosphonium derivatives provide better selectivity than their diphosphonium analogues.[109]

Scheme 49



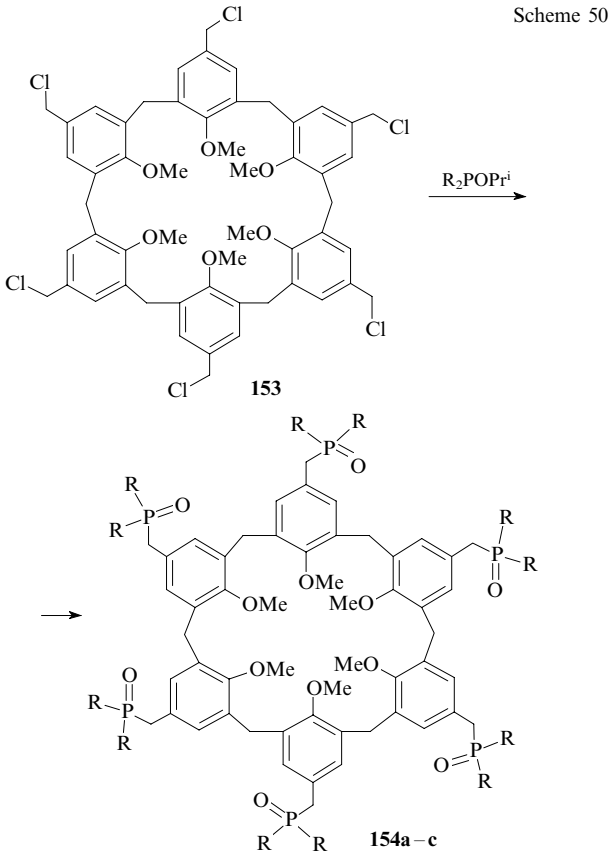
R = Ph, Me; An = Br, PF_6

The reactions of hexakis(chloromethyl)calix[6]arene hexamethyl ether **153** with P^{III} acid isopropyl esters produced derivatives **154a–c** functionalized by six phosphoryl groups at the upper rim (Scheme 50).[110]

Apparently, the cooperative involvement of all phosphoryl groups in the binding of metal cations is responsible for the fact that these compounds have higher extractability for americium and europium ions compared to their acyclic analogues and industrial phosphorus-containing extractants. The observed cooperative effect has no substantial influence on the Am/Eu selectivity. Thus, europium is bound more efficiently than americium (the ratios of the distribution coefficients D_{Am}/D_{Eu} are in the range of 0.18–0.29). Calix[6]arene **154c** containing two electron-donating n-butyl groups at the phosphorus atom exhibits the highest extraction ability in the series of compounds examined in the study.[110] In weakly acidic solutions, the latter compound outperforms trialkyl phosphine oxides containing various alkyl groups and diphenyl-*N*,*N*-di(n-butyl)carbamoyl methylene phosphine oxide widely used in laboratory investigations and industry. However, the extractability of macrocycle **154c** decreases with increasing acidity of solutions. In strongly acidic solutions, diphenylphosphonylcalix[6]arene **154b** is a more efficient extractant than trialkyl phosphine oxide but it is inferior to diphenyl-*N*,*N*-di(n-butyl)carbamoyl methylene phosphine oxide.[110]

The synthesis of calix[*n*]arenes ($n = 4, 6$), which are functionalized by two, four or six dibutylphosphinoylmethoxy groups at the narrow rim and exist in the cone, 1,2-alternate or 1,3,5-alternate conformation, was documented.[105, 111] For instance, the alkylation of calixarenes **107** and **109** with tosylate of dibutyl(hydroxymethyl)phos-

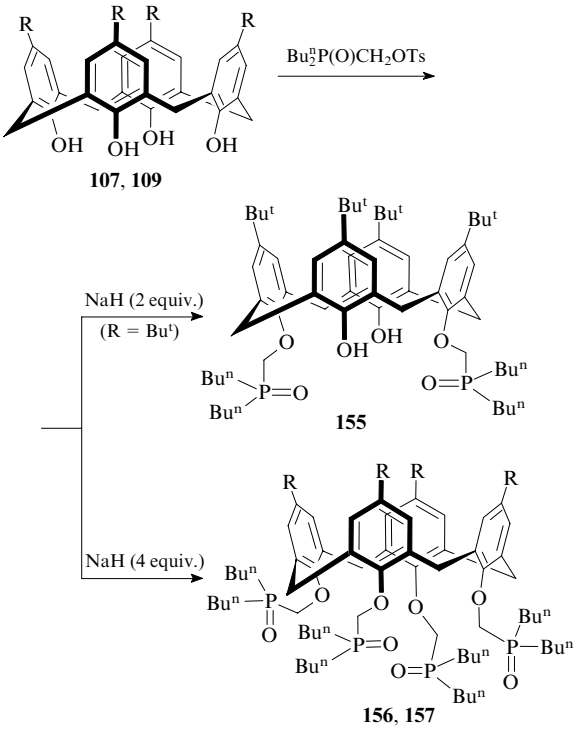
Scheme 50



R = OPr^i (**a**), Ph (**b**), Bu^n (**c**)

phine oxide in the presence of NaH in toluene afforded calix[4]arenes **155**–**157** in the cone conformation bearing two or four $CH_2P(O)Bu^n_2$ groups (Scheme 51).

Scheme 51

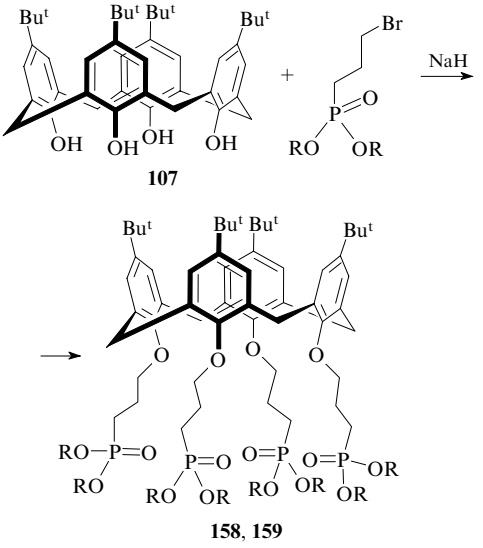


R = H (**109**, **156**, **157**), Bu^t (**107**)

It was found that calix[4]arenes modified by phosphine oxide groups at the lower (more narrow) rim exhibit low extractability for larger lanthanide and actinide cations.[112] The complexation of these compounds with small ions, such as Zn^{2+}, Cu^{2+}, Co^{2+} and Ni^{2+}, is more efficient and results in the formation of stable 1 : 1 complexes.[113] It was also shown that ligand **157** is the most efficient extractant for Ru/Zn complexes in the series of calixarenes **155**–**157**, as well as compared with calix-[4(6)]arenes modified by phosphine oxide groups at the upper rim and the monodentate benzyl(dibutyl)phosphine oxide ligand. This fact can be attributed to the complementarity of the electron-donating phosphine oxide groups and the small Zn^{2+} cation coordinated to the $[RuNO(NO_2)_2OH]^-$ anion, which is the nitroso form of the ruthenium compound predominant in weakly acidic solutions of nitric acid. Therefore, calix[4]arene **157** containing four phosphine oxide groups at the lower rim can be recommended for the selective extraction of ruthenium from weakly acidic highly active waste originating from the reprocessing of spent nuclear fuel.[111]

tert-Butylcalix[4]arenes **158** and **159** substituted at the lower rim by (dialkoxyphosphoryl)propyl groups are highly efficient ionophores for lithium and calcium ions when used as an active material of ion-selective membrane electrodes.[114,115] They also can form stable complexes with Ca^{II}, La^{III}, Eu^{III} and Gd^{III} ions (Scheme 52).

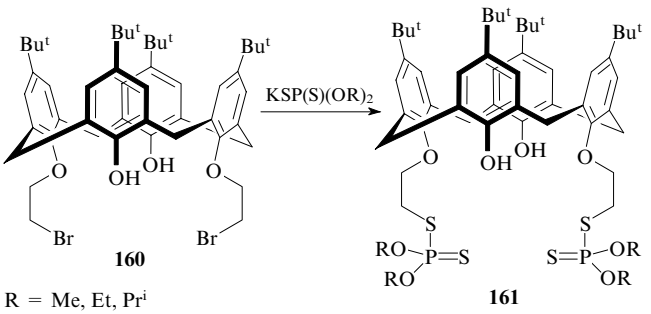
Scheme 52



R = Et (**158**), Pr^i (**159**)

The modification of the spacer of the calix[4]arene template of compound **160** by dithiophosphate groups made it possible to substantially improve the extraction ability of derivatives **161** towards metal ions (Co^{2+}, Cu^{2+}, Zn^{2+}, Pb^{2+}, Hg^{2+}, Ag^+) compared to the starting compound.[116] The best results were obtained for silver ions. This fact can be attributed to the pre-organization of the dithiophosphate groups on the calixarene template existing in the cone conformation and providing the optimal coordination to these ions (Scheme 53).

Scheme 53

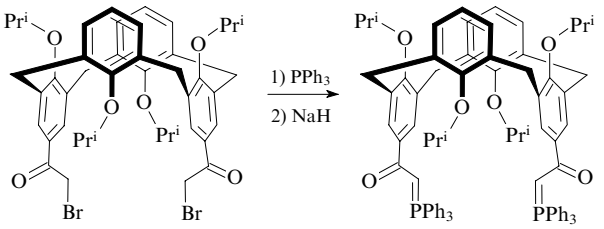


160 **161**

R = Me, Et, Pr^i

The reaction of bromoacetylated derivative **162** with triphenylphosphine followed by the deprotonation of the resulting phosphonium salt with sodium hydride produced calix[4]arene **163** in the 1,3-alternate conformation functionalized by two phosphorus ylide moieties C(O)CH=PPh$_3$ in high yields (Scheme 54).[117]

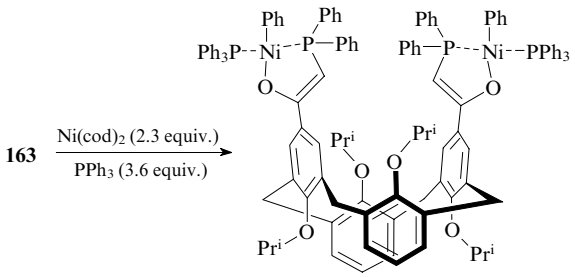
Scheme 54



162 **163**

The reaction of diylide **163** with Ni(cod)$_2$ in the presence of PPh$_3$ gave binuclear complex **164**, which was subjected to reductive elimination of both metal centres during storage to give the starting macrocycle **163**. The use of a small excess of the reactants prevents the reverse reaction (Scheme 55).

Scheme 55



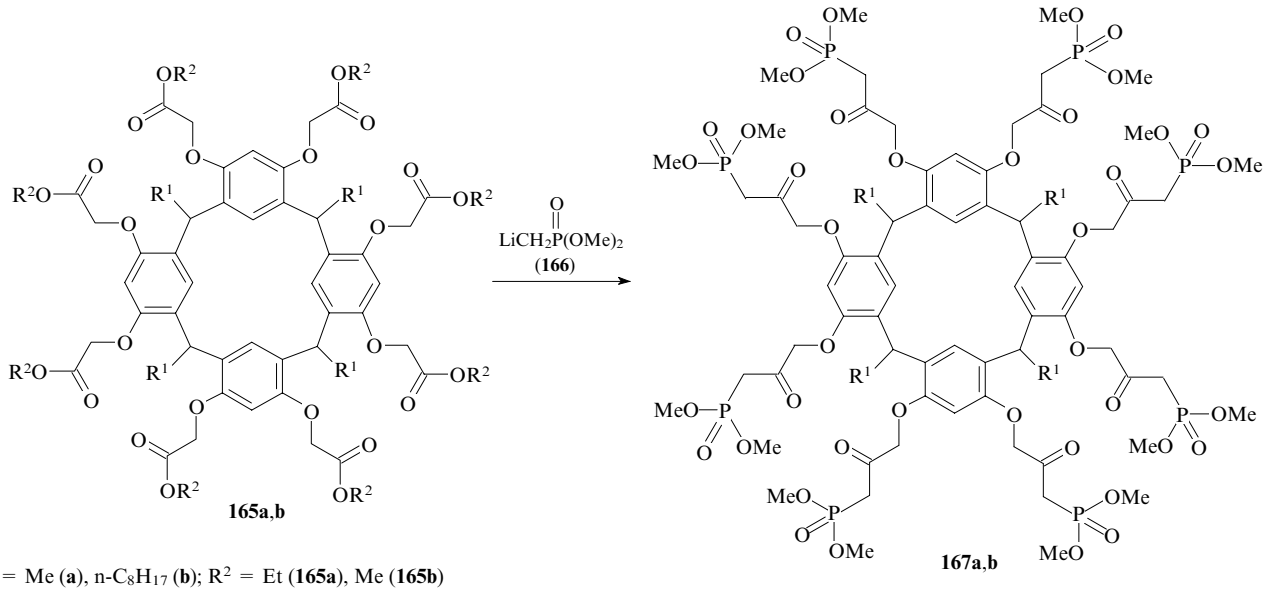
164

Complex **164** is a structural analogue of highly efficient catalysts for the selective oligomerization of linear α-alkenes of the general formula [NiPh(*P*,*O*)L], where L is tertiary phosphine and (*P*,*O*) is a chelating ligand containing phosphanyl enolate moieties. However, catalysts based on monometallic complexes of monoylide-substituted calix[4]arenes, which were synthesized according to this procedure, proved to be more efficient catalysts for the ethylene oligomerization and polymerization compared to binuclear complex **164**. In addition, at 80°C these catalysts exhibit much higher catalytic activity than their linear analogue [NiPh{Ph$_2$PCH=C(O)Ph}PPh$_3$], which is indicative of a great role of the calixarene template.[117]

One of the promising directions of the development of methods for the functionalization of calixarenes is based on the introduction of additional binding sites along with groups containing organophosphorus coordinating moieties.

A facile and efficient method for the introduction of β-keto phosphonate groups into the calix[4]resorcinol template was described by Prosvirkin *et al.*[118] Macrocycles **165a**,**b**, which were prepared by the reactions of monobromoacetic acid esters with calix[4]resorcinols, and dimethyl (lithiomethyl)phosphonate (**166**) served as the starting compounds. The reactions produce compounds **167a**,**b** (Scheme 56).

Scheme 56

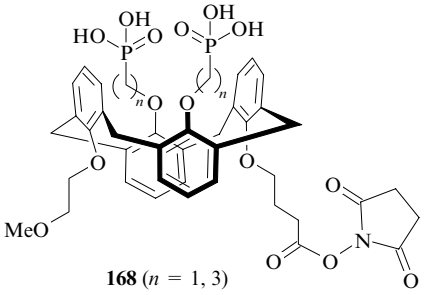


165a,**b** **167a**,**b**

R^1 = Me (**a**), n-C$_8$H$_{17}$ (**b**); R^2 = Et (**165a**), Me (**165b**)

It was shown that ligand **167a** is highly efficient in the extraction of lanthanum ions from an aqueous medium (pH 5.5) into chloroform in the presence of an excess of sodium picrate. The degree of La^{III} ion extraction is higher than 80% at a ligand concentration of 2×10^{-3} mol litre^{-1}. Apparently, this efficiency of the extraction is determined by the complex-forming ability of four chelating keto phosphonate substituents attached at the calix[4]resorcinol template.[118]

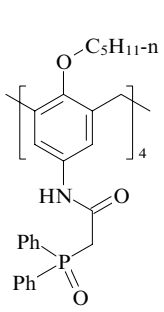
The multistep synthesis of calix[4]arenes **168** in the 1,3-alternate conformation was described.[119] These compounds contain several substituents of different nature, *e.g.*, two chelating phosphonic acid groups and the carboxylic acid moiety in the form of *N*-oxysuccinimide ester.



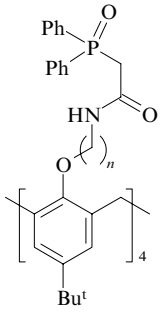
168 (n = 1, 3)

The succinimide group can react with the amino group of the solid substrate thus providing binding of functionalized macrocycles **168** to the surface. The substrate thus modified quantitatively immobilizes uranyl cations to form complexes **168** · UO_2^{2+} of the composition 1 : 1.[119]

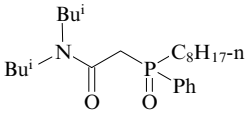
Calix[4]arenes **169** and **170** bearing four carbamoylmethyl phosphine oxide (CMPO) groups at the upper or lower rim can be easily prepared by acylation of the corresponding amino derivatives of *p*-nitrophenyl (diphenylphosphoryl)acetate (yields 65%–80%).[120]



169



170 (n = 2–4)

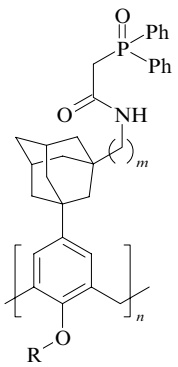


171

n-Octyl(phenyl)-*N,N*-diisobutylcarbamoylmethyl phosphine oxide (**171**), which is used on the industrial scale for the disposal of liquid nuclear waste (TRUEX process),[121, 122] is an efficient extractant for lanthanide and actinide ions; however, it is non-selective with respect to actinides. It should be noted that the latter are much more toxic components in nuclear waste than lanthanides, though they are present in smaller amounts. The CMPO-modified calix[4]-arenes **169** and **170** are not only more efficient extractants for actinides and lanthanides than their linear analogue **171** but also exhibit high selectivity with respect to actinides. The C=O and P=O groups in compounds **169** and **170** serve the binding function, and the preorganization of a set of CMPO groups at the molecular level increases the degree of extraction and the selectivity of the process due to the chelating effect.[120, 123]

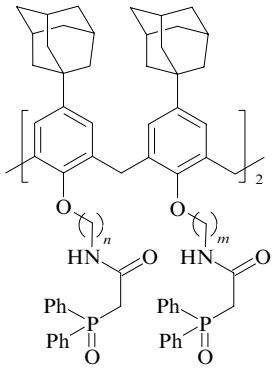
It was found that the degree of extraction of lanthanide (La^{3+}, Eu^{3+}, Yb^{3+}) and thorium (as a model for plutonium) ions from acidic media (1 M HNO_3 in CH_2Cl_2) substantially depends on the spacer length in ligands **170** (n = 2–4). These compounds proved to be more efficient extractants for thorium ions than macrocycle **169**. At the 10^{-4} mol litre^{-1} concentration of ligands **170**, the degree of extraction of thorium ions reaches 100%. The satisfactory extraction parameters for lanthanide ions were obtained only at a higher concentration of the tested ligand (10^{-3} mol litre^{-1}). Modified calix[4]arene **170** with n = 3 is the best selective extractant for the Th^{4+}/Eu^{3+} and Th^{4+}/La^{3+} pairs.[120, 123]

A similar approach to modifications of adamantyl-substituted calix[*n*]arenes by CMPO groups at the upper or lower rim was documented.[124, 125] It was shown that ligands **172** and **173** are also more efficient extractants for lanthanide, thorium and americium ions than industrial CMPO-modified extractant **171**. Among macrocycles **172**, calix[4]-arene, in which the CMPO moieties are linked to the adamantane core through one methylene group (R = Bu^n, n = 4, m = 1) has the best extraction properties towards lanthanides and actinides, whereas the highest selectivity for the Th^{4+}/La^{3+} pair ($D_{Th}/D_{Ln} > 24$) is achieved with the use of the hexameric ligand (R = Me, n = 6, m = 2).[124] In turn, tetrameric ligands **173** containing spacers of different length have better extraction properties towards lanthanides than the above-described analogues **170**; however, the degree of extraction of thorium ions with **173** remains the same or is even lower.[125]



172

R = Me, Pr^n, Bu^n;
n = 4, 6; m = 0–2



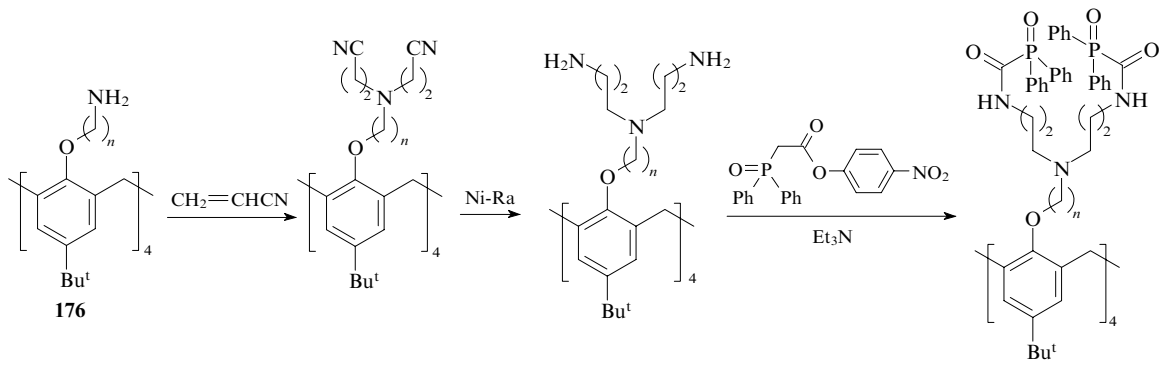
173

n, m = 2–4

It is reasonable to suggest that the high extraction properties of compounds **169**, **170**, **172** and **173** are associated with a high local concentration of CMPO groups. Hence, an attempt was made to increase the amount of CMPO groups in the calix[4]arene template based on the principles of the construction of dendrimeric structures. These attempts culminated in the synthesis of compounds **174** (Scheme 57) and **175** (Scheme 58) containing eight CMPO groups at the upper or lower rim.[126] Calixarenes **176** and **177** functionalized with amino groups were used as the starting compounds.

However, the degree of extraction of lanthanide ions by calixarenes **174** and **175** appeared to be much lower than by ligands **169**, **170**, **172** and **173**. These results show that the simple accumulation of functional CMPO groups in the

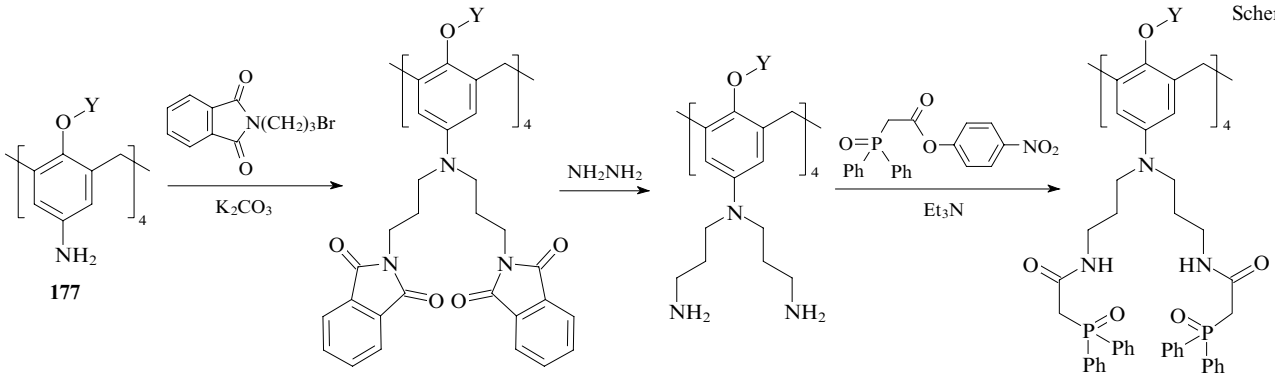
Scheme 57



176 **174**

n = 3, 4

Scheme 58



177 **175**

Y = Pr^n, n-C_5H_{11}

calixarene molecule is not the decisive factor for the improvement of extraction properties.[126]

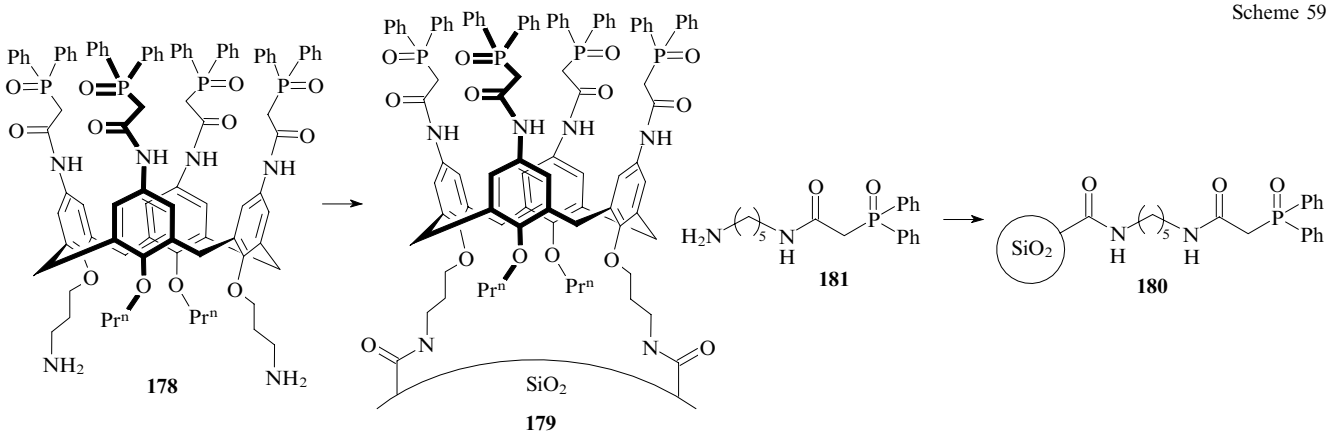
An attempt to attach calixarene ligand **178** containing CMPO and amino groups to the magnetically activated surface of silica gel functionalized by carboxylic acid moieties has been brought to success.[127] Resulting particles **179** exhibit higher efficiency in the extraction of lanthanide and actinide (europium, cerium and americium) ions (the degree of extraction reaches 92%) as compared with nonmagnetic silica gel particles, which were modified in a similar way, and particles **180**, which were prepared with the use of linear CMPO ligand **181** (Scheme 59).

Therefore, it was shown [127] that the preorganization of the chelating functional groups on the appropriate macrocyclic template prior to the binding to the substrate surface plays an important role.

The design of a new type of calixcryptands is an interesting example of the phosphorylation of calixarenes. The macrocyclization of calix[6]arene **182** containing three aminoethyl groups with triphenylphosphine containing three aldehyde groups in the *ortho* positions of the aromatic rings afforded calix[6]triimine **183**. The reduction of the latter with a large excess of $NaBH_4$ gave new PN_3-calix[6]-cryptand **184** in a total yield of 23% (Scheme 60).[128]

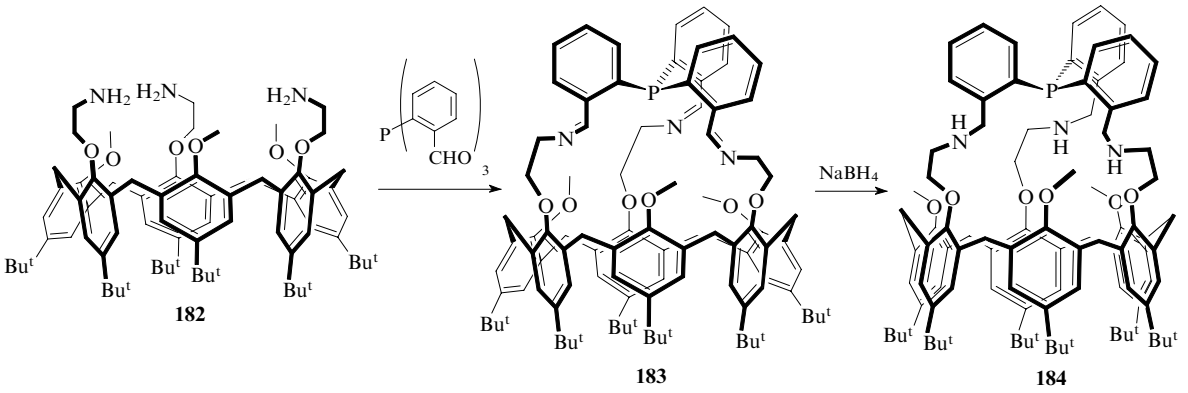
The molecule of host **184** has the C_{3v} symmetry (the cone conformation), which is ideally suitable for molecular recognition mechanisms. This compound is an efficient and selective receptor for binding alkylammonium cations. Thus, a 16-fold increase in the selectivity was observed upon binding of $EtNH_3^+$ cations compared to $Pr^nNH_3^+$. Taking into account the fact that these two guest cations differ by only one methylene group, this selectivity can be considered as sufficiently high.[128]

Scheme 59



178 **179** **181** **180**

Scheme 60



182 **183** **184**

The properties of complexes of calix[6]cryptand **184** with Cu^{I} and Cu^{II} ions were investigated.[129, 130] It was found that the complex $[Cu(\mathbf{184})]^{2+}$ containing also the $Cu^{II}-P$ bond with the five-coordinate metal centre exhibits the unusual affinity for weak σ-donor ligands (for example, MeCN > EtOH), whereas the complex $[Cu(\mathbf{184})]^{+}$ has high affinity for O-donor ligands (EtOH, DMF). An interesting feature of the latter complex is that it is stable to oxygen. Thus, the oxidation of the Cu^{I} metal centre to Cu^{II} does not proceed either in the solid state or in solution.

d. Design of phosphocavitands

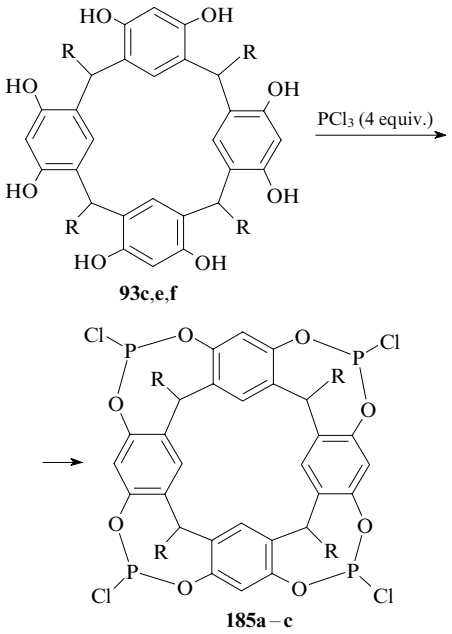
The development of research on the synthesis of phosphorus-containing calixarenes reasonably leads to the design of phosphocavitands belonging to a family of molecular bowls with organophosphorus moieties introduced into the upper rim. In the early 1990s, several research groups independently made first attempts to carry out cyclophosphorylation of calix[4]resorcinols with the use of such conventional reagents as phosphoric and phosphorous acid di- and trichlorides in the presence of tertiary amines.[131 – 134] However, these experiments cannot be considered as successful because the reaction products were contaminated with amine hydrochlorides, whose purification is a very difficult problem.

To synthesize cavitands containing cyclic chloro(thio)phosphate moieties at the upper rim, attempts were made to carry out cyclophosphorylation of calix[4]resorcinols with $POCl_3$ or $PSCl_3$ at different molar ratios of the reactants (from 1 : 1 to 1 : 8) in the absence of bases.[135, 136] However, in all cases either acyclic derivatives or mixtures of products containing both cyclic and acyclic phosphorus-containing moieties were obtained. Their ratio depends on the nature of the solvent and the reaction conditions. Attempts to isolate individual compounds from the reaction mixtures failed.

Then efforts were directed to the synthesis of cavitands containing cyclic chloro(thio)phosphate moieties through the formation of the corresponding cyclic chlorophosphites **185**, and the latter were obtained in high yields by the reactions of calix[4]resorcinols **93** with PCl_3 (Scheme 61).[135 – 137] Compounds **185** are easily oxidized by sulfuryl chloride to the corresponding chlorophosphates, and they bind four equivalents of sulfur to form cyclic chlorothiophosphates upon heating.

The possibility of the construction of phosphocavitands using the amide method for the phosphorylation of calix[4]resorcinols was examined.[138 – 140] This method is experimentally simple and highly efficient and requires readily available reagents. These reactions often proceed even at room temperature to give the target products in high yields, and the secondary amines that formed are easily removed from the reaction sphere.

Scheme 61



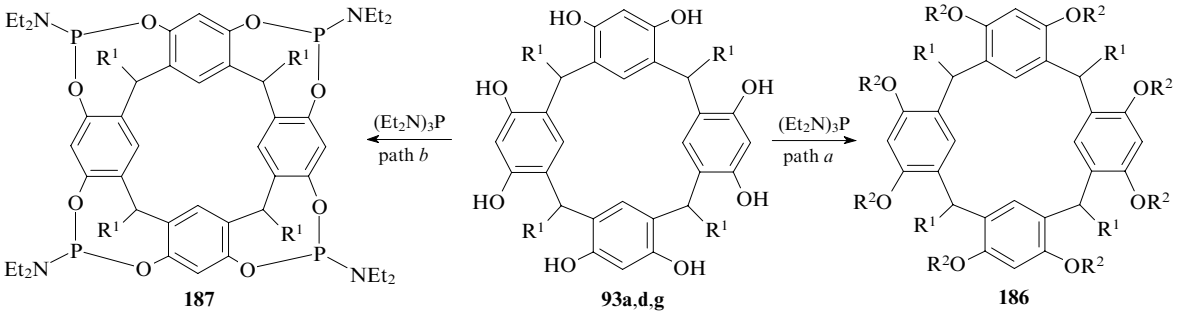
93c,e,f **185a – c**

R = n-C_5H_{11} (**93e**, **185a**), n-C_6H_{13} (**93c**, **185b**), n-$C_{11}H_{23}$ (**93f**, **185c**)

Taking into account the structure and conformational lability of calix[4]resorcinols, the following two possible pathways of their phosphorylation were proposed: path *a*, the simple functionalization at the hydroxy groups (O-phosphorylation); path *b*, the cyclophosphorylation giving phosphocavitands (Scheme 62).[139] The regioselectivity of the reaction was analyzed by studying the reaction of octols **93a**,**d**,**g**, whose molecules contain different substituents in the cyclophane core, with hexaethylphosphoric triamide.

The reactions were carried our in dioxane at room temperature. It was found that the reaction of hexaethylphosphoric triamide with tetraphenyloctol **93d** follows mainly the path *a*. The variation of the octol : amide ratio from 1 : 2 to 1 : 10 showed that the reaction always gives calixarenes **186** with different degrees of phosphorylation as the major products. The alternative process, *viz*., the cyclophosphorylation, proceeds by only 23% even if the phos-

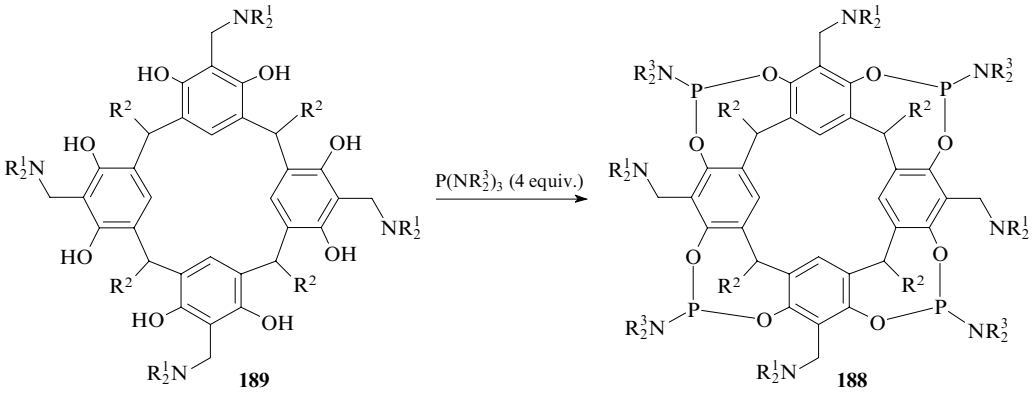
Scheme 62



187 **93a**,**d**,**g** **186**

R^1 = Me (**a**), Bu^n (**g**), Ph (**d**); R^2 = H or $P(NEt_2)_2$

Scheme 63



189 **188**

R^1 = Me, Et, Pr^n; R^2 = Me, Et, Pr^n, n-C_6H_{13}, n-$C_{11}H_{23}$; R^3 = Me, Et

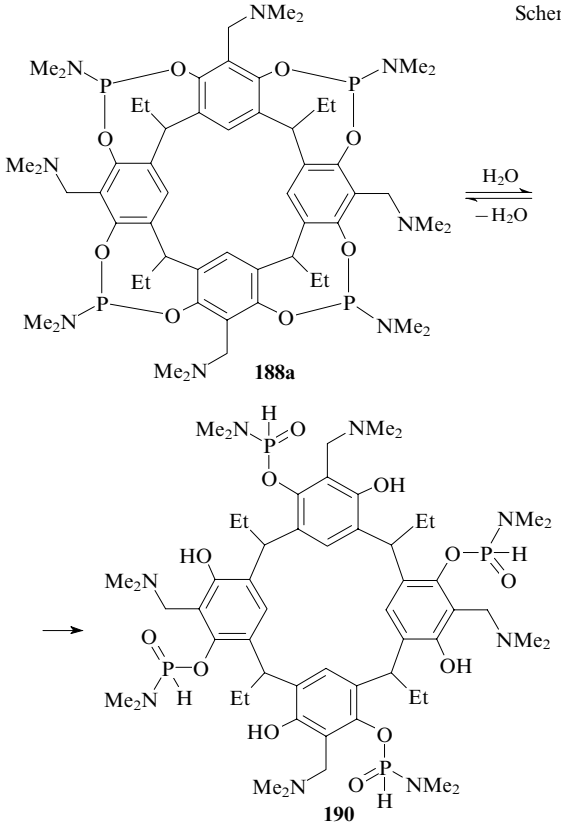
phorylating agent is used in a deficient amount (the ratio is 1 : 2). The corresponding reaction with tetramethyloctol **93a** always affords a mixture of products containing both cyclic (**187**) and acyclic (**186**) derivatives regardless of the reactant ratio. By contrast, the reaction with tetra-n-butyloctol **93g** involves its cyclophosphorylation as the major process, and the reaction with the use of the reactants in the stoichiometirc ratio (1 : 4) follows only the path *b*.

The results of the phosphorylation of octols **93a**,**d**,**g** are attributed to the characteristic features of the preorganization of these macromolecules. Apparently, the conditions for the easy boat – cone conformational transition of the starting calix[4]resorcinols are required for the efficient cyclophosphorylation to occur. The presence of long-chain aliphatic substituents (R^1) should have a favourable effect on the position of the equilibrium, particularly, if the reactions are carried out in polar solvents, for example, in dioxane. In this case, lyophilic interactions between long hydrocarbon chains would be expected to exist, resulting in the predominant formation of the cone conformation, which, in turn, will facilitate the cyclophosphorylation.[139]

Polyfunctional cavitands **188** were synthesized by the reaction of hexaalkylphosphoric triamides with aminoalkylated derivatives of calix[4]resorcinols **189** (Scheme 63).[141 – 144]

The effect of dialkylaminomethyl groups is manifested in that cavitands **188**, unlike their unsubstituted analogues, are easily hydrolyzed in air. It should be noted that cavitand **188a** (R^1 = R^3 = Me, R^2 = Et) containing methyl groups at the nitrogen atoms can undergo the unusual ring-chain transformation with the participation of water molecules. The hydrolysis results in the cleavage of endocyclic P – O bonds in the dioxaphosphocine moieties to form hydrophosphoryl compound **190**. When heated in benzene with azeotropic removal of water, ompound **190** is reversibly transformed into the starting cyclic P^{III}-containing cavi-

Scheme 64



188a **190**

tand. This type of conversions is specific only for this system and does not take place in the case of compounds containing alkyl substituents other than methyl groups at the nitrogen atoms (Scheme 64).[143, 144]

A wide range of P^{III} phosphocavitands containing long aliphatic substituents (C_6-C_9) and such complex exocyclic substituents, as cholesterol, 1,2,3,4-di(isopropylidene)galactose, menthol and glucofuranose moieties and other biologically important molecules, were synthesized by the amide method.[140, 145 – 147]

The effect of methyl substituents in the *ortho* positions of the benzene rings of the calix[4]resorcinol template on the properties of cavitands containing phosphoramidite bridges at the upper rim was investigated.[148] It was shown that an increase in the steric crowding of the upper rim of the starting macrocycle leads to a change in the conformation and symmetry of the phosphoramidite cavitand prepared by cyclophosphorylation. The *ortho*-methyl groups hinder the formation of cavitands with the C_{4v} symmetry (a vase conformation) and facilitate the formation of macrocycles with the C_{2v} symmetry (a kite conformation). In this case, the solubility of these compounds in organic solvent increases, but oxidation reactions are hampered, which is accompanied by a decrease in the yield of phospho(V) cavitands. The C_{2v} symmetry of *ortho*-substituted phosphoramidite cavitands leads to changes in the mutual arrangement of the components of the molecule and facilitates the formation of tetranuclear molybdenum complexes, whereas unsubstituted cavitands form binuclear analogues.

Therefore, the cyclophosphorylation of calix[4]resorcinols with phosphoramidites containing aliphatic substituents is always accompanied by the cleavage of two P – N bonds and the formation of phosphitocavitands.

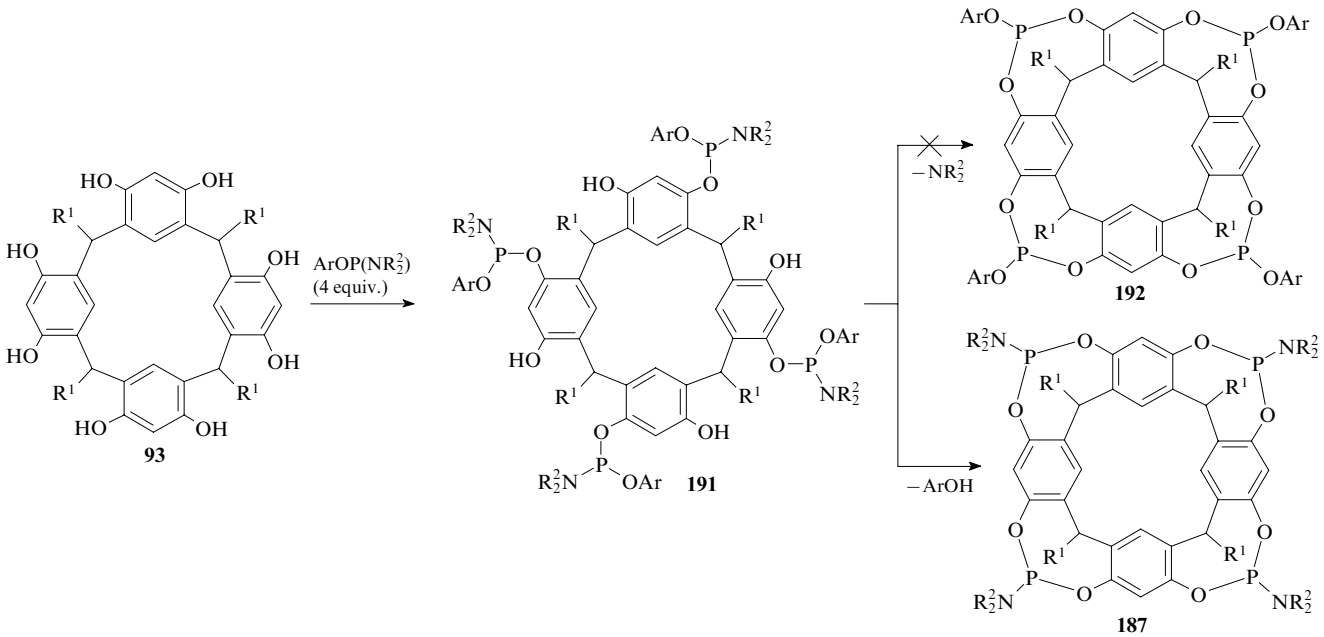
It should be noted that the use of arylphosphorodiamidites resulted in the unusual pathway of cyclophosphorylation of compounds **93** to form products **187** lacking aryloxy groups (Scheme 65).[140, 149, 150]

Apparently, the reaction proceeds in two steps. The first step occurs *via* the classical mechanism of phosphorylation of alcohols and phenols accompanied by the cleavage of one P – N bond to form the corresponding intermediate **191**. Based on traditional views of the reactivity of phosphorodiamidites, the second step should involve the phosphocyclization accompanied by the cleavage of another P – N bond and the formation of phosphitocavitand **192**. However, the reaction of interest proceeds in an unusual way. Thus, the P – O bond in intermediate **191** is cleaved to give phosphoramidite cavitand **187**. This pathway of cyclophosphorylation is independent of the size and nature of the alkyl substituent (R^2), the type of the aryl group in the starting arylphosphorodiamidite or the reactant ratio.

P^{III}-Phosphocavitands, in which the phosphorus atoms have lone pairs, are easily functionalized by means of reactions typical of trivalent phosphorus compounds. Under slight heating, these compounds bind sulfur; at higher temperature, selenium; in the presence of phenyl azide, they also undergo the oxidative imination.[140, 145, 151 – 153]

In the general case, the alkylation of phosphoramidite cavitands affords two type of products, the quasiphosphonium salt and phosphorane, whose ratio depends on the nature of the reactants and the solvent, as well as on the presence of exocyclic substituents at the phosphorus atoms. Substituents in the calixarene template are responsible only for solubility of the compound. The alkylation of phosphoramidite cavitands with alkyl halides takes place only under heating and in the presence of a large excess of the reactant,[152, 154] whereas the reactions of hydrotetrafluoroboric acid derivatives proceed under milder conditions.[155] The protonation of phosphoramidite cavitands with hydrotetrafluoroboric acid in chloroform at room temperature at different reactant rations gives rise to a inseparable mixture

Scheme 65



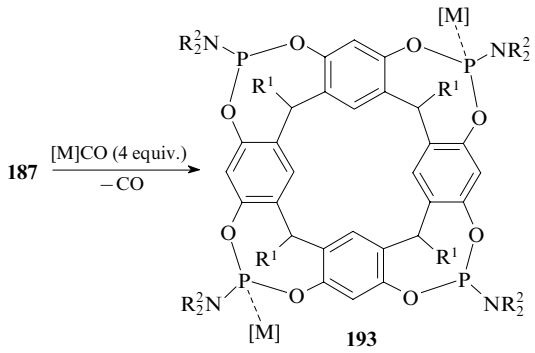
R^1 = n-C_nH_{2n+1} (n = 1 – 6); R^2 = Me, Et; Ar = Ph, 4-MeC_6H_4, 2-$Pr^iC_6H_4$, 2,6-Bu^t_2-4-MeC_6H_2, 1-Naph, 2-Naph; Naph is naphthyl

of products resulting from several competitive reactions. The reaction of phosphoramidite cavitands with triethyloxonium tetrafluoroborate is selective and gives quasiphosphonium salts as the major products.

P^{III}-Phosphitocavitands are also of interest as ligands. The first coordination systems based on phenylphosphonitocavitand and halogen-containing complexes of silver, copper, gold and platinum were synthesized by Canadian researchers.[131, 132] In these complexes, the metal ions coordinate all four phosphorus centres of the phosphonitocavitand.

The reactions of P^{III}-phosphitocavitands with transition metal carbonyls are described in several publications.[140, 156–159] The reactions of phosphoramidite cavitands **187** with certain metal carbonyls (Cr, Mo, W, Mn) produce only the corresponding binuclear complexes **193** even in the presence of a twofold excess of the complex-forming agent upon prolonged heating or under irradiation of the reaction mixture. These complexes contain two uncoordinated trivalent phosphorus atoms and are potential bidentate ligands. However, two metal-containing pentacarbonyl moieties completely shield the cavity of the cavitand and two trivalent phosphorus atoms, which hinders their complexation (Scheme 66).

Scheme 66



R^1 = Me, Pr^n; R^2 = Me, Et;
[M] = $Cr(CO)_5$, $Mo(CO)_5$, $MnCp(CO)_2$, $W(CO)_5$

Phosphoramidite cavitands can form host–guest systems. For example, phosphocavitand **187b** (R^1 = n-C_6H_{13}, R^2 = Et) containing four cyclic phosphoromonoamidite groups at the upper rim forms inclusion complexes with certain amines (triethylamine, diethylamine, *N*,*N*-monoethanolamine, *etc*.) in a molar ratio of 1 : 2 at the chloroform–water interface.[160] It was hypothesized that the binding of amines to the donor centres of the phosphorus-containing cavitand occurs by the single-site binding mechanism.

Thiophosphorylated cavitand **194** containing phenyl substituents at the phosphorus atoms was synthesized from calix[4]resorcinol **93f** with long alkyl substituents. The synthesis involves the cyclophosphorylation of compound **93f** with dichlorophenylphosphine followed by the thionation of intermediate cavitand **192a**. The reaction is stereoselective and gives the isomer, in which all four thiophosphoryl groups are oriented towards the macrocyclic cavity. This isomer efficiently extracts ions of soft metals (Ag^+, Tl^+, Hg^{2+}) from water and organic solvents. Thiophosphorylated cavitand **194** is characterized by the highest affinity for silver ions, which are extracted virtually quantitatively (91%) (Scheme 67).[161]

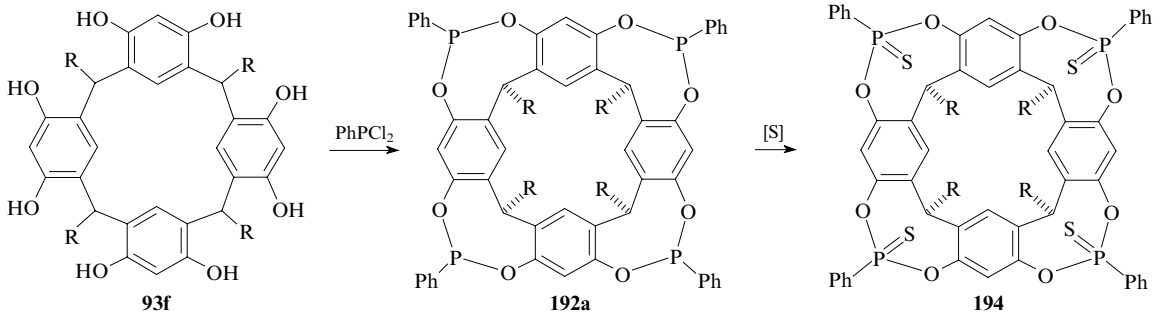
e. Phosphorylation of meta- and paracyclophanes

The phosphorylation of macrocycles related to calix[4]arenes, *viz*., tetrameric metacyclophanes containing four methylene-bridged aromatic units was documented.[162] The Arbuzov reaction with the participation of chloromethylated cyclophane **195** and trialkylphosphites afforded phosphorus-containing tetrameric analogues of calix[4]arenes **196** (Scheme 68).

The corresponding reaction of compound **197** gave bisphosphonate derivatives of cyclophanes **198** containing methylene-bridged two mesitylene and two durene units.[163] An interesting feature of the synthesized macrocycles is their tendency to form solid-state clathrate inclusion compounds with small organic molecules. Due to this property, such compounds can be considered as receptors of hydrophobic guests or water-soluble macrocyclic hosts after the hydrolysis of the phosphonic group to the corresponding monoester or to the free acid having the pH-dependent binding properties (Scheme 69).[72, 162, 163]

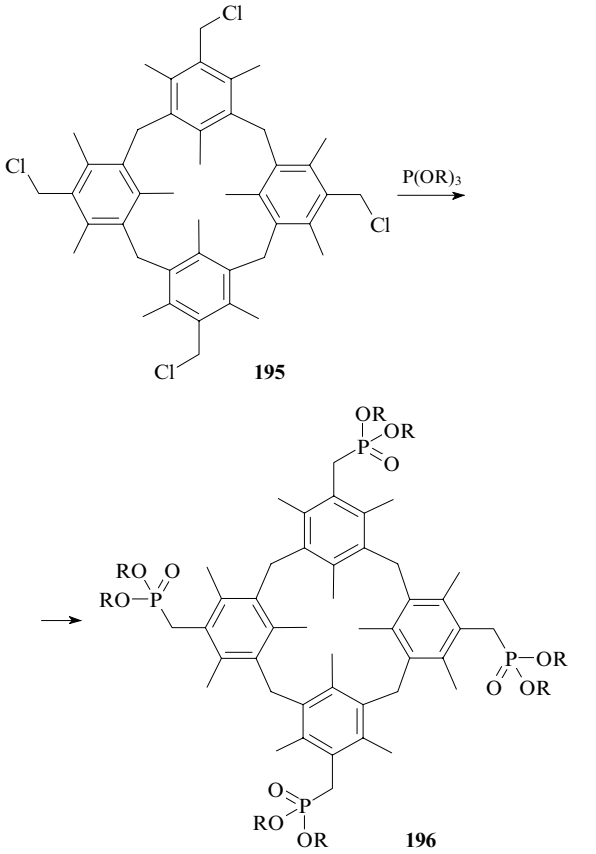
The sequential design of unsymmetrical 2.2]paracyclophane containing two diarylphosphine groups of different types was described.[164] The monometallation of dibromide **199** with n-butyllithium followed by the reaction with chlorodiphenylphosphine gives the corresponding diphenylphosphine derivative sensitive to atmospheric oxygen. The *in situ* sulfination of the intermediate affords air-stable paracyclophane **200**. The similar sequence of the reactions with the participation of the second bromine atom but with the use of bis(3,5-dimethylphenyl)chlorophosphine produ-

Scheme 67



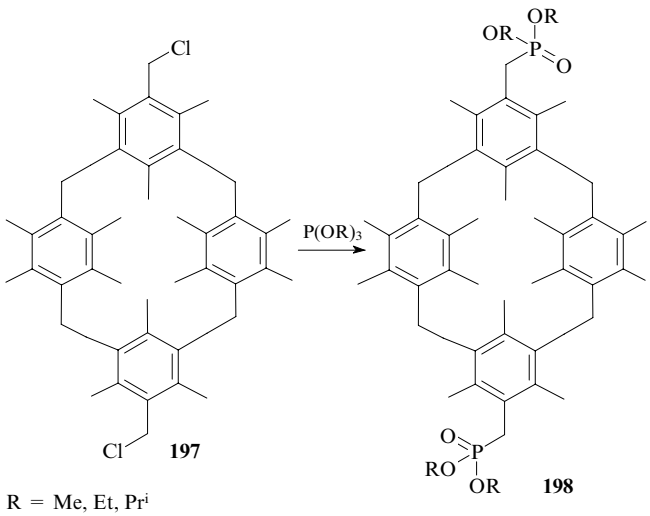
R = n-$C_{11}H_{23}$

Scheme 68



R = Me, Et, Pr^i

Scheme 69

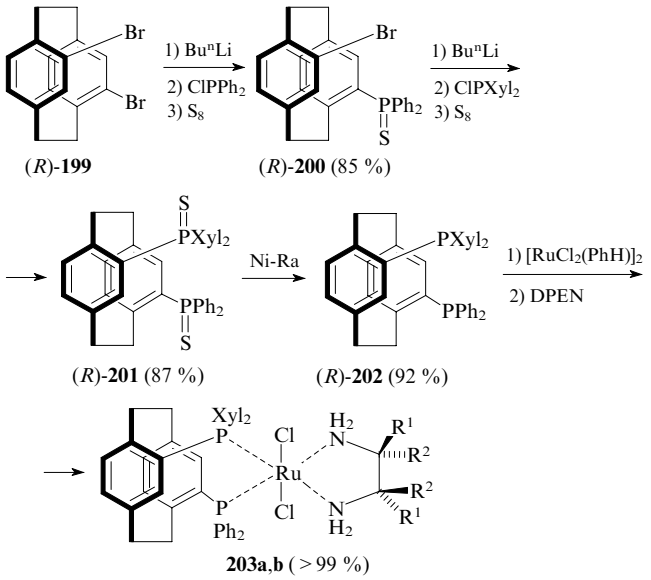


R = Me, Et, Pr^i

ces bis(phosphine sulfide) **201**. After the removal of sulfide groups under mild conditions, the target diphosphine ligand **202** was obtained in high yield (Scheme 70).

Ruthenium complexes **203a**,**b**, which were synthesized by the reaction of diphosphine paracyclophane ligand **202** with $[RuCl_2(PhH)]_2$ followed by the addition of one equivalent of 1,2-diphenylethylenediamine (DPEN), proved to be efficient enantioselective catalysts for the asymmetric hydrogenation of aromatic and heteroaromatic ketones.[164]

Scheme 70

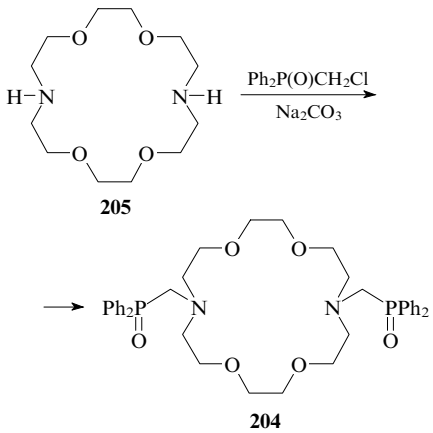


R^1 = H, R^2 = Ph (**a**); R^1 = Ph, R^2 = H (**b**);
Xyl = 3,5-$Me_2C_6H_3$

f. Phosphorylation of crown ethers

Tsivadze *et al.*[165] developed a new method for the synthesis of a prototype of supramolecular machines, phosphoryl-containing lariat crown ether **204**. The latter was synthesized in 71% yield by the phosphorylation of diazacrown ether **205** with (chloromethyl)diphenylphosphine oxide in the presence of dry sodium carbonate (Scheme 71).

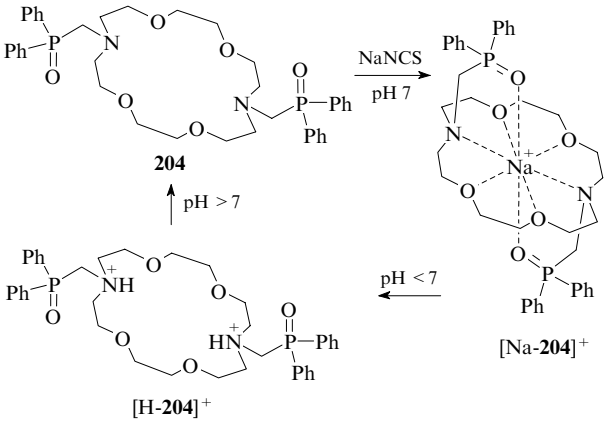
Scheme 71



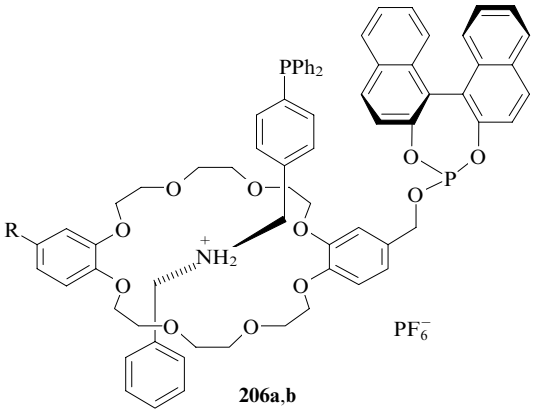
The reaction of compound **204** with sodium thiocyanate in acetonitrile produces the stable coordination compound [Na-**204**](NCS) having the ionic structure in virtually quantitative yield (97%). In this case, the ligand has the maximum denticity. Thus, in the centrosymmetric cation $[Na\text{-}\mathbf{204}]^+$ both the cavity of the macrocycle and the side phosphoryl groups of the ligand are involved in the coordination to the metal atom. The addition of a 10% hydrochloric acid solution to an aqueous suspension of the complex [Na-**204**](NCS) results in the rapid dissolution of the precipitate, and the subsequent alkalification of the solution leads to the precipitation of the starting ligand **204**. Therefore, the equilibrium between the complex and the free ligand can be shifted by varying the pH of the

reaction mixture, which is of obvious interest for the design of various molecular devices (Scheme 72).[165]

Scheme 72



Unusual supramolecular chiral phosphorus-containing pseudorotaxane-type ligands **206a**,**b** were prepared by mixing equimolar amounts of phosphorylated dibenzo[24]-crown-8 and the monodiphenylphosphine-substituted dibenzylammonium salt.[166] The phosphorylation of crown ethers was performed by reducing ester groups with $LiAlH_4$ followed by the reaction of the resulting alcohols with (*S*)-2,2′-binaphthylchlorophosphite.



R = H (**a**), CH_2O—P (**b**)

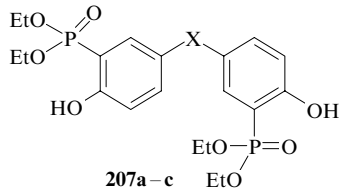
Ligands **206** were used in the *in situ* synthesis of rhodium complexes. The examination of the latter as the catalysts for the asymmetric hydrogenation of a wide range of aromatic α-amino acid esters showed that the complex based on bidentate ligand **206a** exhibits higher catalytic activity and enantioselectivity compared to tridentate ligand **206b** and monophosphorylated crown ether. The reactions proceed under mild conditions in the presence of 0.2 mol.% of the catalytic complex Rh^{I}-**206a** with a conversion of >99% and enantioselectivity from moderate to high (69%–84%) *ee*.[166]

IV. Synthesis of phosphorus-containing macrocyclic compounds with the participation of functional groups involved in organophosphorus molecules

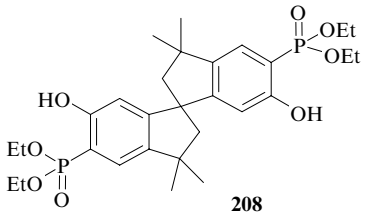
This section considers methods for the synthesis of phosphorus-containing macrocycles that are formed in the reactions with the participation of functional groups in the side chains of organophosphorus reactants.

1. Synthesis of phosphorus-containing macrocyclic polyethers

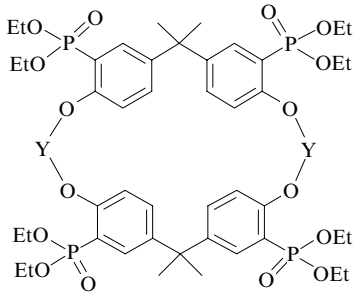
Bis(hydroxyaryldiphosphonates) **207** and **208** exhibiting complex-forming properties with respect to certain cations (for example, lanthanides) were used to synthesize new macrocyclic polyethers.[72, 163, 167–169]

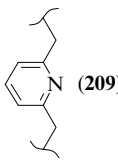
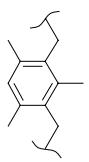
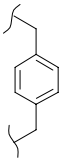


X = CMe_2 (**a**), S (**b**), SO_2 (**c**)



The condensation of bisphenol **207a** with 2,6-bis(bromomethyl)pyridine, 2,4-bis(chloromethyl)-1,3,5-trimethylbenzene and α,α′-dibromo-*p*-xylene affords the corresponding macrocyclic polyethers **209**–**211**. Due to the presence of phosphonate groups, these compounds can form (after the hydrolysis to phosphonic acids) new supramolecular structures through hydrogen bonding.[167]



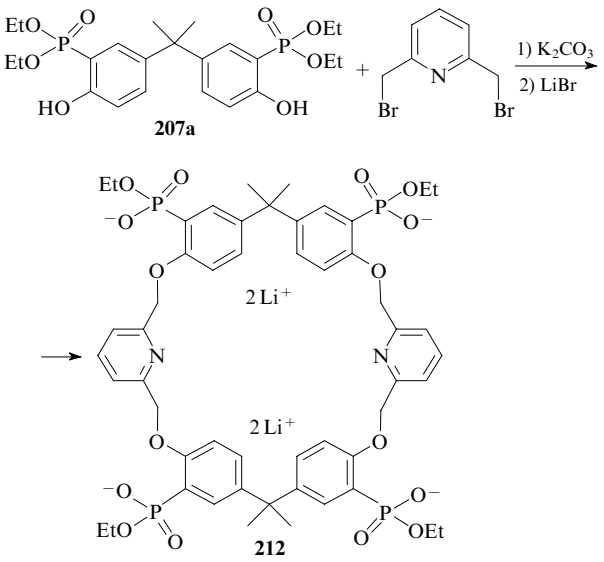
Y =  (**209**),  (**210**),  (**211**)

It should be noted that only macrocycle **209** in the series of the synthesized compounds can form inclusion complexes with neutral molecules. For instance, the crystallization of this compound from a cyclohexane–ethyl acetate mixture

results in the selective inclusion of cyclohexane (in a molar ratio of 1 : 1). Under these conditions, macrocycle **209** can be selectively and almost quantitatively isolated from the reaction mixture ('supramolecular' purification). Macrocyclic polyethers **210** and **211** do not form inclusion complexes with molecules of any organic solvents (benzene, toluene, ethyl acetate, cyclohexane and so on) and can be isolated from the reaction mixtures only by chromatographic methods.[72, 167]

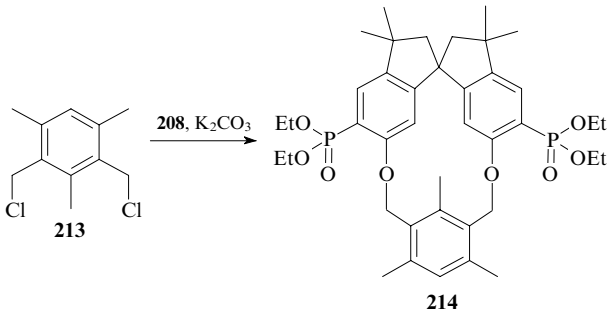
The tetraanion prepared as tetralithium salt **212** (Scheme 73) was found[168, 169] to efficiently bind amino acid esters in water and methanol. Small amino acids (histidine, ornithine and arginine) form complexes with host **212** with a 2 : 1 stoichiometry, whereas lysine forms a 1 : 1 complex with compound **212**.

Scheme 73



The Williamson condensation by the action of inherently chiral spiro-bis(indane) diphosphonate **208** with dihalide **213** afforded cyclophane **214** in high yield (Scheme 74).[72, 170]

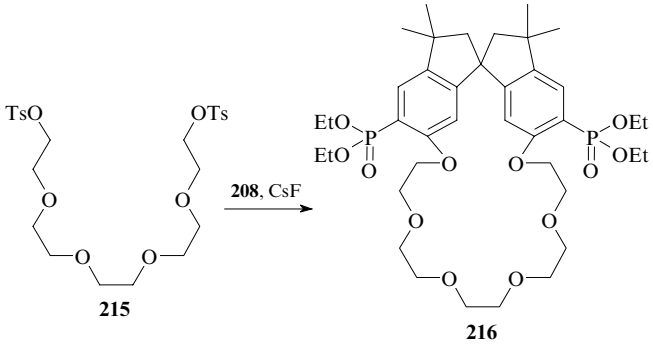
Scheme 74



The spiro-bis(indane) skeleton of molecule **214** provides high rigidity, which should lead to the pronounced preorganization of various binding sites. The corresponding dianion, which was synthesized by the careful monodealkylation of compound **214** with LiBr, displays enantioselective recognition of L-lysine and L-arginine. This compound can be used as the reactant for the quantitative determination of enantiomeric excess of derivatives of these amino acids.[72, 171]

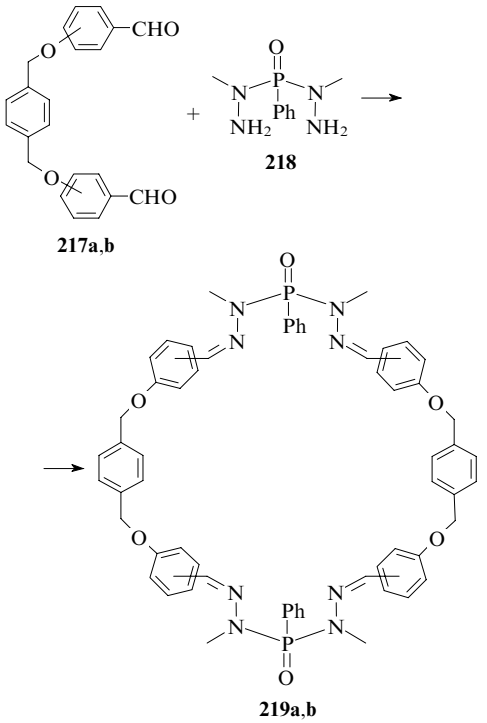
The reaction of spiro-bis(indane) monomer **208** with pentaethylene glycol tosylate (**215**) under high dilution produces chiral crown ether **216**. The latter contains phosphonate moieties in strategically important positions for the efficient and selective molecular recognition of organic dicationic guest molecules (Scheme 75).[163]

Scheme 75



The use of triphenylene dialdehydes **217** and bis(methylhydrazino)phosphonate **218** in the [2 + 2]cyclocondensation made it possible to prepare 42- and 46-membered phosphorus-containing aromatic polyethers **219a**,**b** in 20% yield (Scheme 76).[172]

Scheme 76



Isomers: *meta* (a), *para* (b)

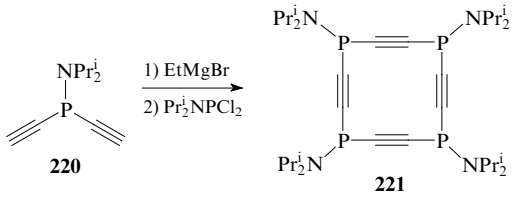
2. Synthesis of macrocyclic polyphosphines and their derivatives

The construction and properties of phospha[*n*]pericyclines ‡ were considered in numerous publications, including a recent review.[173] Acetylene-substituted derivatives of phos-

‡ Phospha[*n*]pericyclines are macrocyclic compounds, whose bridgehead phosphorus atoms are linked by acetylene groups.

phorus(III), for example, *P*,*P*-diethynyl-*N*,*N*-diisopropylphosphoramidite (**220**),[174] were used as building blocks for the synthesis of these compounds. Their successive reactions with ethylmagnesium bromide and dichloro(diisopropylamino)phosphine afford tetraphosphine **221** as a mixture of four stereoisomers in a total yield of ~9%. Apparently, the reaction conditions are more favourable for the formation of linear products. The resulting mixture is highly sensitive to atmospheric oxygen, which made it impossible to isolate and purify isomers. An attempt to stabilize the reaction products by sulfurization led to their complete destruction (Scheme 77).

Scheme 77

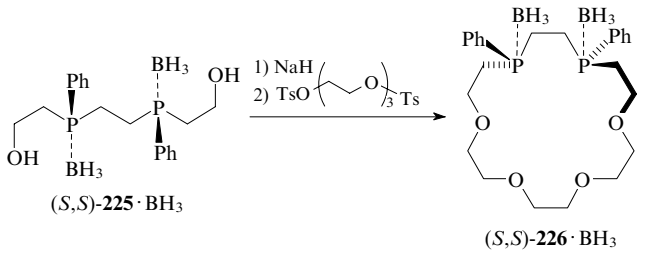


The use of unsaturated diphosphinate **222** for the construction of macrocyclic polyphosphacyclanes was not much more successful (Scheme 78).[175] The oxidative addition under high dilution conditions afforded two types of products, *e.g.*, compounds **223** and **224**. They were isolated by column chromatography as mixtures of the corresponding isomers stable in the solid state. The absence of the signals of acetylenic protons in the ^{1}H NMR spectra of the reaction products is evidence that cyclic compounds are formed as the major products. The high-resolution mass spectrometric study of both fractions confirmed the structures of isomeric mixtures consisting of dimerization (**223**) and trimerization products (**224**).

The first method for the synthesis of optically pure diphosphine crown ethers was employed in the study.[176] Chiral bisphosphines (*S*,*S*)-**225**·BH$_3$ and (*R*,*R*)-**225**·BH$_3$ were used as building blocks. The reaction of compound (*S*,*S*)-**225**·BH$_3$ with sodium hydride and triethylene glycol ditosylate produced optically pure 18-diphosphacrown-6 (*S*,*S*)-**226**·BH$_3$ in 17% yield. The corresponding reaction gave also product (*R*,*R*)-**226**·BH$_3$ in 22% yield (Scheme 79).

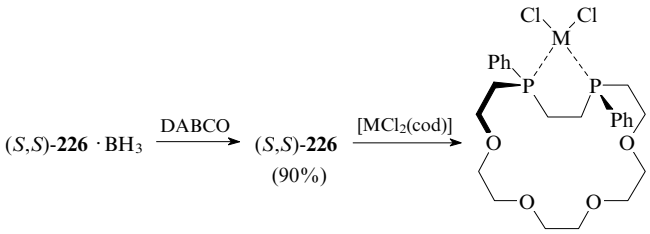
A BH$_3$ molecule can be easily removed by the treatment with amines [for example, with diazabicyclo[2.2.2]octane (DABCO)], resulting in the formation of the corresponding diphosphacrown ether (*S*,*S*)-**226**. The latter can form complexes with Pd^{II} and Pt^{II} under mild conditions, the metal

Scheme 79



centre being coordinated outside the macrocyclic cavity (Scheme 80).[176]

Scheme 80

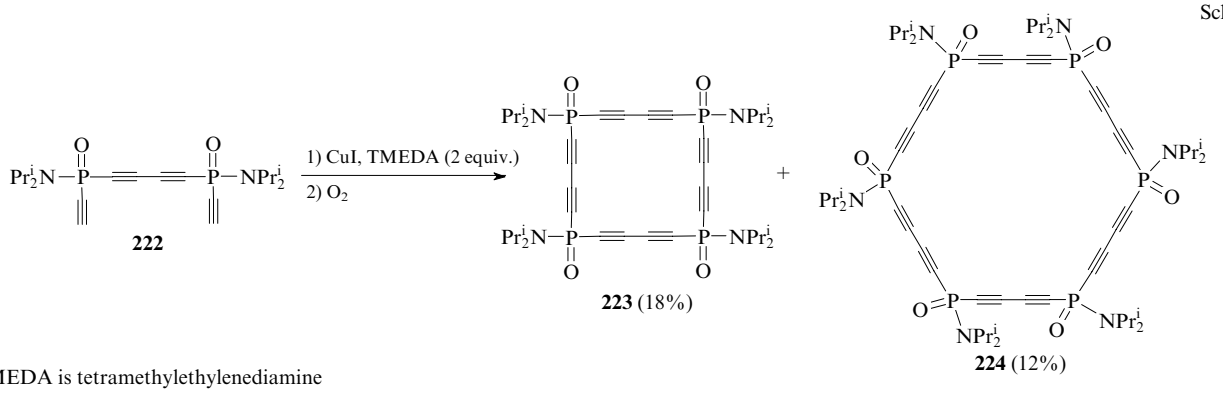


M = Pd (69%), Pt (58%)

Representatives of a new class of compounds containing two diphosphine macrocycles in the cyclophane core were synthesized by the Kazan research team.[46,177–180] This method is based on the Mannich condensation of bis(hydroxymethyl)organylphosphines **227** with primary aromatic dimaines **228** containing two *p*-phenylene moieties linked by one bridging atom or group under high dilution conditions (Scheme 81).

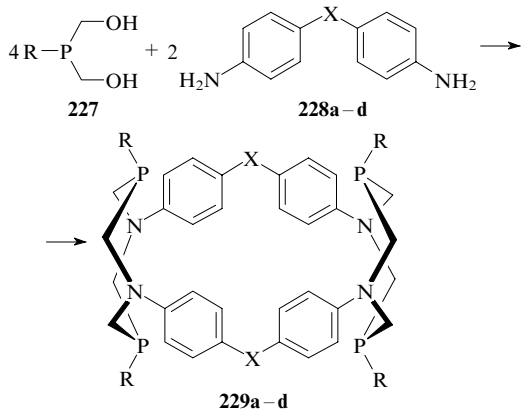
The time required for the condensation to proceed strongly depends both on the nature and concentration of the starting reactants.[179] For instance, the reaction of bis(hydroxyethyl)phenylphosphine (at a concentration of 0.2–0.3 mol litre^{-1}) with 4,4′-thiodianiline should be performed at 110 °C for 4 h to achieve a 42% yield of the corresponding product **229** (R = Ph, X = S). The time required for the corresponding reaction with the weaker nucleophile, bis(4-aminophenyl)sulfone **228c**, to occur is 40 h (yield 18%). Bis(hydroxyethyl)benzylphosphine **227** (R = Bn) unexpectedly appeared to be less active than the phenyl analogue, and its reactions with 4,4′-diaminophenylmethane (**228a**) and 4,4′-thiodianiline (**228b**) take place under heating for >40 h; the yield of the corresponding

Scheme 78



TMEDA is tetramethylethylenediamine

Scheme 81



227 **228a – d** **229a – d**

R = Ph, Bn, Mes, 2,4,6-$Pr^i_3C_6H_2$, L-menthyl;
X = CH_2 (**a**), S (**b**), SO_2 (**c**), O(*m*-C_6H_4)O (**d**)

products **229a**,**b** (R = Bn) is 21%. The reaction of bis(hydroxyethyl)mesitylphosphine **227** (R = Mes) with 4,4′-thiodianiline (**228b**) at a phosphine concentration of approximately 0.08 mol litre^{-1} requires an even longer heating (for 60 – 100 h; the yield of the product was 60%).[178] The condensation of 1,3-bis(4-aminophenoxy)benzene (**228d**) containing the longest and most labile spacer in the series of the above-considered diamines **228** with bis(hydroxyethyl)phenylphosphine **227** (R = Ph) proceeds at a phosphine concentration of 0.45 mol litre^{-1} for 48 h to give the corresponding product **229d** (R = Ph) in 35% yield.

It is hardly probable that polycyclocondensation reactions with the participation of four or more small molecules would give macrocyclic compounds. Rather high yields of macrocycles **229** (up to 60%) attest to the successive covalent self-assembly. It should be noted that the reaction is stereoselective and yields one isomer, in which lone pairs on the phosphorus atoms are directed towards the cylindrical intramolecular cavity. The free volume of this cavity is 110 – 130 Å and it is quite suitable for the inclusion of small organic molecules or their fragments. Thus, it was found that the intramolecular cavity of macrocycle **229b** (R = Mes) in the crystal encapsulates *N*-methyl groups of the solvents *N*,*N*-dimethylformamide and *N*,*N*-dimethylacetamide.[46]

These investigations were successfully continued using *N*-alkyl-2,6-diamino-9,10-dihydro-9,10-ethanoanthracenes as reactants in the condensation with bis(hydroxyethyl)phenylphosphine.[46, 181]

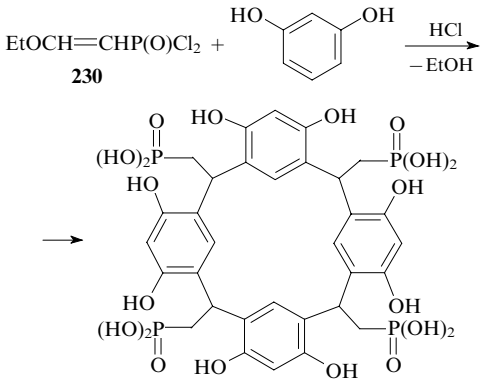
3. One-step formation of the phosphorus-containing calix[4]resorcinol template

Methods for the synthesis of phosphorus-containing calixarenes by the phosphorylation of the calixarene template (O- and C-phosphorylation, the introduction of organophosphorus groups *via* a bridging methylene spacer of the calixarene template) described in Section III have substantial drawbacks. Thus, they involve many steps and are characterized by low selectivity and, as a consequence, low yields of the target products. In addition, macrocyclic compounds synthesized by these methods are, in most cases, hydrolytically unstable, which imposes limitations on their practical applications.

An ingenious solution to this problem was to carry out the condensation of resorcinol and its derivatives with new reactants, such as (thio)phosphorylated acetals, aldehydes and ethoxyvinylphosphonates. This laid at the basis of the one-pot synthesis of new calix[4]resorcinols containing hydrolysis-resistant organophosphorus moieties at the lower rim obtained in high yields.[182 – 192] Investigations of the acid-catalyzed condensation of resorcinol and its derivatives with the above-mentioned (thio)phosphorylated reactants showed that the result of these reactions is determined by the nature of the phosphorus-containing reactant and the reaction conditions. Different types of new compounds can be prepared by varying these parameters. In addition to cyclic polyphenols (calix[4]resorcinols containing phosphorus-containing groups at the lower rim), this approach can be used to synthesize bicyclic phosphonates[193] and linear phosphorus-containing polyphenols of the diarylmethane series.[191, 194]

The acid-catalyzed condensation of resorcinol and 2-ethoxyvinylphosphonic dichloride (**230**) afforded new water-soluble calix[4]resorcinol **231** with four phosphonic acid substituents. The latter compound is an efficient extractant used in the micellar extraction of La^{III}, Gd^{III} and Yb^{III} ions even at a concentration of 4×10^{-4} mol litre^{-1}. The maximum selectivity in the lanthanide series under study is achieved at pH ~2. In particular, under these conditions, ytterbium ions are almost completely bound to ligand **231** (L) to form the insoluble complex Yb(H_{16}L). The degree of extraction of La^{3+} is 18%, whereas the degree of extraction of Gd^{3+} reaches 65%, *i.e.*, gadolinium ions are preferably extracted in the presence of lanthanum and ytterbium ions (Scheme 82).[195]

Scheme 82

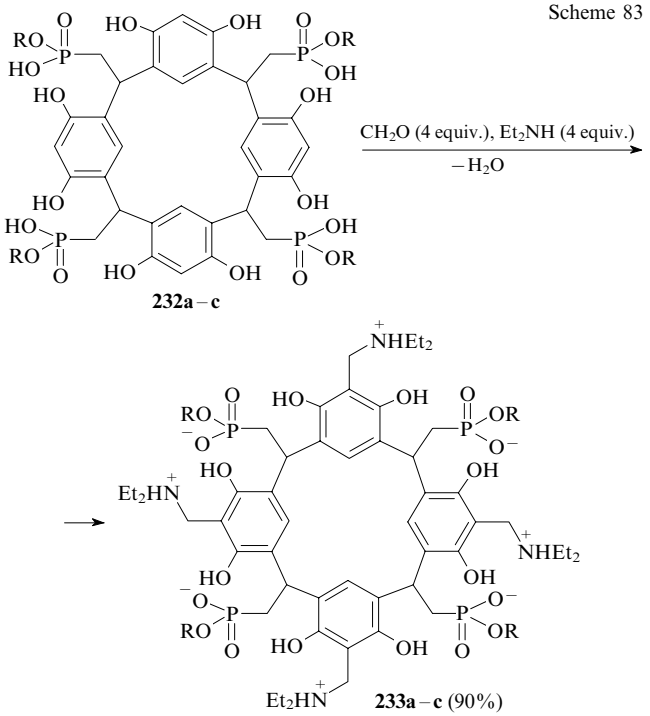


230 **231** (92%)

Phosphorus-containing esters of calix[4]resorcinol **232a – c** synthesized by the above-described method can easily be modified at the upper rim, for example, by the aminoalkylation in the Mannich reaction, resulting in an increase in their synthetic potential and the extension of the scope of the practical application (Scheme 83).[196]

Polyfunctional derivatives **233a – c** exhibit better complex-forming properties compared to their precursors due to the presence of new coordination sites (alkylammonium groups) at the upper rim in addition to four organophosphorus moieties at the lower rim. These compounds have pronounced surface-active properties surpassing the characteristics of known and widely used surfactants (for instance, trimethylammonium bromide). Thus, the critical

Scheme 83



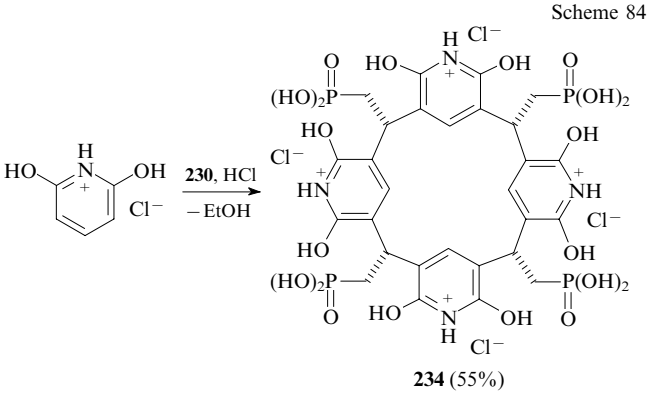
R = Et (**a**), Pr^n (**b**), Bu^n (**c**)

micelle concentration of macrocycles **233a–c** is at least an order of magnitude lower than that of classical surfactants.[197–200] This means that at low concentrations in water, these compounds can form supramolecular ensembles. The latter apparently have a layered structure and are head-to-tail self-assembled through interactions between ammonium groups of one aminomethylated calix[4]resorcinol molecule and phosphonate anions of another molecule.[200]

This characteristic feature of aminoalkylated derivatives of phosphorus-containing calix[4]resorcinols was employed in investigations aimed at improving the dispersion of carbon nanotubes in water to find new technological aspects of their application.[201] In addition, it was shown [197–200] that self-associated supramolecular systems based on phosphorylated calix[4]resorcinols **232** and their aminomethylated derivatives **233** exhibit high catalytic activity in the hydrolysis of phosphonic acid esters and phosphorylation of polyethyleneimines.

In an extension of this research, the condensation of dichlorovinylphosphonate **230** was carried out with an analogues of resorcinol, 2,6-dihydroxypyridine hydrochloride, resulting in the formation of calix[4]pyridine hydrochloride **234** containing four phosphonic acid groups at the lower rim (Scheme 84).[202]

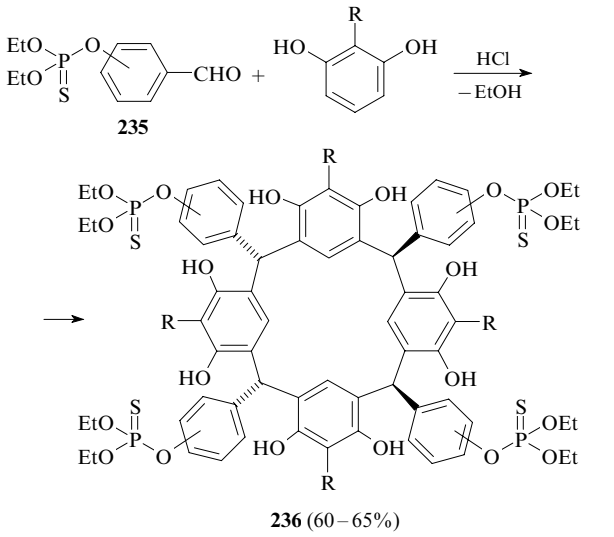
Scheme 84



This is the only example of the one-pot synthesis of phosphorus-containing macrocycles containing pyridine rings instead of benzene groups in the calixarene templates.

The condensation of resorcinol and its analogues with new (thio)phosphorylated derivatives of benzaldehyde yielded calix[4]resorcinols containing phosphonate, phosphonium and thiophosphate groups at the lower rim.[192, 203–205] In particular, the reactions of thiophosphorylated aromatic aldehydes **235** with resorcinol and its derivatives are strictly stereoselective and afford one configurational isomer of **236** adopting a chair conformation with the *rctt* configuration of thiophosphorylated substituents (Scheme 85).[192]

Scheme 85



R = H, Me, OH; isomers: *meta*, *para*

It should be noted that the introduction of thiophosphorylated groups into the calixresorcinol template has earlier been a laborious process. Generally, it was performed by the attachment of sulfur to trivalent phosphorus atoms of calix[4]resorcinols or cavitands pre-phosphorylated at the upper rim.[82, 140, 145, 151, 152, 161]

V. Conclusion

An extensive development of the chemistry of phosphorus-containing macrocyclic compounds in the past years was stimulated by the use of these compounds for the design of new types of supramolecular and coordination systems, investigations of mechanisms of molecular recognition of various ions and neutral organic molecules, unusual transformations performed with the aim of studying the fundamental reactivity of the synthesized compounds, *etc*. Since such macrocycles contain phosphorus atoms in different valence states, various ensembles with a three-dimensional architecture can be synthesized. Organophosphorus moieties, which are introduced into a macromolecular system and exhibit high coordination ability, can substantially enhance particular properties of the molecule as a whole and impart basically new features to the latter.

This review not only shows trends in the development of known methods for the synthesis of phosphorus-containing

macrocycles of different nature but also considers highly efficient approaches to the construction of such compounds. A rapid progress in synthetic methods gives impetus to the search for novel technological aspects of application of these compounds, from the construction of new systems exhibititing pronounced catalytic, receptor and other properties to the design of supramolecular devices, whose principle of action is based on specific reactivity of organophosphorus groups introduced into the macrocycle.

This review has been written with the financial support of the Russian Foundation for Basic Research (Project Nos 11-03-00416 and 12-03-31002).

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