

Heteroatom-Bridged Calixarenes

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Dedicated to Prof. Dr. Martin A. Bennett on the occasion of his 65th birthday

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Macrocycles have always played an important role in supramolecular chemistry. Macrocycles with rigid subunits, known as calixarenes, are an important subclass of these compounds. While carbon-bridged calixarenes have been studied intensively and are used for practical applications,

heteroatom-bridged calixarenes have entered the stage more recently. This review summarizes the current knowledge of synthesis and properties of heteroatom-bridged calixarenes in the year 2000.

Introduction

Macrocyclic compounds are of great importance in supramolecular chemistry whenever selective molecular recognition is desired.^[1] The reason for this is obvious; selective recognition requires intermolecular forces that are strong enough to stabilize the assembly, but at the same time allow the dynamic formation and breaking of intermolecular bonds to reach the aggregate that represents the thermodynamic minimum. Weak bonds, such as hydrogen bonds, electrostatic interactions, or kinetically labile coordination to metal ions, fulfill this requirement. However, compared to covalent or metallic bonds, these interactions are usually weak and contribute only a small enthalpic stabilization energy to the aggregate. Therefore, the loss of entropy in the assembly process becomes a significant factor in determin-

ing the stability of the supramolecular structure.^[2] Macrocyclic preorganization reduces the loss of entropy in aggregate formation by achieving a more restricted conformation as compared to acyclic compounds. This makes macrocycles good host compounds in recognition and self-assembly processes; indeed, this phenomenon has long been known as the macrocyclic effect.^[3]

From the large number of macrocycles with potential binding abilities, compounds with rigid, aromatic or heteroaromatic subunits have received special attention. Fully or partially conjugated macrocycles of this kind, such as porphyrins **1**, are widely found in nature, with hemoglobin and chlorophyll the most common. A nonconjugated macrocycle possessing sub-heterocyclic pyrrol rings **2** was synthesized more than 100 years ago by Baeyer from pyrrol and acetone.^[4] Somewhat later the formation of cyclic condensation products from *para-tert*-butylphenol and formaldehyde was discovered, but it took another 50 years before the structures of the different calixarenes were determined and protocols for their selective synthesis were developed.^[5]

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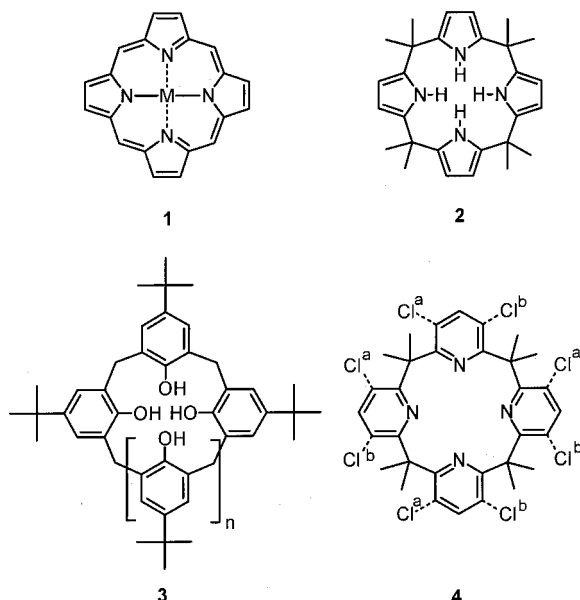


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Burkhard König received his doctorate in 1991 from the University of Hamburg under the direction of Prof. de Meijere. He continued his scientific education as a postdoctoral fellow with Prof. M. A. Bennett, Canberra, Australia, and Prof. B. M. Trost, Stanford, U. S. A. In 1996 he obtained his "Habilitation" at the Technical University of Braunschweig and since 1999 he has been Professor at the University of Regensburg. His current research interests focus on intermolecular interactions, which naturally includes the chemistry of macrocycles.

MICROREVIEWS: This feature introduces the readers to the authors' research through a concise overview of the selected topic. Reference to important work from others in the field is included.

The chemistry of mainly calix[4]- ($3, n = 1$), calix[6]- ($3, n = 3$) and calix[8]arenes ($3, n = 5$) has been thoroughly studied, and the search for new calixarenes is still ongoing, as illustrated by the recent synthesis of calix[4]pyridines **4**.^[6] The reasons for the very successful application of heteroaromatic and aromatic calixarenes as artificial receptor molecules are apparent: Depending on their conformation they provide an inner cavity for inclusion of guests, functional groups can be selectively introduced to build binding sites in three dimensions, and the parent calixarene macrocycles are in many cases available in large quantities from simple starting materials (Scheme 1).



Scheme 1. Conjugated and nonconjugated macrocycles with rigid subunits: porphyrin (**1**), *meso*-octamethylcalix[4]pyrrole (**2**), *para*-*tert*-butylcalix[3+*n*]arene (**3**), and chlorocalix[4]pyridine (**4**)

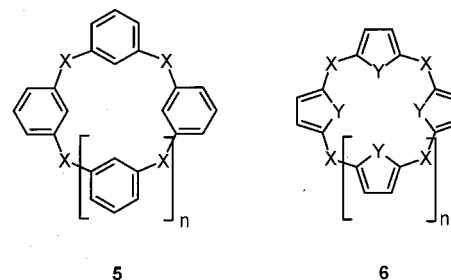
Calixarenes in which the carbon methylene bridge between the arene or heteroarene units is replaced by a heteroatom are much less studied. For such compounds the name hetero-calixarenes will be used in this article. The introduction of a heteroatom as the bridge provides an additional opportunity to tune the ring size, conformation, and binding properties of the macrocycle. Synthetic approaches to both classes of compounds are rather different. While the main synthetic routes to carbon-bridged calixarenes are condensation reactions of arenes or heteroarenes and carbonyl compounds, this reaction is in most cases not suitable for the introduction of heteroatom bridges.

In this account we will summarize recent reports of the synthesis and the binding properties of heteroatom-bridged calixarenes that have appeared in the literature. We include our own investigations on silicon-, sulfur-, and germanium-bridged macrocycles.

Results and Discussion

Most heteroatom-bridged calixarenes discussed in this paper are described by the two general formulae **5** and **6**

shown in Scheme 2. The substitution pattern of the arene rings in **5** is not restricted to *meta*-, *ortho*- and *para*-substituted rings as part of the macrocycle and mixtures of substitution patterns are included. The arene ring may contain additional heteroatoms. As a classification scheme, we will use the bridging heteroatoms X in the order of the main groups of the periodic table. As five-membered heterocyclic rigid subunits of the calixarene, furans ($Y = O$), thiophenes ($Y = S$) and *N*-methylpyrrols ($Y = \text{Me}-N$) are considered. Macrocycles with three ($n = 0$) to six ($n = 3$) rigid arene or heteroarene units are covered in this review.

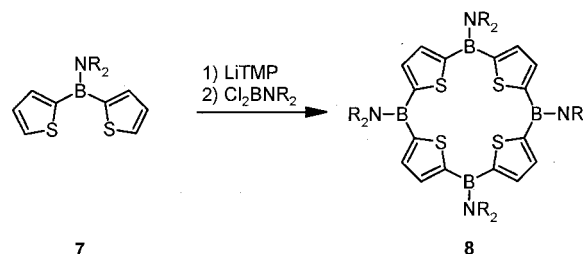


Scheme 2. General formulae of heterocalixarenes covered in this review

1. Group IIIA Elements

1.1 Boron

The first boron-bridged tetrathiaporphyrinogen **8** has been reported only recently.^[7] The macrocycle was synthesized in remarkable 62% yield from *N,N*-dimethylbis(2-thienyl)borylamine **7** via the dilithio compound. No polymer formation was observed in the reaction although this was the initial objective of the experiment. The X-ray structure analysis shows that all four bridging boron atoms do not lie in a single plane, as it is the case for the analogous carbon-^[8] and silicon-bridged compounds (Scheme 3).



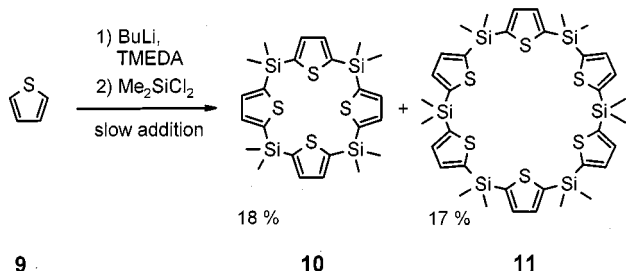
Scheme 3. Synthesis of a boron-bridged tetrathiaporphyrinogen; LiTMP = lithium-2,2,6,6-tetramethylpiperidid; R = *i*Pr

2. Group IVA Elements

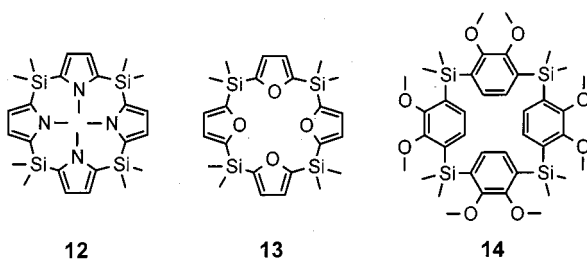
2.1 Silicon

The element closely related to carbon, silicon, has been widely used for the synthesis of macrocycles with rigid aromatic or heteroaromatic subunits. The first report appeared in 1973 by Kauffmann et al.^[9] who obtained a macrocycle **10** consisting of four thiophene rings bridged by dimethylsilyl groups from the reaction of a lithiated dimethylsilyl-

bridged bis(thiophene) in 16% yield. Later silicon-bridged macrocycles, such as **10** and **11**, were reported by Corriu and Moreau as by-products in polymerization reactions (Scheme 4).^[10] We have further developed protocols for silicon-bridged macrocycles, which now allow the synthesis of a wide variety of lipophilic macrocycles with weak coordination sites. In this strategy carbo- or heterocyclic dianions react with bis(electrophiles), such as Me_2SiCl_2 .^[11] The low solubility of the dianions in petroleum ether solvent and the very fast reaction of the slowly added bis(electrophile) generate *pseudo*-dilute conditions. The synthesis of macrocycles therefore proceeds under high substrate concentrations. Variation of the heterocyclic dianion yields the macrocyclic structures **12** and **13** (Scheme 5).



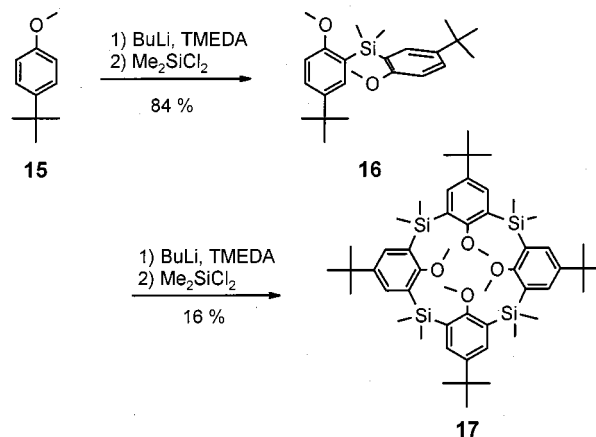
Scheme 4



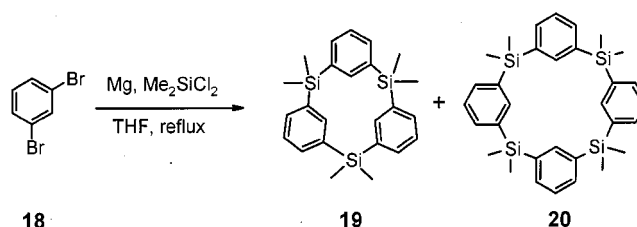
Scheme 5

An extension of the synthesis to sila[14]paracyclophanes **14** or silicon-bridged calix[4]arenes **17** is possible by a two-step route: Aromatic anions, generated by *ortho*-lithiation, react with Me_2SiCl_2 to give silicon-bridged dimers **16** (Scheme 6). Double deprotonation of **16** generates the dianion for cyclization. Metal salt extraction experiments from aqueous solutions revealed a much smaller affinity towards the silicon-bridged macrocycles as compared to crown ethers. In some cases high selectivities were observed, but it was not possible to establish a rational structure-selectivity relationship.

Yoshida et al.^[12] have obtained the unsubstituted parent trisilacalix[3]arene (trisila[1.1.1]*meta*-cyclophane) **19** and tetrasilacalix[4]arene **20** (tetrasil[1.1.1.1]*meta*-cyclophane) from 1,3-dibromobenzene (**18**), Me_2SiCl_2 , and magnesium in 12 and 2% yield, respectively (Scheme 7). The X-ray structure analysis revealed that **19** adopts a saddle structure and **20** a 1,2-alternate structure in the solid state. An isomer of **19**, trisila[1.1.1]*ortho*-cyclophane, has been previously prepared by Sakurai et al.^[13] Mass spectrometry showed that **19** and **20** do form complexes with silver cations. Association constants have not been reported.^[12]



Scheme 6

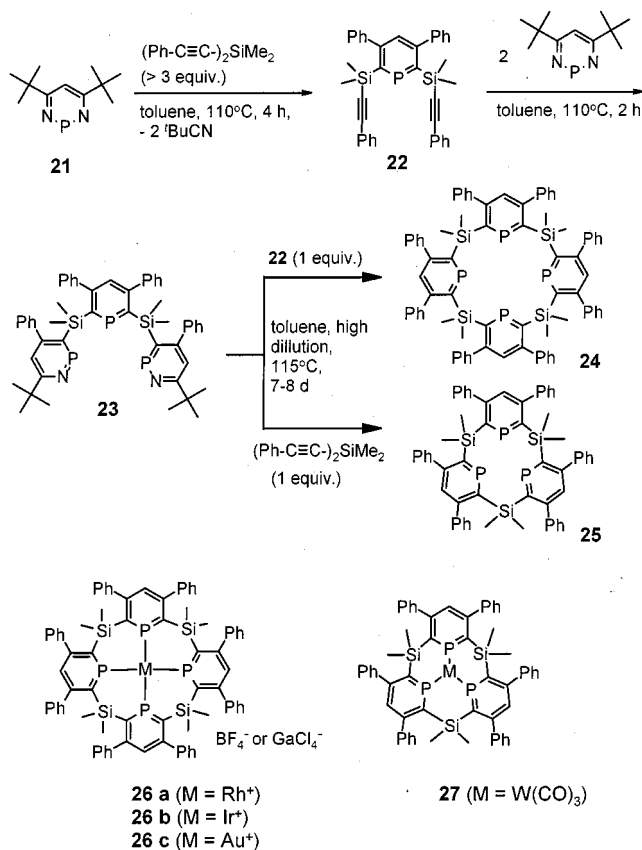


Scheme 7

A successful synthesis of silicon-bridged dicoordinate phosphorous macrocycles was reported by Mathey, Le Floch, and co-workers.^[14] They used a previously established, versatile route to phosphinines^[15] based on the [4+2] cycloaddition of alkynes with 1,3,2-diazaphosphanes for the synthesis. The 1,3,2-diazaphosphinine **21** was first allowed to react with a threefold excess of dialkynylsilane to give **22** in 60 to 70% yield (Scheme 8). Next, compound **22** was allowed to react with two equivalents of diazaphosphinine **21** to give **23**. Under high dilution conditions **23** reacted with one equivalent of **22** to give the calix[4] derivative **24** or the calix[3] derivative **25** under similar conditions, both in 20% yield. The macrocycles act as ligands with strong π -acceptor properties. From compound **24** the rhodium and iridium complexes **26a** and **b** have been prepared and from macrocycle **25** the $\text{W}(\text{CO})_3$ complex **27**. Reaction of **24** with AuI gave the first macrocyclic gold(I) complex **26c**, which can be reduced with sodium or potassium to a paramagnetic gold(0) complex.^[14c]

2.2 Germanium

Extension of the reaction of the bis(carbanions) with Me_2SiCl_2 to Me_2GeCl_2 revealed significant differences: While the reaction of monolithiated heterocycles, such as furan, thiophene or *N*-methylpyrrole with Me_2GeCl_2 gave Me_2Ge -bridged dimers in good yield, the reaction of 2,5-dianions with Me_2GeCl_2 mostly yielded a mixture of linear oligomers instead of macrocycles. However, reaction of stoichiometric amounts of Me_2GeCl_2 with the 5,5'-dianion of **28** and **30** gave macrocycles **29** and **31**, respectively (Scheme 9), both in low yield.^[16] The reaction of other dianions of Me_2Ge -bridged aromatic and heteroaromatic



Scheme 8

dimers yielded mixtures of linear oligomers exclusively. The size and distribution of the oligomers was investigated by gel permeation chromatography. The monomodal distribution in all cases indicates a regular, unbranched structure for the oligomers, with an average size being from 4 to 17 repeating units. The UV spectra of Me₂Ge- and Me₂Si-bridged arenes and heteroarenes show a small, but distinct bathochromic shift of λ_{max} with increasing molecule size. The extent of this shift differs only slightly for Me₂Si- and Me₂Ge-bridged molecules, which shows the similar abilities of these elements to electronically link the π-systems by σ-conjugation.^[17]

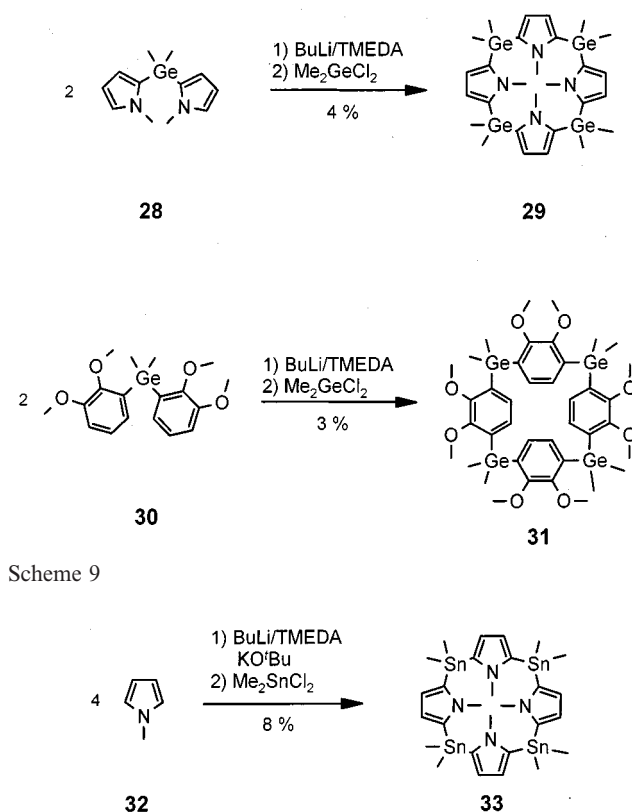
2.3 Tin

Tin can substitute for silicon or germanium in the macrocycles. Compound **33** was synthesized from the *N*-methylpyrrol dianion and Me₂SnCl₂ as described before (Scheme 10).^[11b] The nearly identical NMR spectra of **33** and **12** indicate similar structures for both compounds. However, macrocycle **33** is rather unstable and decomposes rapidly if stored in air.

3. Group VA Elements

3.1 Nitrogen

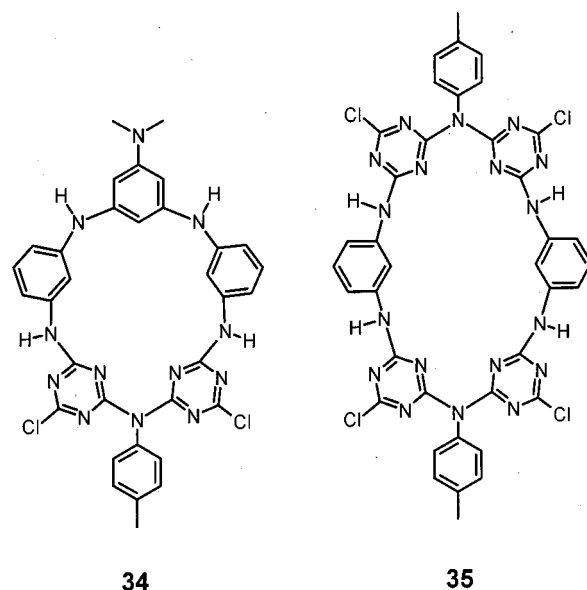
The nitrogen-bridged macrocycles **34** and **35** with aromatic subunits have been obtained from the reaction of trichlorotriazine with primary amines and diamines in step-



Scheme 9

Scheme 10

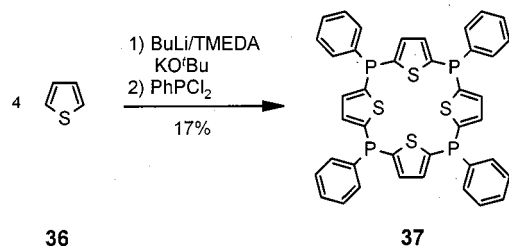
wise procedures (Scheme 11).^[18,19] The synthetic strategy allows for the incorporation of a wide variety of substituents. A first example of nitrogen-bridged calixarenes of structure **5** with X = NCH₃ (*n* = 1) has been reported in the literature very recently,^[20] but so far no information about the binding properties is available. The advances in methods for the formation of nitrogen-carbon bonds to arenes^[21] makes it likely that many more such compounds will soon be available.



Scheme 11

3.2 Phosphorus

The reaction of PhPCl_2 with the 2,5-dianion of thiophene gave macrocycle **37** in 17% yield (Scheme 12).^[11b] The ^{31}P resonance shows the formal oxidation level to be +3 for the phosphorus bridge. However, the sensitivity of the compound towards oxidation did not allow for metal extraction studies.

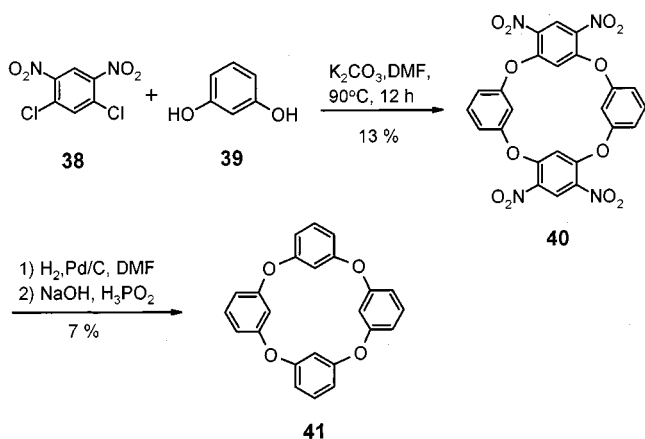


Scheme 12

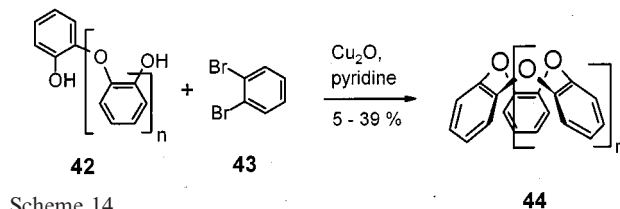
4. Group VIA Elements

4.1 Oxygen

Several oxygen-bridged calixarenes have been prepared. Such compounds, which can be described as fully aromatic crown ethers, have been prepared to investigate the influence of a more rigid structure and less basic binding sites on the binding selectivity of crown ethers towards metal cations. The synthesis uses either nucleophilic aromatic substitution of activated arenes^[22] (Scheme 13) or Ullmann-type reactions of bis(hydroxyaryl) ethers **42** with 1,2-dibromobenzene (**43**) in the presence of copper salts and pyridine (Scheme 14).^[23] The structure of **44** with $n = 1$ has been determined in the solid state and was found to have a C_2 -symmetric saddle form. Crown compounds **44** ($n = 4,5$) were tested by extraction methods for their extraction abilities, but no complexes were formed with lithium, sodium, potassium, calcium, or ammonium cations.



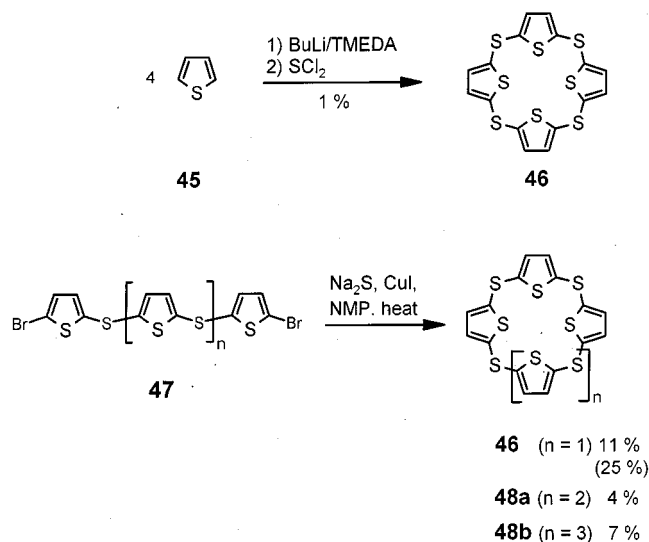
Scheme 13



Scheme 14

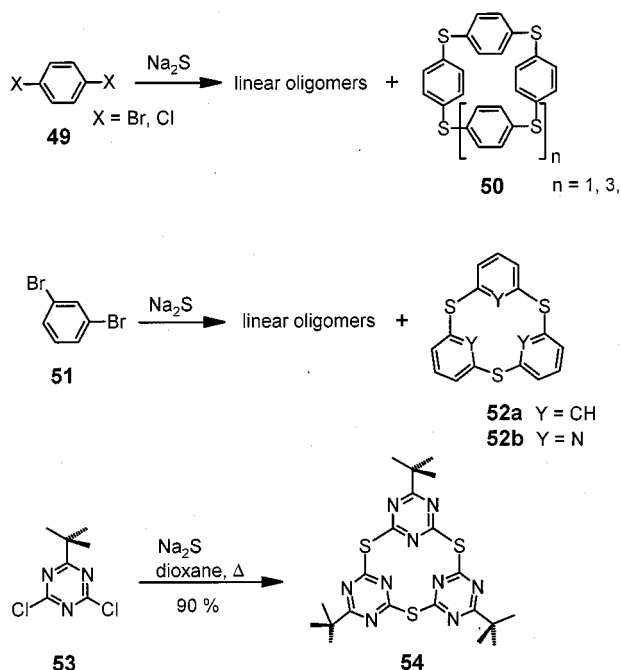
4.2 Sulfur

A large variety of sulfur-bridged calixarenes and heterocalixarenes have appeared in the literature. A simple extension of the previously described synthesis via 2,5-dilithiothiophenes to bis(electrophiles), such as SCl_2 yields thiacalix[4]arene **46**, although in very low yield (Scheme 15).^[24] The reaction of dibromo derivatives of linear sulfur-bridged thiophenes with Na_2S and copper salts in NMP as reported by Nakayama et al. gave access to **46** in higher yield and gave larger thiacalixarenes **48**.^[25]

Scheme 15. Synthesis of sulfur-bridged thiacalixarenes; the yield of compound **46** increases to 25% if CuI is replaced by Cs_2CO_3

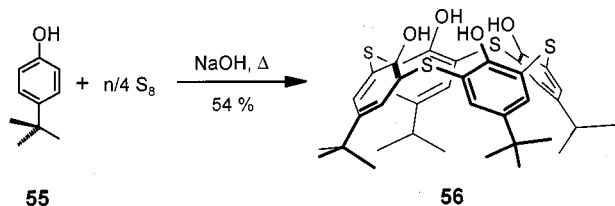
The reaction of *para*- or *meta*-dichlorobenzene or -dibromobenzene and sodium sulfide results in the formation of linear polyphenylene sulfides that contain small amounts (ca. 3%) of sulfur-bridged macrocycles of various ring sizes. From the low molecular weight fractions, several macrocycles, such as **50** or **52a**, with 3–6 benzene units have been isolated by extraction, chromatography and recrystallization, and characterized spectroscopically (Scheme 16).^[26] An X-ray structure analysis has been reported for compound **52a**. The analogous thiacalix[3]pyridine **52b** was obtained from intermolecular condensation of 6-chloropyridine-2-thione in the presence of P_2S_5 , but no yield was reported.^[27] In 90% yield a sulfur-bridged calix[3]azine **54** was synthesized from 6-*tert*-butyl-2,4-dichloro-1,3,5-triazine (**53**) and Na_2S in dioxane. The X-ray analysis of the molecule revealed a surprisingly flat structure with each triazine

ring participating in π -stacking interactions with neighboring molecules.^[28]



Scheme 16

Most reports have appeared on the synthesis and properties of tetrahydroxytetrathiacalix[4]arenes. The synthesis of tetrahydroxy-*para-tert*-butyltetrathiacalix[4]arene (**56**) starts from *para-tert*-butylphenol (**55**), as in the parent methylene-bridged system. Heating of **55** with elemental sulfur and NaOH in tetraethylene glycol dimethyl ether results in the

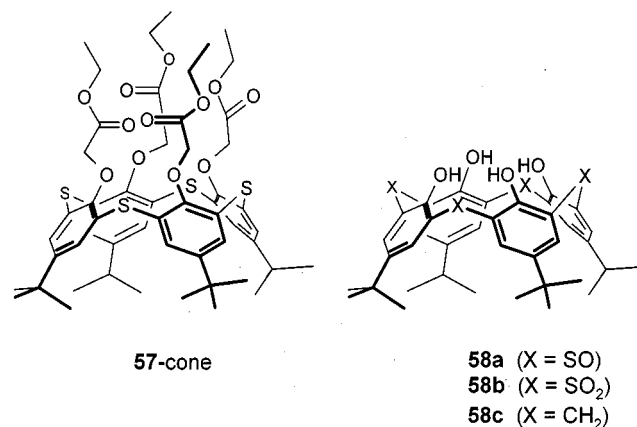


Scheme 17

formation of **56** in 54% yield (Scheme 17). Small amounts of the corresponding thiacalix[5]- and thiacalix[6]arenes were isolated by HPLC.^[29] The synthesis of all possible isomers of *para-tert*-butylcalix[4]arenes in which methylene bridges were partly replaced by sulfur linkages has also been reported.^[30] The X-ray structure analysis of **56** shows the inclusion of dichloromethane in the cavity under the conditions of crystallization. The molecule has a cone conformation in the solid state.^[31] The compound is an interesting ligand for metal ion coordination. An antiferromagnetic copper complex with copper acetate is obtained in DMF. The X-ray structure analysis shows a square cluster of four copper(II) ions with phenoxy and sulfur bridges sandwiched between two fully deprotonated calixarenes, thus forming a ditopic, divergent receptor.^[32] Zinc(II) ions are coordinated by the bridging sulfur atom and the phenolic oxygen atom to form a complex coordination structure.^[33] The high affinity of **56** for transition metal ions was

also demonstrated by quantitative extraction of Co^{2+} , Cu^{2+} , and Zn^{2+} salts from the aqueous phase into chloroform.^[34] Alkylation of the hydroxy groups of tetrahydroxythiacalixarenes has been used to lock the macrocycle conformation and thereby tune complexation properties. Depending on the counterion of the base used in the alkylation reaction, the conformer distribution is altered from the cone as the major product with sodium ions to the 1,3-alternate conformation with cesium ions present. The results suggest that a template effect is the main controlling factor. X-ray structure analysis of the 1,3-alternate conformer showed the formation of channels in the solid state.^[35] NMR investigations showed a higher conformational flexibility for the tetraethyl ether of thiacalix[4]arene in comparison with the methylene-bridged calixarene. The larger cavity of the sulfur-bridged macrocycle is a likely rationale for this observation.^[36] Extraction studies with the different conformers of tetrakis[(ethoxycarbonyl)methoxy]thiacalix[4]arene **57** (Scheme 18) showed a higher affinity of the cone conformer for sodium ions, whereas the 1,3-alternate conformer extracts preferentially potassium and rubidium ions. The extraction ability of the partial cone conformer was found to be lower for all metal ions.^[37] The stoichiometry of the complex of cone-**57** with sodium ion was determined to be 1:1 with the stability constant of $10^{2.85} \text{ L mol}^{-1}$ in 50% (v/v) $\text{CDCl}_3/\text{CD}_3\text{OD}$. For details of percentage cation extracted and experimental conditions, see ref.^[37]

Water-soluble sulfonated tetrathiacalix[4]arenes have been used for the removal of small halogenated organic substances, such as CH_2Cl_2 or CHCl_3 , from water. By formation of a ternary complex of the negatively charged thiacalixarene, an anion-exchange resin and the halogenated organic compound, almost perfect removal of organic pollutants, with removal rates of more than 99.9% from water, was achieved.^[38] Thiacalix[4]arene derivatives, which are modified with di- and tridansyl moieties, have been prepared to investigate their metal-sensing abilities in aqueous solution. Such molecules with two dansyl groups are able to detect metal cations in aqueous solution by variation of the fluorescence intensity, but observed selectivities are low.^[39]



Scheme 18

Oxidation of **56** with H_2O_2 in glacial AcOH yielded sulfonylcalixarene **58b** in 59% yield (Scheme 18). The X-ray analysis revealed the formation of a three-dimensional network of hydrogen bonds between the OH and SO_2 groups, whereby the calixarenes adopt a 1,3-alternate conformation.^[40] Stepwise oxidation of **55** to sulfinyl- and sulfonylcalix[4]arenes was achieved with stoichiometric amounts of NaBO_3 in chloroform.^[41] Extraction experiments (see Table 1) showed that sulfonylcalix[4]arene **58b** completely lost the ability of thiacalix[4]arenes, such as **56**, to extract transition metal ions. With **58b**, alkaline earth metal ions, in particular Ca^{2+} , are extracted. Interestingly, sulfinylcalixarene **58a** shows affinity for both transition and alkaline earth metal ions in extraction experiments.^[41]

Table 1. Percentage of extracted transition metal and alkaline earth metal cations by calixarenes from the aqueous phase into chloroform; for detailed experimental conditions, see ref.^[41]

Compound	Transition metal (pH = 8.0)			Alkaline earth metal (pH = 10)			
	Co^{2+}	Ni^{2+}	Cu^{2+}	Zn^{2+}	Mg^{2+}	Ca^{2+}	Ba^{2+}
58c	5	1	1	6	0	0	3
56	99	97	99	99	1	0	7
58a	99	99	17	99	99	91	99
58b	9	2	4	10	60	100	80

Conclusion

The introduction of heteroatoms as bridging atoms in calixarene macrocycles offers additional opportunities to modify their properties, affinity and selectivity for binding ions or molecules. So far, the number of known heteroatom-bridged calixarenes is still rather limited compared with carbocyclic calixarenes, and the relation of macrocyclic structure to selectivity of binding is obvious in only very few cases. However, if ongoing research in this field will provide the knowledge to better predict binding properties, as it is the case for crown ethers and cryptands, designed heteroatom-bridged calixarenes will have the potential to serve as selective ionophores and host molecules for many applications.

Acknowledgments

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