

Review Article

Calixarene Complexes with Transition Metal Ions

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Abstract

Selected calixarene complexes with transition metal ions are described showing their syntheses and possible applications, especially in the aspect of the environmental protection.

Introduction

Calixarenes attract an attention as convenient receptors for neutral molecules and ions. They are a theme of a great number of reports [1–5], so dealing with simple calixarenes [6–8] as well as resorcinarenes [9, 10] or cavitands [11]. One should also mention analogues of these compounds, i.e. thiacalixarenes [12, 13], oxacalixarenes [14, 15] and azacalixarenes [16, 17]. Calixarene complexes with alkali metal ions [18–20], especially cesium [21, 22] are promising in the nuclear waste management, and those with heavy metal ions [23, 24] are useful in view of the environmental protection.

The present paper dealing with metalocalixarenes is related to our reviews concerning metalocyclodextrins [25] and metalloporphyrins [26] and is a continuation of our papers on calixarenes [27–31], resorcinarenes [32] and cavitands [33, 34].

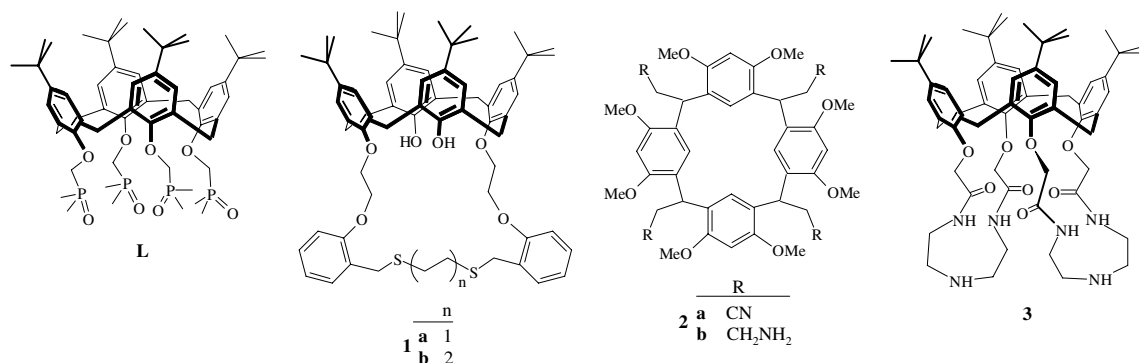
Since the number of calixarene complexes with metal ions [35], and among them of those with transition metal ions [36–41] is enormous, we present here selected calixarene complexes with transition

metal as well as with lanthanide and actinide ions showing their syntheses and properties, and possible applications. Title complexes are interesting from both theoretical and practical aspects, for example they are used in the removal of lanthanides and actinides from industrial and nuclear waste [42, 43]. It should also be pointed out that transition metal complexes of calixarenes are convenient models for mimicking biological processes [44].

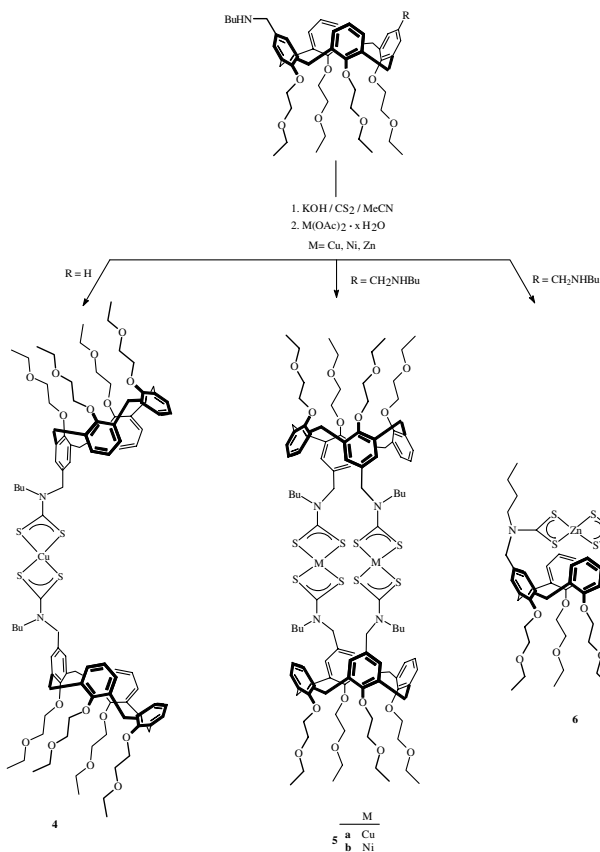
The paper shows works that appeared from 2001 to mid-2004 and is a continuation of our former review on this theme with references cited up to 2000 [45].

The following complexes are described in the present review:

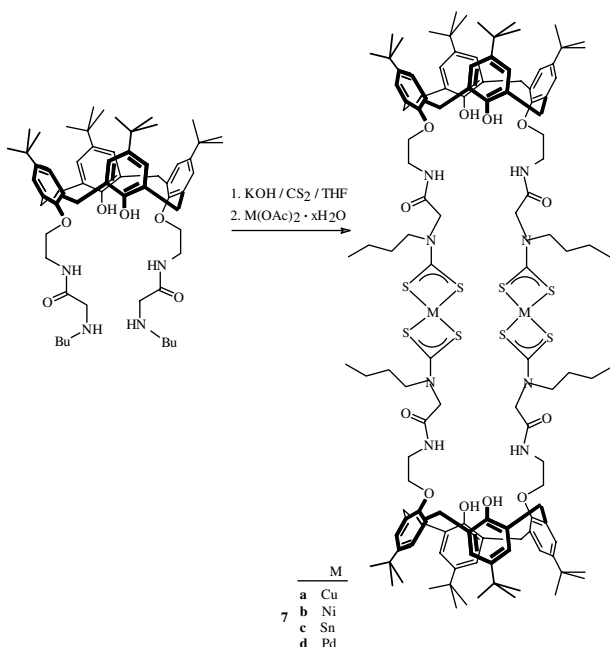
- Calixarene complexes with copper, silver, cadmium and mercury ions,
- Calixarene complexes with iron, ruthenium, rhodium and palladium ions,
- Calixarene complexes with molybdenum, tungsten and titanium ions,
- Calixarene complexes with lanthanide and actinide ions.



Scheme 1.



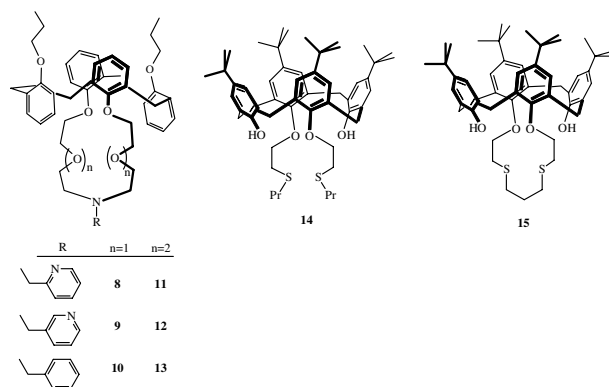
Scheme 2.



Scheme 3.

Calixarene Complexes with Copper, Silver, Cadmium and Mercury Ions

It was established that calixarene Cu²⁺ [46] and Zn²⁺ [47] complexes may be used in analytical chemistry as



Scheme 4.

luminescent sensors for these metal ions. Calixarene **L** forms 1:1 (metal/ligand) complexes **CuCl₂L · 4H₂O**, **Cu(ClO₄)₂L · 4H₂O** and **M(ClO₄)₂L · 2H₂O**, where M = Co, Ni and Zn, as well as the 2:1 (metal/ligand) complex **Zn₂Cl₄L**, isolated from ethanolic solutions [48] (Scheme 1). The same metal/ligand stoichiometry is maintained in solution, as it was shown by ES-MS (electrospray mass spectrometry) results. IR and ³¹P NMR spectroscopy, as well as X-ray diffraction studies confirm the coordination of metal ions through the phosphoryl groups.

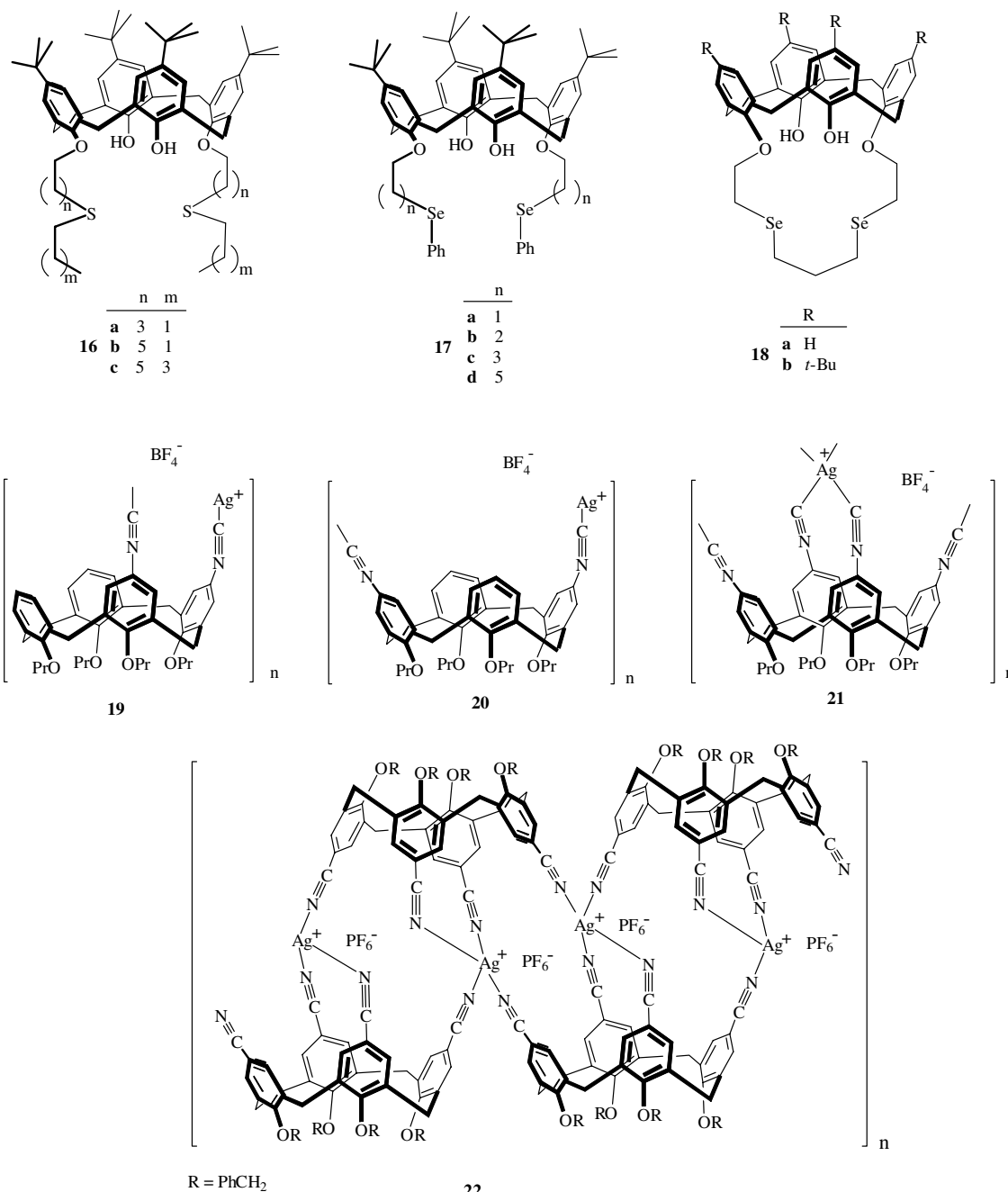
Calixarenes **1a**, **b** containing sulfur atoms in the crown moiety form with Cu²⁺ and Ag⁺ ions in MeCN the 1:1 complexes [49]. The complex **Cu · 1a** is stronger than **Cu · 1b** while the complex **Ag · 1a** is weaker than **Ag · 1b**. The high selectivity of Cu²⁺ over Mg²⁺, Na⁺, K⁺, Cr³⁺, Mn²⁺, Fe²⁺, Co²⁺, Ni²⁺ and Cd²⁺ ions was observed (Scheme 1).

Resorcinarenes **2a**, **b**, both in cone conformation, interact with Cu²⁺ ions [50]. Compound **2a** forms with Cu²⁺ as 1:1 complex **Cu · 2a**, and for **2b** the EPR spectrum shows the existence of **Cu · (2b)₂** and suggests its octahedral geometry. Both complexes are stabilized by cation-π interaction (Scheme 1). It was found that **3** forms 1:2 complexes with Cu²⁺, Co²⁺, Ni²⁺ and Zn²⁺ picrates [51] (Scheme 1).

Calixarene complexes **4–6** and **7**, functionalized with dithiocarbamate groups at wide and narrow rims, respectively, have been synthesized in one-pot procedures (Schemes 2 and 3). It was established that bimetallic copper^{II} bis(calixarene) complexes **5a** and **7a** can electrochemically sense carboxylate and dihydrogen phosphate anionic guests [52].

Calixarene complexes with silver ions are a topic of numerous reports [53–59]. The investigation of complexing properties of **8–13** has shown that their binding constants for Ag⁺ ion decrease in the order **8** > **11** > **10** > **9** > **13** > **12** [60]. It was observed that **14** and **15** bind selectively Ag⁺ over other metal ions, stronger in the case of **14** [61] (Scheme 4).

Ion-selective electrodes based on calixarenes **16–18** [62, 63] show excellent Ag⁺ selectivity over Na⁺, K⁺, NH₄⁺, Mg²⁺, Ca²⁺, Ni²⁺, Zn²⁺, Cu²⁺, Cd²⁺ and



Scheme 5.

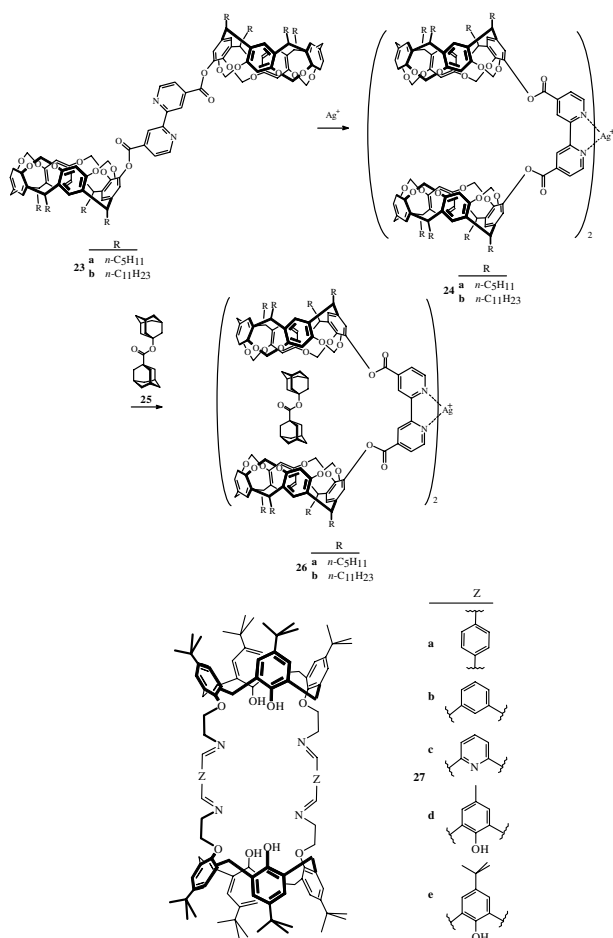
Pb²⁺ ions, except for Hg²⁺, having a relatively weak interference (Scheme 5). In the study of silver^I complexes **19**–**21** it was found that they exist as oligomers or polymers, the structure of **21** resembling that of polymer **22** [64] (Scheme 5).

The complexation of bipyridine bridged bis(resorcinarene) **23** with Ag⁺ ion leads to hemicarcerand-like structure **24** which can bind non-polar organic molecules [65]. It was observed that the treatment of **23** with **25** serving as a guest does not lead to complexation. However, when Ag(MeCN)₂BF₄ was added to this solution, **25** was bound to give **26** *via* CH- π interactions

and solvophobic effects, this process being an example of an allosteric recognition (Scheme 6).

The investigation of complexing properties of bis-calixarenes **27a–e** with Ag⁺, Na⁺, K⁺, Ca²⁺ and Pb²⁺ ions has shown that they bind Ag⁺ more efficiently than other metal ions [66]. Compounds **27a** and **27c** are promising for the construction of silver ion selective electrodes and PVC membranes; they are highly selective for Ag⁺, even over Hg²⁺ (Scheme 6).

It was observed that metal ions can oscillate through the calixtube [67, 68]. Calixtubes consisting of 2–5 calixcrown molecules and complexing metal ions able to



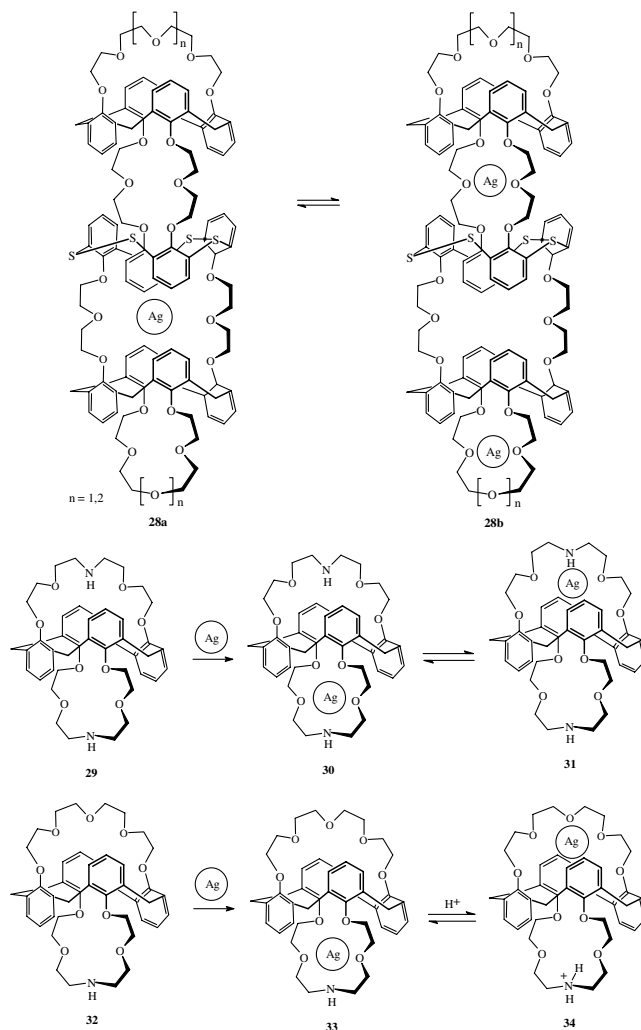
Scheme 6.

shuttle along the tube may be considered as metal-containing calix-nanowires [19, 69]. Silver ion shuttling involving cation- π interactions in trimers **28a**, **b** was established by means of variable-temperature NMR spectra [70] (Scheme 7).

Complexing properties of **29** have been investigated. It was found that the Ag^+ ion shuttles in **29** between both azacrown loops to give **30** and **31** complexes (Scheme 7). However in the case of **32**, the Ag^+ ion prefers to be situated in the azacrown loop affording complex **33**, and the protonation is required for the tunneling of the Ag^+ ion from azacrown to the crown ether ring, resulting in the complex **34**, this process being due to the electrostatic repulsion of Ag^+ and NH_2^+ group [68] (Scheme 7).

In the study of calixarene-based fluorescent sensors [71] it was observed that the fluorescence of **35** is partially quenched by photoinduced electron transfer (PET) from azacrown ring to pyrene (Scheme 8). When Ag^+ or Cu^{2+} ions are bound with **35**, fluorescence is enhanced since lone pairs of azacrown no longer participate in PET, and due to this blocking of PET the chelation-enhanced fluorescence (CHEF) takes place.

Compound **36** containing crown ether and azacrown ether moieties shows CHEF with Ag^+ and Cu^{2+} ions.

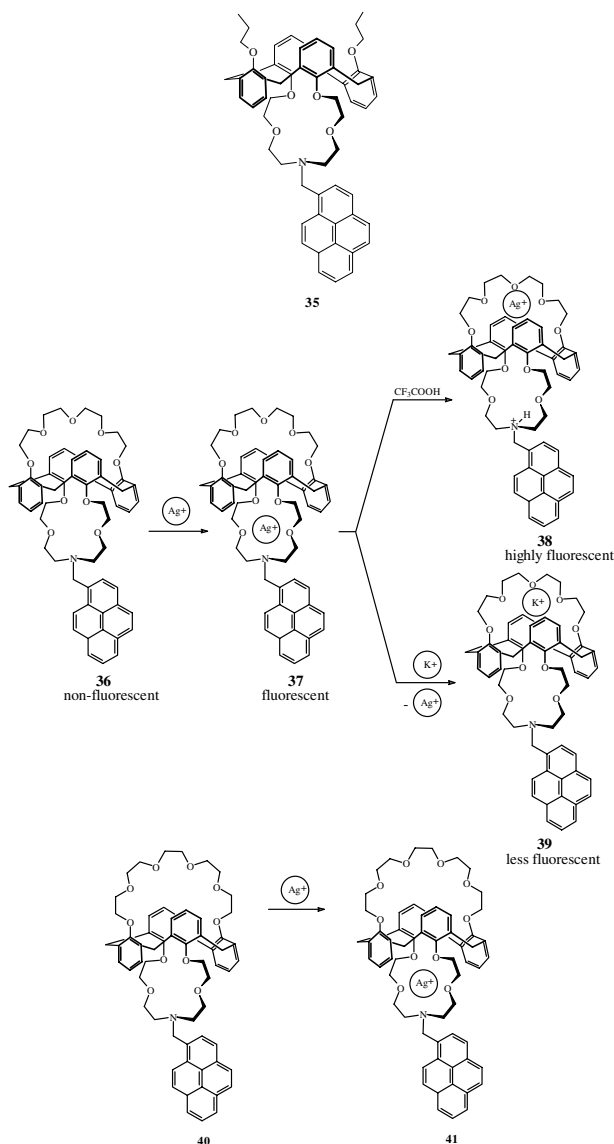


Scheme 7.

When **36** is bound with Ag^+ , this ion chooses for complexation the azacrown, and not the crown ether loop to give **37**; as a result the large CHEF effect is observed and the fluorescence increases.

The fluorescence may be further enhanced when CF_3COOH is added to the solution of **36** and Ag^+ affording **38**, this fact being due to the protonation of the azacrown nitrogen atom. In this process Ag^+ ion is moved to the crown ether moiety by intramolecular tunneling through the calixtube (Scheme 8).

The addition of the K^+ ion to an ethanolic solution of **36** and Ag^+ results in a “molecular taekwondo”, described below. The fluorescence of **36** in ethanol is almost completely quenched by PET. When Ag^+ was added to give **37**, the CHEF effect was observed. The addition of K^+ which prefers crown over azacrown loop, yielding **39** resulted in the fluorescence quenching, due to the throwing out of Ag^+ from azacrown and binding of K^+ with crown ether and not with azacrown ether. In this way PET is no more blocked, and quenching takes place (Scheme 8). This “coming-in and kicking-out” process, called



Scheme 8.

“molecular taekwondo” may be easily monitored by fluorescence changes [72]. The same observation was made with **36** for $\text{Cu}^{2+}/\text{K}^+$ pair, *i.e.* the throwing out of Cu^{2+} from azacrown and complexation of K^+ in the crown ether.

However, when **36** was replaced by **40** containing [18]crown-6 instead of [15]crown-5, the complexation of Ag^+ in the azacrown moiety took place to give **41** but the addition of K^+ did not result in the fluorescence quenching. This observation is explained by the larger size of crown ether, too big for K^+ complexation, therefore K^+ cannot throw out the Ag^+ ion, which remains in azacrown, and no fluorescence quenching occurs (Scheme 8). The [18]crown-6 cavity is suitable for Cs^+ , and the same experiment made with Cs^+ instead of K^+ causes the fluorescence quenching. The above “molecular taekwondo” processes are promising in the design of chemosensors.

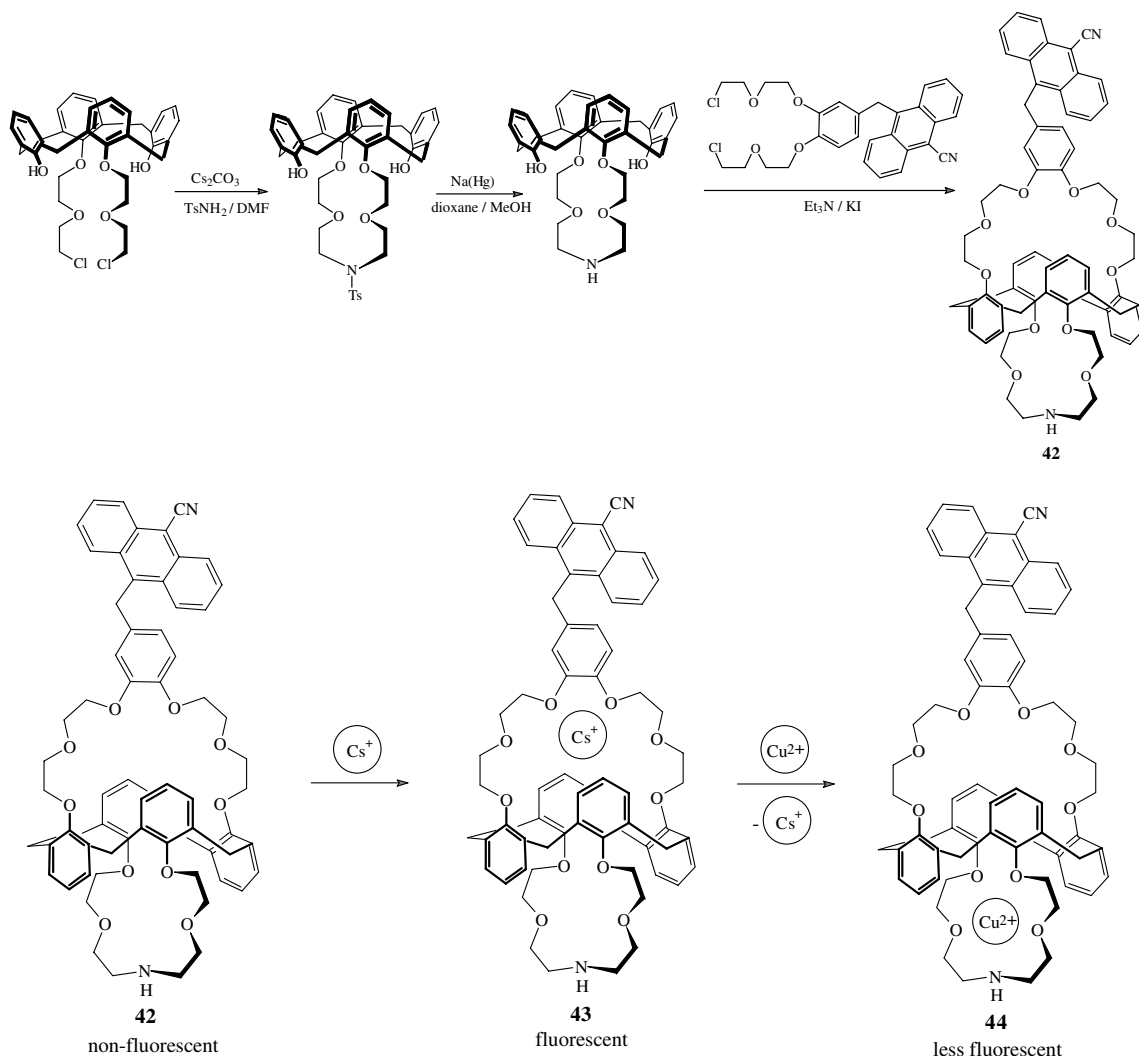
The synthesis of calixarene **42** has been reported (Scheme 9). It displays large CHEF effect with Cs^+ , Rb^+ and K^+ complexed in the crown ether bearing anthracenyl group [73]. In this case, the fluorophore anthracenyl is situated in crown ether, and not in azacrown, as was situated pyrenyl group, therefore the “taekwondo” occurs in an opposite mode than it was shown in Scheme 8. When Cu^{2+} is added to an ethanol/dichloromethane solution of **42** and Cs^+ forming **43**, the fluorescence quenching takes place, since complexation of Cu^{2+} into the azacrown ether to give **44** induces the throwing out of Cs^+ from the crown ether; PET is no longer blocked by Cs^+ and fluorescence is quenched (Scheme 9).

In the study of Au^{3+} calixarene complexes [74], calix[6]arenes **45–48** have been tested for binding Au^{3+} ions as AuCl_3 and AuCl_4^- [75] (Scheme 10). Calix[6]arenes are convenient extractants for chloro complexes of metal ions; they show higher selectivity than calix[4]arenes and allow the pH control of extraction and back extraction [76]. Because of its too low solubility in organic solvents, **45a** cannot be used for extraction, however the solubility can be improved by thionation affording **45b** or by replacement of *t*-butyl by *t*-octyl group to give **46**. The protonated **47** forms with Au^{3+} complex **49** (Scheme 10). For ligands **45b–48** both extraction and back-extraction from hydrochloric acid solutions are quantitative, therefore they may be used not only for separation but also for analytical purposes. Extraction constants of **45b–48** decrease in the order **47** > **48b** > **45b** > **48a** and the complexation is fast.

Compounds **45b**, **47** and **48b** show high selectivity for Au^{3+} over Zn^{2+} , Co^{2+} , Ni^{2+} , Pb^{2+} and especially over Fe^{3+} ions, while alkali, alkaline earth and Al^{3+} ions are not extracted under these conditions. The loaded metal is quantitatively back-extracted by a pH change or by a competing ligand, *e.g.* thiourea. Since **45b–48** extract Au^{3+} selectively from highly acidic media, their application in hydrometallurgy is environmentally friendly; ores can be leached with acidic thiourea solution and oxidized [77] instead of cyanide leaching [78].

Investigating Au^+ calixarene complexes [79], the luminescent complexes **50** have been synthesized; they show binding properties towards K^+ and Na^+ ions [80] (Scheme 10).

Numerous calixarene complexes with Zn^{2+} [48, 51, 52, 81, 82] and Cd^{2+} [83] were prepared; in these investigations calixarene **51** has been synthesized and its complexing properties towards Hg^{2+} , Pb^{2+} , Cd^{2+} and Na^+ ions examined [83] (Scheme 11). Calixarene **51** shows high selectivity towards Hg^{2+} and Pb^{2+} ions over Na^+ and Cd^{2+} ions, which are not complexed at all. The size effect, *i.e.* longer ionic radii of Hg^{2+} and Pb^{2+} as compared with those of Na^+ and Cd^{2+} seems to be insufficient for such a selectivity, here the softness of Hg^{2+} and Cd^{2+} should be taken into account; Hg^{2+} ion being softer than Cd^{2+} is more efficiently complexed by **51**. The stoichiometries of Hg^{2+} and



Scheme 9.

Pb^{2+} complexes with **51** determined by the mole ratio and the Job methods are 1:1. Since **51** discriminates Hg^{2+} and Pb^{2+} from Cd^{2+} and Na^+ ions, it may be used as a chromatographic selector.

It was observed that **52** shows selective complexation of Cd^{2+} and Hg^{2+} ions over alkali metal (Li^+ , Na^+ , K^+ , Rb^+) and Pb^{2+} ions and is promising for the detection of toxic Hg^{2+} and Cd^{2+} ions in the treatment of industrial waste streams [84]. In the search for calixarenes useful in the cadmium extraction [85], calixarene **53** was synthesized [23]; at pH 8 it extracts completely Cd^{2+} and Pb^{2+} over Cu^{2+} , Co^{2+} and Ni^{2+} ions (Scheme 11).

Complexing properties of fluorogenic ionophores **54** and **55** have been investigated. It was found that **54b** shows recognition of Hg^{2+} ions over Cu^{2+} , Pb^{2+} and Zn^{2+} ions, higher than in the case of **55**. A higher fluorescence of **Hg·54b** as compared with that of **54b** was observed, therefore **54b** is promising for the detection of Hg^{2+} ions [86] (Scheme 11).

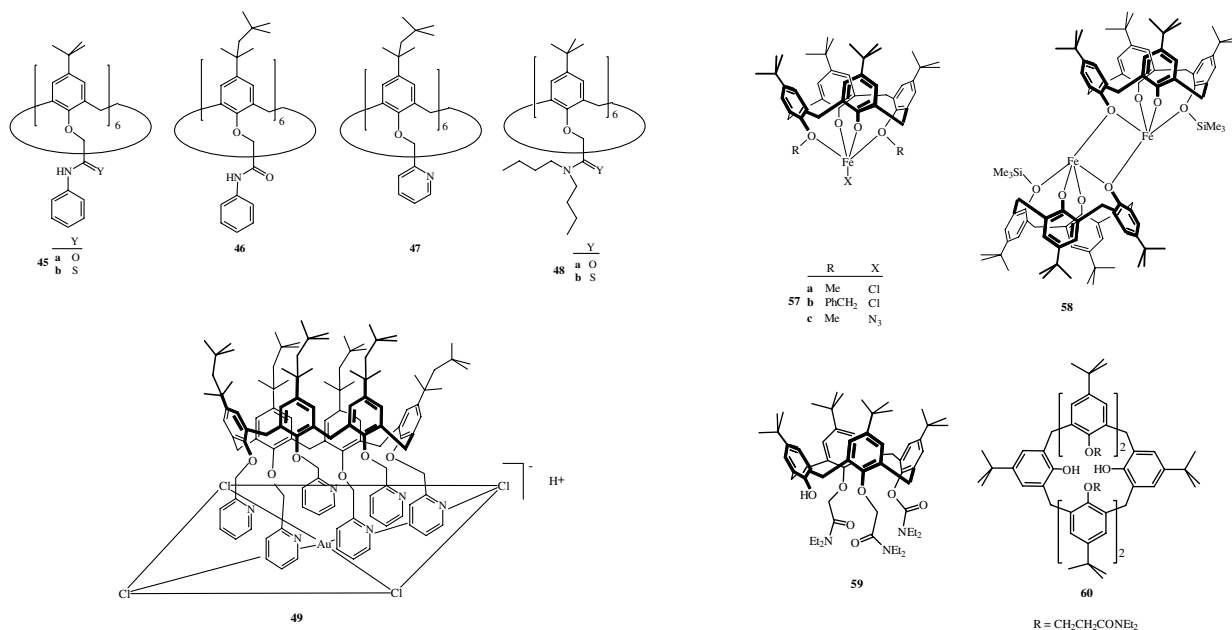
The Hg^{2+} ions in waste water are a difficult environmental problem. In this aspect the transport of

Hg^{2+} from an aqueous solution into an aqueous receiving solution through a liquid membrane containing biscalixarene **56** as a carrier has been investigated [87]. The membrane entrance and exit rates increase with temperature and with stirring rate. As solvents CH_2Cl_2 , CHCl_3 and CCl_4 were used, the highest transport efficiency occurring for CH_2Cl_2 (Scheme 11).

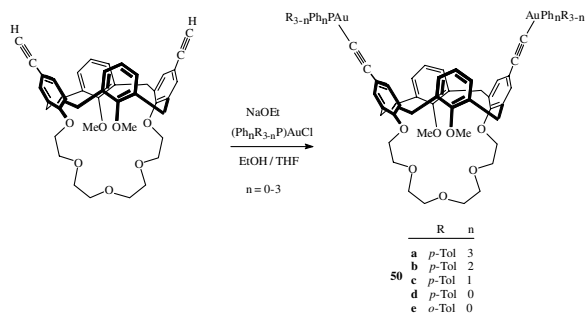
Calixarene Complexes with Iron, Ruthenium, Rhodium and Palladium Ions

Calix[4]arene iron^{III} mononuclear complexes **57** and dinuclear complex **58** have been synthesized and their structure confirmed by X-ray diffraction results [88] (Scheme 12). It was established that calixarene **59** forms with FeCl_3 the complex $[\text{Fe}(\mathbf{59}\text{-H})(\text{FeCl}_4)_2]$ and with $\text{Fe}(\text{ClO}_4)_2$ the complex $[\text{Fe}(\mathbf{59}\text{-H})(\text{ClO}_4)_2]$; calixarene **60** gives with $\text{Fe}(\text{ClO}_4)_2$ the complex $[\text{Fe}(\mathbf{60}\text{-H})(\text{ClO}_4)_2]$ [89] (Scheme 12).

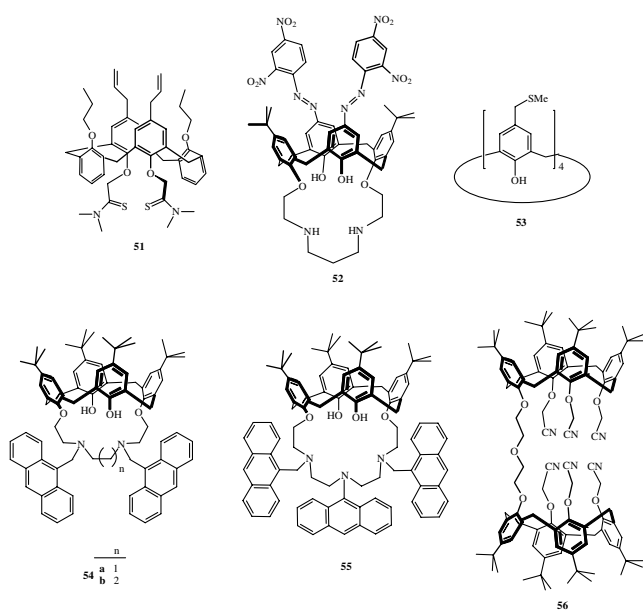
One should also mention here that calix[4]pyrrole Schiff base macrocycles **61** and **62** react with iron²⁺



Scheme 12.



Scheme 10.



Scheme 11.

mesitylene Fe₂Me₄ to give μ -oxo bis-Fe³⁺ complexes **63** and **64**, respectively [90, 91] (Scheme 13).

Complexes **65a–c** are examples of calixarenes bridged at the upper rim by ferrocene unit, promising as anion

receptors [92, 93]; complexes **66–68** may serve as electrochemical sensors for anions, dihydrogen phosphate displaying larger cathodic shifts than chloride and benzoate [94] (Scheme 14).

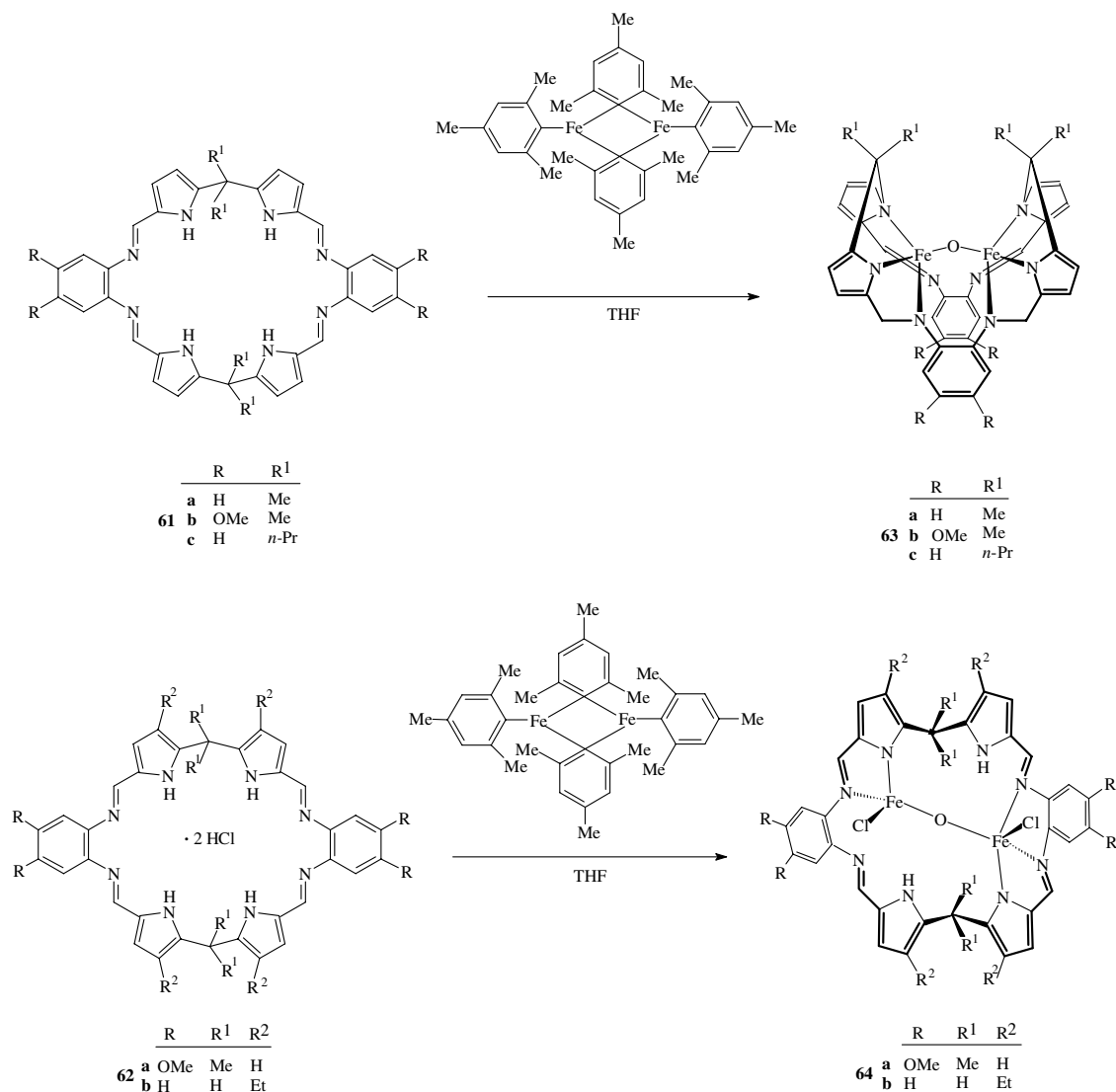
The synthesis of compound **69** was reported; it binds potassium ions as well as chloride, benzoate and dihydrogen phosphate anions [95]. It was observed that dipotassium complex of **69** shows the enhanced anion complexing properties due to the electrostatic effects and favorable preorganization (Scheme 15).

Investigating cobalt and nickel complexes of calixarenes [82] it was established that cavitands **70** and **71** modified with pyrene units may be used as fluorescent sensors for Ni²⁺ and Co²⁺ ions [96], respectively (Scheme 16).

In the study of biomimetic coordination ability of the calix[6]arene bearing three methylimidazole units **72** [97], its complexation with Co²⁺ and Ni²⁺ ions was performed [98]. Calixarene **72** gives with Co²⁺(H₂O)₆(ClO₄)₂ the tetrahedral Co²⁺-aqua complex **73**, whereas with [Ni(H₂O)₆(ClO₄)₂] the five-coordinate square-based pyramidal complex **74** was obtained (Scheme 16).

The reaction of **73** with EtOH affords **75** and with EtCN four-coordinate tetrahedral complex **76** is formed, being in equilibrium with a five-coordinate trigonal bipyramidal complex **77** containing a second nitrile ligand outside the cavity, in a *trans* position to the first one (Scheme 16).

The above Co²⁺ and Ni²⁺ complexes are flexible species, resembling carbonic anhydrase, i.e. a mononuclear zinc enzyme with a *tris*(histidine) coordination core. They are convenient models for Michaelis adducts, reproducing structural features of enzyme active sites, except for the *cis* coordination of the exogenous ligands.



Scheme 13.

Mono-, di- and tetraphosphinocalix[4]arenes **78**, **79** and **80**, respectively, have been synthesized from tetrabromocalixarene **81** by one-pot procedures [74] (Scheme 17). Compound **80** may be also prepared in two step procedure involving the introduction of four phosphoryl groups by reaction of **81** with $\text{Ph}_2\text{POEt}/\text{NiBr}_2$ and the subsequent reduction of the formed phosphine oxide with PhSiH_3 [99]. Complexing properties of these compounds, along with diphosphinocalix[4]arene **82** have been investigated [74].

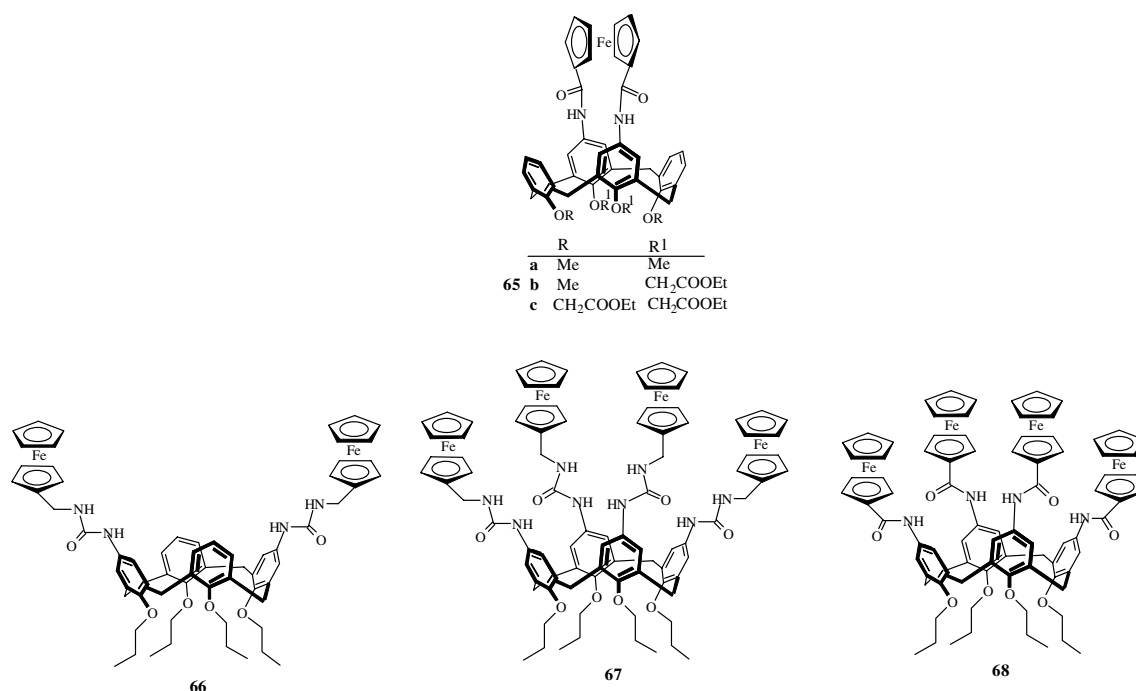
The reaction of **78** with $\text{RuCl}_2(p\text{-cymene})_2$ leads to mononuclear complex **83**. Since **78** bears three bromine atoms at the upper rim, its cavity is expanded; in **83** the metal ion complexation occurs at the cavity entrance. On the contrary, in the complex **84** formed from the calixarene having a shorter cone, the coordinated RhCp^*Cl_2 group ($\text{Cp}^* = \text{C}_5\text{Me}_5$) is situated outside the cavity [100] (Scheme 17).

Reactions of **82** affording mononuclear complexes of rhodium and palladium **85** and **86**, respectively and of platinum **87** and **88**, as well as those leading to dinuclear complexes of ruthenium and palladium **89** and **90** (Scheme 18) have been made. It should be noted that the reaction of **82** with $[\text{PtCl}_2(\text{cod})]$ yields the *cis* complex **87**, while in the case of $[\text{PtCl}_2(\text{PhCN})_2]$ the *trans* complex **88** is formed.

Reactions of **79** give complexes of ruthenium and platinum **91** and **92** and reactions of **80** afford tetranuclear complexes of gold, ruthenium and palladium **93**, **94** and **95**, respectively (Scheme 19).

Among rhodium and iridium complexes of calixarenes [101] one should mention dinuclear complexes of Rh (**96a**, **96b**) and of Rh and Ir (**96c**) [102] (Scheme 20).

Numerous calixarenes bound with dimetal units are known [103, 104], for example those containing Rh_2 [105], Mo_2 [105] and Ru_2 [106] units. Dirhodium compounds show varied catalytical activities [107, 108].



Scheme 14.

Reaction of calix[4]arene tetraanion **97** with [Rh₂(*cis*-L)₂(MeCN_{eq})₄(MeCN_{ax})₂](BF₄)₂ and tetraethylammonium ion leads to the capsule **98** linked by four dimetal units, Rh₂(L)₂ (where L = *N,N*-di-*p*-anisylformamidinate) and incorporating tetraethyl ammonium ion [109] (Scheme 20).

Calixarenes **99a–c** are inherently chiral. They react with [Rh(nbd)(thf)₂](BF₄) (where nbd = norbornadiene) to give complexes **100a–c** (Scheme 21) and with [Pd(η³-MeC₃H₄)(thf)₂](BF₄) (where thf = tetrahydrofuran) to give complexes **101a–c** [110].

Compounds **100a–c** catalyze hydrogenation of dimethyl itaconate, and compounds **101a–c** are catalysts

of the alkylation of 1, 3-diphenylprop-2-enyl acetate with dimethyl malonate. For **100** and **101** it was established that the enantioselectivity increases with the size difference between calixarene substituents.

No asymmetric induction was observed in the case of **101c**, bearing two identical chiral substituents, while with **101a** and **101b** the asymmetric induction occurs. Therefore it may be suggested that the presence of asymmetric carbon atoms as the only source of chirality has only little influence on the enantioselectivity.

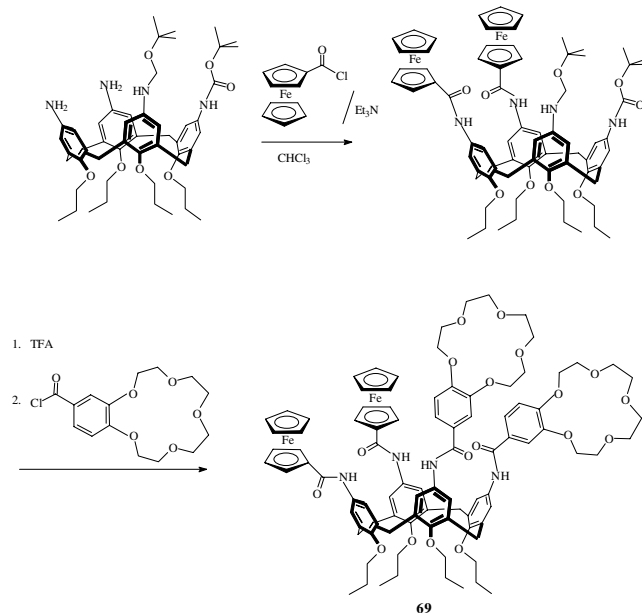
For comparison purposes, the catalytic activity of the rhodium complex **102** (for hydrogenation of dimethyl itaconate) and of chiral palladium complexes **103a, b** (for the alkylation of 1, 3-diphenylprop-2-enyl acetate) has been investigated (Scheme 21).

The hydrogenation rate decreases in the order **100a** > **100b** > **100c** > **102**. The low catalytic activity of **102** is explained by the pocket-like rhodium environment hindering the access of the olefin.

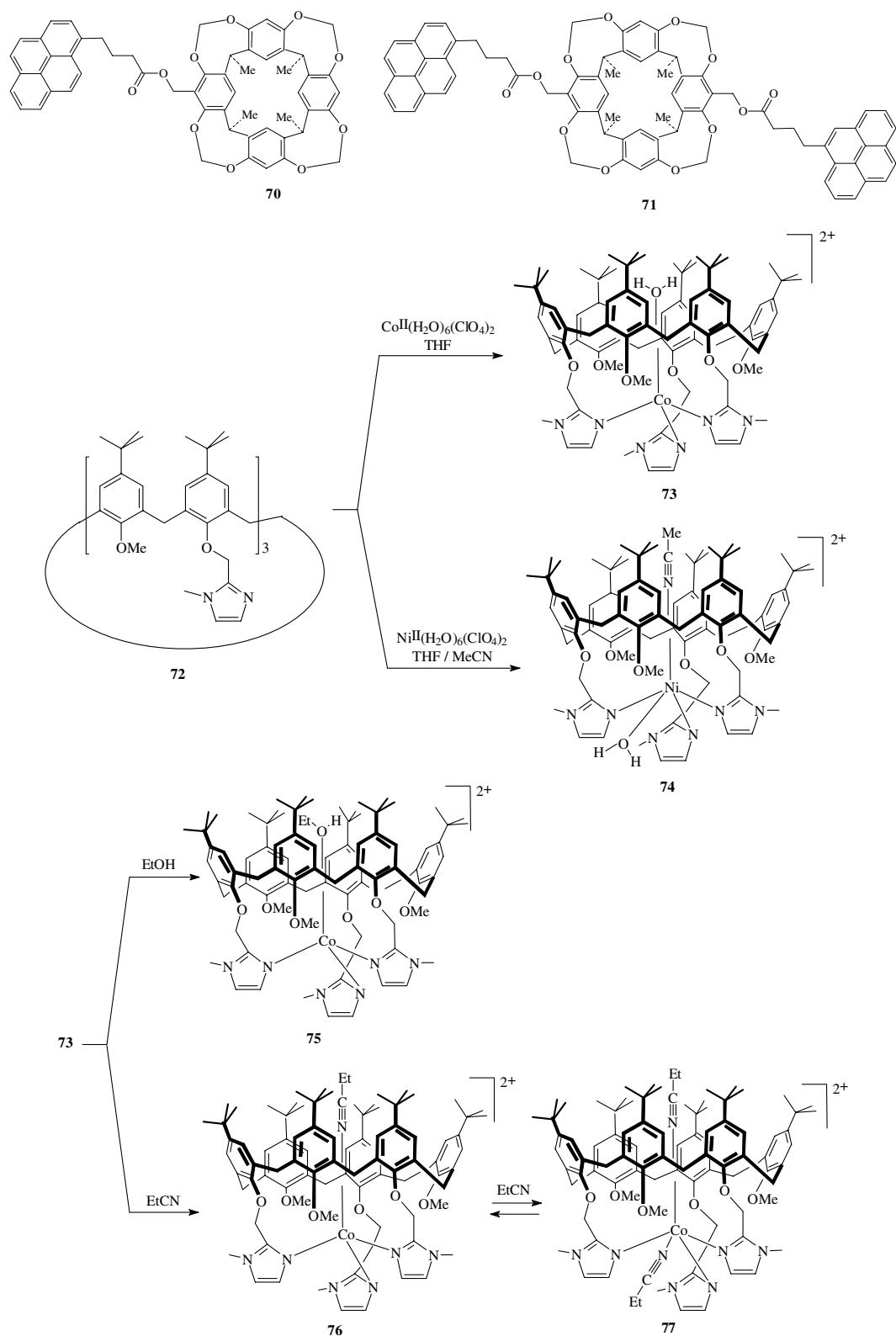
The low enantiomeric excess values observed with **101c** and **103a, b** in the alkylation result from the large separation between the stereogenic centres and the metal unit, and from the flexibility of the pendant amide which prevent effective induction.

The pyridylation of calixarene **104** affords **105** [111]. When **105b** was treated with palladium²⁺, the complex **106** was formed (Scheme 22). The X-ray crystal structure of **106** shows its metal-mediated self-organization resulting in formation of hexameric supracycles which are assembled into hexagonal tubes [111].

Complexes of calixarenes **107–109** with Pd²⁺ have been investigated by electrospray mass spectrometry (ESMS) [112, 113]. Calixarene **107** gives with one equivalent of PdCl₂ or with *trans*-Pd(py)₂Cl₂ the mono-



Scheme 15.

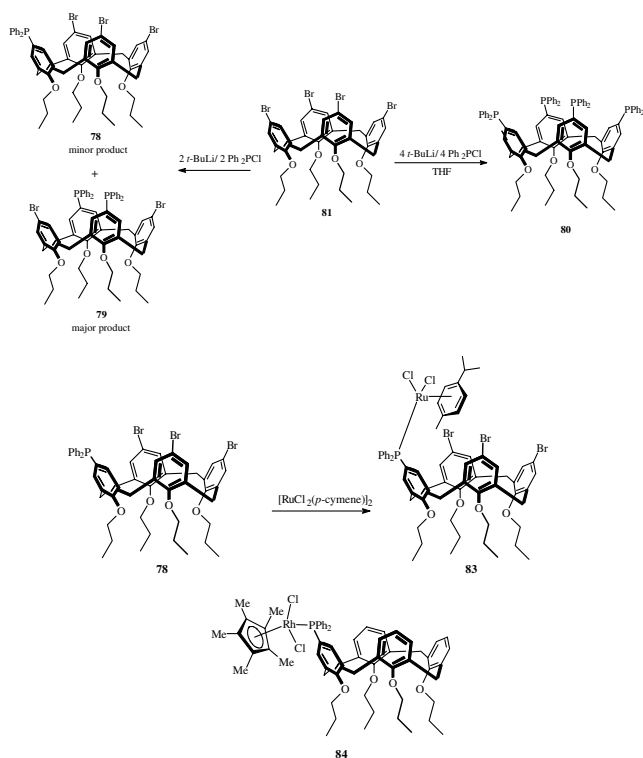


Scheme 16.

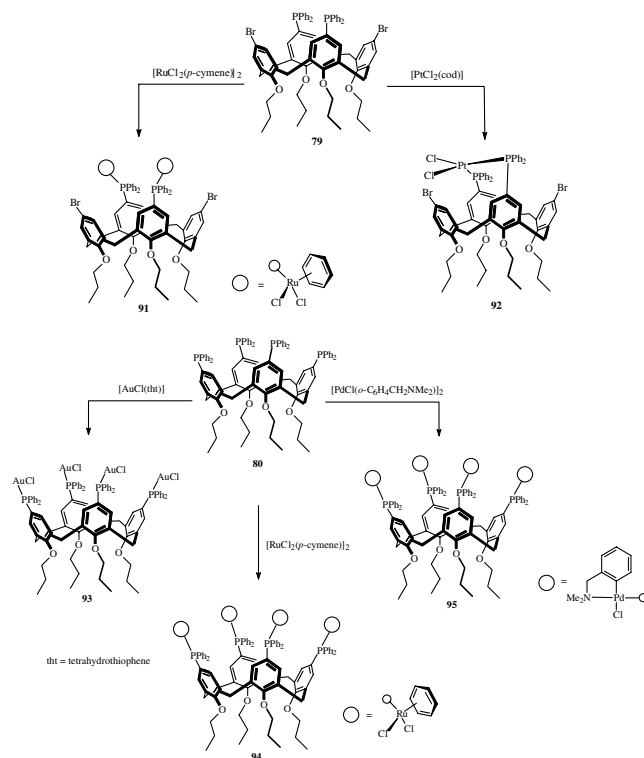
nuclear complex $\text{Pd}(\mathbf{107})\text{Cl}_2$, whereas with two equivalents of PdCl_2 the binuclear complex $\text{Pd}_2(\mathbf{107})\text{Cl}_4$ was formed (Scheme 23).

The same binuclear complex $\text{Pd}_2(\mathbf{107})\text{Cl}_4$ was obtained as the final product of the reaction of $\mathbf{108}$ (*i.e.* $\mathbf{107}$

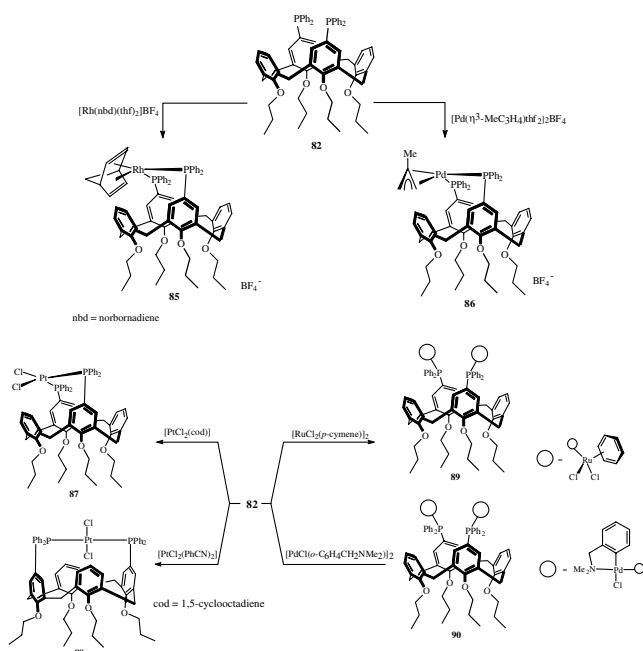
substituted by two BOC groups) with PdCl_2 proceeding *via* $\mathbf{110}$; during this process two BOC groups were successively removed. The reaction of $\mathbf{108}$ with PdCl_2 at room temperature gives $\text{Pd}(\mathbf{108})\text{Cl}_2$ in which two BOC groups remain. The treatment of this compound with



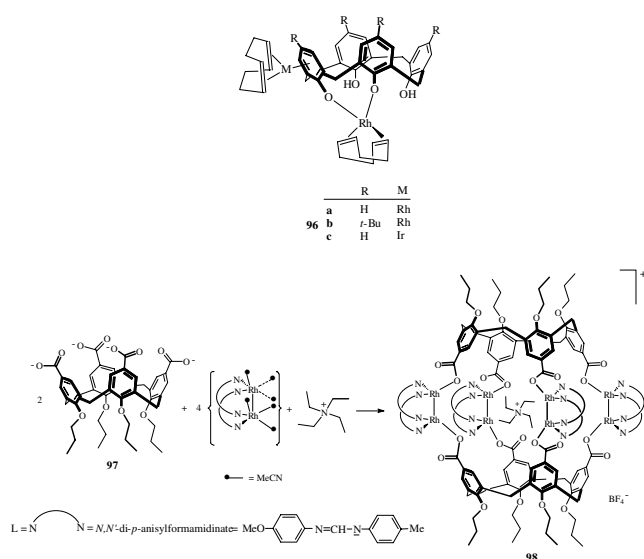
Scheme 17.



Scheme 19.



Scheme 18.



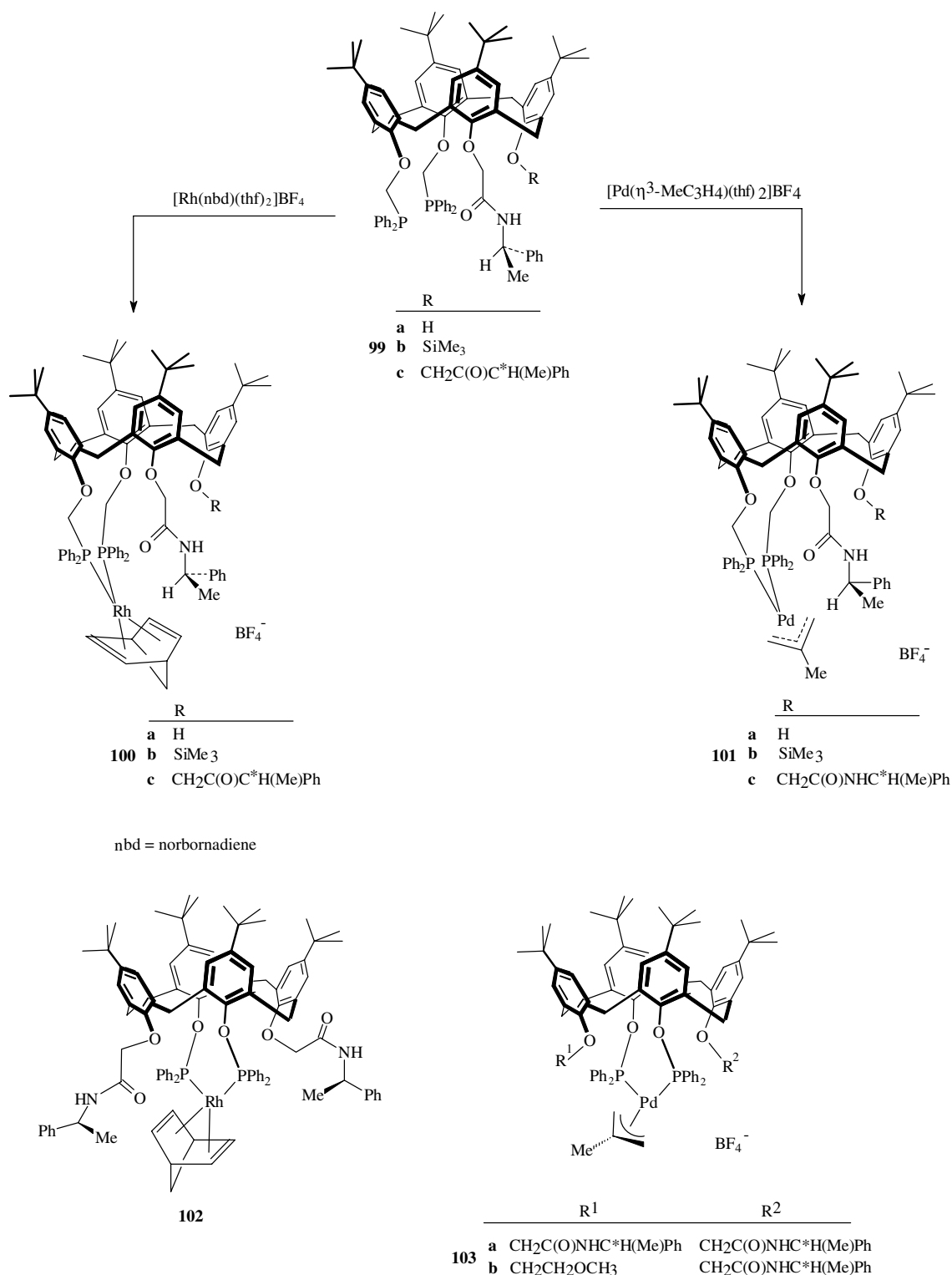
Scheme 20.

PdCl₂ in refluxing MeOH leads to **110** in which one BOC group was removed (Scheme 24).

The reaction of **109** bearing di- N-BOC-glycine units with PdCl₂ proceeds *via* **111** to give **112**; it was shown that in this case the BOC groups may also be successfully cleaved, and the Pd²⁺ complex **112** is not formed until both BOC groups are removed (Scheme 24).

The above results indicate that the detachment of BOC groups proceeds at higher temperature and is induced by PdCl₂, acting as a Lewis acid. This method is promising for the direct synthesis of Pd²⁺ complexes of calixarenes from species substituted at the lower rim by BOC-protected amino acids or peptides without previous treatment of BOC groups.

The reaction of cavitan **113** with [Pd(en)(NO₃)₂] leading to supramolecular bowls **114** and **115** has been made [114] (Scheme 25).

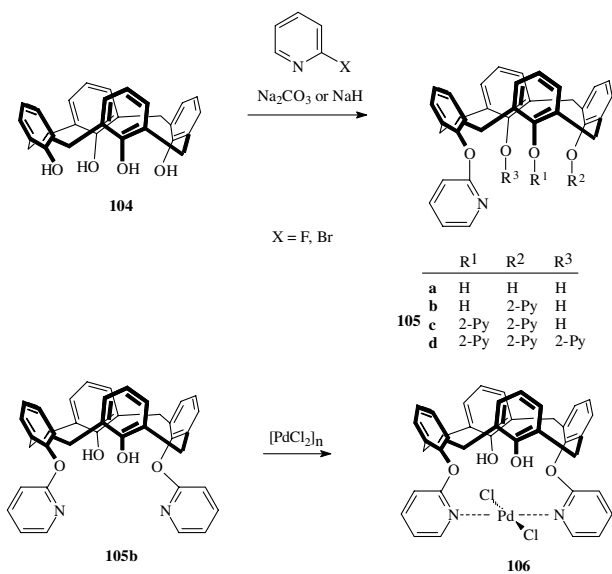


Scheme 21.

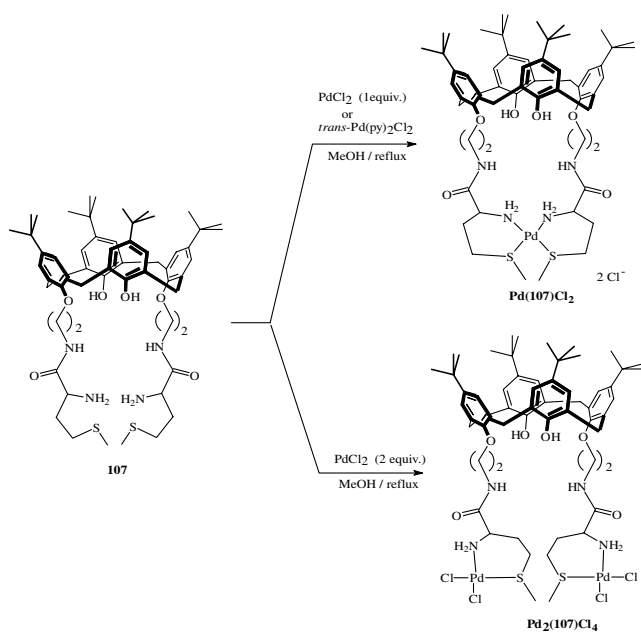
Self-assembly [115, 116] and especially metal-directed self-assembly [117] are interesting in the formation of two- and three-dimensional structures. The self-assembly of coordination cages both in solution [118–120] and immobilized on gold surfaces [118] has been studied. Mixing of cavitand **116** and $[M(dppp)(OTf)_2]$ (where $M = Pd, Pt$ and $dppp =$

1, 3-bis(diphenylphosphino)propane) gave cages **117a, b** able to bind to a gold surface by their thioether groups (Scheme 26).

The formation of coordination cages on gold may be performed by two ways: a) the direct insertion of cages formed in solution into a SAM (self-assembled monolayer) of 11-mercaptoundecanol on gold leading to



Scheme 22.

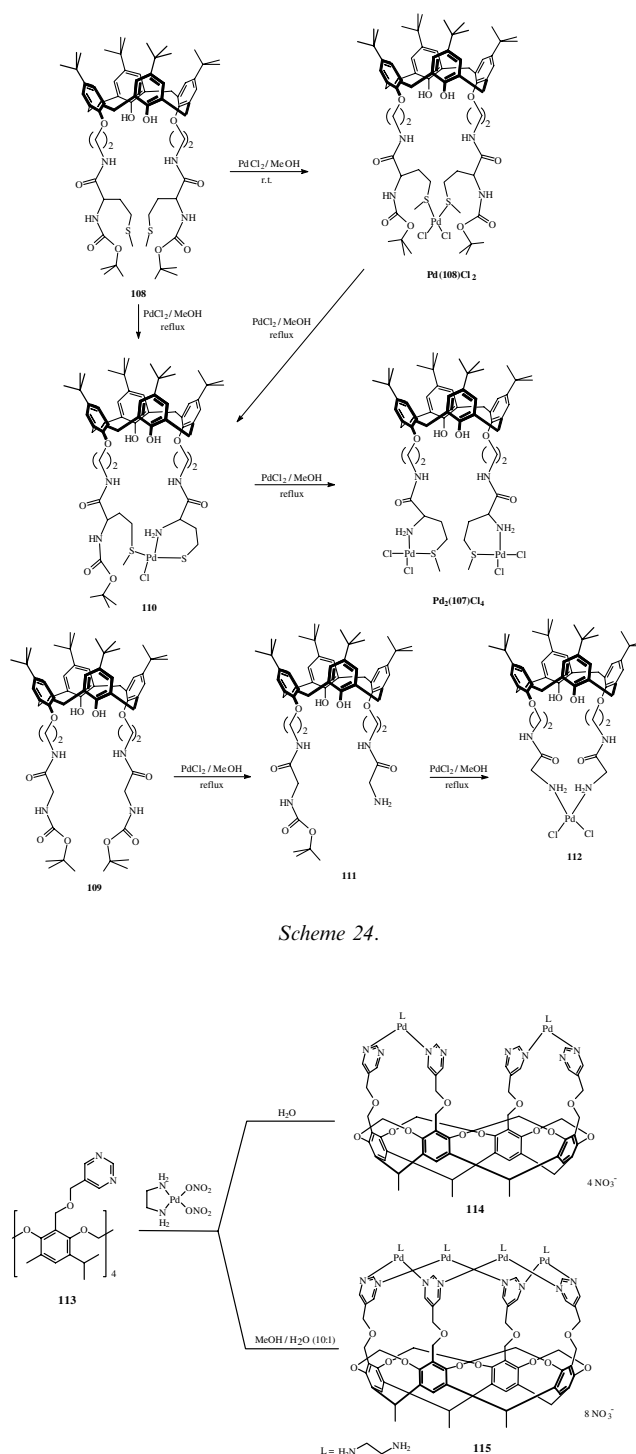


Scheme 23.

immobilized homocages; b) the insertion of the thio ether – footed cavitaund into an 11-mercaptoundecanol SAM, followed by assembly of cages *via* complexation of a different cavitaund from solution, leading to immobilized heterocages.

The insertion and assembly processes were monitored with AFM (atomic force microscopy) by measuring the height of cavitaunds (2,5 nm) and cages (5, 8 nm). When SAM of **116** is exposed to a solution of cage **118** in CH_2Cl_2 , the assembly of heterocage **119** on gold takes place, its formation involving the ligand exchange (Scheme 26).

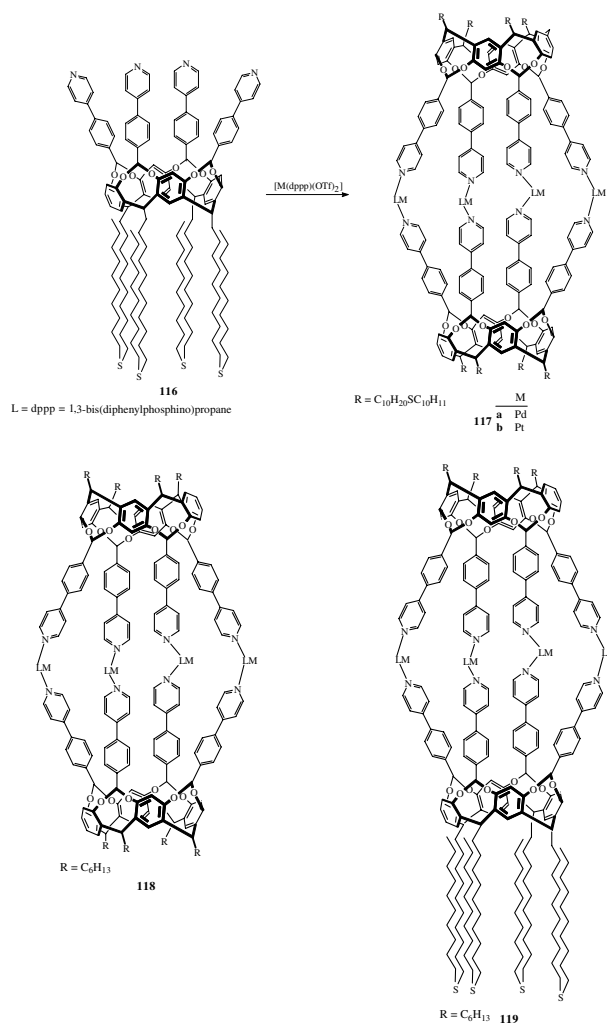
A disassembly of cages **117a** immobilized on gold surface was made by exposing a gold substrate with inserted **117a** to a solution of triethylamine in CH_2Cl_2 .



Scheme 24.

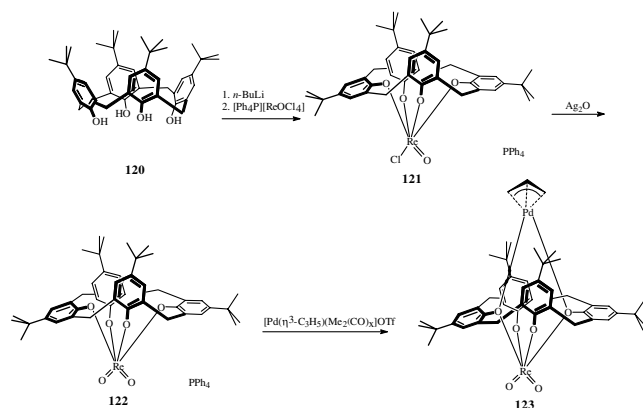
Scheme 25.

Since triethylamine competes with Pd coordination centres, it may disassemble a part of cages **117a** with the formation of free cavitaunds **116** and $[\text{Pd}(\text{dppp})(\text{NEt}_3)_2(\text{OTf})_2]$ molecules. This observation confirms the fact that metal-directed self-assembly of cages is a reversible process. So homo- and heterocages are interesting, for example homocages may be used to attach gold colloids from solution and form “sandwich” structures.

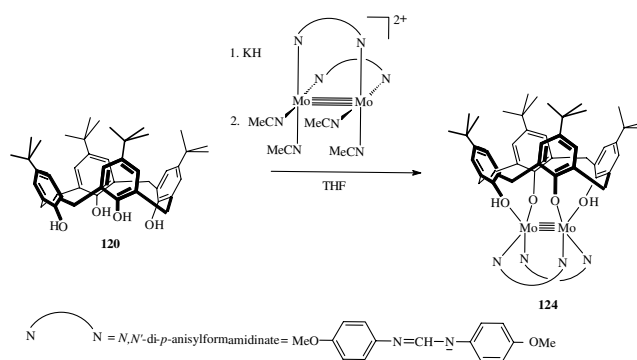


Scheme 26.

Calixarene **120** affords mononuclear Re⁴⁺ and Re⁷⁺ complexes **121** and **122**, respectively [121]. They are rather rare calixarene-rhenium complexes in which the metal atom is directly bound to the body of calixarene, although calixarene derivatives containing a rhenium complex moiety as a pendant group are known [122,



Scheme 27.



Scheme 28.

[123]. Compound **122** has an anionic character, therefore it may give the heterodinuclear Re–Pd complex **123** by treatment of its ethanolic solution with the solvated allyl–palladium complex Pd(η^3 -C₃H₅)(Me₂CO)_x](OTf), where OTf = OSO₂CF₃. Such heterodinuclear complexes of calixarenes are not so common as homodinuclear species [124] (Scheme 27).

Calixarene Complexes with Molybdenum, Tungsten and Titanium Ions

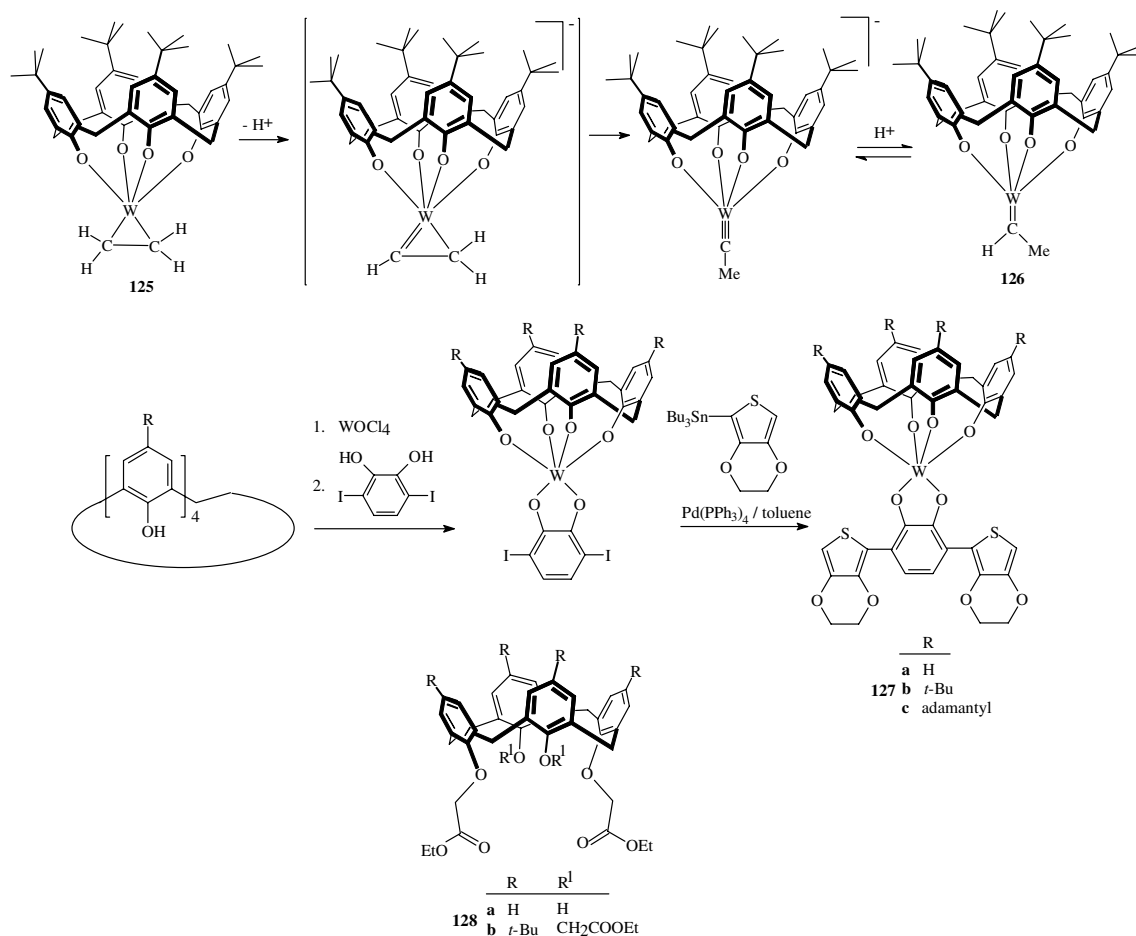
Reaction of calix[4]arene **120** with [Mo₂(*cis*-L)₂(MeCN)₄](BF₄)₂ where L = N, N'-di-*p*-anisylformamidinate leads to dimolybdenum complex **124** [103] (Scheme 28).

In the study of calixarene-tungsten complexes the deprotonation – protonation reaction of compound **125** leading to **126** has been investigated by density functional calculations [125] (Scheme 29).

Rigid calixarene tungsten complexes **127a–c** have been obtained [126] (Scheme 29). Complex **127c**, containing four adamantyl units has a large deep cavity and shows a specific recognition of *p*-xylene. Polymeric films incorporating **127c** electropolymerized in the presence of *p*-xylene show higher conductivity than films deposited in the absence of *p*-xylene. These highly conductive polymers are promising in the design of sensors for aromatic analytes.

One should also mention organic–inorganic assemblies formed from calixarenes **128** and Keggin polyoxotungstate sodium salt (Na₃PW₁₂O₄₀) by host–guest interaction between organic host and the sodium ion [127]. For their preparation solutions of **128** in CHCl₃ and Na₃PW₁₂O₄₀ in MeOH were mixed. The obtained assemblies have a porous structure showing guest-sorption capabilities (Scheme 29).

Titanium calixarene complexes are catalysts of various reactions. It was observed that compounds **129** and **130** catalyze epoxidation of allylic alcohols, their catalytic properties being enhanced in the presence of 4 Å molecular sieves [128]; the epoxidation of geraniol **131** leading to epoxyalcohol **132** may serve as an example (Scheme 30). Titanium⁴⁺ complexes of calixarenes **104** and **120a, b** are effective catalysts in aldol reaction of Chan's diene **133**.



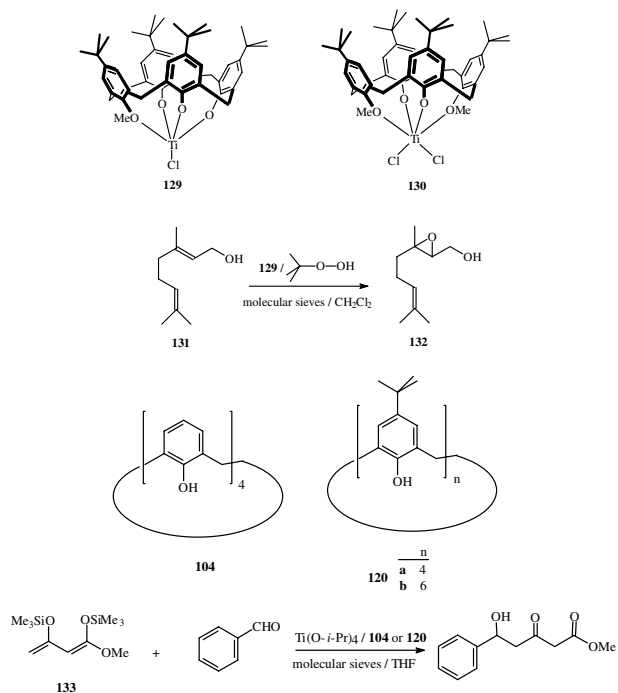
Scheme 29.

These compounds are formed *in situ* by treatment of appropriate calixarene with $\text{Ti}(\text{O } i\text{-Pr})_4$ [129] (Scheme 30).

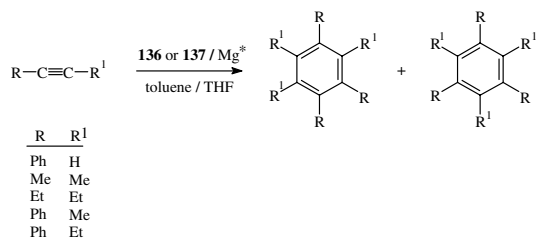
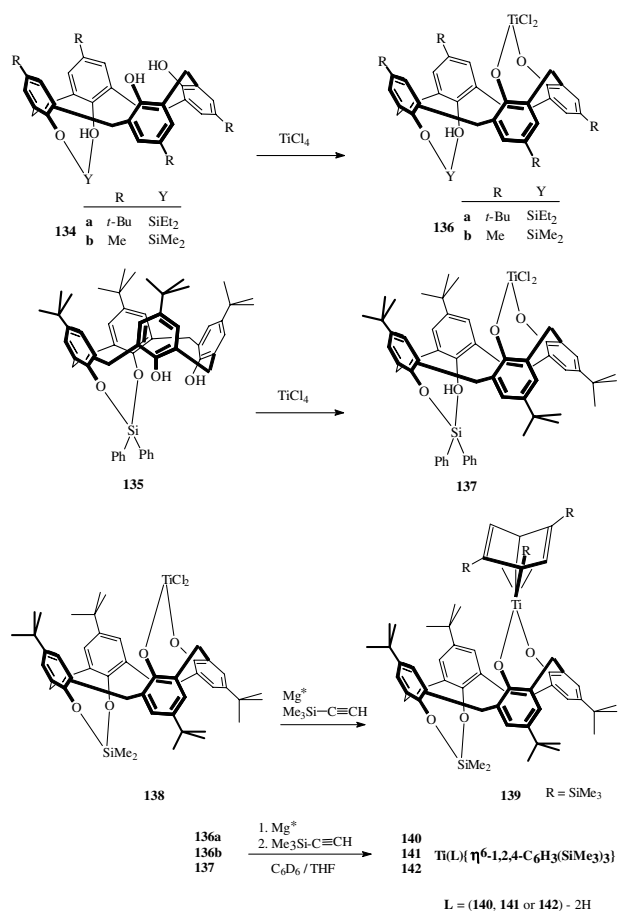
Reactions of proximally bridged calixarenes **134** and **135** with TiCl_4 afford titanium dichloride complexes **136** and **137** [130]. It should be noted that in the synthesis of **137** the cone conformation of **135** changes into 1, 2-alternate one (Scheme 31).

The reduction of **138** with activated magnesium (Mg^*) in the presence of $\text{Me}_3\text{SiC}\equiv\text{CH}$ gives titanoboradiene complex $\text{Ti}(\text{L})\{\eta^6\text{-1, 2, 4-C}_6\text{H}_3(\text{SiMe}_3)_3\}$ **139** ($\text{L} = \text{138-2H}$). Activated magnesium Mg^* was generated from $\text{C}_{14}\text{H}_{10}\text{Mg}(\text{THF})_3$ by release of anthracene in C_6D_6 containing 2% THF. Similar reduction of **136** and **137** leads to titanoboradiene complexes **140-142** (Scheme 31). It was observed that complex **139** catalyzes cyclotrimerization of terminal alkynes leading to 1, 2, 4-substituted benzenes at room temperature [131], and complexes **136** and **137** in the presence of Mg^* catalyze cyclotrimerization of terminal and internal alkynes (Scheme 31).

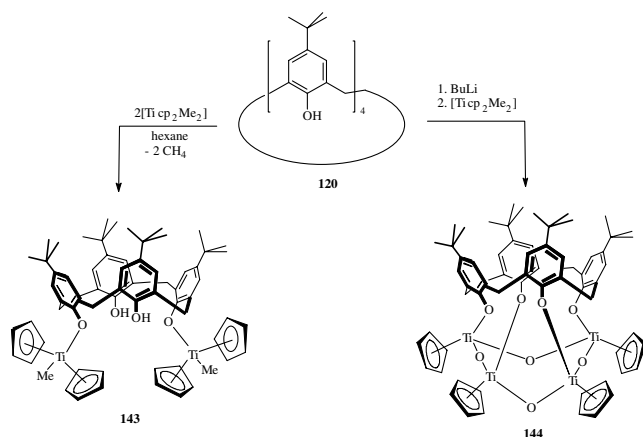
In the study of titanocenecalixarenes [132] syntheses of dinuclear and tetranuclear titanium⁴⁺ calix[4]arene complexes **143** [133] and **144** [134], respectively, have been made (Scheme 32). Reactions of **145** with *p*-tolyl isocyanate, CO_2 and CS_2 give monometallic **146** and



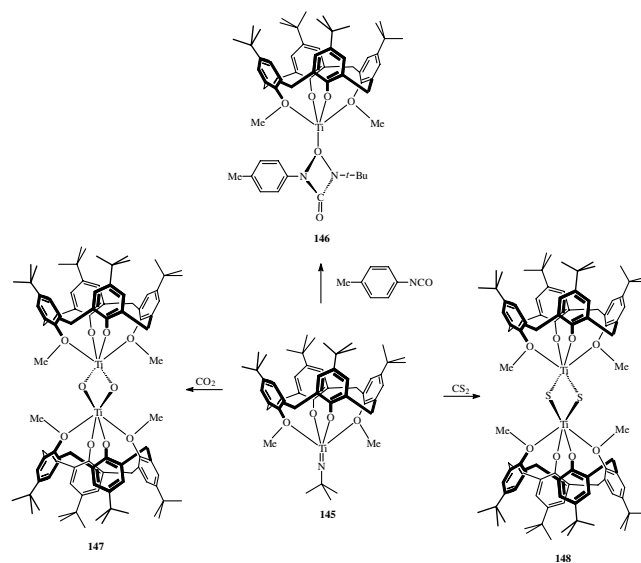
Scheme 30.



Scheme 31.



Scheme 32.



Scheme 33.

bimetallic **147** and **148** complexes, respectively [135] (Scheme 33).

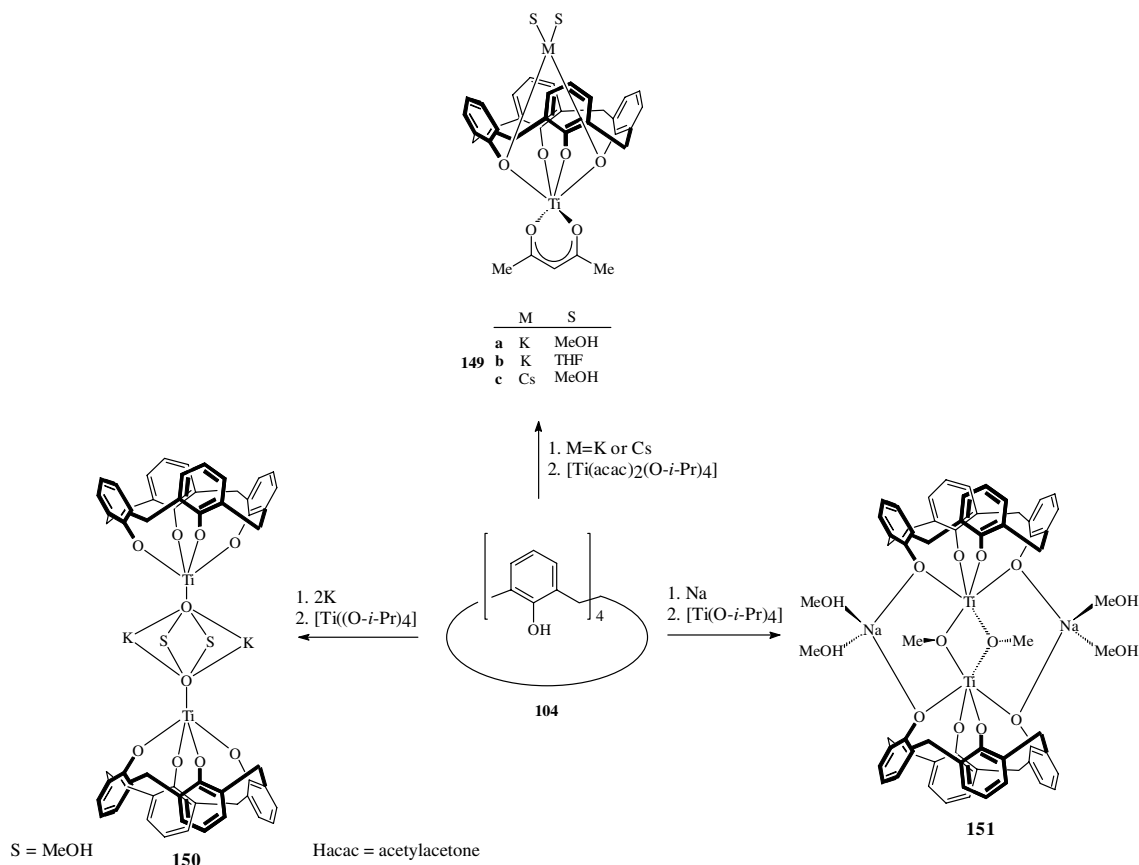
Many heterobimetallic alkali metal ion / transition metal ion complexes of calixarenes have been reported [136]. The partial deprotonation of calixarenes by alkali metal was used for the synthesis of monomeric and dimeric titanium⁴⁺ complexes. Deprotonation disrupts the strong H-bonded array of calixarene phenolic groups and solubilizes the formed calixarene anion.

Using calixarene **104** as a starting material, in the case of K and Cs, the monomeric Ti⁴⁺ complexes **149** are obtained, the oligomer formation being inhibited by an acetylacetonate ligand. In the absence of acetylacetonate the reaction leads to the dimeric complex **150**. With the use of Na the dimeric complex **151** is formed [137] (Scheme 34).

In investigation of larger calixarenes, the synthesis of the unsymmetrical dimeric 1:1 Ti/K complex **152** built up from a Ti-O-Ti core with each titanium⁴⁺ centre octahedrally coordinated with calix[5]arene and acac molecules has been reported [138] (Scheme 35).

Titanium-strontium, titanium-barium and zirconium-barium calix[6]arene complexes **153**, **154** and **155**, respectively, have been obtained by deprotonation of calix[6]arene with strontium or barium and the subsequent treatment with Ti(O-*i*-Pr)₄ (for **153** and **154**) or with Zr(O-*n*-Bu)₄ (for **155**) [139, 140] (Scheme 35). Calix[4]arenes form complexes with metal ions, usually in cone conformation [141]. Since the conformation of larger, calix[6–8]arenes is more flexible than that of calix[4]arenes, their complexes have not been so intensively studied as those of calix[4]arenes [124, 132, 142].

Deprotonation of calixarenes **104** or **120a** with potassium, and the subsequent reaction with [Ti(acac)₂(O-*i*-Pr)₂] leads to monomeric Ti/K complex **156**. Reaction with Ca, Sr, or Ba metals followed by the



Scheme 34.

addition of $[\text{Ti}(\text{acac})_2(\text{O}-i\text{-Pr})_2]$ affords dimeric complexes **157** or **158**, respectively (Scheme 36). In the above procedures the use of inert atmosphere is not necessary. Dimers **157** and **158** sublime under high vacuum, annealing of the sublimate to give a crystalline perovskite phase [143].

Calixarene Complexes with Lanthanide and Actinide Ions

In the preparation of radioactive stents to be used for the treatment of restenosis, the β -emitting isotopes, for example ^{90}Y have been incorporated into sulfur-containing adsorbates; in this way the gold surface may be covered with a self-assembled monolayer (SAM). It was established that **159**, incorporating yttrium $^{3+}$ as a potential radioisotope may serve as such an adsorbate [144] (Scheme 37).

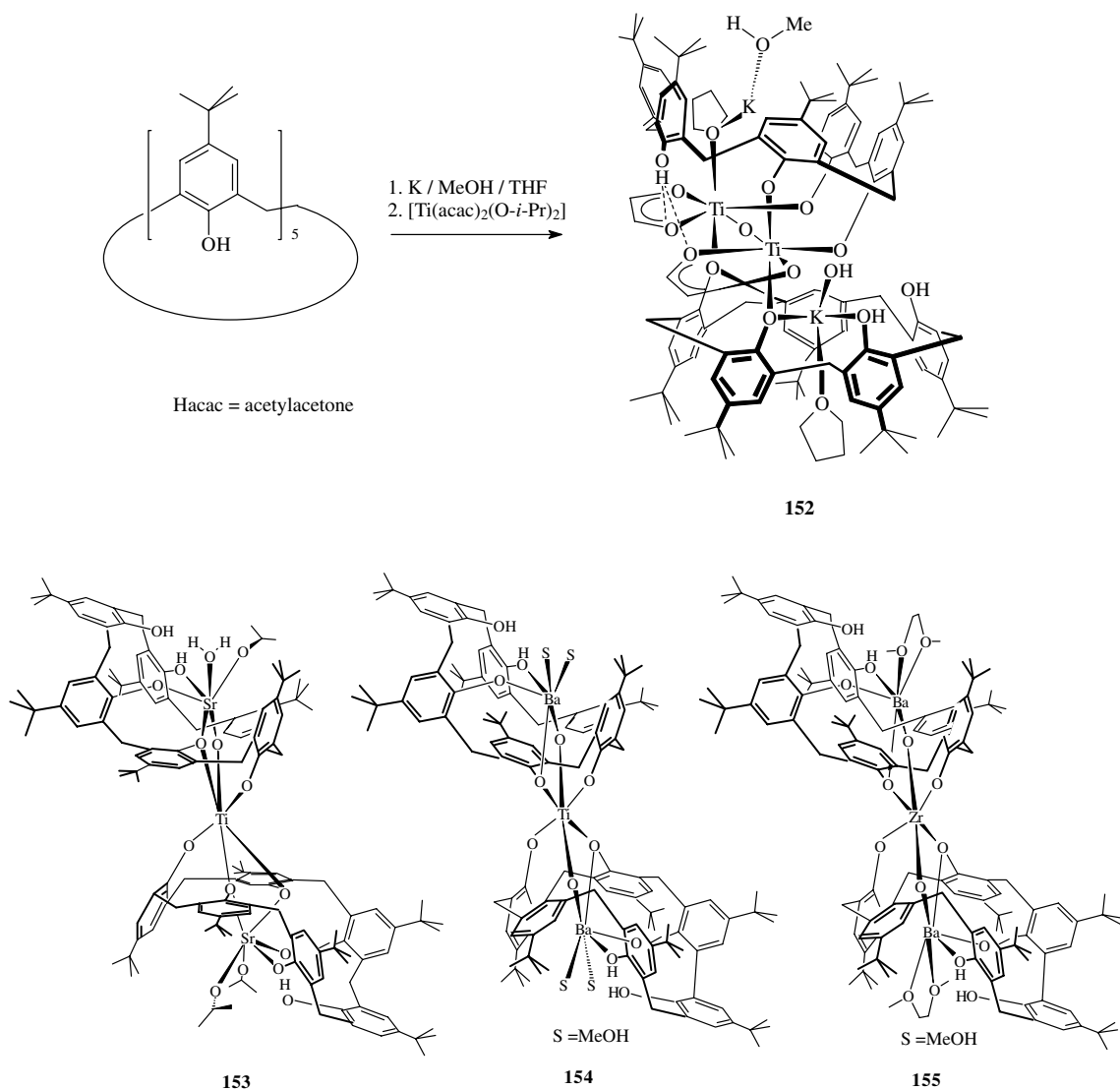
The synthesis of scandium and lutetium calixarene complexes **160a** and **160b, c**, respectively, has been made [145] (Scheme 37). It was observed that the reaction of sodium sulfonatocalix[4]arene **161** with scandium $^{3+}$ triflate in the presence of [18]crown-6 affords the crystalline complex incorporating capsules **162** [146] (Scheme 37).

Numerous lanthanide [147–149] complexes, e.g. those of La^{3+} [150], Eu^{3+} [151], Gd^{3+} [152] and

Tb^{3+} [153] are known. In the study of complexation of the water-soluble *p*-sulfonatocalix[4]arene **163** by the La^{3+} ions [154, 155], the 1:1 complex formed was thermodynamically characterized by ^{139}La NMR analysis. The complexation occurs in acidic medium (pH 2) and is entropy driven [154–156] (Scheme 37).

Reduction of calixarene **164** affording **165** and the subsequent Schiff base formation lead to calixarene **166** (Scheme 38). The stability constant values for complexation of **166** with light lanthanide $^{3+}$ nitrates (La–Gd) have been obtained from calorimetric titrations in acetonitrile [157]. It was found that **166** shows higher binding properties for lanthanides studied (except for La^{3+}) than **164** and **165** do, the highest in the case of Eu^{3+} , due to the exact match of this ion with pseudocavity formed by narrow rim and flexible vanillin side-arms. The above selectivity of complexation of Ln^{3+} ions is promising for the separation of the lanthanide family species.

The Ln^{3+} complexation in nonaqueous media is useful in separation and purification of lanthanides. It should be pointed out that in view of the industrial development of lanthanide complexes as optics and magnetic materials, their recycling is of a great importance. The complexation of calixarenes **167–169** with trivalent cations La^{3+} , Pr^{3+} , Nd^{3+} , Eu^{3+} , Gd^{3+} , Tb^{3+} , Er^{3+} , Ho^{3+} , Yb^{3+} , Sc^{3+} , and Y^{3+} has been investigated in two dipolar aprotic media—in acetonitrile



Scheme 35.

as a protophobic solvent and in DMF as a protophilic solvent [42] (Scheme 38).

^1H NMR and conductance measurements show the 1:1 stoichiometry of complexes. Stability constants of complexes have been determined by UV spectrophotometric titration and by competitive potentiometric titrations, the latter method based on a competitive reaction between Ln^{3+} ion and an auxiliary Ag^+ ion. The complexation is enthalpically controlled.

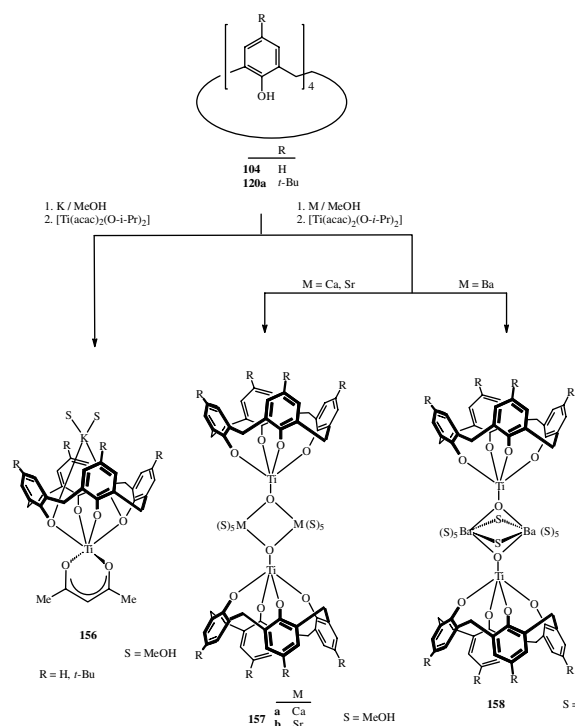
The basicity of **167–169**, and as a result, the stability constants of their Ln^{3+} complexes increases in the order **167** < **168** < **169**. Stability constants and derived standard Gibbs energies, enthalpies and entropies show that **168** is not able to distinguish among the trivalent cations in MeCN due to a considerable enthalpy–entropy compensation effect, however **169** distinguishes between these cations in MeCN, and to a lesser extent in DMF.

Complexation of resorcinarenes **170** with Tb^{3+} in liquid monolayers and multilayered LB films deposited on hydrophobic substrates has been investigated

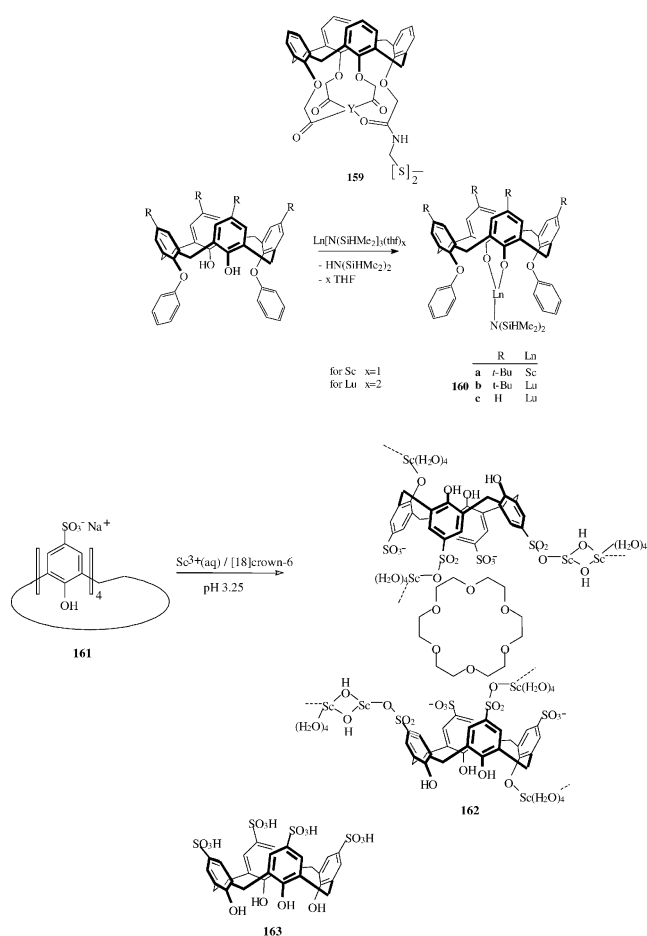
(Scheme 38). Compounds **170** have been used to prepare liquid monolayers on subphases of Milli-QTM water and Tb^{3+} aqueous solution [158]. LB films on hydrophobic substrates have been characterized using UV–VIS and emission spectroscopies. The UV–VIS spectra have shown the same structural conformation of molecules in solution and in LB films. Analysis of emission spectra obtained from the solution and the LB films indicates the formation of excimer aggregates in the films.

It was observed that calixarene fluoroionophores **171** and **172** form complexes with Nd^{3+} , Yb^{3+} and Eu^{3+} ions in acetonitrile solution [159] (Scheme 38).

In the study of larger calixarenes the reaction of calix[9]arene **173** with PCl_5 has been made. The formed **174** affords upon hydrolysis the threefold bridged *p-t*-butylcalix[9]arene phosphate **175**, existing in three conformations A–C. The treatment of **175** with the shift reagent $[\text{Eu}(\text{fod})_3]$, (where fod = tris(1, 1, 1, 2, 2, 3, 3-heptafluoro-7, 7-dimethyl-4, 6-octanedionate)) yields the complex of a proposed structure **176**, resulting from



Scheme 36.



Scheme 37.

the attack of europium ion on P¹O and P³O groups of **175B** [160] (Scheme 39).

The reaction of sodium *p*-sulfonatocalix[6]arene and pyridine *N*-oxide with ytterbium³⁺ nitrate pentahydrate in water affords the *p*-sulfonatocalix[6]arene/pyridine *N*-oxide/ytterbium³⁺ complex **177** with the calixarene molecule in the “up-down” conformation [161]. Complex **177** may self-assemble into extended sheets *via* hydrogen bonding and CH- π interactions, by formation of C-shaped dimers similar to that of calix[4]arene analogue **178** [162] (Scheme 39). It should be pointed out that *p*-sulfonatocalix[6]arenes are more flexible [163, 164] than their *p*-sulfonatocalix[4]arene analogues, and therefore they have been not so intensively investigated as the latter ones.

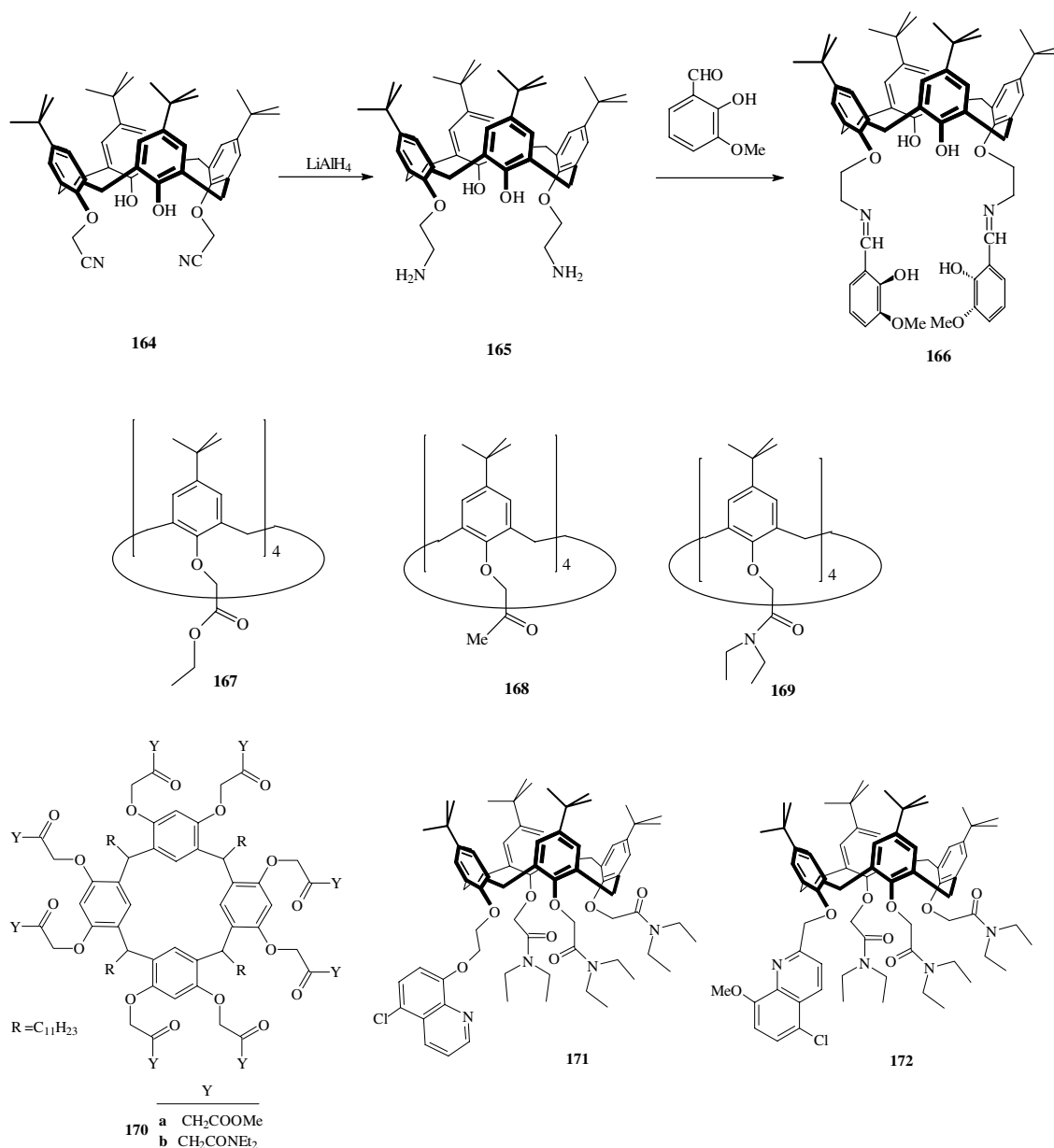
Lanthanide *p*-sulfonatocalix[6]arene crown ether complexes **179** and **180** have been synthesized and their conformations studied [163]. Complexes **179** and **180** have the calixarene in the “up-up” double core conformation (Scheme 40). Complex **179** has a “ferris wheel” arrangement in which europium centres are coordinated to a sulfonate group and to the crown ether, in a similar way as in the case of *p*-sulfonatocalix[4]arene [165]. Complex **180** forms a molecular capsule enveloping two crown ether molecules. One should also mention compound **181**, which is an example of La³⁺ complex with palladacalix[4]arene [166] (Scheme 40).

Chemistry of actinides is of importance in the aspect of nuclear waste remediation [167, 168]. Having in mind that phosphorus-containing calixarenes are useful in the separation of lanthanides and actinides [169, 170], compounds **182** [171], **183** [171] and **184** [172] have been synthesized and their distribution coefficients for the extraction of La³⁺, Ce³⁺, Nd³⁺, Sm³⁺, Eu³⁺ and Am³⁺ investigated. It was found that **182** and **183** show higher extraction efficiency of actinides and lanthanides from a strongly acidic aqueous phase to an organic phase than **185**, used as an industrial extractant.

In the extraction of lanthanides (La, Ce, Nd, Sm, Eu) and americium ions from aqueous nitric acid to *o*-nitrophenyl hexyl ether, **183a** has proven to be more efficient extractant for all cations than **184a**; both **183a** and **184a** show a significant selectivity for the extraction of Am³⁺ over Eu³⁺, higher for **184a** than for **183a** (Scheme 41).

Compounds **186** and **187** have been synthesized for the two-phase solvent extraction of lanthanide and uranyl ions from aqueous wastes [173] (Scheme 41). Electrospray MS shows that smaller lanthanide ions form with calixarenes investigated the 1:1 complexes, while in the case of larger Ln ions the 2:2 complexes are obtained. Compound **187a** forms with uranyl ion a dimeric complex (UO₂)₂(**187a-2H**)₂. It was found that de-*t*-butylated (**186a**) and dinitro (**186b**) calixarenes are more efficient extractants of uranyl ion than **187a-c**.

It was established that calix[6]arene **188** forms with UO₂(NO₃)₂·6H₂O three complexes: [UO₂(**188**)]⁻, [UO₂(**188**)H] and [UO₂(**188**)OMe]²⁻ [43] (Scheme 41).



Scheme 38.

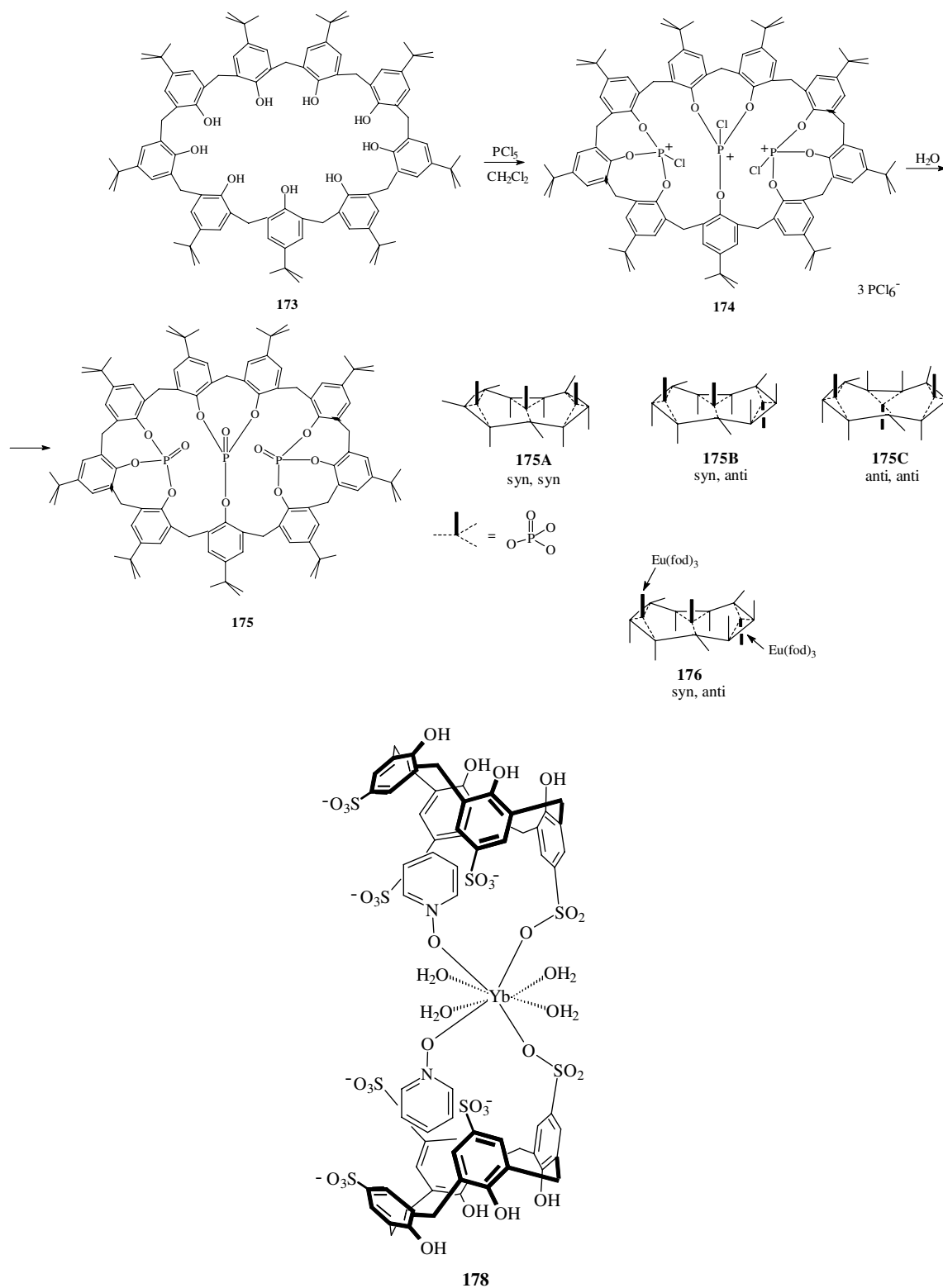
The synthesis of the complex **189** has been made; it crystallizes as a cyclic trimer, with the three uranium atoms forming approximately an equilateral triangle in which each edge is bridged by two chlorine atoms. Complex **189** is a rare example of a mixed chloro aryloxide of uranium⁴⁺ [174] (Scheme 42).

In order to investigate the influence of a lanthanide ion on the reaction of calix[6]arenes with $[\text{UO}_2\text{Cl}_4]^{2-}$ ions, the mixture of *t*-Bu-calix[6]arene (**H₆L**, i.e. **120b**) and $[\text{HNC}_5\text{H}_5]_2[\text{UO}_2\text{Cl}_4]$ was treated with $\text{La}(\text{OTf})_3$ in pyridine; as a result two complexes **190** and **191** were formed.

Compound **190** is a heterotrimeric complex $[\text{U}\{\text{H}_2\text{L}\}\text{LaCl}_2(\text{NC}_5\text{H}_5)_2]$ organized around a U^{4+} center, coordinated by two calix[6]arene molecules in a 1, 2,

3-alternate conformation. Each of both La^{3+} ions is coordinated by a hydroxyl group, four pyridine molecules and two chloride anions (Scheme 42). Compound **191** is a heterodecametallic complex $[\text{ULa}_9\text{O}_8\text{Cl}_{15}(\text{OTf})_6(\text{NC}_5\text{H}_5)_9]^{4-}$ organized around a UO_6 moiety, in which all six O^{2-} ligands bind lanthanum ions. The central core of **191** is shown in a simplified way in Scheme 42.

It should be pointed out that **190** and **191** are rather uncommon 4f–5f heterometallic complexes. In the above reaction the $\text{U}=\text{O}$ bond has been activated at room temperature; the uranyl cation (UO_2)²⁺ has been transformed into U^{IV} in **190** and into central UO_6 unit in **191** [175].

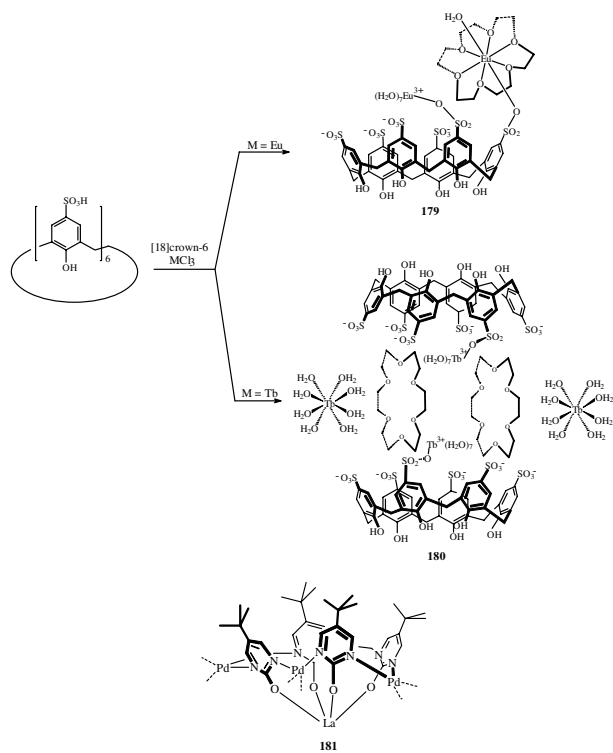


Scheme 39.

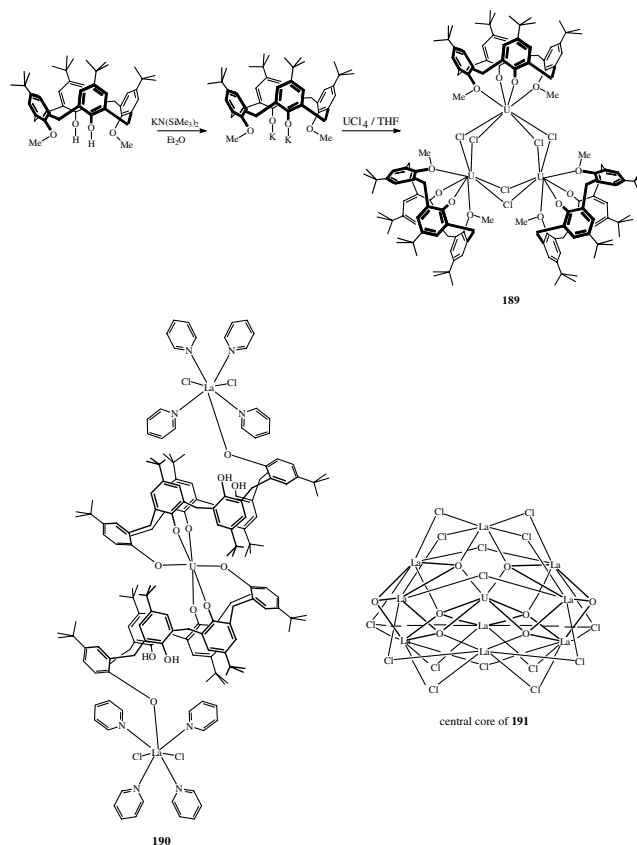
Conclusion

The chemistry of calixarenes, including calixarene transition metal complexes is developing rapidly. This area attracts attention so from theoretical as practical points of

view. Calixarene transition metal complexes are promising for construction of electronic devices and sensors. By using in the removal of metal ions from waste they are valuable in the environment protection, their application in the nuclear waste management being of a great importance.

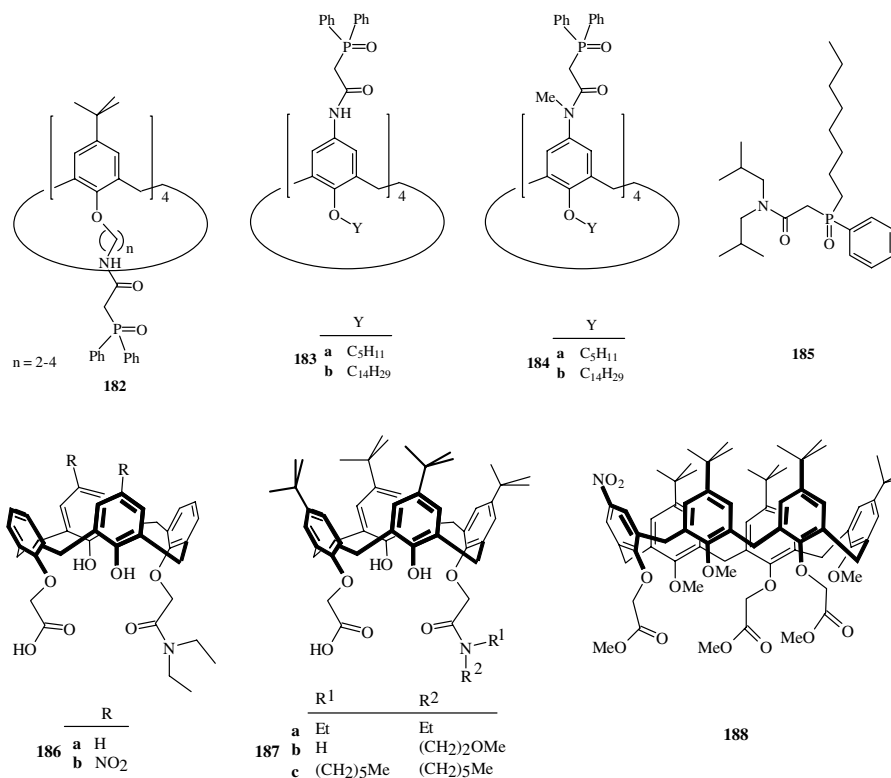


Scheme 40.



Scheme 42.

The large number of recently appeared works concerning calixarene transition metal complexes is a reflection of their interesting properties and possible applications [176–180].



Scheme 41.

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