Chemistry of Cavitands

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Abstract: In the paper selected examples of cavitands are presented showing their binding properties. In the first part cavitands with one or two extended walls are described, the second part concerns deep cavitands, and in the third part examples of cavitands forming open capsules are given.

Keywords: Binding, capsule, cavitand, conformation, receptor.

INTRODUCTION

Cavitands are a topic of numerous reports due to their interesting receptor properties [1-5]; they are formed from resorcinarenes or pyrogalloarenes by linking the adjacent hydroxyl groups of the wide rim mostly with a methylene group, although phosphocavitands [6] are also known. These species have enforced cavities able to confine suitable organic compounds or ions; their cavity is an extended π surface while the upper rim often forms a seam of hydrogen bonds.

The present review is a continuation of our former papers concerning cavitands [7,8] as well as calixarenes as metal-ion receptors [9,10] and components of calixarene assemblies [11]; resorcinarenes [12], calixpyrroles [13] and calixarenes bearing azaromatic moieties [14] have also been reported.

In the paper at first cavitands with one or two extended walls, larger than other walls are described, the second part deals with deep cavitands; finally some examples of cavitands forming open capsules are shown. The review does not cover works concerning various types of capsules [15,16] nor tubes [17,18] formed from calixarenes. The references are cited mainly of reports appeared since 2005.

1. CAVITANDS WITH ONE OR TWO EXTENDED WALLS

The binding properties of salen functionalized cavitand (**1a**) and its metal-free analogue (**1b**) were studied and compared with those of the salen unit (**2**). Investigating behavior of choline and its derivatives it was observed that cavitand (**1a**) catalyzes the acetylation of choline (**3**) with acetic anhydride [19]; this reaction performed in the presence of **1a** is faster than in the case of the salen unit (**2**). The cavitand (**1a**) was also used in the hydrolysis of *p*-nitrophenyl choline carbonate (**4**) [20]. The hydrolysis occurred by water contained in commercial CH_2Cl_2. Similarly as in the case of acetylation of choline it was found that the reaction in the presence of **1a** is faster than in the case of **2** and of the metal-free cavitand (**1b**).

Cavitands (**1a**) and (**1b**) have the vase conformation; the seam of hydrogen bonds formed by six secondary amide groups stabilizes this shape, however the dynamic exchange is possible, i.e. guests may enter and depart by the folding and unfolding of the cavitand. The guests bearing a tri-methylammonium group, such as choline derivatives bind strongly within cavitands, their trimethylammonium group sealing one portal. It was found that **1a** forms with 1,2-dioleyl-sn-glycero-3-phosphocholine (**5**) the inclusion complex in which the zinc ion is coordinated to the phosphate group of **5** [21-23]. The results of isothermal titration calorimetry (ITC) indicate that the binding constant of **1a** with **5** is higher than those of **2** and of the cavitand (**6**) with **5** [24-26]. The above observations show the synergic effect between the metal center and the cavity. It should be pointed out that the trimethyl-ammonium group of **5** is situated deeper in the cavity of **1a** than in the cavity of **6**.

Partially bridged (i.e. containing four non bridged hydroxyl groups) cavitand (**7**) is a receptor for steroids (**8a-c**) and (**9a-c**) [27]. Only unsaturated steroids are bound, their association strength being higher when the ring A is flattened and carbonyl group is present in the 3 position and hydroxyl groups in 11 and 17 positions; CO and OH groups form hydrogen bonds with resorcinarene skeleton. It was found that the association constants of **7** with steroids (**8**) and (**9**) increase in the order **8a** < **8b** < **9b** < **9a** < **8c** < **9c**.

Cavitands can be reversibly switched between vase and kite conformations upon variation of temperature, pH or metal-ion addition. For such investigation cavitand (**10**) bearing two donor (D) units at both ends and cavitand (**11**) bearing donor and acceptor (A) units at both ends have been synthesized [28]. Cavitands (**10**) and (**11**) exist in the vase conformation in $CDCl_3$ or $CHCl_3$ above 25°C; however upon lowering the temperature to -60°C or upon addition of TFA they adopt the kite conformation. Vase and kite conformations of **11** are schematically shown.

The presence of BODIPY (dipyrromethaneboron difluoride) group in the molecule enables the observation of switching of **10** and **11** by fluorescence resonance energy transfer (FRET). The fluorescence spectrum of **10** is nearly identical in the vase and kite forms, in the case of **11** however it differs considerably. Upon addition of TFA to **11**, the acceptor fluorescence diminishes, while the donor fluorescence doubles its intensity. In kite conformation of **11** the separation of donor and acceptor is ca 7 nm; due to this increased length of the spacer FRET is strongly reduced. This behavior results from the fact that the kite conformation of **11** is very rigid and strongly limits the available conformational space.

The *O*-alkylation reactions of cavitands (**12**) and (**13**) with **14**, i.e. the zwitterionic dioxane derivative of cobalt bis (dicarbollide) anion (**15**) lead to cavitands substituted with anion (**15**) at upper rim, i.e. **16**, and at lower rim i.e. **17** [29]. The ion (**15**) belongs to borane clusters of a very high thermal and chemical stability, which are similar to inorganic superacids [30,31]. It should be pointed out that **16** and **17** are well soluble in a large variety of solvents; they

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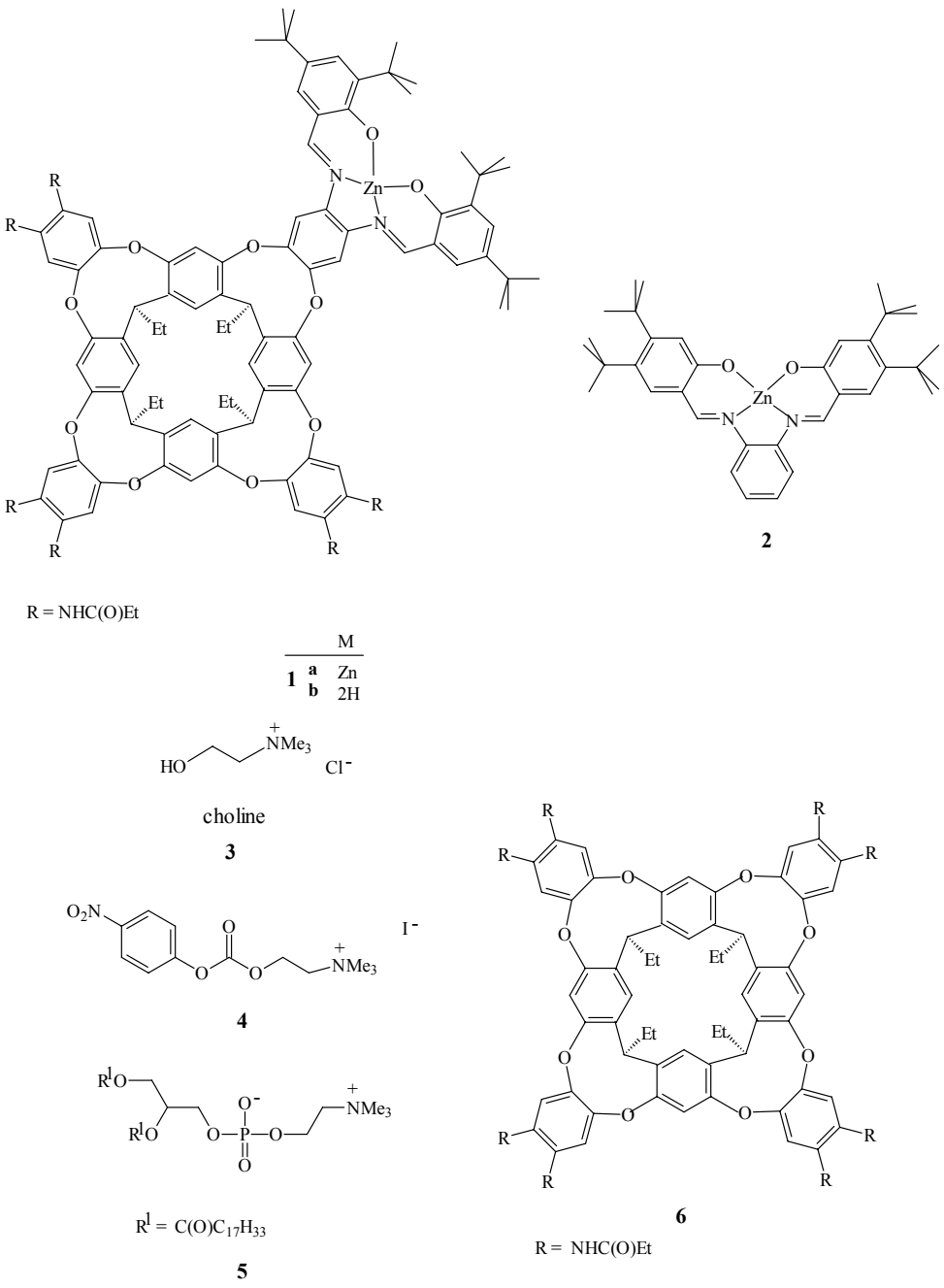


Scheme 1.

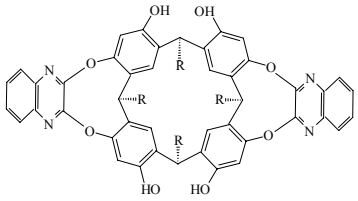
are bowl-shaped structures with properties of anions of strong, non-oxidizing inorganic acids and are of interest for design of cation-binding systems.

2. DEEP CAVITANDS

Cavitands (**18**) are deep, vase-like compounds able to encapsulate neutral and cationic guests of a suitable size. They contain on the upper rim eight secondary amide groups forming seam of hydrogen bonds which stabilizes the vase cavity; the interior of cavity has a π-electron rich surface.

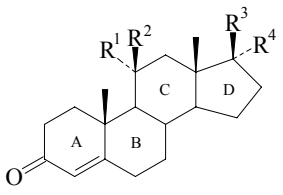
Cavitand (**18c**) served as a reaction vessel for α-deuteration of activated olefins with the use of methyl acrylate (**19**); the catalysis of this reaction was investigated [32-34]. Methyl acrylate (**19**) reacts with DABCO or quinuclidine serving as catalysts in the cavitand (**18c**) in acetone-d_6 to give α-D-methyl acrylate (**20**); it was observed that the deuteration is accelerated in the presence of cavitand. The rate acceleration may be explained by molecular modelling. Molecular mechanics minimization of the bound enolate formed after addition of catalyst shows a reorganization of the amide groups on the rim allowing the flexible cavitand walls to fold inward. As a result, the cavitand provides stabilization for the addition intermediate (**21**); due to this stabilization the deuteration is faster.

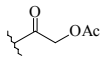
It was found that the cavitand (**18b**) may serve as a molecular reactor for Menschutkin reaction, for this purpose the quaternization of quinuclidine with a series of electrophiles was made. It was found that this reaction is facilitated when performed in the cavity of **18b** [24]. In its resting state, in acetone, the cavitand

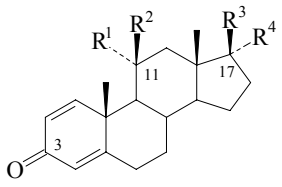


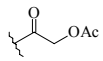
R = $C_{11}H_{23}$

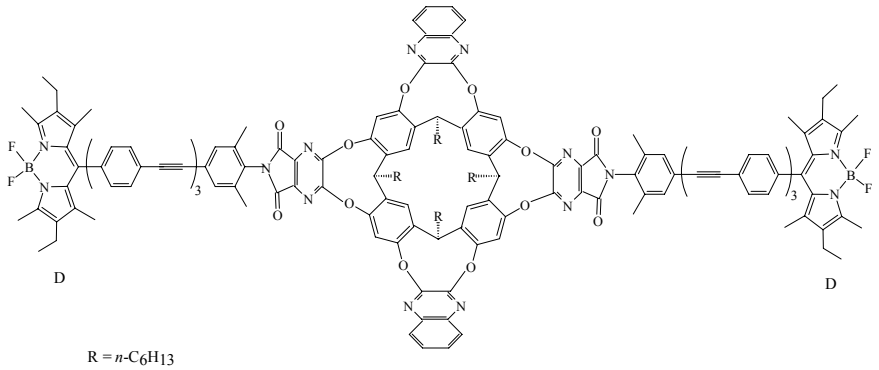
7



		R^1	R^2	R^3	R^4
8	**a**	H	H	H	
	b	H	H	H	
	c	H	OH	OH	

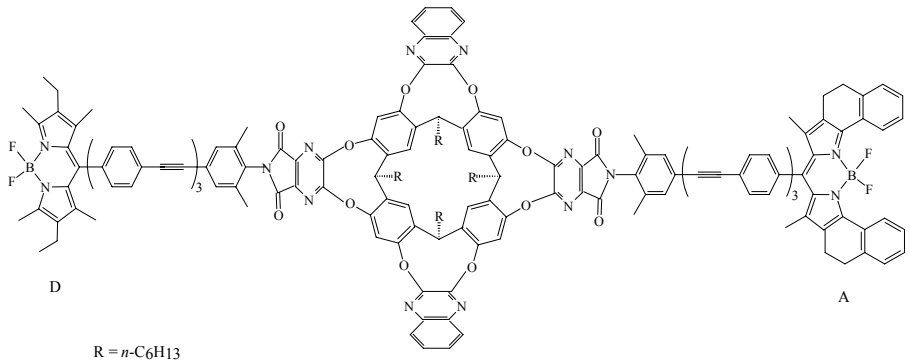


		R^1	R^2	R^3	R^4
9	**a**	H	H	H	H
	b	H	H	H	
	c	H	OH	OH	



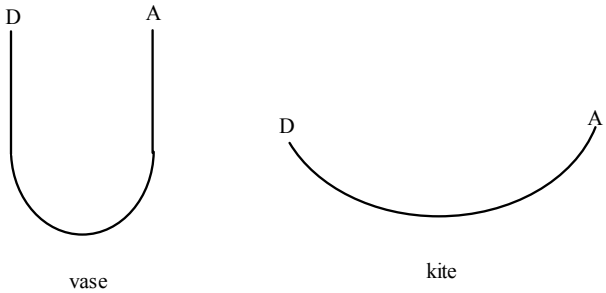
R = *n*-C_6H_{13}

10



R = *n*-C_6H_{13}

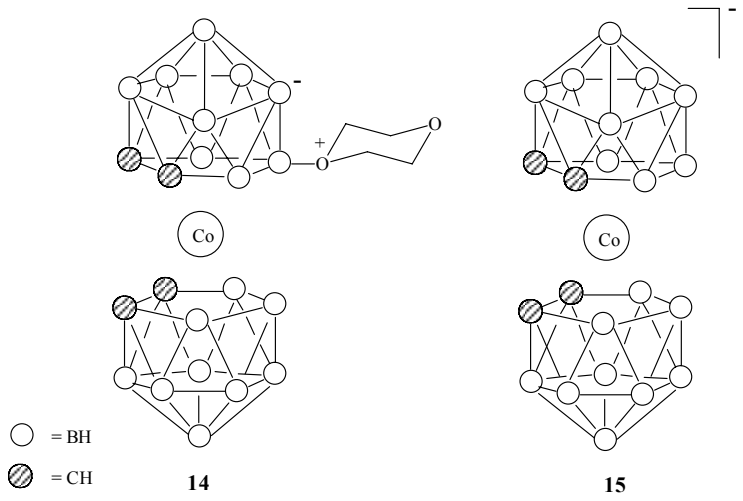
11



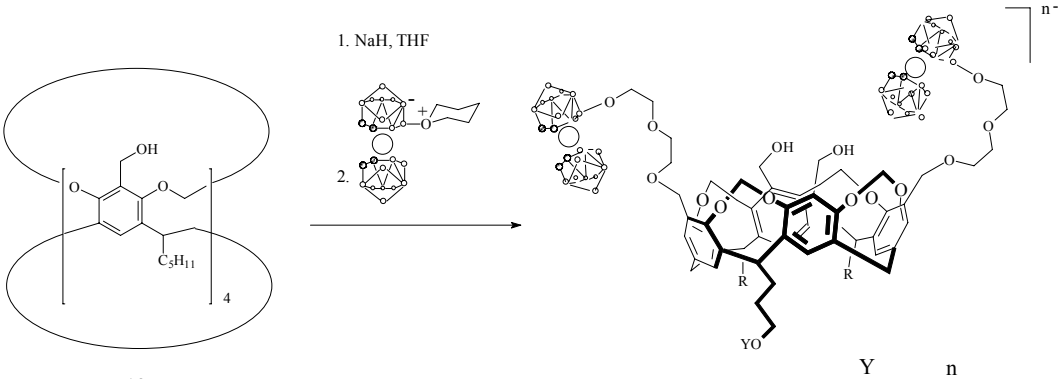
11

Schematically shown conformations of **11**

Scheme 2.

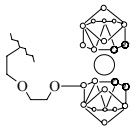


14 **15**

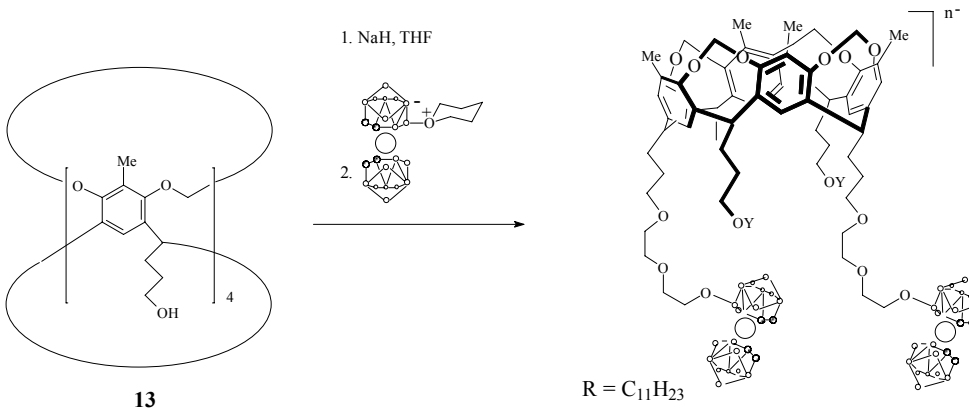


12

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

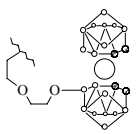
	Y	n
a	H	2
b		4

16



13

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

	Y	n
a	H	2
b		4

17

Scheme 3.

(**18b**) includes two molecules of acetone which exchange rapidly with the bulk solvent. Quinuclidine is a guest competing with acetone solvent by displacing its molecules. The formed inclusion complex of quinuclidine in **18b** reacts with the electrophile RX (the S_N2 reaction) to give N-alkylquinuclidinium embedded in **18b**. The reaction of quinuclidine with RX performed in **18b** is faster than that made in the absence of **18b**; the rate enhancement decreases in the order BuBr > BuCl > *i*-PrBr > allyl chloride.

Cavitand (**22**) containing four dichloropyrazine flaps exists only as a vase conformer, however, cavitand (**23**) containing four quinoxaline flaps exists as two stable vase and kite conformers. Protonation or metal ion coordination of the quinoxaline N-atoms of **23** favors its kite conformation due to electrostatic repulsion of adjacent cationic sites [35].

Properties of cavitand (**24**) bearing four benzimidazole flaps have been investigated. It was found that **24** can form very stable vase structures in which the cavity is enforced by intermolecular hydrogen bonding with four complexed molecules containing hydroxyl groups X-OH, such as water, methanol, acetic acid and trifluoroacetic acid. The stability of the vase structure of **24**·$(XOH)_4$ depends on the hydrogen bond donor strength of HOX which is comparable with their acidity. When hydrogen bond donor strengths of X-OH are high, the hydrogen bonds formed between hydroxyl groups and nitrogen atoms of the neighboring benzimidazole fragments are strong, and vase structures of **24**·$(XOH)_4$ are stable. An example of such structure is **24**·$4H_2O$.

The annular tautomerism of **24**·MeOH results from the proton exchange between NH groups and nitrogen atoms of the neighboring benzimidazole fragments; the equilibrium between two tautomers A and B exists. It was observed that cavitand (**24**) forms inclusion complexes with 4-methylbenzamide guests (**25**) and (**26**).

In order to investigate binding properties of cavitands bearing a charge on the upper rim, the complexation of cavitands (**27**) and (**28**) with adamantane derivatives was studied [36]. Cavitand (**27**) is soluble in water at pH 2.6; however under neutral conditions or at pH 4 the water solubility disappears. It was observed that **27** exists in the kite conformation; neither the presence of suitable guests, such as adamantane or adamantanecarboxylic acid nor elevated temperature (60°C) could induce the vase conformation. However when co-solvents such as DMSO, THF or MeOH were added, the vase conformation appeared.

Adamantane derivatives (**29**-**34**) were used as guests of cavitands (**27**) and (**28**). It was found that cavitand (**27**) binds negatively charged **29** and **30** stronger than **28** due to unfavorable electrostatic interactions in the case of **28**. Cavitands (**27**) and (**28**) show similar binding affinities with neutral adamantanes (**31**) and (**32**); cavitand (**27**) does not form complexes with positively charged adamantanes (**33**) and (**34**), however in the case of **28** a strong complexation occurs.

The deep, water-soluble cavitand (**28**) is stabilized in the vase conformation by an array of hydrogen bonds of water molecules situated at its upper rim. These hydrogen bonds do not allow the unfolding of the cavitand into kite conformation. The cavitand encapsulates *n*-alkanes (pentane to dodecane) *via* hydrophobic forces; alkanes coil in a helical manner to fill the space properly and tumble rapidly on the NMR timescale inside the cavity of **28** [37]. The complexation of **28** with sodium dodecyl sulfate (SDS) micelles has been investigated by NMR diffusion ordered spectroscopy (DOSY) [38]. Usually the guests with long alkyl chains adopt a coiled conformation to achieve a better fit with hydrophobic cavity of the cavitand. It was observed that **28** in water, at low concentrations includes SDS, however above cmc (critical micellar concentration) the roles of the host and the guest are reversed since SDS incorporates the cavitand.

Three tetrabenzamidazole cavitands (**35**-**37**) have been prepared and their binding properties with *n*-alkylammonium guests (**38**-**42**) have been studied [23]. The crystal of **35** obtained from CH_2Cl_2/EtOH has a vase conformation stabilized by four EtOH molecules which form hydrogen bonds with benzimidazole units. The cavity is filled with two additional EtOH molecules, one is embedded deep inside the cavity, and the second one is situated between benzimidazole and phenyl region. The cavitand (**35**) is one of the largest cavitands known, its volume of 300 $Å^3$ allows the inclusion of long alkyl ammonium salts. The structure of **37a** is similar.

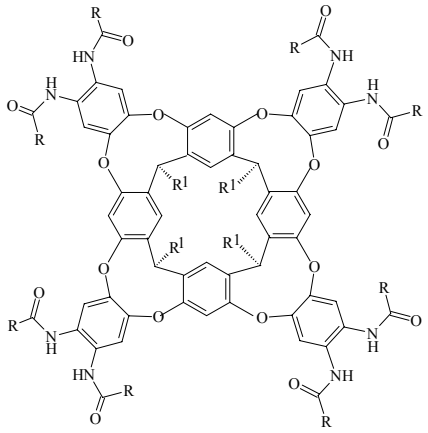
The binding constants of complexes of **35** with **38**-**42** decrease in the order **41** > **40** > **42** > **39** > **38**. The C_{4v} conformation of cavitand (**35**) is stabilized by the inclusion of guests (**40**-**42**) due to additional CH.... π interactions. It was found that cavitand (**43a**) catalyzes the aminolysis of *p*-nitrophenyl choline carbonate (**4**) [39]. It should be noted that the model 2-pyridone itself or the pyridine cavitand (**43b**) do not catalyze this reaction.

The isothermal microcalorimetry (ITC) study has shown that propyl ureidocavitand (**44a**) and propyl thioureidocavitand (**44b**) form inclusion complexes with formate to valerate anions in MeCN [40]. It was observed that glucose- and galactose containing thioureido cavitands (**45a**) and (**45b**), respectively, bind the acetate anion in MeCN/H_2O 1:1 more strongly than **44a** or **44b** do. The saccharide-functionalized acetylated thioureido cavitands (**46**) react with sodium methoxide to give nonacetylated species (**47**); glucose (in the case of **47a,c**), galactose (in the case of **47b**) and cellobiose (in the case of **47d**) served as saccharides.

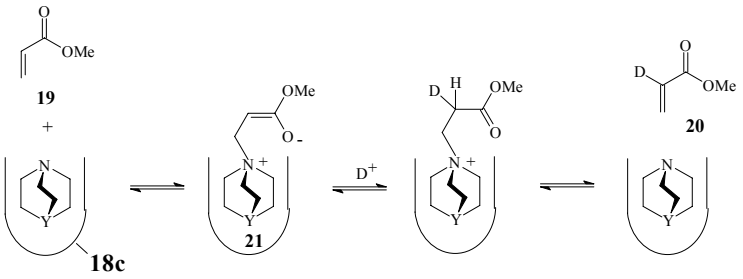
For comparative purposes gluco-thiamethyl cavitands which do not contain thiourea linker, i.e. **48** (acetylated) and **49** (nonacetylated) were used; deacetylation of **48** affording **49** proceeds as above, by sodium methoxide. It was observed that the solubility of **46** in MeCN is higher than that of the propylthiourea cavitand (**44b**). The solubility of **47** in water is higher than that of gluco-thiamethylcavitand (**48**) and increases in the order **47a** < **47b** < **47c** < **47d**, the very high water solubility of **47d** being due to the presence of four disaccharide moieties in the molecule.

The complexation of anions by acetylated species (**46**) and (**48**) and by deacetylated species (**47**) and (**49**) was investigated by ESI-MS (electrospray ionization MS) in acetonitrile and in a 1:1 acetonitrile/water mixture [41]. Due to the linear relationship between the square root of the intensity of the signal and the concentration of the formed 1:1 host-guest complex, novel methods (direct titration and competition experiments) have been developed for determination of K_a values. For **46a** and **46b** in MeCN the K_a values decrease in the order $Cl^- > HSO_4^- > NO_3^- > Br^- > I^-$; for **47a** and **47b** this sequence is $Cl^- > HSO_4^- > Br^- > NO_3^- > I^-$. In all cases studied, the preference for Cl^- ion was observed. It was established that the Br^- and I^- ions are more weakly complexed than Cl^- due to their softer character, in spite of their larger size; it was found also that the spherical Cl^- ion fits better into thiourea binding pocket than the tetragonal HSO_4^- or trigonal NO_3^- ions.

Functionalization of deep cavitand (**50**) was performed using directed *ortho* metalation [42]. Cavitand (**50**) has eight readily accessible aromatic hydrogen atoms situated in *ortho* positions to

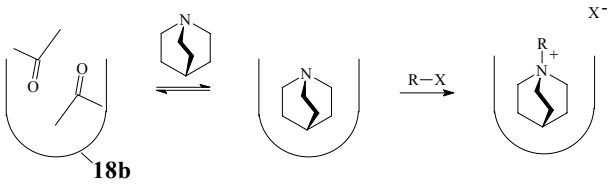


		R	R^1
18	**a**	Me	Et
	b	Et	Et
	c	Me	$C_{11}H_{23}$

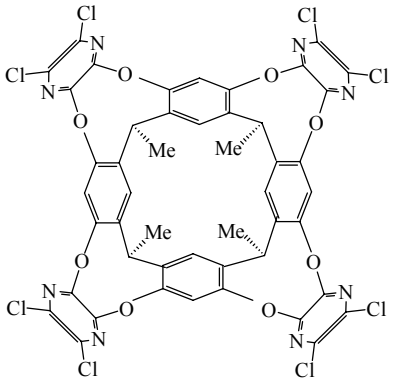


18c

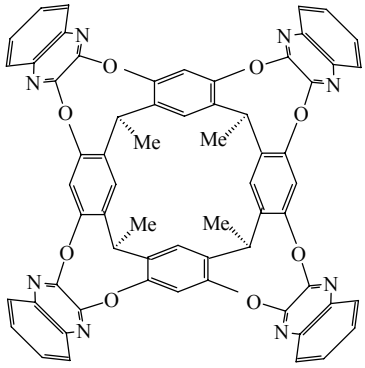
	Y
DABCO	N
quinuclidine	CH



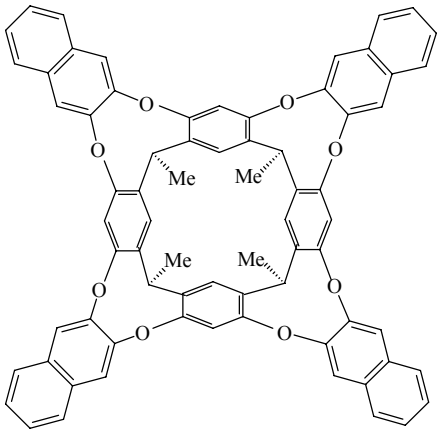
18b



22
vase

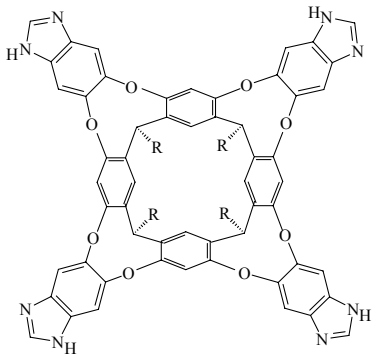


23
vase



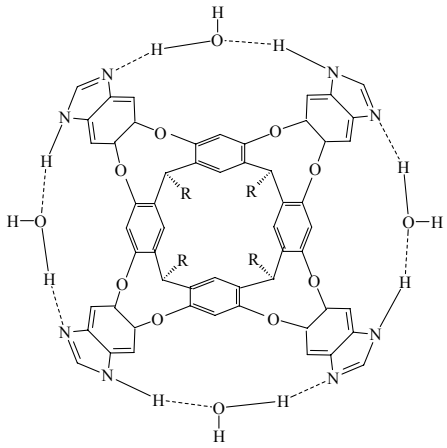
23
kite

(Scheme 4) contd…..



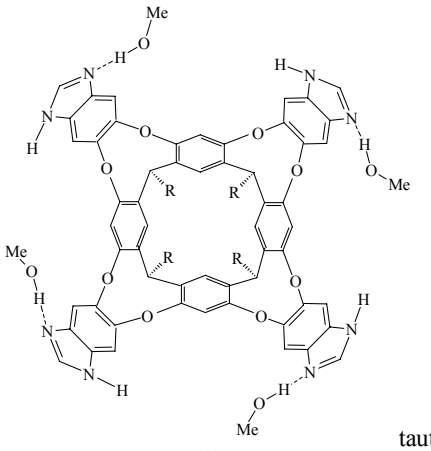
R = $C_{11}H_{23}$

24



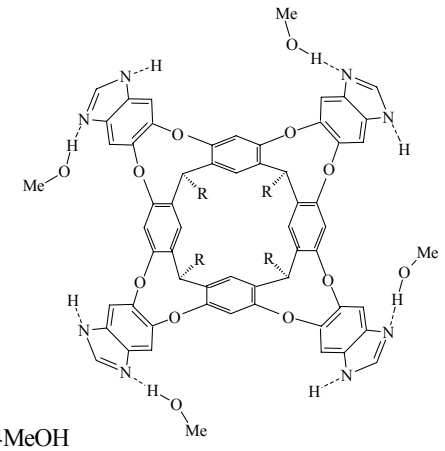
R = $C_{11}H_{23}$

24 · 4 H_2O



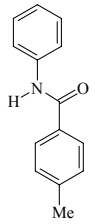
R = $C_{11}H_{23}$ A

tautomerism



B

tautomers of **24**·4MeOH



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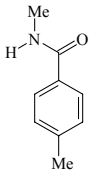

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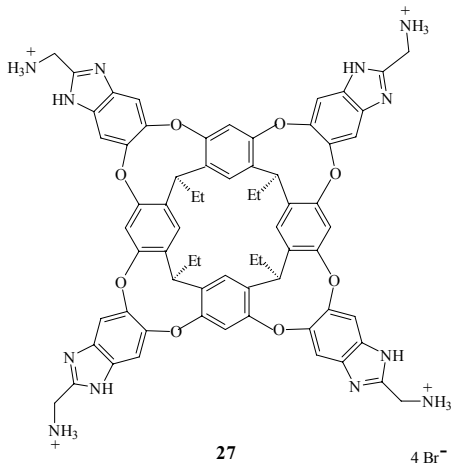
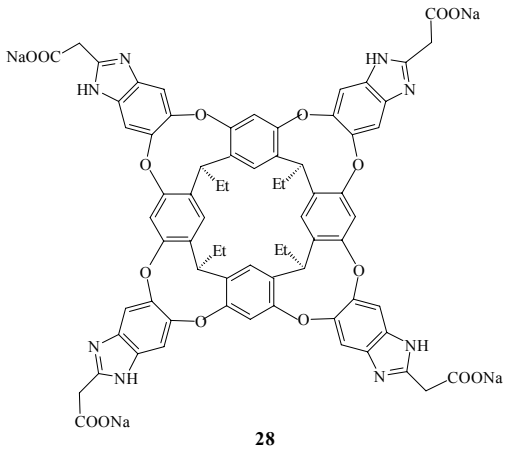


27 4 Br^-



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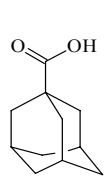

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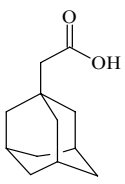

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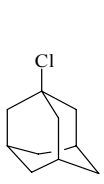

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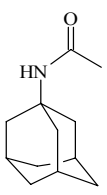

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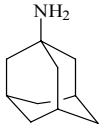

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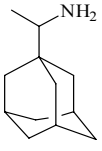
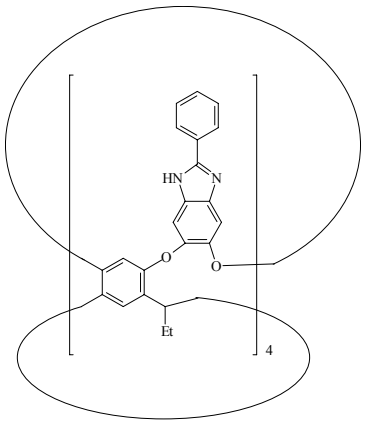


34

Scheme 4.



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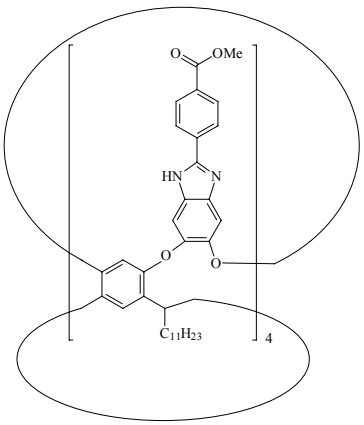

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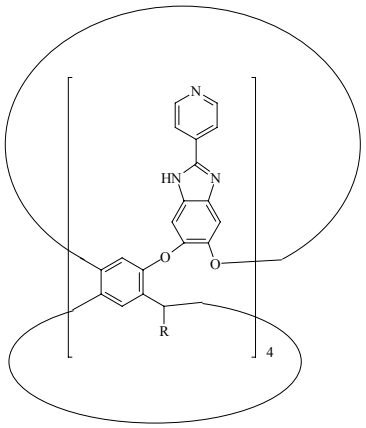
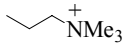
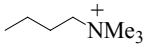
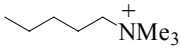
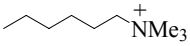
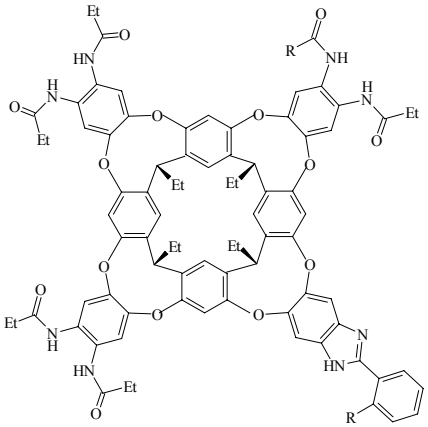
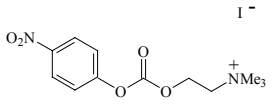


37

	R
a	Et
b	$C_{11}H_{23}$

	R $\overset{+}{N}Me_3$ Br^-		R
38		Br^-	Et
39		Br^-	*n*-Pr
40		Br^-	*n*-Bu
41		Br^-	*n*-C_5H_{11}
42		Br^-	*n*-C_6H_{13}

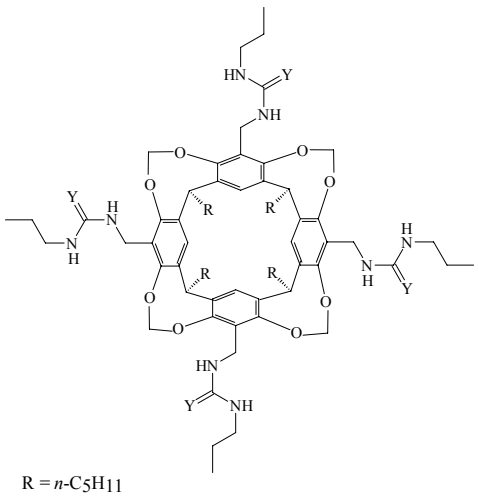




4

	R
a	
b	

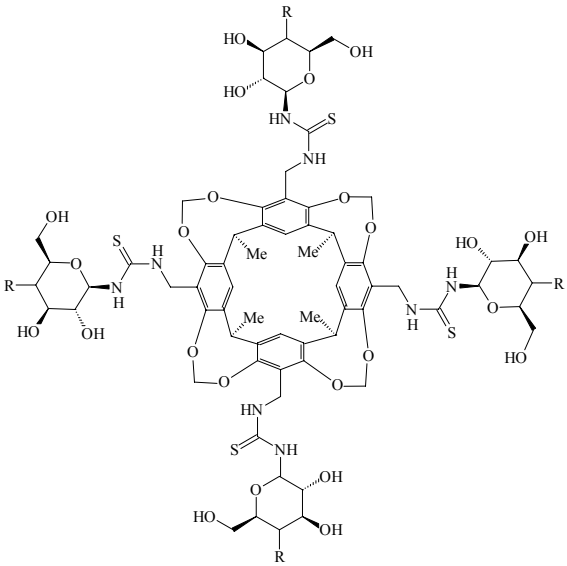
43



R = *n*-C_5H_{11}

	Y
a	O
b	S

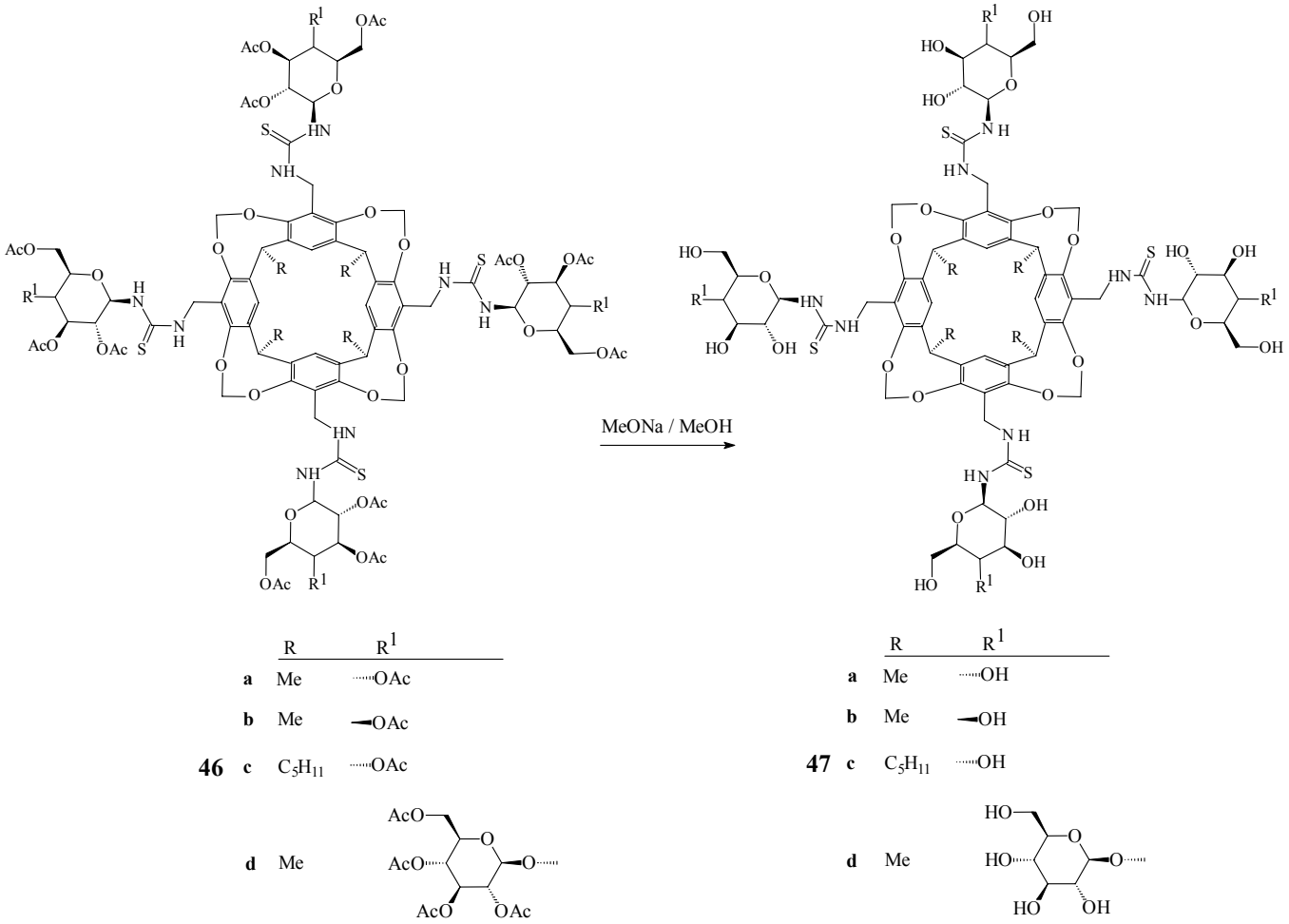
44



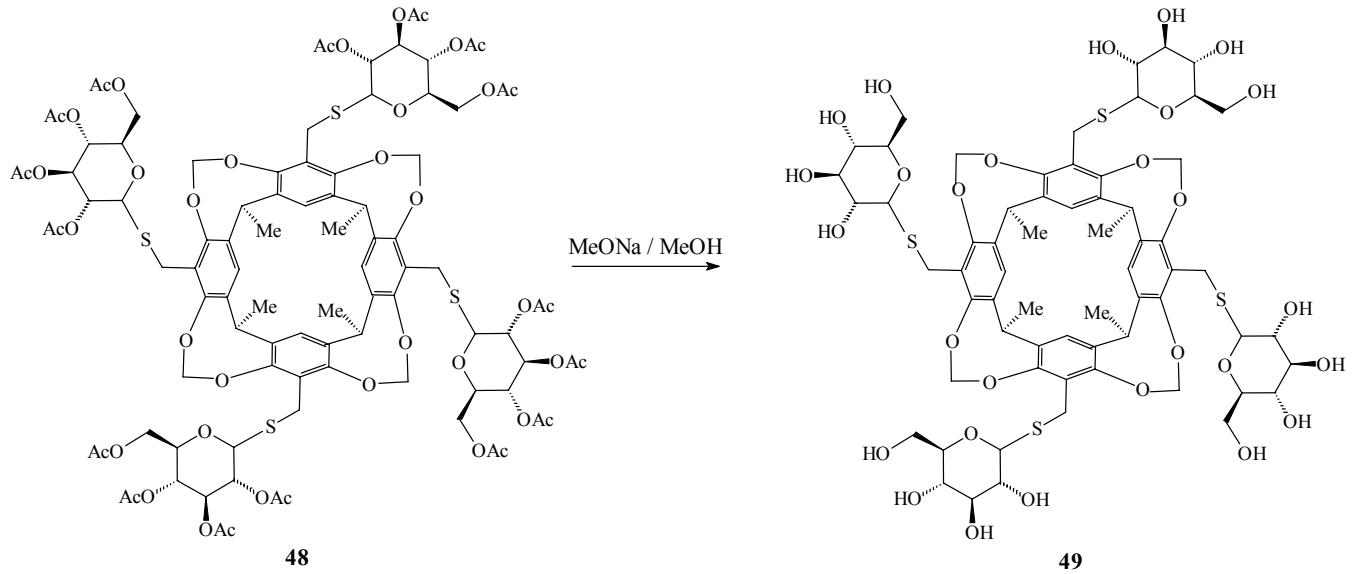
	R
a	····OH
b	▬OH

45

(Scheme 5) contd…..

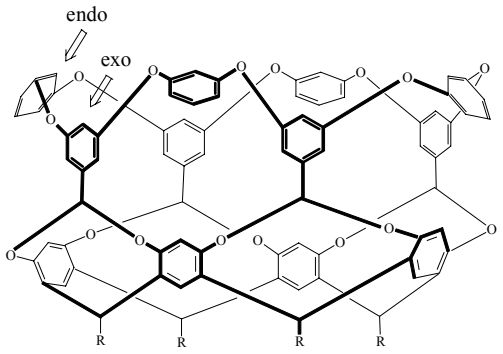


46 **47**



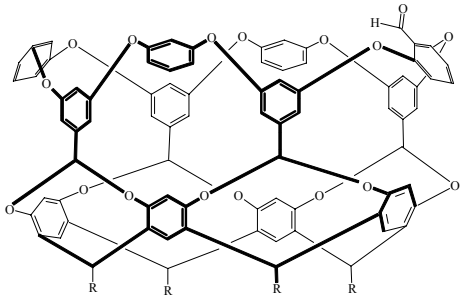
48 **49**

Scheme 5.



R = CH_2CH_2Ph

50



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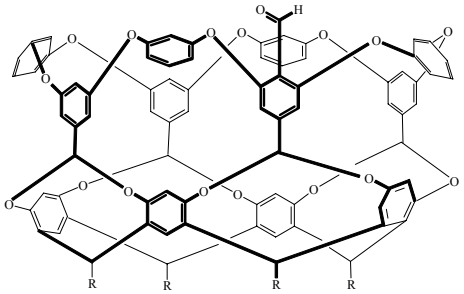

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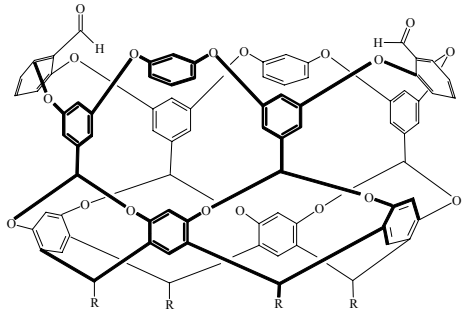

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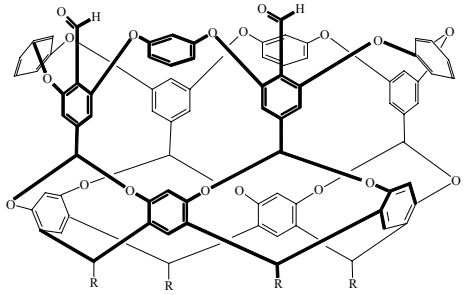

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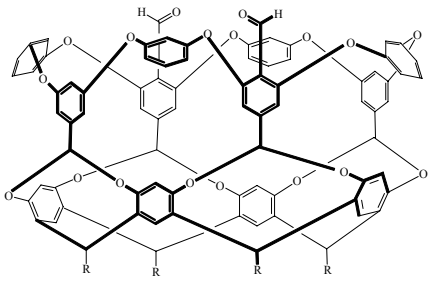

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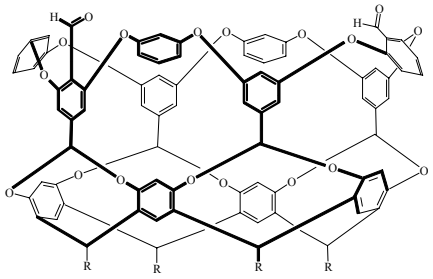

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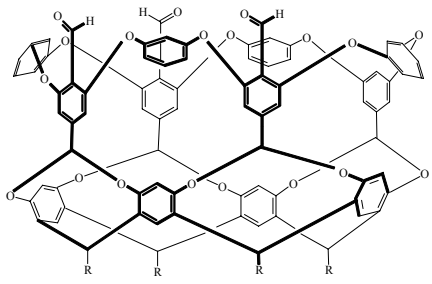

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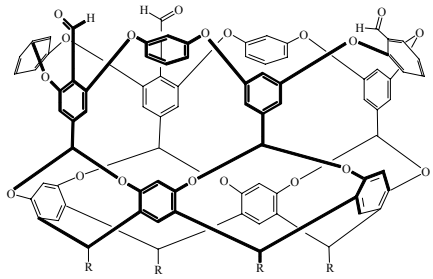
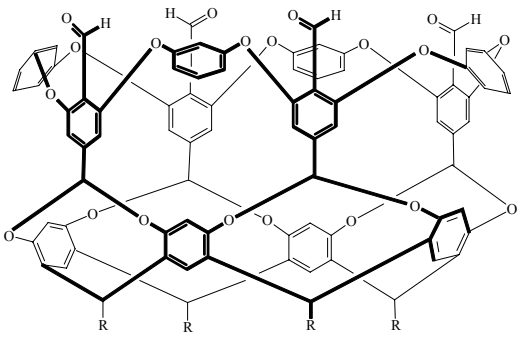


58

(Scheme 6) contd…..



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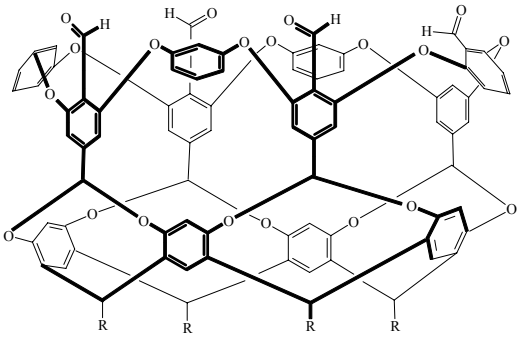

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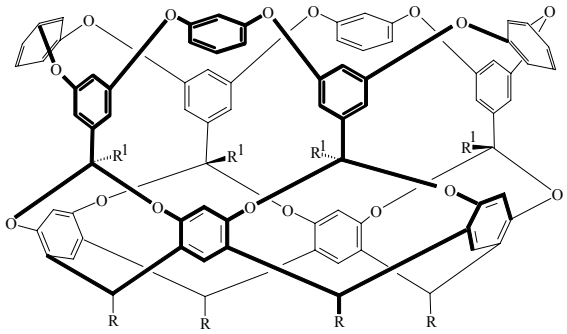
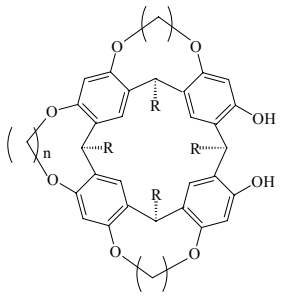


	R	R^1
a	CH_2CH_2Ph	H
b	CH_2CH_2Ph	D

61

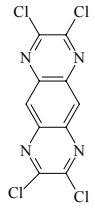
Scheme 6.



68

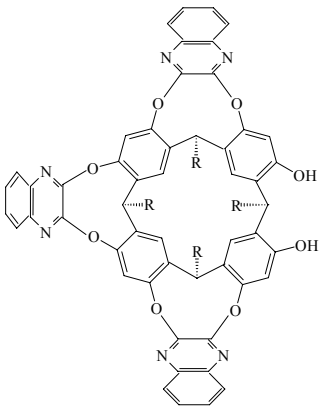
n = 1-3

+



70

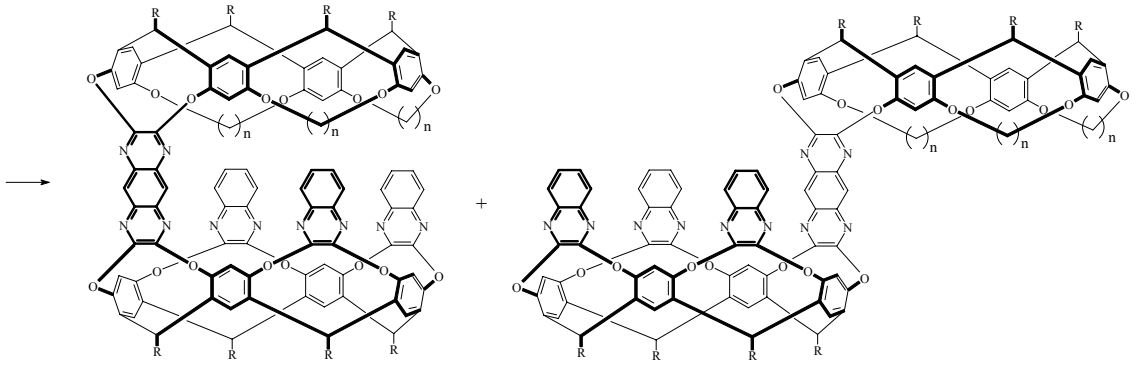
CsF / DMF



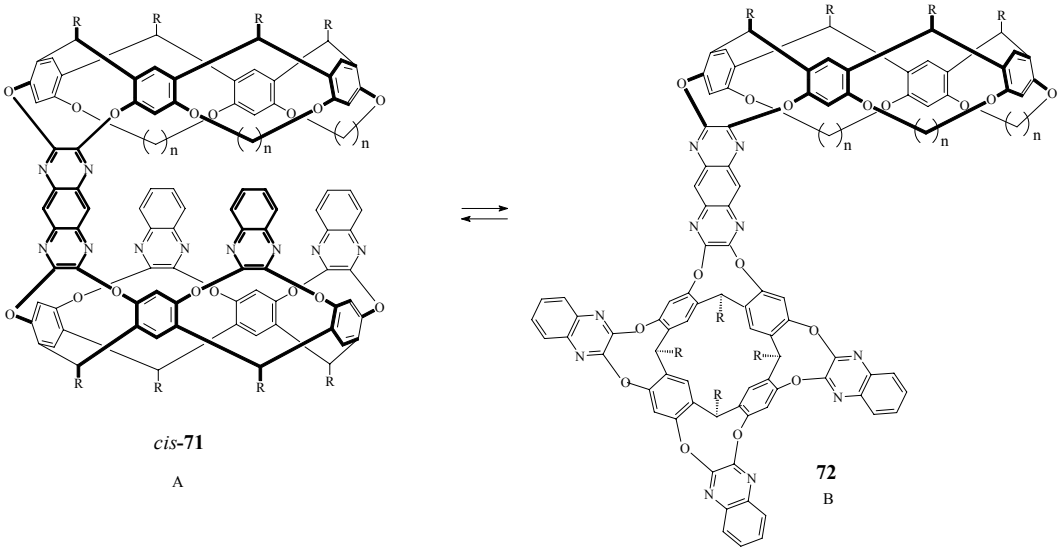
69

R = *n*-C_5H_{11}

(Scheme 7) contd…..



cis-**71** *trans*-**71**

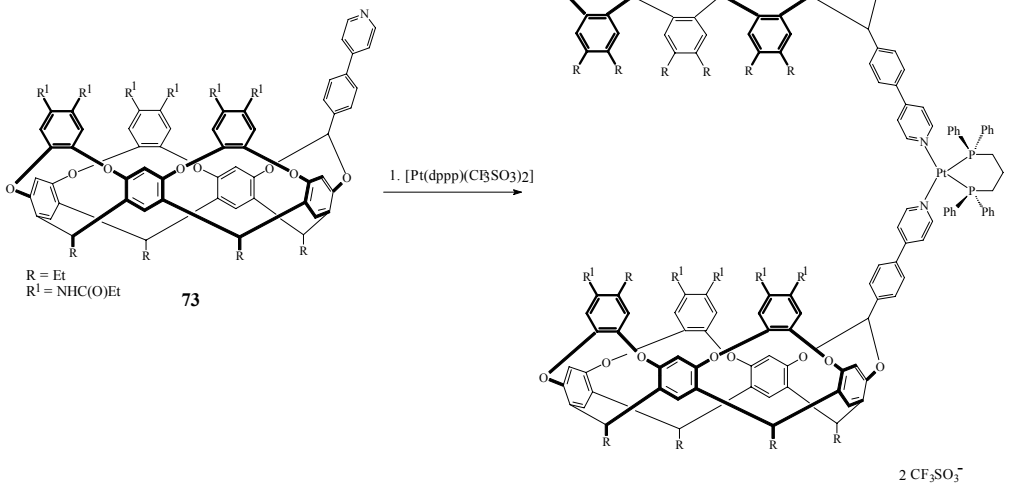


cis-**71**

A

72

B



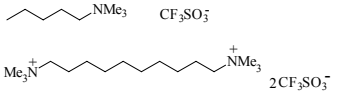
R = Et
R^1 = NHC(O)Et

73

1. [Pt(dppp)(CF_3SO_3)2]

2 $CF_3SO_3^-$

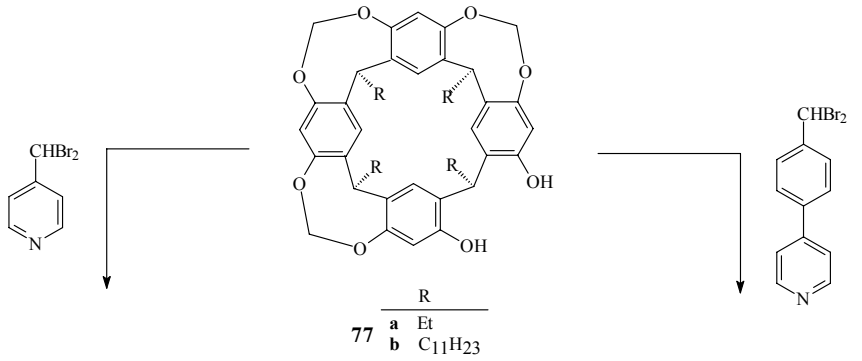
cis-**74**



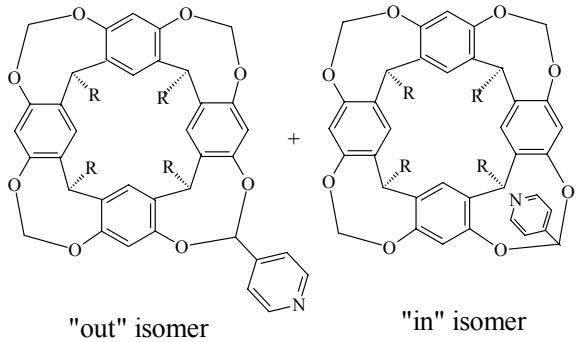
75

76

Scheme 7.



	R
77 **a**	Et
b	$C_{11}H_{23}$

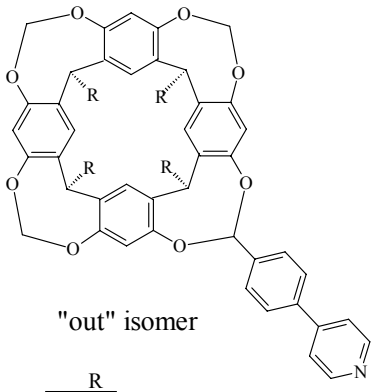


"out" isomer

"in" isomer

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

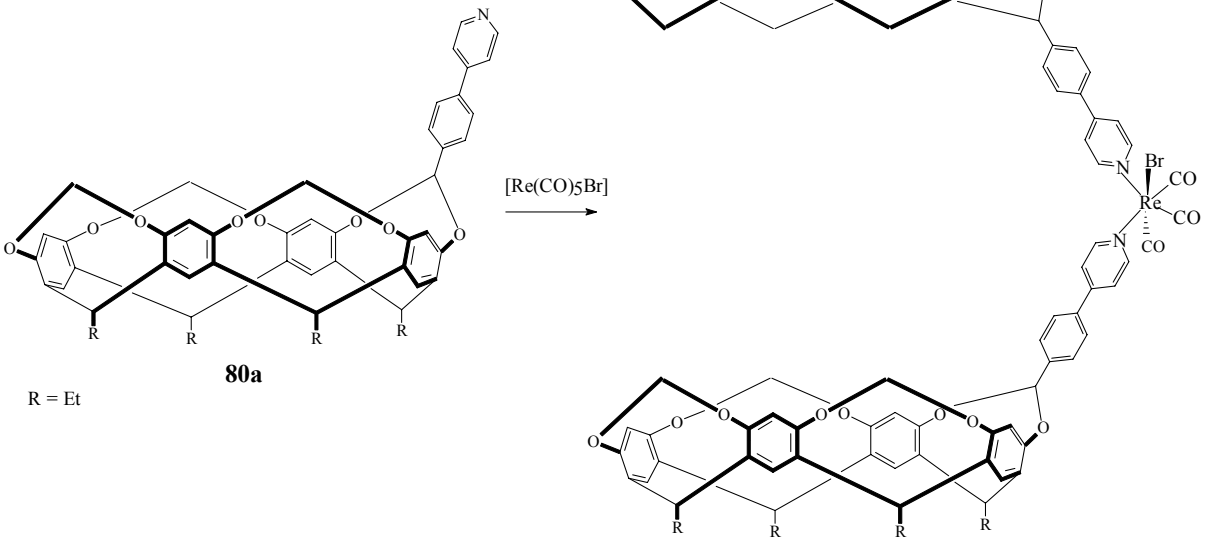
79



"out" isomer

	R
78 **a**	Et
b	$C_{11}H_{23}$

	R
80 **a**	Et
b	$C_{11}H_{23}$



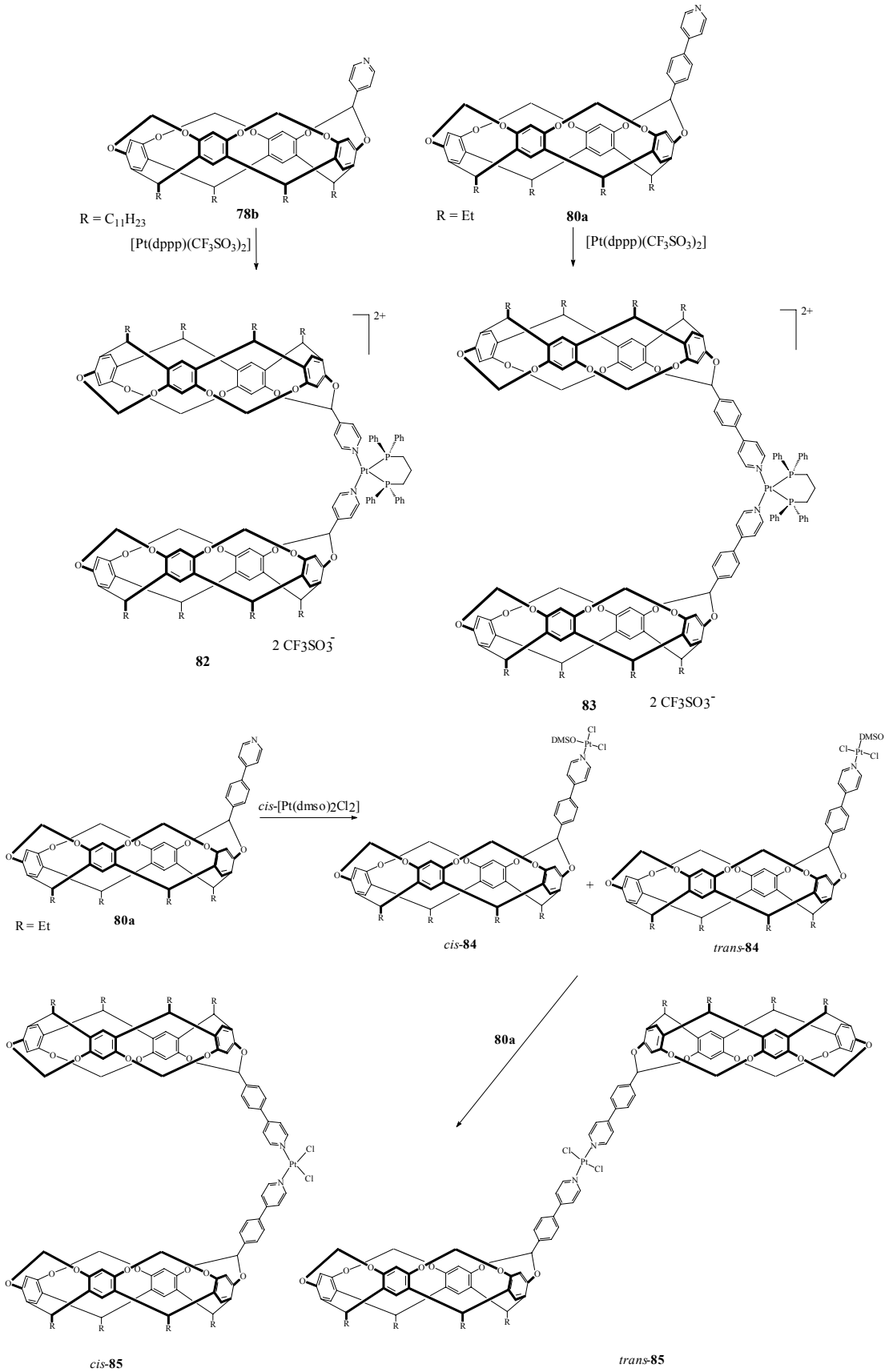
80a

R = Et

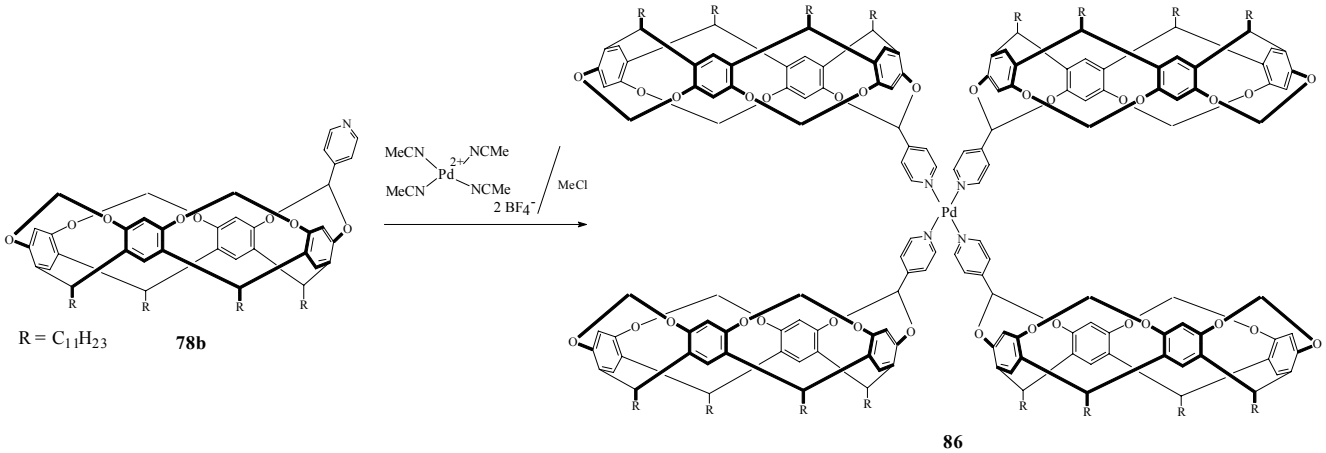
$2\ CF_3SO_3^-$

81

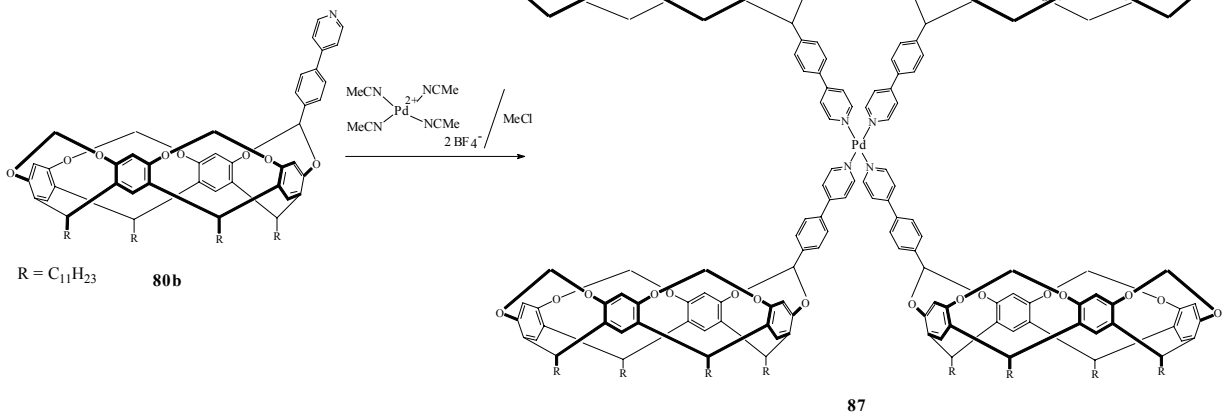
(Scheme 8) contd…..



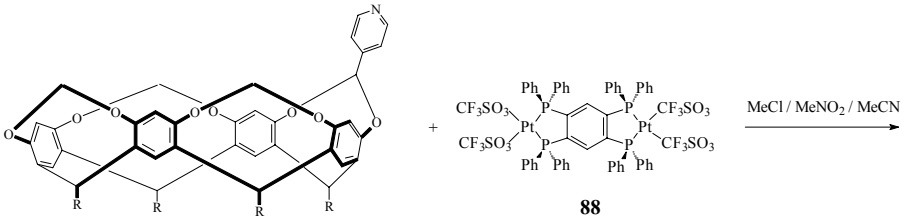
Scheme 8.



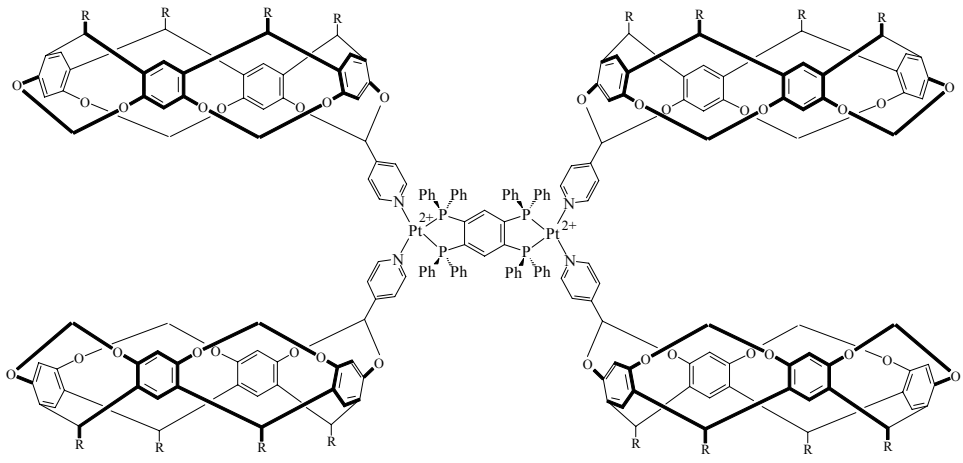
R = $C_{11}H_{23}$ **78b** **86**



R = $C_{11}H_{23}$ **80b** **87**



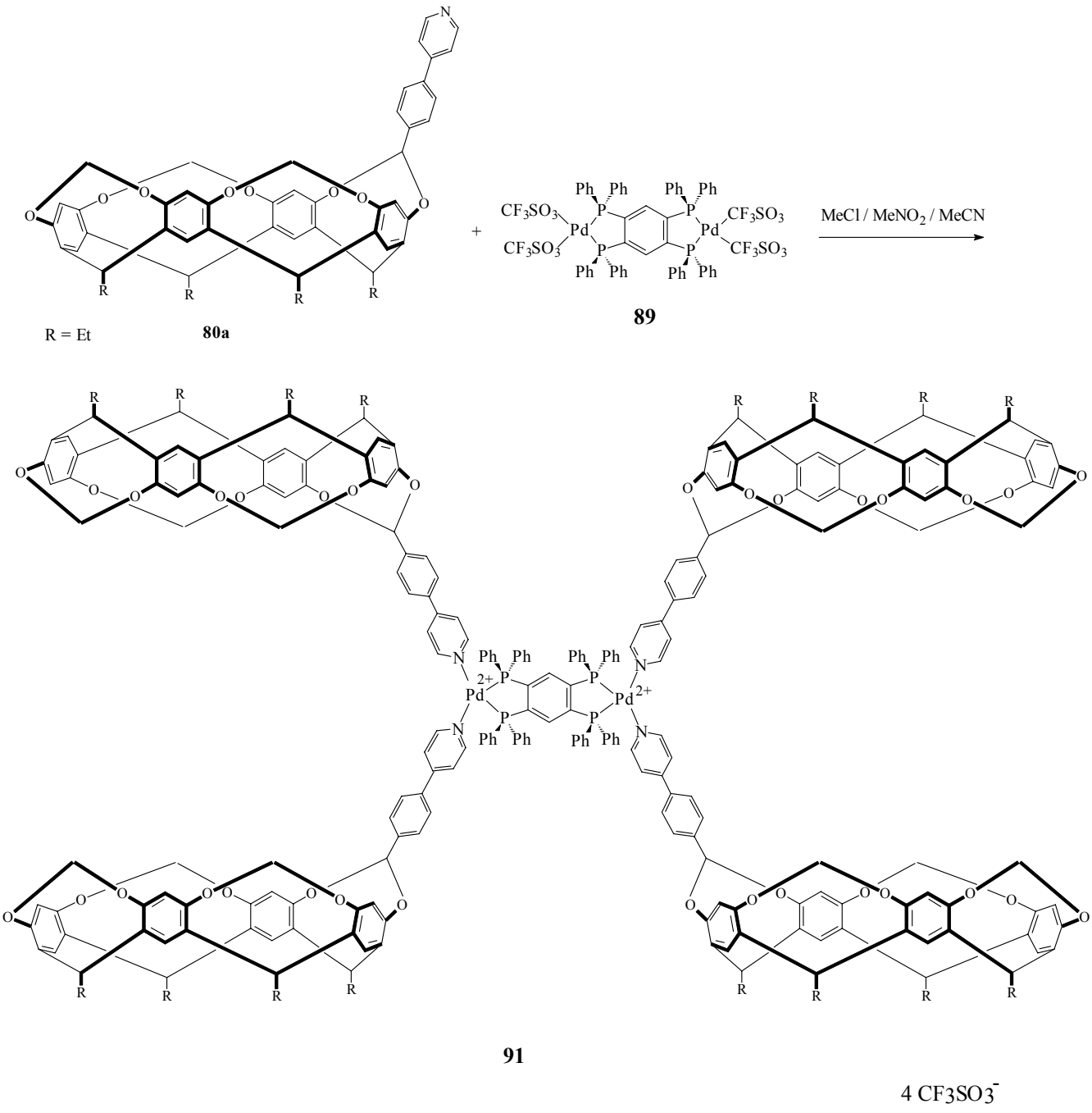
R = Et **78a** **88**



90

4 $CF_3SO_3^-$

(Scheme 9) contd…..



Scheme 9.

two oxygen atoms. These hydrogen atoms are weakly acidic, therefore they can be removed by directed *ortho* lithiation, and the formed carbanions may be quenched with electrophiles. The treatment of cavitand (**50**) with *n*-butyl, *sec*-butyl and *t*-butyllithium followed by quenching with DMF affords aldehydes.

In the case of *n*-butyllithium mono-*endo* and mono-*exo* aldehydes (**51**) and (**52**), A/C-*endo* dialdehyde (**53**), two inseparable A/B and A/C *exo* dialdehydes (**54**, **55**) and chiral A-*exo*, B-*endo* dialdehyde (**56**) (and its enantiomer) have been obtained. In the case of *sec*- or *t*-butyllithium the ABC tri-*exo* trialdehyde (**57**), A/B-*exo*-C-*endo* trialdehyde (**58**), tetra-*exo* aldehyde (**59**) and chiral A/B/C-*exo*-C-*endo* (**60**) (with its enantiomer) were formed.

The above results show that the *exo* substitution is preferred over *endo*. It should be noted that products with two aldehyde groups A,B-*endo* or A-*endo,* A-*exo* substituted are not favored, this behavior resulting from the fact that the high-energy dicarbanion intermediate would bear two negative charges in a too close

proximity (one exception is **60**). Therefore the compounds A,B-*endo* and A-*endo*, A-*exo*, A-*endo* can not be formed; as a result the formation of pentaaldehydes is not possible, and the number of substituted products is considerably reduced [43]. The above results are promising for functionalization of receptor molecules.

Deep cavitands (**61**) have been examined for their affinity to halogenated guests bromo- and iodocyclopentane (**62a,b**), bromo- and iodocyclohexane (**63a,b**), bromo- and iodocyclo-heptane (**64a,b**), bromo- and iodocyclooctane (**65a,b**), 2-bromoadamantane (**66**) and *exo*-2-bromonorbornane (**67**) [44]. The presence of halogen atom in the guest enhances the association, for example 2-bromoadamantane (**66**) binds stronger than adamantane. It was observed that **61a** and **61b** bind iododerivatives (**62b-65b**) stronger than bromoderivatives (**62a-65a**). The cavitand (**61b**) binds guests (**62b-65b**) as well as **66** and **67** more strongly than the host (**61a**), the binding of **61a** and **61b** towards guests (**62a-65a**), however, is similar.

3. CAVITANDS FORMING OPENED CAPSULES

Reaction of partially bridged (i.e. containing two non bridged hydroxyl groups) cavitands (**68**) and (**69**) with tetraazaanthracene (**70**) leads to opened capsules (*cis*-**71**) and (*trans*-**71**) consisting of "bottom" and "cap" vase cavitands [45]. It was found, however, that opened capsules (*cis*-**71**) may undergo the reversible change of the vase conformation of the "bottom" cavitand into its kite conformation to give **72**; it is the A/B switching, occurring *via* pH or temperature variation. For example, the switch A ∅ B proceeds under acidic (TFA) conditions in toluene and in benzene. The reverse process (B ∅ A) occurs by acid neutralization with a base (Et_3N or K_2CO_3) or by addition of polar solvents (acetone-d_6 or TMF-d_8). The switch A ∅ B proceeds at 23°C in $CDCl_3$ and the switch B ∅ A at 57°C.

Cavitand (**73**) has a deep vase-like cavity formed through a network of hydrogen bonds; the presence of a phenylpyridyl group enables coordination of **73** with [Pt(dppp)$(CF_3SO_3)_2$] affording the thermodynamically stable opened capsule (*cis*-**74**) [46]. The exclusive synthesis of only *cis* isomer is due to the presence of bidentate dppp ligand. Methyl ammonium and diammonium salts (**75**) and (**76**), respectively, were used as guests of **74**. It was found that **74** forms with **75** the 1:2 complex and with **76** the 1:1 complex, the latter being more stable than the former one.

For the synthesis of opened capsules and their dimers, at first reactions of partially bridged cavitand (**77**) with 4-(dibromomethyl)pyridine and with 4-(dibromotolyl)pyridine leading to cavitands (**78**), (**79**) and (**80**), respectively, have been performed. In order to obtain opened capsules, the cavitands (**78**) and (**80**) have been submitted to metal coordination; for this purpose only "out" isomers are useful [47]. The reaction of **80a** with [$Re(CO)_5Br$] leads to formation of the opened capsule (**81**). Cavitands (**78b**) and (**80a**) react with [Pt (dppp)$(CF_3SO_3)_2$] to give opened capsules (**82**) and (**83**), respectively. The reaction of **80a** with *cis*-[Pt$(dmso)_2(Cl_2)$] affords *cis/trans* mixture of **84**, converted by treatment with second equivalent of **80a** into compounds (*cis*-**85**) and (*trans*-**85**).

The reaction of **78b** and **80b** with [$Pd(MeCN)_4(BF_4)_2$] affords dimeric opened capsules (**86**) and (**87**)**,** respectively, stable only in their mother MeCl solution. However, cavitands (**78a**) and (**80a**) treated with platinum and palladium dinuclear precursors (**88**) and (**89**) yield dimeric opened capsules (**90**) and (**91**), respectively, which are stable both in solution and in the solid state. The above results show that the use of dinuclear metal precursors (**88**) and (**89**) is very convenient for design of complex molecular architectures.

CONCLUSION

Due to their interesting binding properties and possibility to form capsules, cavitands are attracting the attention of researchers. Since the number of reports concerning this class of compounds is increasing rapidly [48-50], the present review does not mean to be exhaustive, only selected, the most representative examples are shown.

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