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Review

Calixarene Complexes with Transition Metal, Lanthanide and Actinide Ions

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Selected calixarene complexes with transition metal as well as lanthanide and actinide ions are described, showing their syntheses and possible applications.

Key words: actinides, calixarenes, complexes, lanthanides, nickel, platinum, rhodium, tantalum, transition metals, tungsten.

INTRODUCTION

Due to their structure and properties, calixarenes are a topic of many works.[1-8] Numerous metal ion complexes of calixarenes are known,[9-14] among them those with transition metal ions.[15-18] Title complexes are interesting from both theoretical and practical viewpoints, for example they are used in the extraction of lanthanides and actinides from nuclear waste.[19,20]

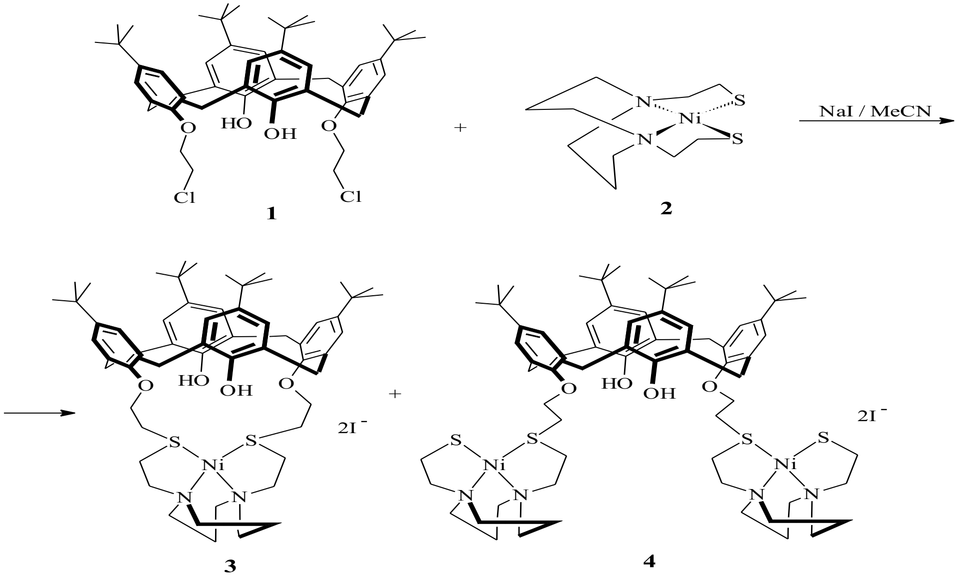
The following complexes are described in the present review:

- calixarene complexes with nickel, copper, zinc and silver ions,
- calixarene complexes with chromium, tantalum, tungsten and niobium ions,
- calixarene complexes with lanthanide and actinide ions,
- calixarene complexes with ruthenium, rhodium, palladium and platinum ions.

References of works that appeared during the years 1998-2000 are cited.

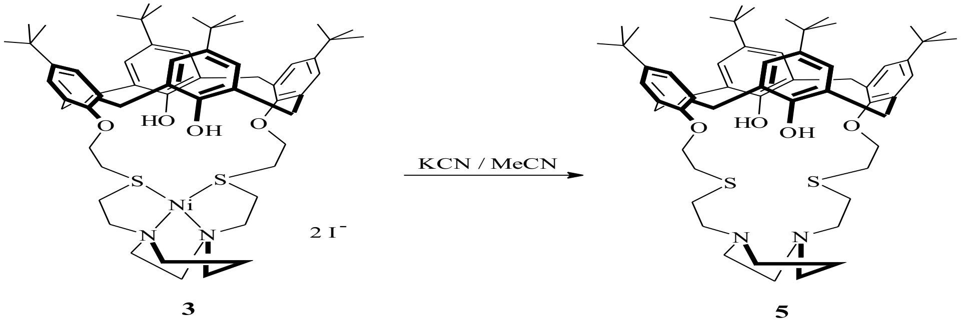
CALIXARENE COMPLEXES WITH NICKEL, COPPER, ZINC AND SILVER IONS

Nickel-thiolato-calixarene complexes have been investigated.[21] The reaction of dichloroethylcalix[4]arene (**1**) with nickel(II)thiolate (**2**) in the presence of NaI affords nickel(II) and bis-nickel(II)-calixarene complexes (**3** and **4**), Scheme 1.



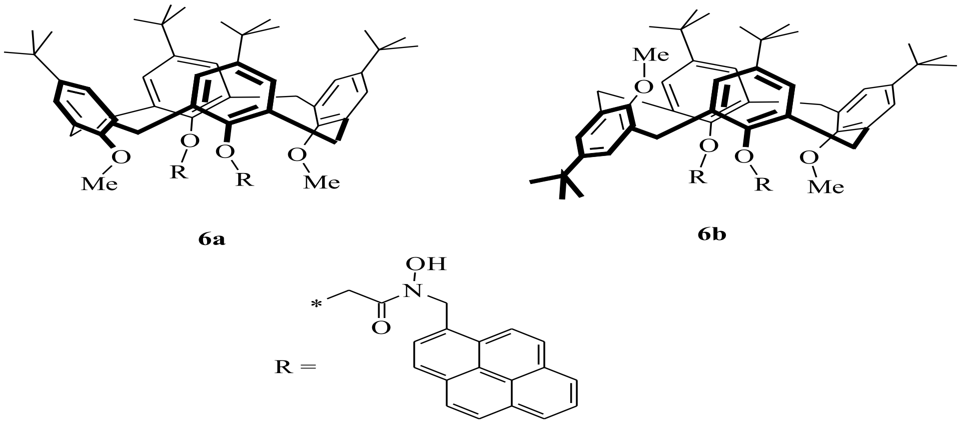
Scheme 1.

Nickel ion can be removed from complex **3** by treatment with KCN. The formed free ligand **5** of a crown ether structure contains two nitrogen, two oxygen and two sulfur electron-donors convenient for further complexation (Scheme 2).



Scheme 2.

In the study of fluorescent chemosensors for optical detection of transition metal ions, bispyrenylcalixarene **6** has been synthesized.[22] This compound exists in $CDCl_3$ solution at room temperature as a mixture of cone and partial cone conformers **6a** and **6b** (Scheme 3).



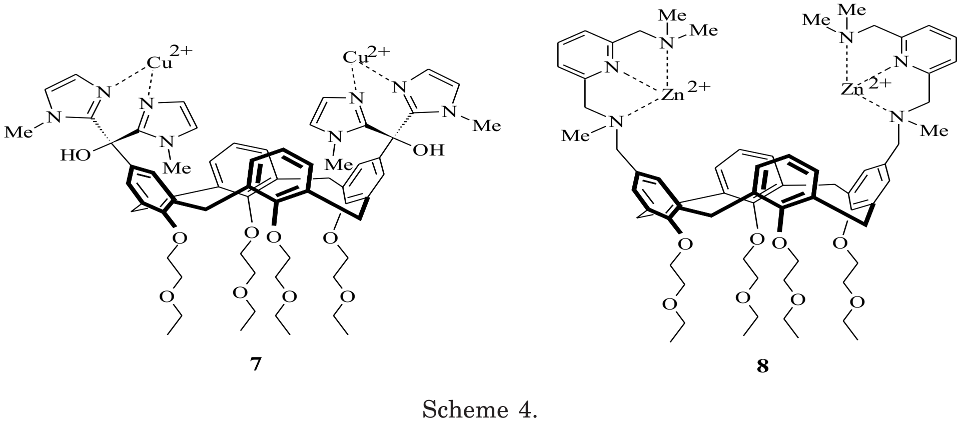
6a

6b

Scheme 3.

Fluorescence intensity in methanol-water solution is sensitive to pH and the presence of transition metal ions. Addition of Cu^{2+} and Ni^{2+} ions induces a strong, pH dependent quenching of fluorescence of **6**. Calixarene **6**, acting as an excimer-forming photoresponsive ligand is therefore a selective chemosensor for the detection of Cu^{2+} and Ni^{+} ions. The proton induced decomplexation makes it possible to distinguish Cu^{II} and Ni^{II} ions in solution *via* fluorescence emission enhancement.[22]

Dinuclear Cu^{II} and Zn^{II} complexes **7** and **8** (Scheme 4) have been investigated as enzyme models of phosphodiesterase.[18,23,24]

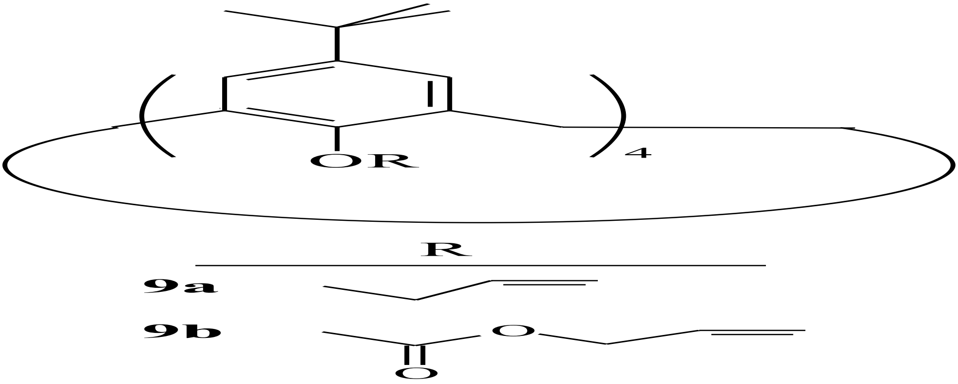


7

8

Scheme 4.

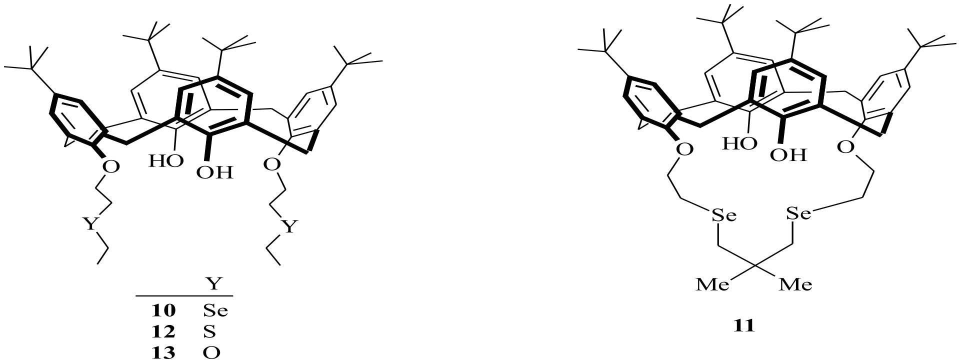
Soft metal ions, such as Ag$^+$, have high affinity to π-coordinating groups, *e.g.* to allyl or phenyl. *t*-Butyl[4]arenes have been chosen as examples of such neutral carriers containing π-coordinating substituents for Ag$^+$ sensors. It was observed that tetraallylether **9a** has good ionophoric properties; it shows very high silver ion selectivity against sodium ion. The calixarene tetraallylester **9b**, however, has only low silver ion selectivity with a considerable sodium ion interference (Scheme 5).[25,26]



Scheme 5.

Selenium containing calixarenes **10** and **11** have been synthesized and their complexing abilities have been investigated.[27] For comparative purposes, sulphur and oxygen analogues of **10**, *i.e.* calixarenes **12** and **13**, have been prepared (Scheme 6).[27]

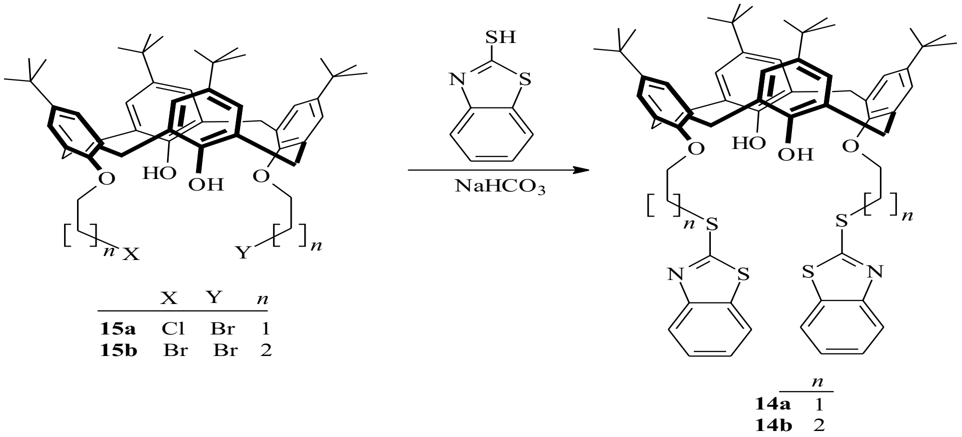
The highest Ag$^+$ extraction selectivity was found for selenium calixarenes **10** and **11**, and for sulphur compound **12**, while oxygen calixarene **13** shows only very low affinity to Ag$^+$ ion. These complexing properties of selenium calixarenes are of interest in their application for the detection of Ag$^+$ ions



Scheme 6.

and for the recovery of Ag^+ from industrial waste water.[27] A rather unexpected observation was that there was almost no affinity of calixarenes **10–13** towards Pb^{2+} ion, whose size is similar to that of Ag^+.[27,28]

In order to obtain calixarene based ion-selective electrodes sensitive to soft heavy metal ions such as Ag^+, Pb^{2+} and Hg^{2+}, calixarene should be functionalized with groups containing nitrogen and sulphur atoms; in this case, the binding of soft heavy metal ions is higher than that of alkali metal ions. For this purpose, compounds **14a,b** bearing benzothiazolylthioalkoxy moieties have been synthesized by treating calixarenes **15a,b** with 2-mercaptobenzothiazole (Scheme 7).[29] Calixarenes **14a,b** adopt cone conformations; it was found that they are convenient ionophores for silver ion-selective electrodes.[29]



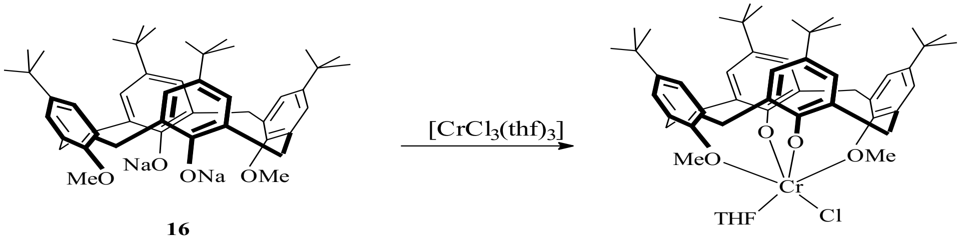
	X	Y	*n*
15a	Cl	Br	1
15b	Br	Br	2

	n
14a	1
14b	2

Scheme 7.

CALIXARENE COMPLEXES WITH CHROMIUM, TANTALUM, TUNGSTEN AND NIOBIUM IONS

In the study of the calixarene chromium complexes, the reaction of **16** with $[CrCl_3(thf)_3]$ leading to [Cr{*p*-*t*-Bucalix[4](O)$_2$(OMe)$_2$}(Cl)(thf)] was carried out (Scheme 8).[30]

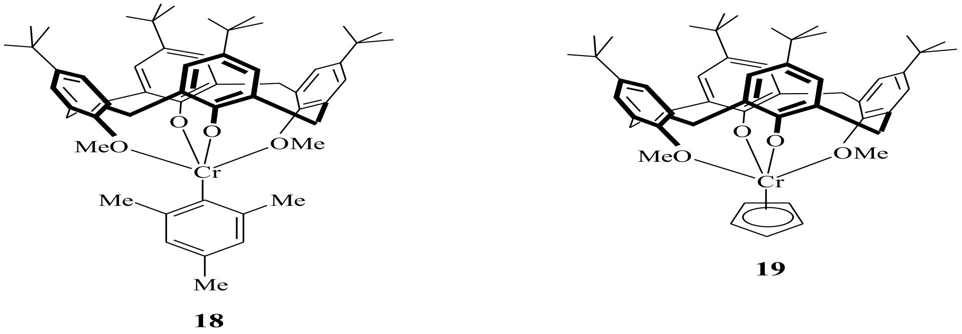


16

17

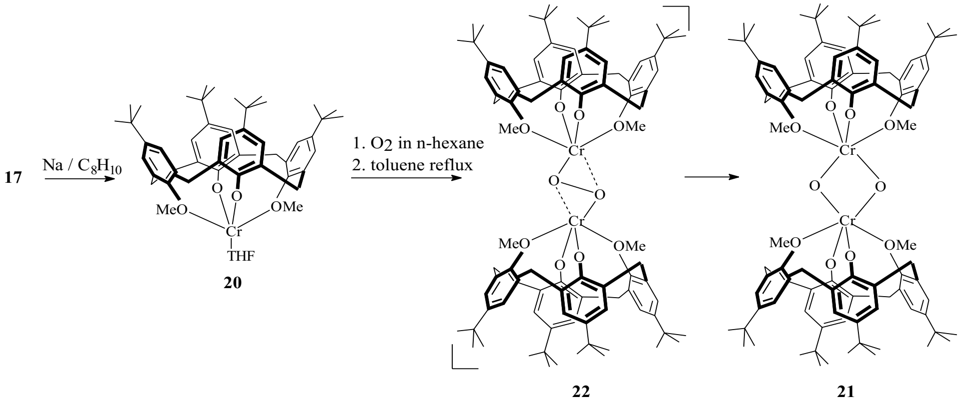
Scheme 8.

Complex **17** reacts with LiMes and NaCp to give mesityl and cyclopentadienyl derivatives **18** and **19**, respectively (Scheme 9).[30] Complex **18** crystallizes with toluene in 1:2 ratio, one toluene molecule being hosted in the calixarene cavity.



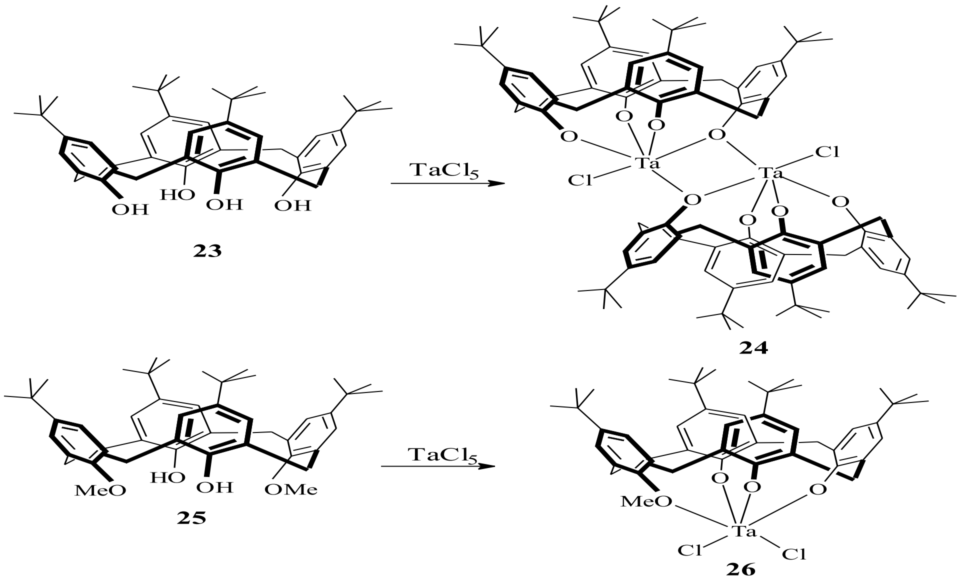
Scheme 9.

The reactivity of Cr^{III} in **18** and **19** is very low, even under photochemical or thermal conditions. Compound **17**, however, undergoes one electron reduction leading to **20** by treatment with sodium in the presence of naphthalene in THF. Complex **20** crystallizes with THF in 1:2 molar ratio, one of the two THF molecules being encapsulated in the calixarene cavity. This species is air sensitive, it readily undergoes oxidation to give **21** *via* a bridged peroxodichromium derivative **22**, undergoing a cleavage of the O–O bond (Scheme 10).[30]



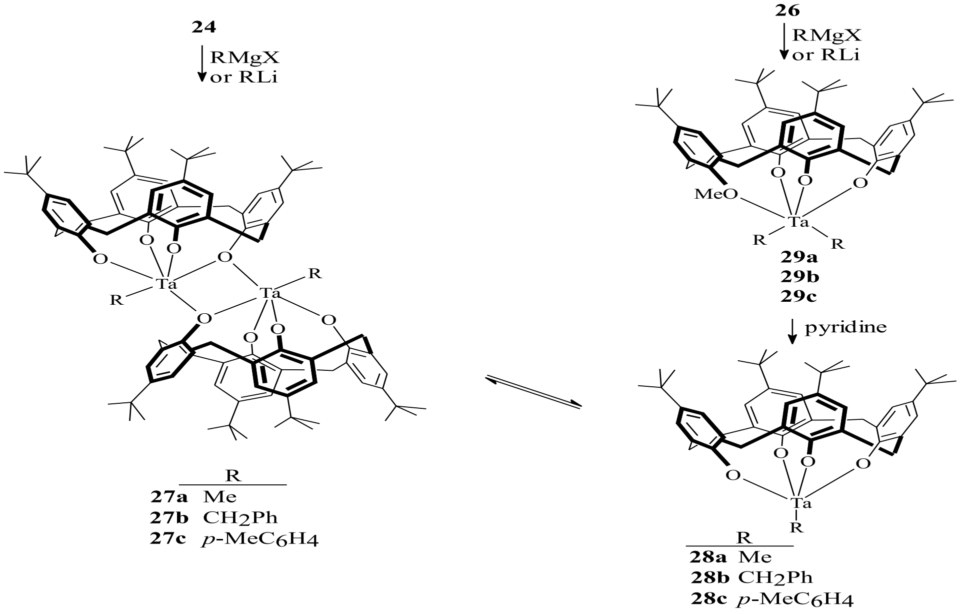
Scheme 10.

The reaction of calixarene **23** with $TaCl_5$ affords the bis-tantalum complex **24**, and the reaction of **25** with $TaCl_5$ results in its demethylation leading to complex **26** (Scheme 11).[31]



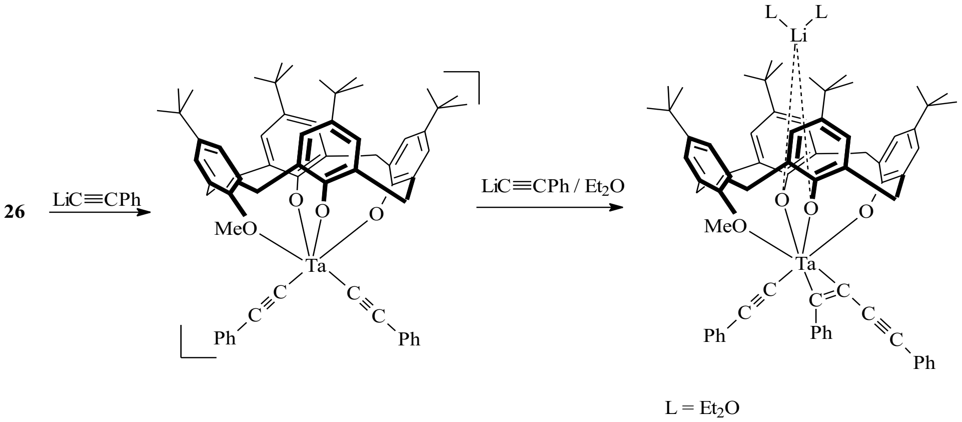
Scheme 11.

The alkylation of **24** gives **27a-c**, which are in equilibrium with their monomeric forms **28a-c**. Similar alkylation of **26** leads to **29a-c**, which in the presence of pyridine undergo demethylation to give **28a-c** (Scheme 12).[31]



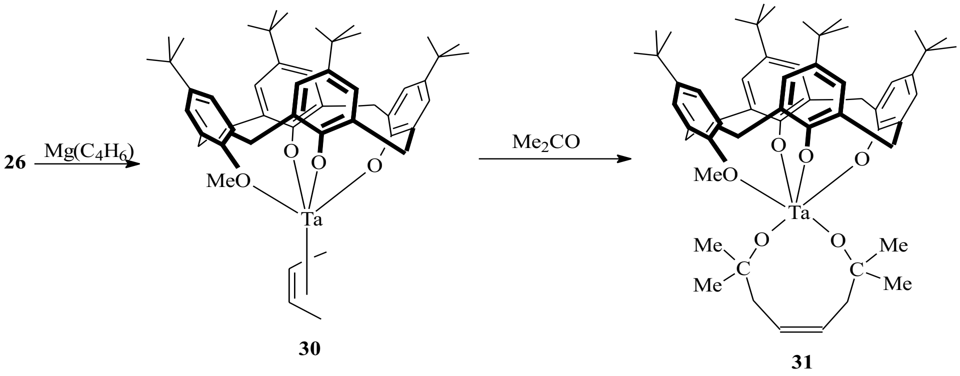
Scheme 12.

Complex **26** may be used for the synthesis of derivatives containing unsaturated carbon groups bonded with metal, as shown in Scheme 13.[31]



Scheme 13.

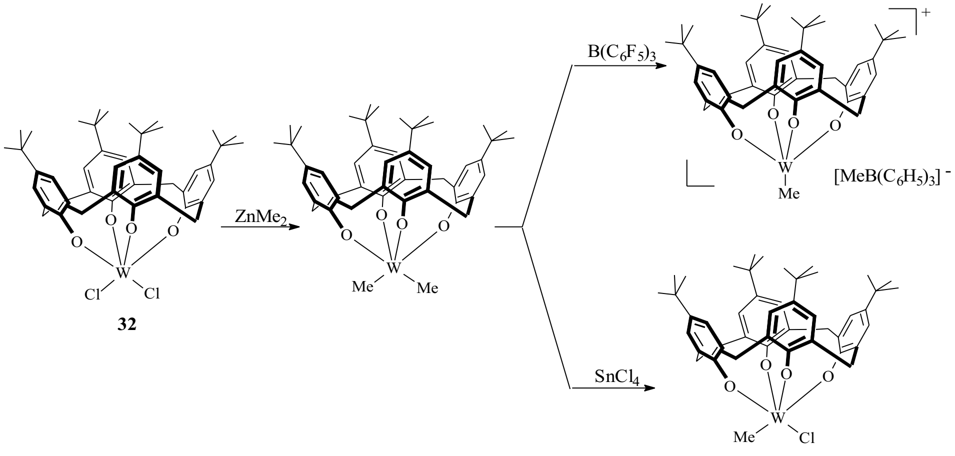
The reaction of **26** with $Mg(C_4H_6)$ leads to the tantalum-butadiene complex **30**, converted by treatment with acetone into dioxo metallacycle **31** (Scheme 14).[31]



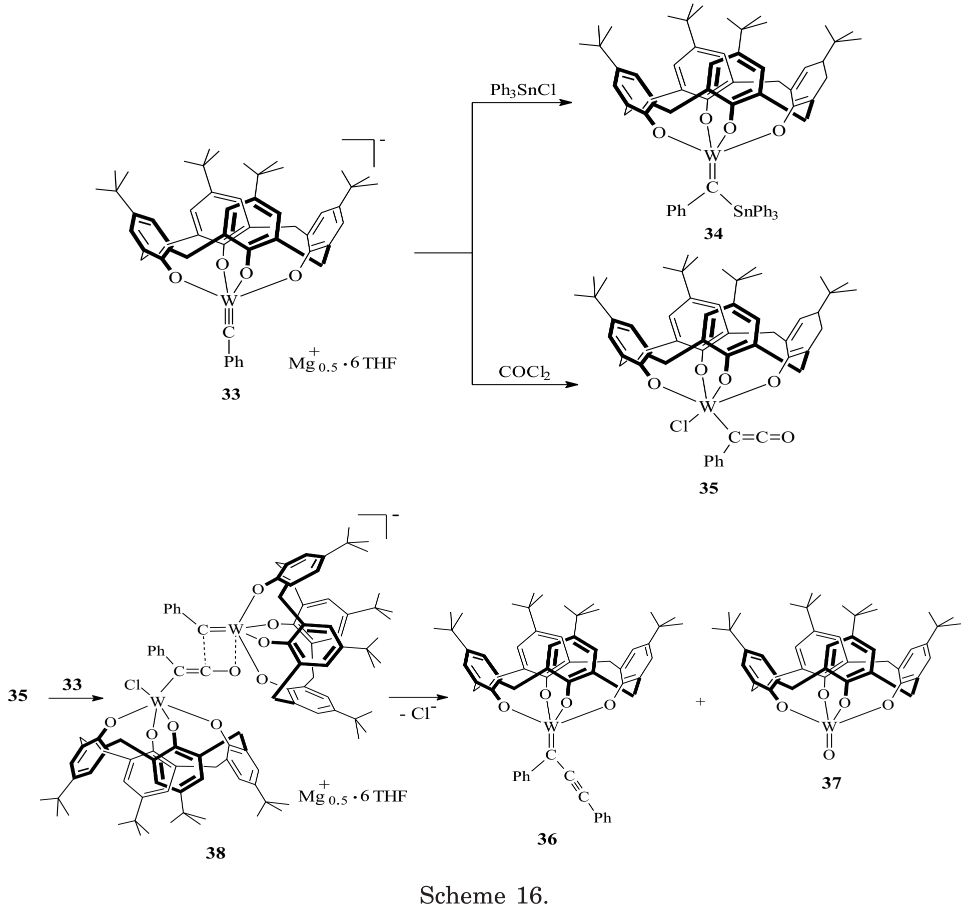
Scheme 14.

In the study of tungsten complexes of calixarenes, the following reactions of **32** were performed (Scheme 15).[32,33]

It was observed that complex **33** reacts with Ph_3SnCl to give **34**, useful in transmetalation reactions with transition metal derivatives.[34,35] The reaction of **33** with phosgene affords the ketenyl derivative **35**, which by treatment with another molecule of **33** gives an equimolar mixture of **36** and **37**; this reaction proceeds *via* intermediate **38** (Scheme 16).[34]

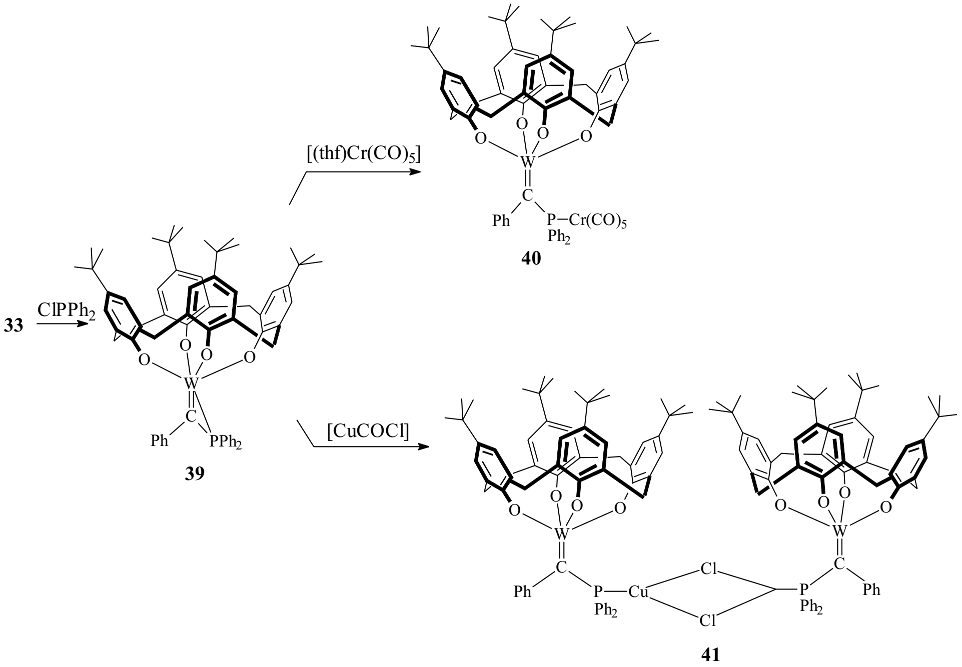


Scheme 15.



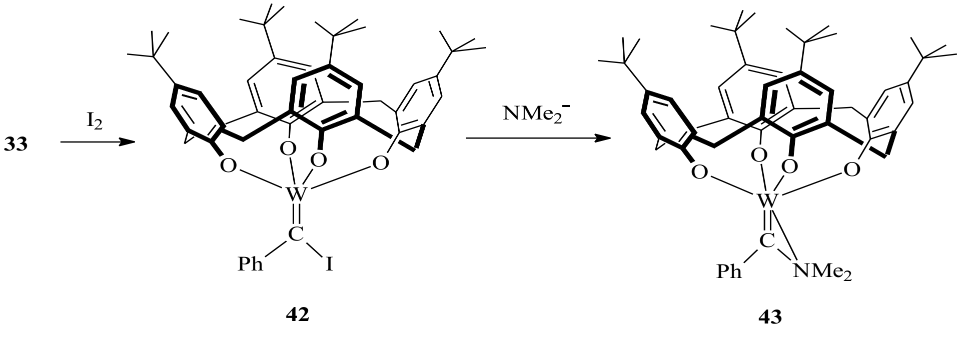
Scheme 16.

Complex **33** may be used for the synthesis of phosphanylalkylidenes and their transformation into dimetallic complexes; its reaction with $ClPPh_2$ gives **39**, which by treatment with $[(thf)Cr(CO)_5]$ and [CuCOCl] affords dimetallic complexes **40** and **41**, respectively (Scheme 17).[34]



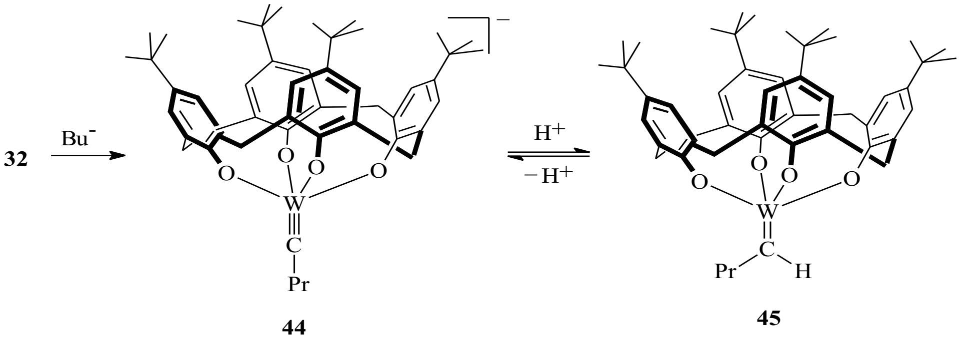
Scheme 17.

Oxidation of **33** by I_2 leads to complex **42**, in which the iodine atom may be replaced by various organometallic nucleophiles. For example, the reaction of **42** with $NaNMe_2$ affords aminoalkylidene **43** (Scheme 18).[34]



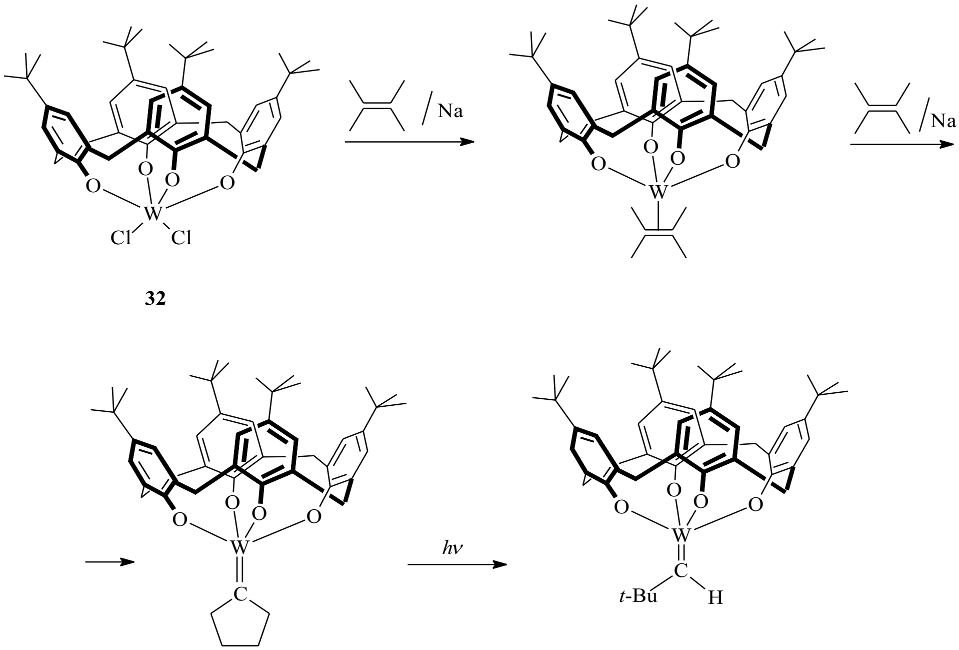
Scheme 18.

Treatment of complex **32** with butyl carboanion gives rise to alkylidyne **44**, which was converted into alkylidene **45** by protonation (Scheme 19).[36]



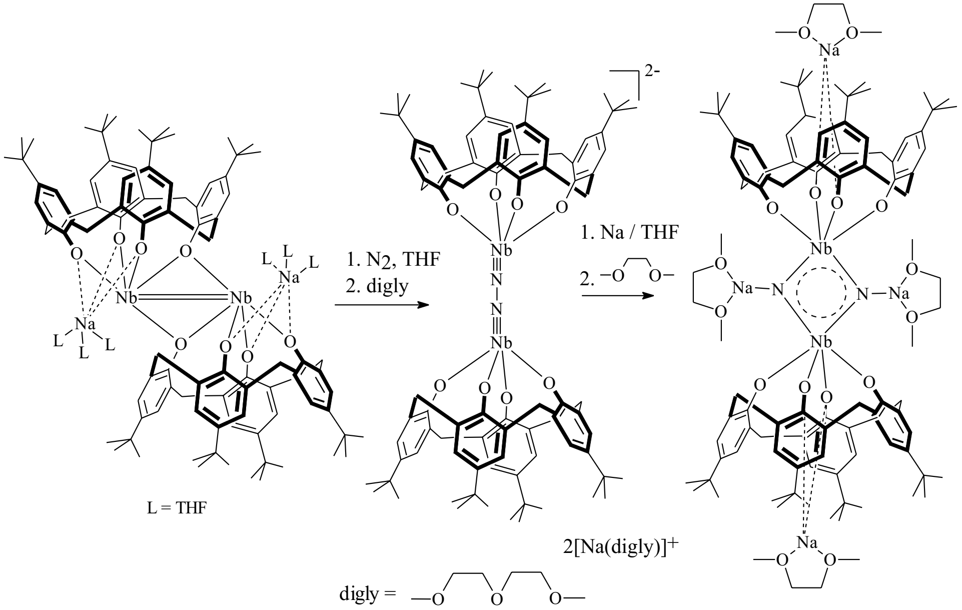
Scheme 19.

The following reactions (Scheme 20) of **32** have also been performed.[32,35]



Scheme 20.

Activation of small molecules like O_2, N_2, CO and CO_2 by metallacalixarenes is possible; an example of dinitrogen activation and cleavage is shown (Scheme 21).[36,37]



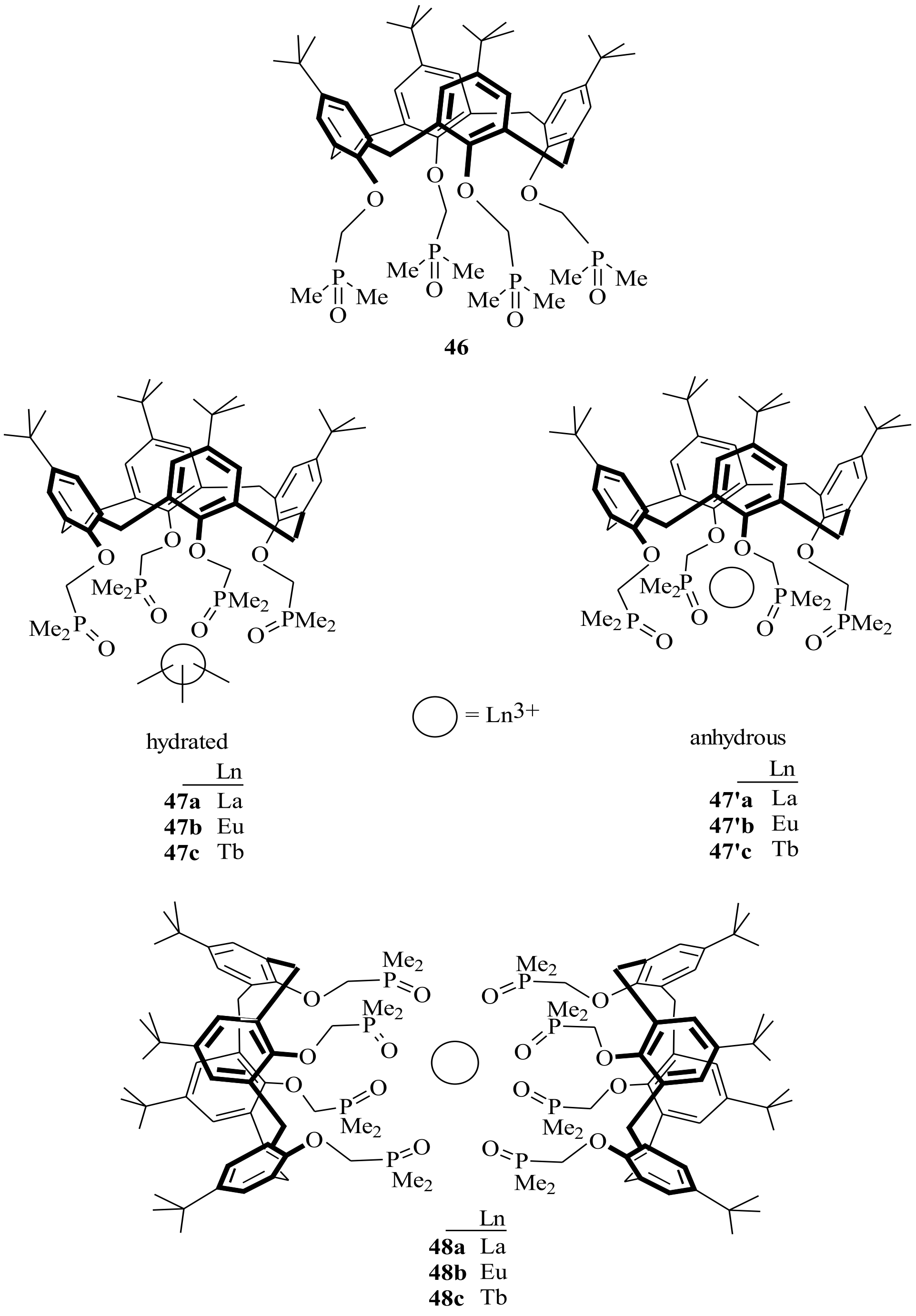
Scheme 21.

CALIXARENE COMPLEXES WITH LANTHANIDE AND ACTINIDE IONS

Lanthanide complexes of calixarenes have been investigated.[38,39] Complexation of trivalent lanthanide ions by calixarenes is promising in terms of their use for the design of luminescent devices and for the extraction of lanthanide ions from nuclear waste. It was observed that calixarenes with phosphorus-containing pendant arms[40] are better extractants for lanthanides(III) and actinides(IV) than TOPO (trioctylphosphine oxide) or CMPO ((*N,N*-diisobutylcarbamoylmethyl)octylposphine oxide) used in the nuclear waste management. Calixarene **46** forms with Ln^{3+} ions (Ln = La, Eu, Tb) 1:1 hydrated and anhydrous complexes **47** and **47'** as well as 2:1 complexes **48** (Scheme 22).[40-42]

In the hydrated 1:1 complex **47a** the La^{3+} ion is coordinated by the four P=O groups and by water molecules, while in the anhydrous complex **47'a** the La^{3+} ion is situated deeper in the calixarene cavity.

In the study of extractants for lanthanides and actinides contained in nuclear waste, calixarene **49** (Scheme 23), functionalized at the upper rim by CMPO analogue, was investigated.[43] Calixarene **49** is a more powerful extractant than CMPO and shows high selectivity for lighter lanthanides and actinides.[44] For this purpose, calixarenes **50** (Scheme 23) functionalized



46

hydrated

	Ln
47a	La
47b	Eu
47c	Tb

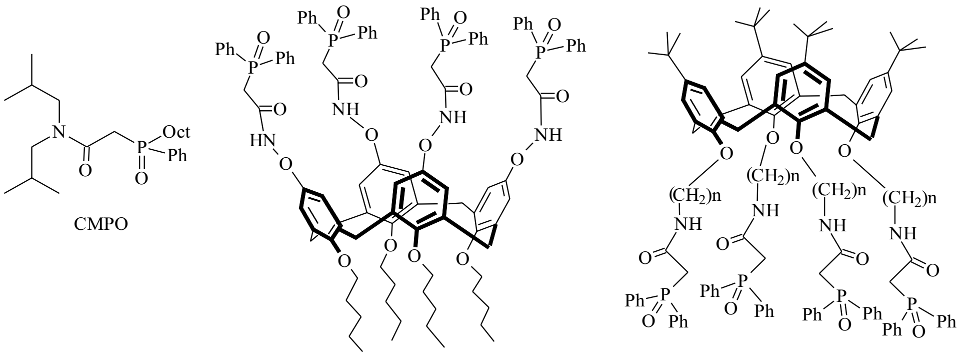
○ = Ln^{3+}

anhydrous

	Ln
47'a	La
47'b	Eu
47'c	Tb

	Ln
48a	La
48b	Eu
48c	Tb

Scheme 22.



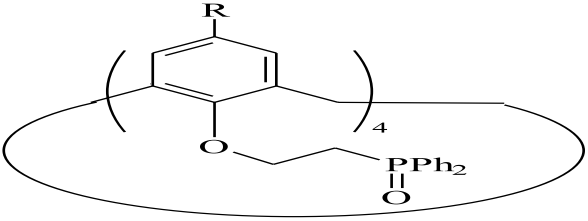
49

	n
50a	2
50b	3
50c	4

Scheme 23.

by CMPO analogue at the lower rim are also promising. It was found that calixarenes **50** show increased extraction of La^{3+}, Eu^{3+}, Yb^{3+} and Th^{4+}. Compounds **49** and **50** are selective extractants of thorium over lanthanides, **50b** being the most selective extractant for Th^{4+}/Eu^{3+} and Th^{4+}/La^{3+}.[45]

Calixarenes **51a-f** (Scheme 24) bearing phosphine oxide moieties have been investigated in view of their complexing properties towards trivalent lanthanides (exemplified by europium(III)) and tetravalent actinides (exemplified by thorium(IV)), separations of lanthanides and actinides being of great importance in the management of nuclear waste.[46] Calixarenes **51a** and **51d** exist in stable cone conformations in solution, while compounds **51a,c,e,f** are conformationally mobile.



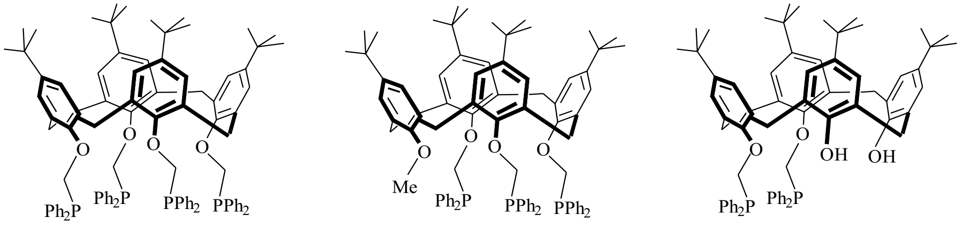
	R	n
51a	t-Bu	4
51b	t-Bu	6
51c	t-Bu	8
51d	H	4
51e	H	6
51f	H	8

Scheme 24.

It was established that calixarenes **51a-f** are more efficient extractants for europium and thorium than TOPO and CMPO, with the exception of europium extraction by **51c**. Extraction of europium is lower than that of thorium. Dealkylated calixarenes **51d-f** are more efficient than alkylated compounds **51a-c** for both europium and thorium extraction.[46]

CALIXARENE COMPLEXES WITH RUTHENIUM, RHODIUM, PALLADIUM AND PLATINUM IONS

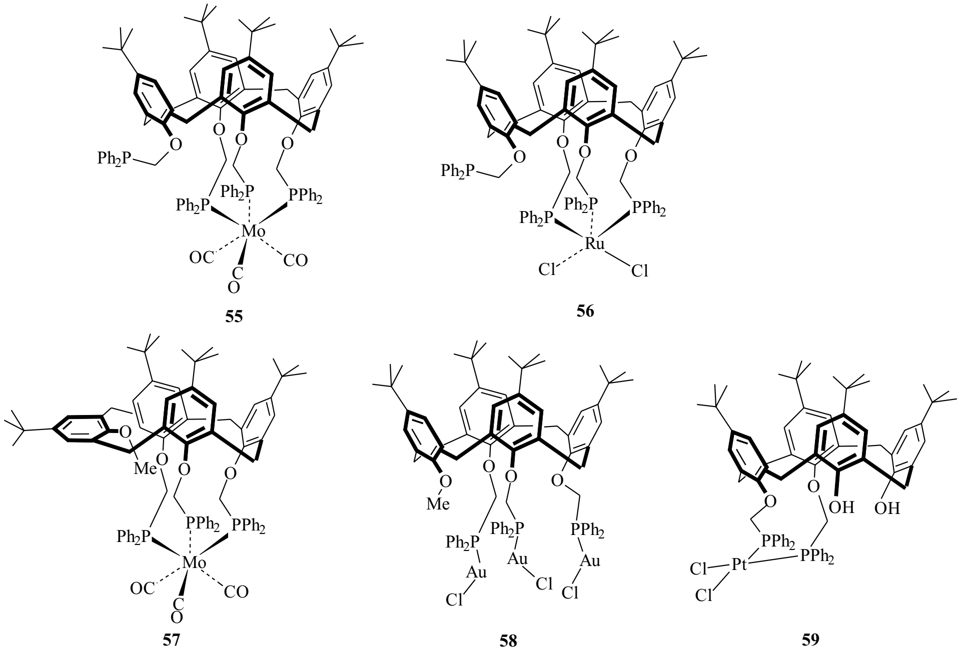
Complexes of calix[4]arenes **52-54** (Scheme 25) containing phosphine moieties have been investigated.[47,48]



52 **53** **54**

Scheme 25.

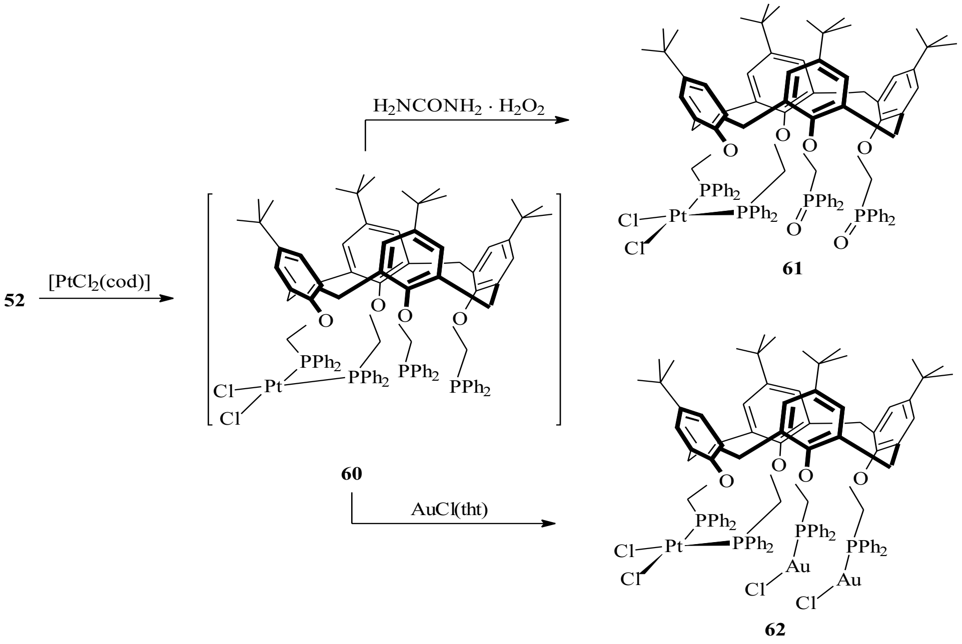
Reactions of **52** with [Mo(CO)$_3$(C$_7$H$_8$)] and [RuCl$_2$(dmso)$_4$] lead to complexes **55** and **56**, compound **53** treated with [Mo(CO)$_3$(C$_7$H$_8$)] and with AuCl(tht) (tht = tetrahydrothiophene) affords complexes **57** and **58**, and calixarene **54** reacts with [PtCl$_2$(cod)] (cod = cycloocta-1,5-diene) to give **59** (Scheme 26).



55 **56** **57** **58** **59**

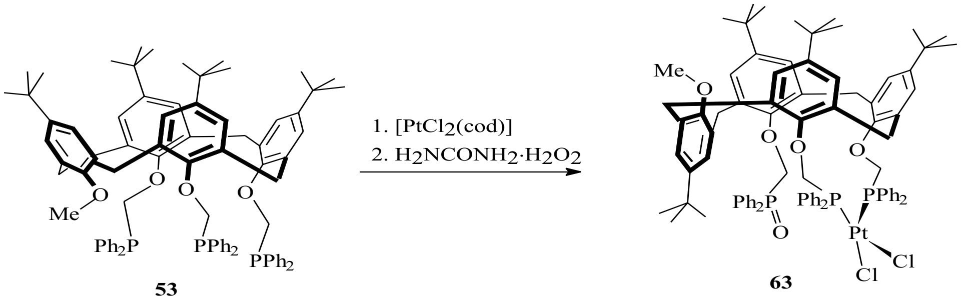
Scheme 26.

Treatment of **52** with [PtCl$_2$(cod)] results in formation of **60**, which could not be isolated due to oligomerization. To prevent oligomerization, the mild oxidation of uncoordinated phosphine groups by addition of urea · H_2O_2, leading to **61**, may be applied. Another method involves complexation of the remaining phosphine groups with [AuCl(tht)], affording the trinuclear complex **62** (Scheme 27).



Scheme 27.

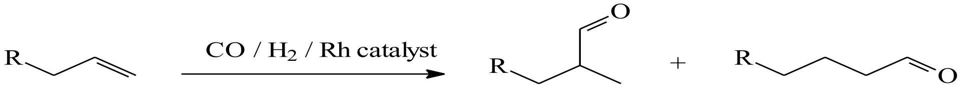
Using the first procedure, the reaction of **53** with [PtCl$_2$(cod)] and the subsequent oxidation with urea · H_2O_2 leading to **63** were performed (Scheme 28).



Scheme 28.

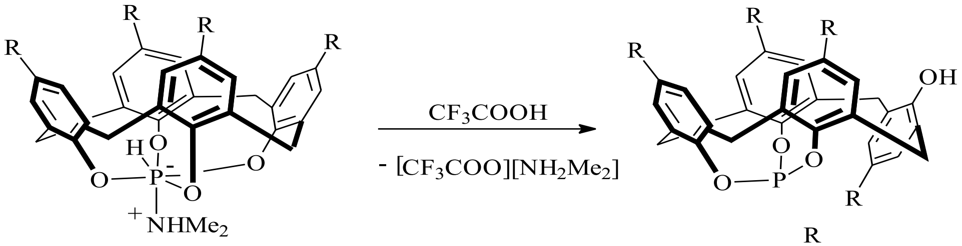
In complexes **59** and **61–63**, the platinum centre is a part of a 12-membered metallamacrocycle.[47]

It was found that P-bridged calixarenes $\mathbf{L_{a,b}}$ form rhodium complexes with $[Rh(CO)_2(acac^*)]$ ($acac^*$ = *t*-BuCOCHCO-*t*-Bu) which are catalysts of the following hydroformylation reaction (Scheme 29).[49]



Scheme 29.

Calixarenes $\mathbf{L_{a,b}}$ were synthesized from compounds **64a,b** by treatment with CF_3COOH (Scheme 30).[50] Calixarenes $\mathbf{L_{a,b}}$ are thermally stable even in refluxing toluene and are not hydrolyzed by aqueous HCl or NaOH.[50]

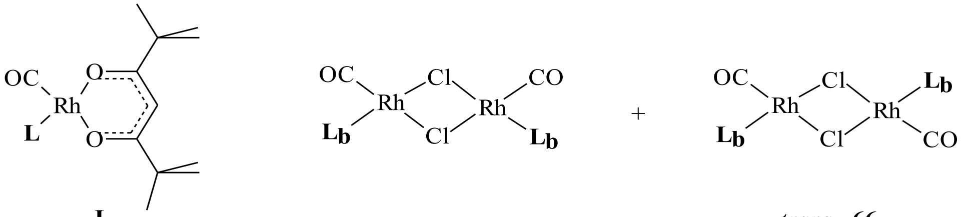


	R
64a	H
64b	*t*-Bu

	R
La	H
Lb	*t*-Bu

Scheme 30.

Dissolved in CH_2Cl_2 calixarenes $\mathbf{L_{a,b}}$ were treated with $[Rh(CO)_2(acac*)]$ to give complexes **65a,b** while the reaction of $\mathbf{L_b}$ with $[Rh_2(\mu\text{-}Cl_2)(CO)_4]$ afforded a 1:4 mixture of *cis*-**66** and *trans*-**66** (Scheme 31).[51]



	L
65a	**La**
65b	**Lb**

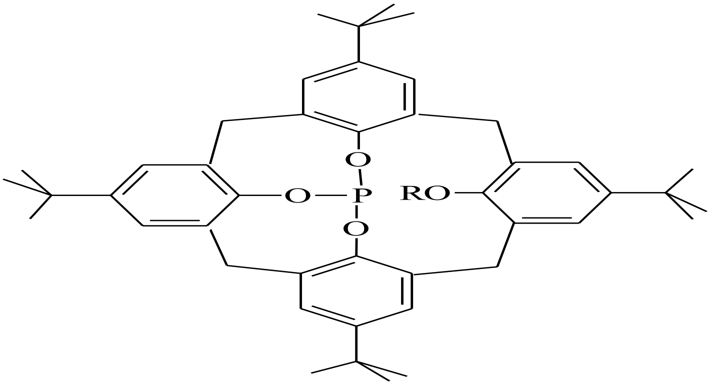
cis - **66**

trans - **66**

Scheme 31.

Rhodium complexes of $\mathbf{L_a}$ and $\mathbf{L_b}$ were tested as catalysts of the hydroformylation of 1-hexene. It was found that they are very active and chemoselective catalysts, however their regioselectivity is low.[49-51]

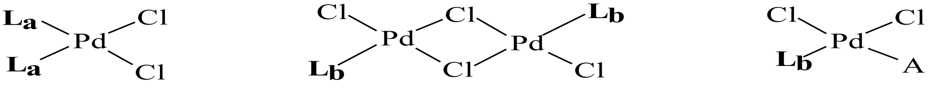
Calixarenes **67–70** (Scheme 32) form with $[Rh(CO)_2(acac*)]$ very active catalysts for hydroformylation of 1-octene, their efficiency being influenced by the conformation of the ligand.[49,50,52]



	R
67	*i*-Pr
68	CH_2Ph
69	C(O)Me
70	C(O)Ph

Scheme 32.

It was established that also palladium, iridium, platinum and gold complexes of $\mathbf{L_a}$ and $\mathbf{L_b}$ are promising with regard to their use as hydroformylation catalysts.[49-51] Reaction of $\mathbf{L_a}$ with $[PdCl_2(NCPh)_2]$ affords **71**, while $\mathbf{L_b}$ gives binuclear palladium(II) complex **72** under these conditions, the latter being converted into **73–75** by ligands A (A = CO, MeCN, *t*-BuCN) (Scheme 33).



71

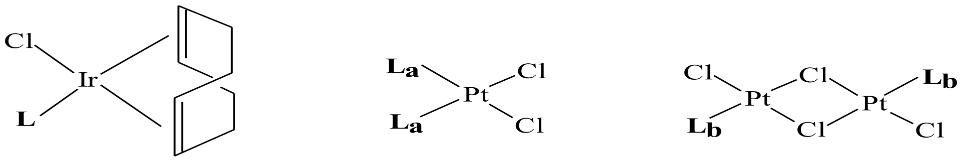
72

	A
73	CO
74	MeCN
75	*t*-BuCN

Scheme 33.

Calixarenes $\mathbf{L_a}$ and $\mathbf{L_b}$ react with $[Ir_2(\mu\text{-}Cl)_2(cod)_2]$ to give complexes **76a,b** and the reaction of $\mathbf{L_a}$ with $K[PtCl_3(C_2H_4)]$ results in mononuclear species **77**, while in the case of $\mathbf{L_b}$ the binuclear platinum(II) complex **78** is formed (Scheme 34).

Treatment of $\mathbf{L_a}$ and $\mathbf{L_b}$ with $[Pt(nor)_3]$ (nor = η-norbornene) in CH_2Cl_2 leads to non-isolable mixtures of complexes **79a,b** and **80a,b**,[50,53] and complexes **81a,b** are obtained with [AuCl(tht)] (Scheme 35).[50]

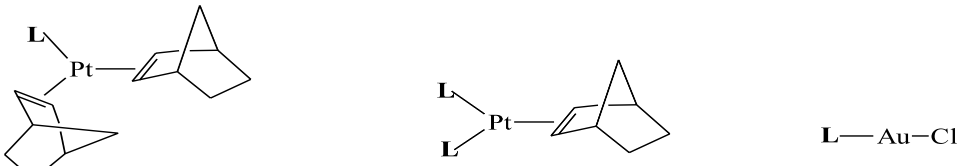


	L
76a	L_a
76b	L_b

77

78

Scheme 34.



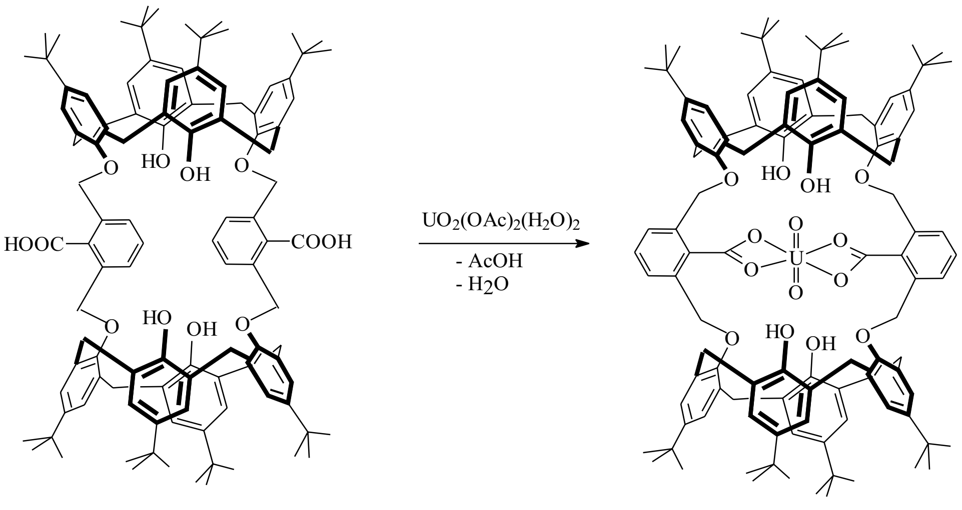
	L
79a	L_a
79b	L_b

	L
80a	L_a
80b	L_b

	L
81a	L_a
81b	L_b

Scheme 35.

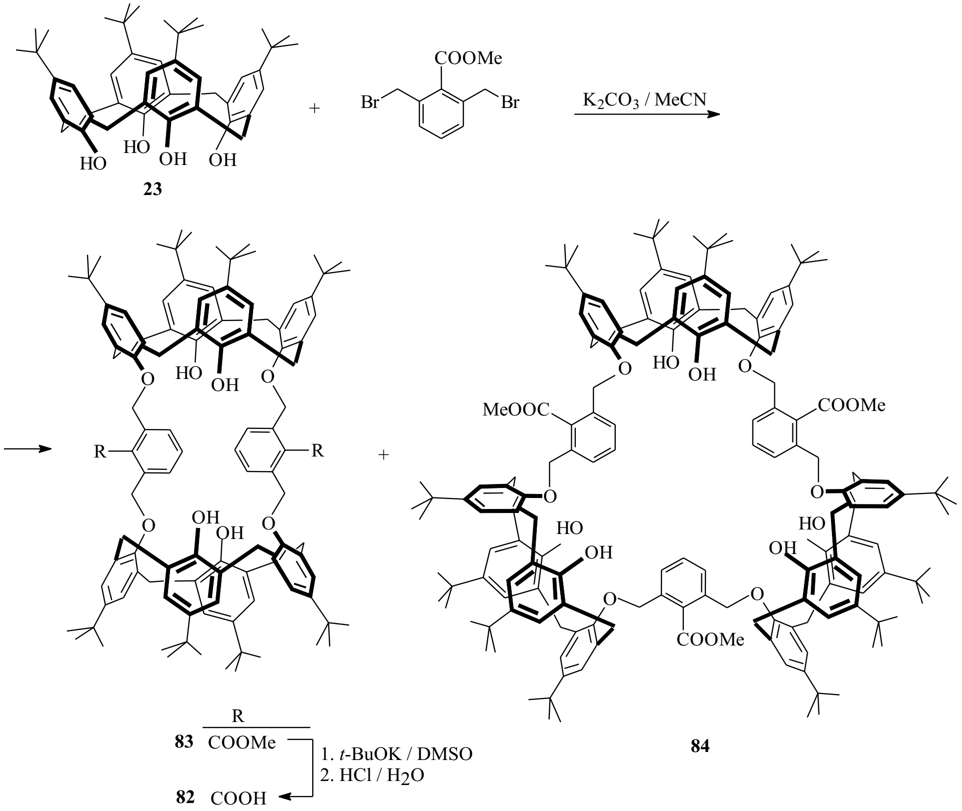
In the study of selective extraction of uranium dissolved in seawater in the form of uranyl cation UO_2^{2+}, it was observed that the biscalix[4]arene-based receptor **82** binds and extracts uranyl cation into organic solvent media.[54] The complexation of uranyl proceeds as follows (Scheme 36).



82

Scheme 36.

The synthesis of **82** involves condensation of calix[4]arene **23** with methyl 2,6-bis(bromomethyl) benzoate leading to dimer **83** and trimer **84**; the hydrolysis of the former affords receptor **82** (Scheme 37).



23

	R
83	COOMe
82	COOH

84

Scheme 37.

CONCLUSION

Investigations of calixarene complexes with transition metal as well as lanthanide and actinide ions are developing rapidly. In the above paper, an attempt has been made to present a concise survey of this theme. The described species are attracting growing attention, among others due to their usefulness in nuclear waste management, important in environmental protection.

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SAŽETAK

Kompleksi kaliksarena s prijelaznim metalima, ionima lantanoida i aktinoida

Wanda Śliwa

Opisani su odabrani kompleksi kaliksarena s ionima prijelaznih metala, lantanoidâ i aktinoidâ, te njihova priprava i mogućnosti primjene.