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Calixarene and resorcinarene ligands in transition metal chemistry

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Contents

Abstract

This is an exhaustive review of calixarenes containing transition metals. General preparative routes to calixarene ligands suitable for transition metal complexation are briefly reviewed. The aspects concerning their coordinative properties are organized according to the site and type of donor atom(s) involved in complexation. Emphasis has been placed on synthetic aspects so as to allow the reader to acquire a useful knowledge of the construction of transition

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metal complexes derived from calixarenes. Structural aspects have been systematically discussed for those complexes which have been characterized by X-ray analysis. Many interesting features of calixarene-derived ligands have been emphasized, e.g. the ability to act as bulky ligands or to behave as a polyoxo surface and the possibility to form novel supramolecular assemblies and to associate a catalytic centre with a potential receptor cavity. It is shown that transition metals are ideal partners for shaping or assembling calixarenes, thus allowing the construction of a number of large molecular systems, leading to various applications, notably liquid crystals, sensors for analytical purposes or molecular filters. © 1997 Elsevier Science S.A.

Keywords: Calixarene; Resorcinarene; Transition metal chemistry; Supramolecular chemistry

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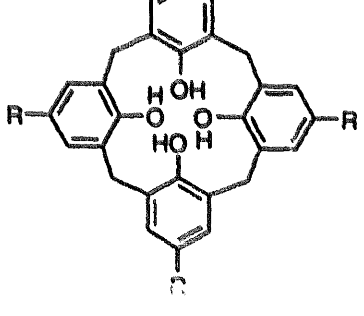
1. Introduction

Calixarenes have a long history, stretching back to 1872 when Adolph von Baeyer reported reactions between phenols and aldehydes [1–3]. Many of the products could not be identified at that time, and it took almost 70 years before the Austrian chemists Zinke and Ziegler assigned cyclic tetrameric structures to the products (**1**) resulting from the base-induced condensation of *p*-substituted phenols with formaldehyde [4,5]. Another class of cyclic tetramers (**2**), obtained from the acid-catalysed reaction of resorcinol with aldehydes, was identified by Niederl and Vogel in 1940 in the US [6]. Compounds of type **1** were termed calixarenes by C.D. Gutsche in 1978, from the Greek χυλιξ, thus describing the so-called cone (or bowl-shaped) conformation which these macrocycles often adopt [7]. Compounds of type **2** were called calixresorcinarenes or calixresorcarenes.With time, the term calixarene was used to describe all cyclic oligomers obtained from phenols or resorcinols, whatever their conformation or size. In this review, we use Gutsche's abbreviated nomenclature, of the type *p*-R-calix[*n*]arene, where the bracketed number indicates the size of the oligomer and R is the name of the group para to the hydroxyl group of the phenol used for the condensation reaction [8]. For simplicity, compounds in which R≡H are named calix[*n*]arenes.



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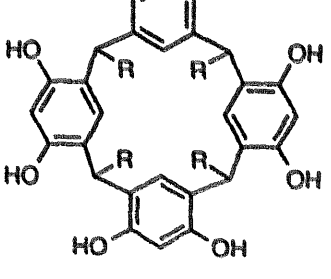

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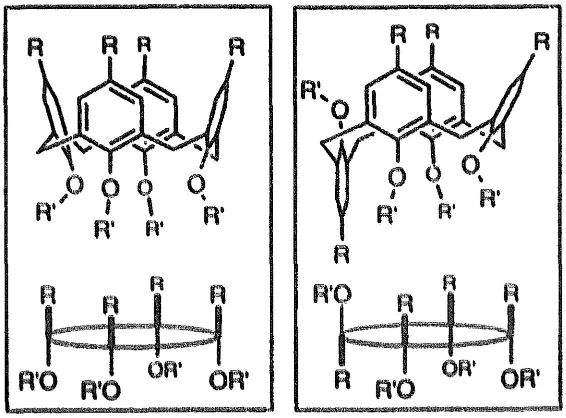
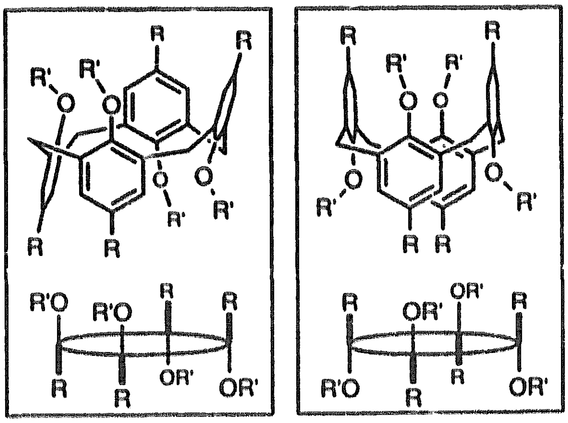
The investigations of Gutsche and coworkers during the 1970s led to an efficient synthetic methodology allowing easy access to large quantities of pure *p*-tert-butylcalix[*n*]arenes [9–11]. This work, as well as that of Hayes and Hunter [12], Kämmerer and coworkers [13–17] and Böhmer et al. [18–20] who, unlike Gutsche, proposed the synthesis of calixarenes by defined reaction sequences, initiated a number of studies dealing with the functionalization and structural modification of calixarenes. One characteristic feature of calixarenes is that they possess cavities which can be exploited for the formation of molecular complexes with small molecules. *p*-R-Calix[4]arenes, for example, form four types of cavity according to the relative orientation of the four phenoxy rings (Scheme 1), but inclusion compounds have been encountered only with cone conformers (in this review, the nomenclature used to specify an inclusion compound has the compound reference number immediately followed by the guest in parentheses). Much work has also demonstrated the ability of calixarene-based ligands to function as ion carrier molecules, sensors for analytical purposes or models for in vivo reactions of enzymes. The sensitivity of the calixarene structure to guest binding is well exemplified by the properties of calix[4]arenecrowns-6, e.g. **3** [21] and **4** [22], in the 1,3-alternate conformation. Such ligands are exceptionally selective for caesium ions (α(Cs/Na)$>$33 000 for **3**, α(Cs/Na)$>$49 000 for **4**), a result which is highly relevant for ^{137}Cs complexation, and hence for the recovery of nuclear waste.



cone

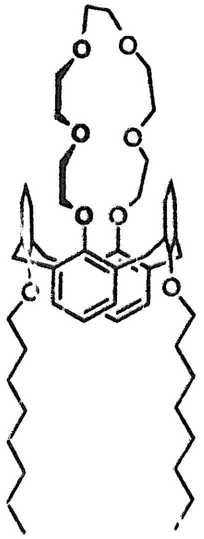
partial-cone



1,2-alternate

1,3-alternate

Scheme 1.



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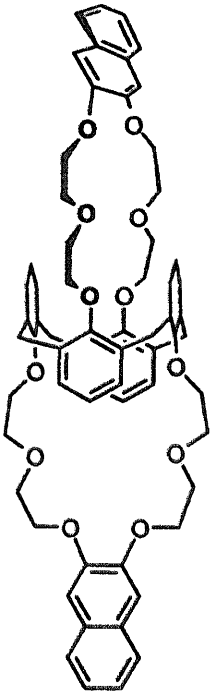

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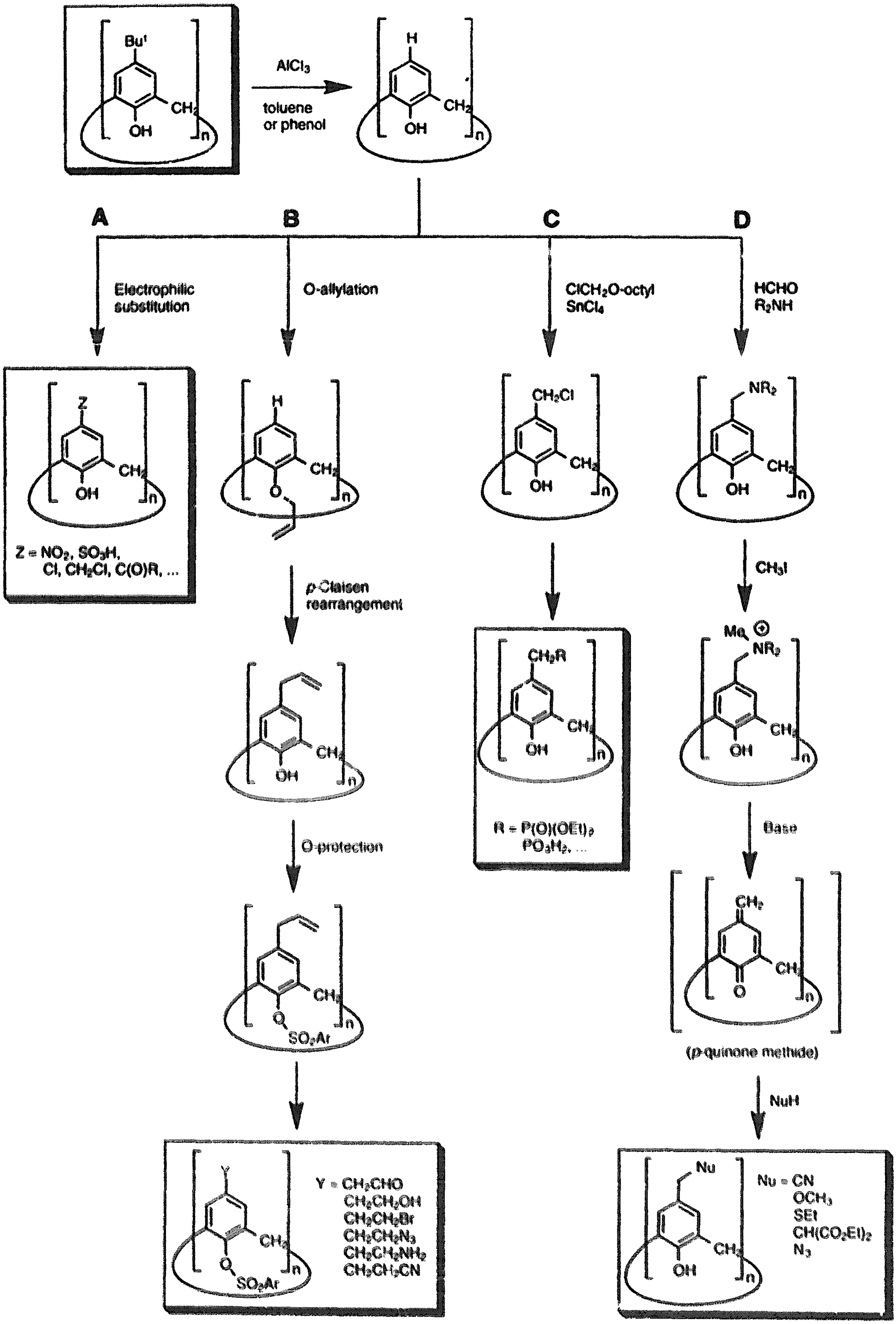
Despite the importance of calixarenes in host–guest chemistry, transition metal ions have been employed rarely in association with these ligands. Indeed, the first transition metal complexes containing a calixarene unit were only reported in 1985 [23]. In this review, we show how calixarene ligands can be used as pre-organizing matrices for the construction of mononuclear or polynuclear transition metal complexes and also illustrate their potential applications in catalysis and materials science. This overview will also include copper, silver, gold and mercury complexes. Some excellent articles describing the preparation and features of calixarenes [24–29], as well as their binding properties towards alkali, alkaline earth and rare earth metals [30–32], have already been reported.

2. General comments on synthetic and structural aspects of calixarene- and resorcinarene-derived ligands

What are the factors that govern the coordinative properties of a calixarene-derived ligand? Obviously, the most simple fashion in which to bind a metal centre is via one or more phenolic oxygen atoms; however, in most cases, the coordination chemistry of calixarenes results from the presence of functional groups arranged around the calixarene periphery, i.e. attached either to the phenolic oxygen atoms or to the carbon atoms in the para position. Many publications have been devoted to the functionalization of the phenolic oxygen atoms of calixarenes [8,33–35] and resorcinarenes [36]. This is often achieved by direct acylation [37,38] of the phenol group or by performing a Williamson-type alkylation allowing the straightforward introduction of groups, such as $-CH_2C(O)R$ ($R \equiv$ alkyl [39–41], $R \equiv$ aryl [40], $R \equiv$ O-alkyl [40–44], $R \equiv N(alkyl)_2$ [41,45–47]), $-CH_2CH_2OR$ [42,48,49], $-CH_2P(O)Ph_2$ [50,51], $-CH_2$pyridyl [52–54], $-CH_2CN$ [41,44], $-CH_2C{\equiv}CH$ [44], etc., which may, if necessary, be functionalized further [41,55,56]. If calixarenes functionalized at specific oxygen atoms are needed, we need to control both the degree of alkylation and the site(s) which will be modified. This can be done using carefully selected reaction conditions [57], notably by employing an optimum base–solvent couple and by controlling the stoichiometry [58]; very efficient strategies are now available for double functionalization of distal [44] or proximal [52,59] positions in *p*-R-calix[4]arenes. Alternatively, it may be advantageous to introduce, in a preliminary step, easily removable protective groups, such as methyl and benzyl groups, which can specifically be removed with Me_3SiX ($X \equiv$ Cl, Br [60], I [61]), or the C(O)Ph group which can be displaced with NaOH [37]. Once these groups have been specifically attached to the calixarene matrix, further functional groups can be introduced at the remaining non-functionalized OH groups. De-protection of the primarily modified phenolic oxygen atoms yields the selectively functionalized calixarene ligands.

General routes for the construction of *p*-tert-butylphenol-derived calixarenes having functional groups located at the para positions of calixarene are outlined in Scheme 2. These methodologies start by de-alkylation of the tert-butyl groups, using $AlCl_3$–toluene or $AlCl_3$–phenol as catalyst [37,62–64]. Via electrophilic substitution [64], the H atoms in the para positions can be selectively or totally (route A) replaced by groups, such as NO_2 [65], Cl, Br [66], I [67], SO_3^- [68,69] and $C(O)CH_3$ [37], themselves giving access to a large variety of other functional calixarenes [28]. Another route, **B**, exploits the possibility of transferring an O-bound allyl group to the para position (*p*-Claisen rearrangement) on heating the allylic ether in refluxing *N,N*-dimethylaniline [70]. The *p*-sited allyl group can be chemically modified via classical methods, giving access to interesting functionalized compounds. In route **C**, a chloromethyl group is introduced with chloromethyl *n*-octyl ether and $SnCl_4$ [71]. Subsequent replacement of the chloride results in the formation of a variety of potential ligands. In the so-called *p*-quinone methide route (**D**), the calixarene precursor is first transformed into a Mannich base with formaldehyde and a dialkylamine [72,73]. The resultant amino group itself can be easily displaced by quaternization, followed by reaction with two equivalents of a nucleophile. The formation of an intermediate *p*-quinone methide in this latter functionalization step is probable.

It is worth reminding the reader unfamiliar with the synthetic aspects of calixarenes that alkylation reactions at the lower rim (phenolic part), as described above, may be accompanied by structural changes in the matrix [60]. However, in most cases, homo-tetrafunctionalized *p*-R-calix[4]arenes may conveniently be obtained in the cone conformation, especially if the crowding of the substituent is larger than that of an ethyl group. This inhibits flipping of the phenolic rings through the calixarene cavity, thereby preventing conformational exchange.


Bu^t
AlCl3
toluene
or phenol
H
CH2
OH
n
A
B
C
D
Electrophilic
substitution
O-allylation
ClCH2O-octyl
SnCl4
HCHO
R2NH
Z
Z = NO2, SO3H,
Cl, CH2Cl, C(O)R, ...
CH2Cl
NR2
p-Claisen
rearrangement
CH3I
Me ⊕ NR2
CH2R
R = P(O)(OEt)2
PO3H2, ...
O-protection
Base
SO2Ar
CH2
O
(p-quinone methide)
NuH
Y
Y = CH2CHO
CH2CH2OH
CH2CH2Br
CH2CH2N3
CH2CH2NH2
CH2CH2CN
Nu
Nu = CN
OCH3
SEt
CH(CO2Et)2
N3

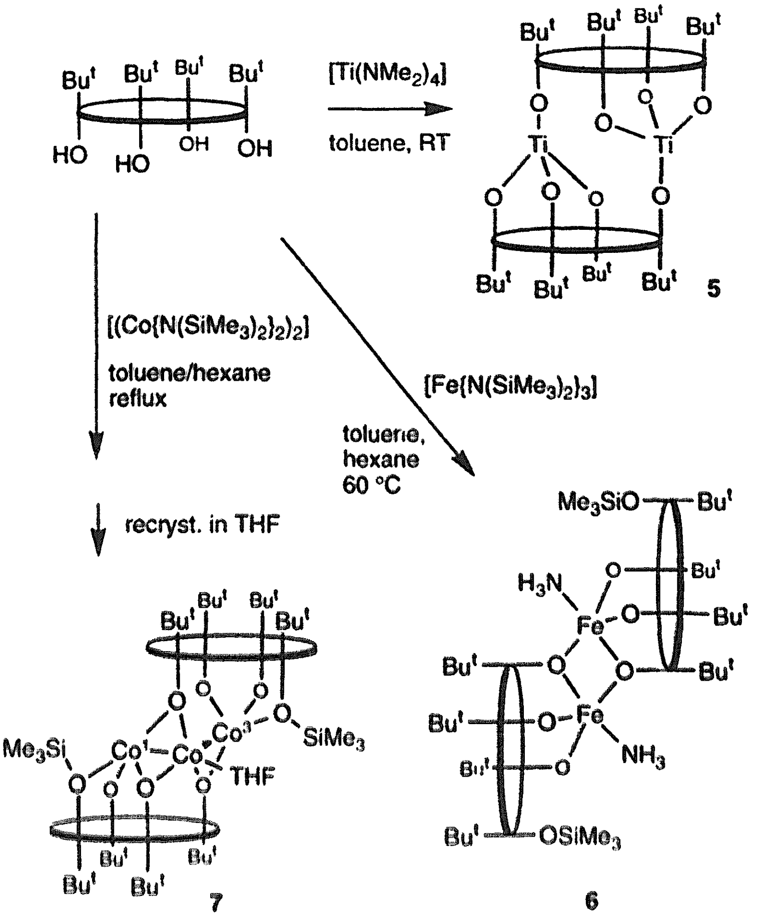
Scheme 2.

3. Exploiting the binding properties of phenolic oxygen atoms

3.1. Complexes with O-bound metals derived from p-R-calix[4]arenes

Compounds **5**–**7** are the first reported transition metal complexes based on calixarenes [23]. They were obtained by reacting *p*-tert-butylcalix[4]arene with the amido complexes $[Ti(NMe_2)_4]$, $[Fe\{N(SiMe_3)_2\}_3]$ and $[(Co\{N(SiMe_3)_2\}_2)_2]$ respectively (Scheme 3). While the formation of complex **5** may be interpreted in terms of deprotonation of the phenolic groups and subsequent elimination of Me_2NH, the pathways by which **6** and **7** are formed appear to be more complex. These latter reactions involve $SiMe_3$ shifts from N to O with the possible formation of NH_3 and/or $NH(SiMe_3)_2$ (note the iron atoms of **6** each contain an NH_3 ligand). As revealed by an X-ray diffraction study, complex **5** is a centrosymmetric dimer. For each calixarene subunit, adopting a cone conformation, three oxygen atoms are bound to the same titanium atom, the fourth being coordinated to the second metal centre. This leads to Ti atoms with a somewhat distorted tetrahedral geometry (the O–Ti–O angles range from 97.7(1)° to 127.0(1)°). According to a variable temperature study, the conformation of the calixarene fragments appears to be rigid on the nuclear magnetic resonance (NMR) timescale. The solid state structure of the dinuclear iron complex **6** is also centrosymmetric. In this complex, the three phenolato oxygen atoms of each calixarene are bound to an iron centre; in addition, one is coordinated to the second iron atom. The coordination sphere around the iron atoms contains an NH_3 molecule formed during the reaction and may be described as distorted trigonal pyramidal. The solid state structure of the trinuclear cobalt complex **7** has also been investigated. The main features of this unique complex are the presence of three cobalt atoms in an open cluster arrangement (Co(1)–Co(2), 2.760(4) Å; Co(2)–Co(3), 2.744(3) Å), stabilized by a terminal tetrahydrofuran (THF) molecule bound to the central cobalt atom (Co(2)), two terminal $OSiMe_3$ groups (one at Co(1) and the other at Co(3)) and terminal aryloxy and doubly bridging aryloxy groups. It is worth mentioning that complex **5** crystallizes with three toluene molecules in the asymmetric unit, one lying inside the cone cavity in a fashion similar to that found for *p*-tert-butylcalix[4]arene(toluene) [74]. For the cobalt complex **7**, which crystallizes with five toluene molecules, two solvent molecules are involved in host–guest interaction.

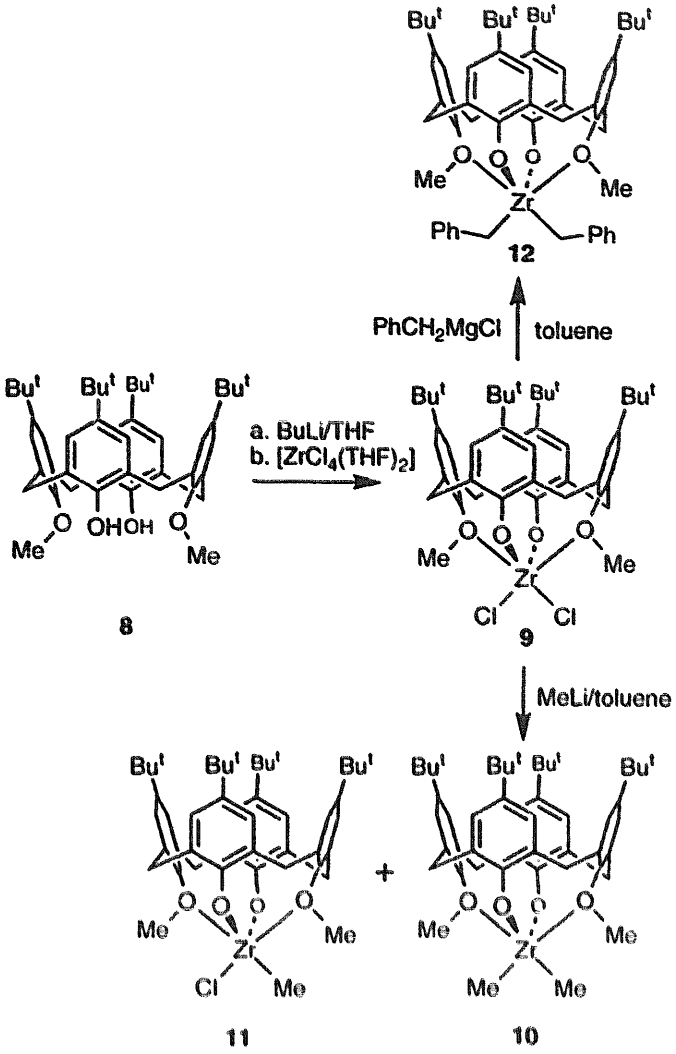
A series of mononuclear zirconium complexes having the metal centre coordinated to the four oxygen atoms of a dianionic calixarene ligand were prepared from dimethoxy-*p*-tert-butylcalix[4]arene (**8**) (Scheme 4) [75]. The reaction of **8** with BuLi in THF, followed by the addition of $[ZrCl_4(THF)_2]$, resulted in the formation of the C_{2v} symmetrical complex **9** having the metal centre bound to two phenolate anions and two methoxy oxygen atoms. Alkylation of **9** with one equivalent of MeLi gave a mixture of **9**, **10** and the monoalkylated complex **11** in an approximate 1 : 1 : 2 ratio. The same proportions were obtained by mixing equimolar amounts of **9** and **10**. The monoalkylated complex could not be obtained in pure form. The dialkylated complexes **10** and **12** (the latter was obtained by reacting **9** with $PhCH_2MgCl$ in toluene) display a high thermal stability. While **10** is photochemically



Scheme 3.

stable, **12** is photolabile. In the X-ray crystal structure of **10**, the calixarene ligand adopts an elliptical shape, as required by a hexacoordinated zirconium centre. The extremely short Zr–O(phenoxy) bond lengths (1.974(3) and 1.964(3) Å vs. 2.401(3) and 2.410(4) Å for the other two Zr–O distances) and the high values of the corresponding Zr–O–C_{ipso} angles (161.4(3)° and 167.3(3)° respectively) support strong metal–oxygen π bonds. Reaction of **12** with CO affords the relatively unstable η^2-ketone complex **13**. Another reaction in which the dianionic calixarene ligand displays ancillary behaviour is the oxidation of **12** with $[Fe(\eta^5\text{-}C_5H_5)_2]^+$, resulting in cleavage of one benzyl group and formation of the cationic alkyl complex **14**. The C_s symmetrical η^4-butadiene complexes **15** and **16** are formed when **9** is reacted with $[Mg(C_4H_6)(THF)_2]$ and $[Mg(C_{10}H_{14})(THF)_3]$ respectively. As shown by X-ray crystal structure analysis, the butadiene ligand of **16**, which adopts a cis conformation, may be regarded as π^2, η^4. For none of these latter complexes was cis–trans isomerization of the butadiene ligand observed.

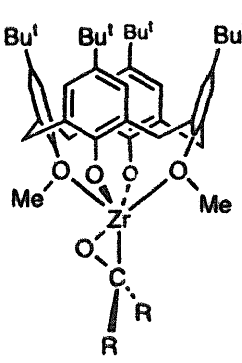
The possibility of using *p*-tert-butylcalix[4]arene as a polyoxo matrix for group V elements was demonstrated by reacting this macrocycle with $NbCl_5$ in *n*-hexane (Scheme 5) [76]. This reaction leads to complex **17**, which was characterized by IR and ^1H NMR. Its reaction with CH_3COOH gave the acylated complex **19**. The Ta



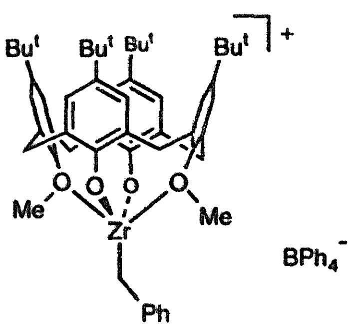
Scheme 4.

analogue of **19** (**20**) could be obtained in a single step without isolating intermediate **18**. Attempts to perform the synthesis of **19** in a single step, namely in *n*-hexane solution containing CH_3COOH or small amounts of H_2O, surprisingly led to the tetranuclear complex **21**. An X-ray structural analysis of **21** showed that this centrosymmetric molecule contains hexacoordinated Nb atoms and that the calixarene moieties adopt a cone conformation.

Further examples of mononuclear *p*-R-calix[4]arene complexes in which a Ta or Nb atom is bound to all four phenolate oxygen atoms were published by Acho et al. [77]. Thus complexes **22**–**24** were obtained either by reacting the corresponding deprotonated calixarene with the cyclopentadienyl metal tetrachloride or by heating the calixarene macrocycle with the metal chloride in refluxing toluene for 2 days. For all three complexes, the ^1H NMR spectra indicate a four-fold symmetry of the calixarene moiety. However, single X-ray structural analyses carried out for **22** and **23(toluene)**, revealed that, in the solid state, the calixarene units deviate from C_4



13 R = PhCH$_2$



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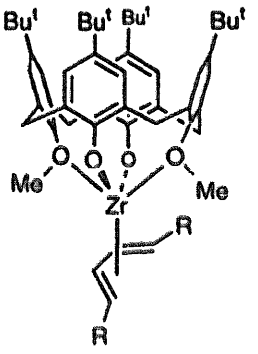
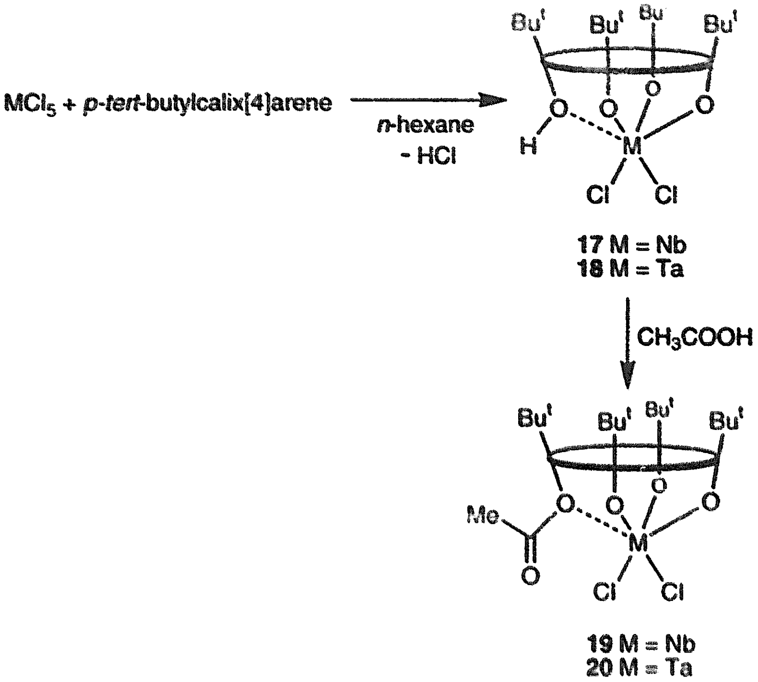


15 R = H
16 R = Ph

symmetry, producing an elliptical cavity shape. In each molecule, the Ta atom is unsymmetrically bound to the four oxygen atoms (see Scheme 6): two distal Ta–O bond distances (average 1.89(2) Å in both structures) are significantly shorter than the others (average 2.005(5) Å for both complexes) and two Ta–O–C$_{calix}$ angles are almost linear with the other two being close to 125°. Consistent with Fenske–Hall calculations, this de-symmetrization around the Ta atom probably originates from PhO–Ta π electron donation, which tends to compensate the electron deficiency of the 14-electron metal centre. This interpretation appears to be quite reasonable in view of the fact that the calix skeleton in the "inclusion" complexes **23(H$_2$O)** and **23(CH$_3$CN)**, containing a water molecule and an acetonitrile molecule bonded to the Ta centre respectively, is considerably more symmetrical, as revealed by X-ray diffraction studies. A further interesting aspect of the elliptical shape of the calixarene in **23(toluene)** is that this cavity nicely facilitates the sideways partial incarceration of toluene. This contrasts with the usual orientation of toluene molecules, characterized by their methyl group pointing towards the calixarene cone [74].

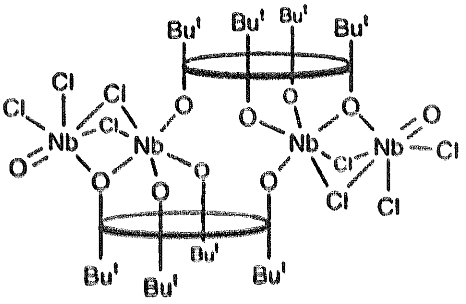
The coordination chemistry of *p*-R-calix[4]arenes was also investigated towards group VI metals. Reaction of Mo(O)Cl$_4$ with two equivalents of *p*-tert-butylcalix[4]arene (abbreviated L-(OH)$_4$) in *n*-hexane yielded, after extraction with CH$_2$Cl$_2$, the blue diamagnetic molybdenum-oxo complex **25** (Scheme 7), in which the Mo=O functionality is bonded to four phenoxy oxygen atoms [78]. This product



17 M = Nb
18 M = Ta

19 M = Nb
20 M = Ta

Scheme 5.



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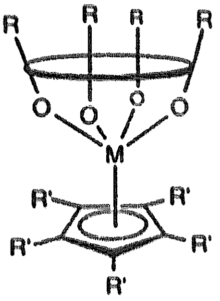
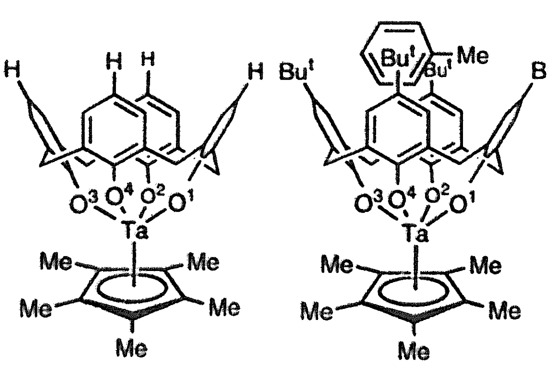


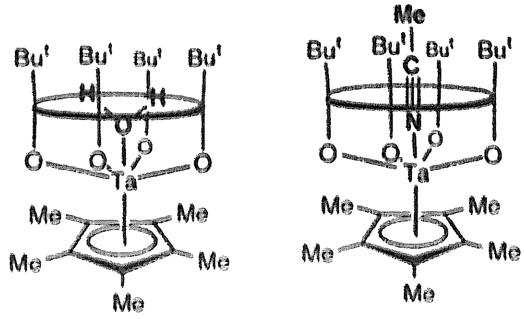
22 M = Ta, R = H, R' = Me
23 M = Ta, R = Bu^t, R' = Me
24 M = Nb, R = Bu^t, R' = H



22 **23(toluene)**

Ta-O^1	1.902 (4) Å	Ta-O^1	1.879(3) Å
Ta-O^2	2.010(3) Å	Ta-O^2	2.002(3) Å
Ta-O^3	1.871(4) Å	Ta-O^3	1.893(3) Å
Ta-O^4	2.000(3) Å	Ta-O^4	1.999(3) Å
O^1-Ta-O^3	127.0(2)°	O^1-Ta-O^3	123.6(1)°
O^2-Ta-O^4	155.1(1)°	O^2-Ta-O^4	155.2(1) °

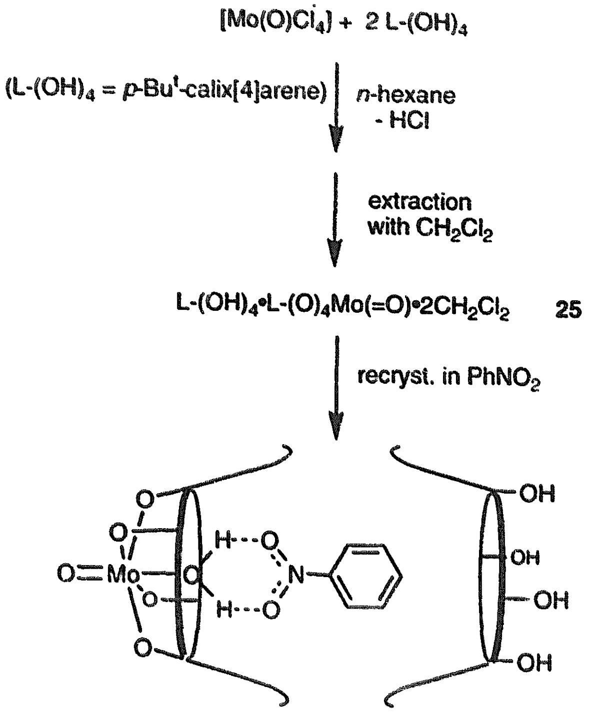
Scheme 6.



23(H$_2$O) **23(CH$_3$CN)**

was also formed when other stoichiometries were used. Recrystallization of **25** from PhNO$_2$ afforded the green complex **26**, in which a nitrobenzene molecule is trapped between a free calixarene and a calix-molybdenum-oxo unit (Scheme 7). X-Ray structural analysis confirmed this assembly and showed that the Mo atom is in a pseudo-octahedral environment of oxygen atoms, one of the coordination sites being occupied by the oxygen atom of a water molecule trapped inside the cavity, and being weakly bonded to the nitrobenzene molecule. The Mo atom lies slightly above the O$_4$ plane (distance to the plane, 0.337(3) Å) and is directed towards the exterior of the cavity.

Treatment of WOCl$_4$ with *p*-tert-butylcalix[4]arene, or its debutylated analogue, yielded complexes **27** and **28** respectively (Scheme 8) [79]. Recrystallization of **28** from CH$_3$COOH or "wet" CH$_2$Cl$_2$ gave inclusion complexes **28(CH$_3$COOH)** and **28(H$_2$O)** respectively with hexacoordinated W atoms. In both complexes, the clathrated solvent molecule is bound to the metal centre. As in **26**, the metal centres lie



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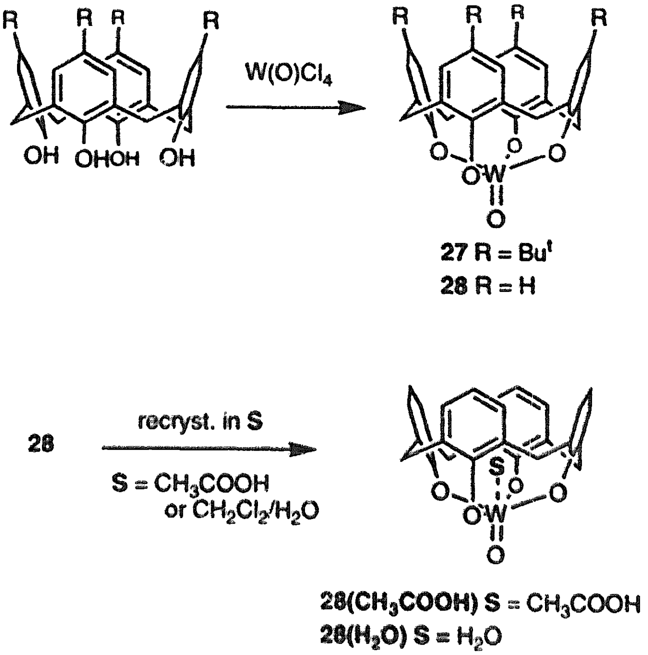
Scheme 7.

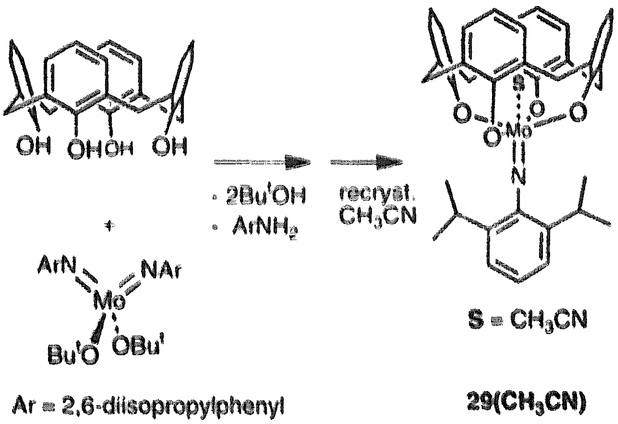
slightly out of the corresponding O_4 plane. The synthesis of a structurally related Mo complex (**29**) has recently been reported, involving the treatment of [Mo(NAr)$_2$(OBu^t)$_2$] (Ar ≡ 2,6-diisopropylphenyl) with calix[4]arene (Scheme 9) [80]. Recrystallization of **29** from CH_3CN afforded the inclusion complex **29(CH$_3$CN)**. It was proposed that this reaction, by analogy with that of complexes of the type [Mo(NR)$_2$(OBu^t)$_2$] with diols, proceeds via initial displacement of two tert-butoxide ligands. As shown by an X-ray study, the Mo atom is displaced from the O_4 plane towards the axial imido ligand by 0.252 Å.

The reaction of p-tert-butylcalix[4]arene in benzene with WCl_6 yielded the W^{VI} complex **30(C$_6$H$_6$)** (Scheme 10) [79]. Treatment of the latter complex with $AlCl_3$ in CH_3COOH resulted in the expected debutylation, with the subsequent formation of **28(CH$_3$COOH)**. As shown by an X-ray study, the calixarene matrix of this latter complex adopts a rather symmetrical bowl-shaped structure, whereas the coordination geometry of the tungsten atom in **30(C$_6$H$_6$)** leads to an elongated vase shape of the calixarene ligand. This is exemplified by the markedly different angles between the two pairs of opposite aryl rings: 126.1(2)° and 49.0(2)° in **30(C$_6$H$_6$)** vs. 83.2(1)° and 59.2(1)° in **28(CH$_3$COOH)**.

The rigid geometry of tungsten-oxo-calix[4]arenes has been exploited for the formation of liquid crystalline phases. Thus the tungsten complexes **31** and **32** with 8 and 12 dodecyloxy sidechains respectively were found to exhibit discotic columnar phases [81,82]. The high stability of the mesophases, which persist over an approximately 200 °C temperature range, has been assigned to the rigidity of the bowl.

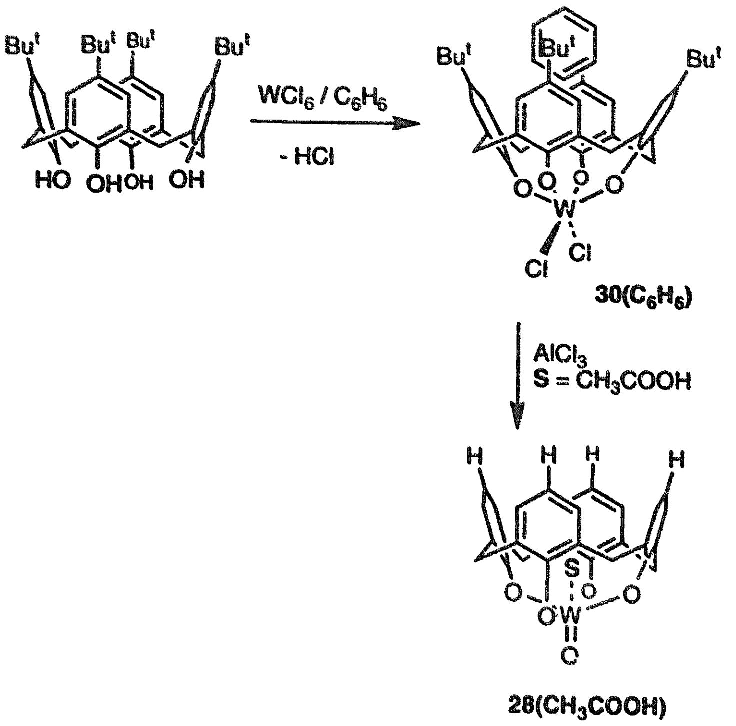


Scheme 8.



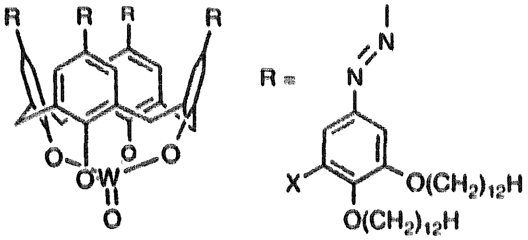
Scheme 9.

Indeed, complexation prevents the formation of non-cone conformers, and hence favours columnar head-to-tail organization in which the tungsten-oxo groups protrude into the cavity of a neighbouring mesogen. The mesomorphic behaviour can be modified dramatically by host–guest complexation. Thus, for instance, while **31** exhibits a discotic mesophase from 135 to 330 °C, the inclusion complex **31(DMF)** melts directly to an isotropic phase at 115 °C. The same phenomenon, occurring at the same critical temperature, was observed for **31(pyridine)**, showing that the important criterion for mesomorphism suppression is the presence of a filled cavity and not the nature of the guest. Further heating (200–250 °C) of the DMF complex results in the slow dissociation of the included molecule and the concomitant forma-



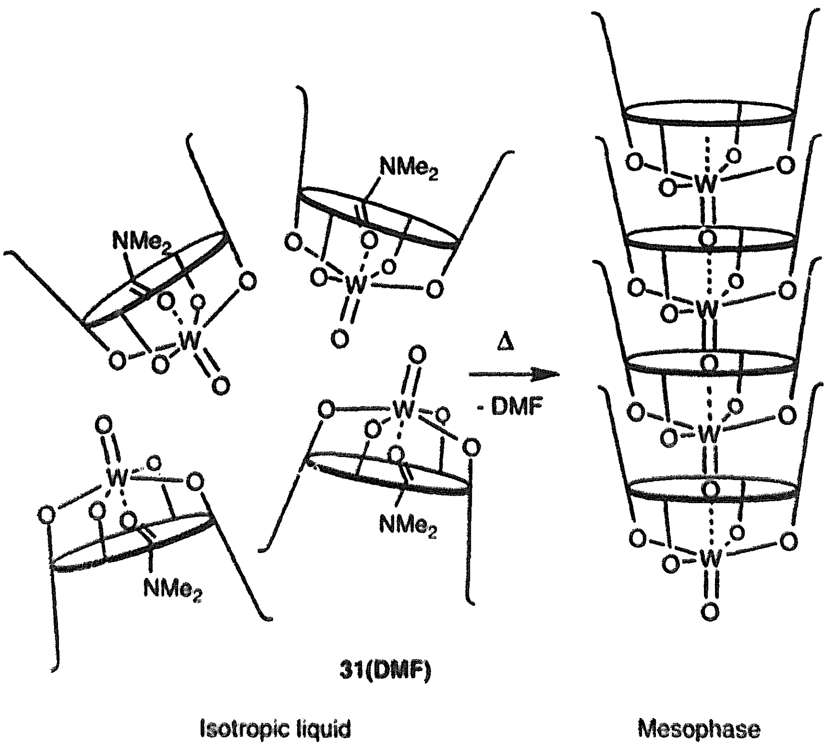
Scheme 10.

tion of the discotic phase (Scheme 11). Obviously, this type of mesophase could be interesting for the preparation of new materials having ferroelectric properties [83].



31 X = H
32 X = O(CH$_2$)$_{12}$H

Another interesting contribution to the controlled formation of supramolecular assemblies of *p*-R-calix[4]arenes is represented in Scheme 12. Reaction of **30** with sodium phenolate or catecholate in THF gave the diphenato complexes **33** and **34** respectively [84]. As established by X-ray analysis, the aromatic ring of one of the two phenato ligands protrudes into a neighbouring calixarene cavity, thus leading to a polymeric chain structure. Structural details are given for **33** only. The tungsten atom deviates slightly from an ideal octahedral geometry, and the calixarene adopts a shape characterized by an elliptical cone section with the two facing aryl rings being almost parallel (**A** and **C**) and the two others (**B** and **D**) being unsymmetrically pushed away from the macrocycle. The guest aryl ring is nearly parallel to rings **A** and **C** (dihedral angle AC, 25.3(2)°) and perpendicular to **C** and **D**. The W–O(ring

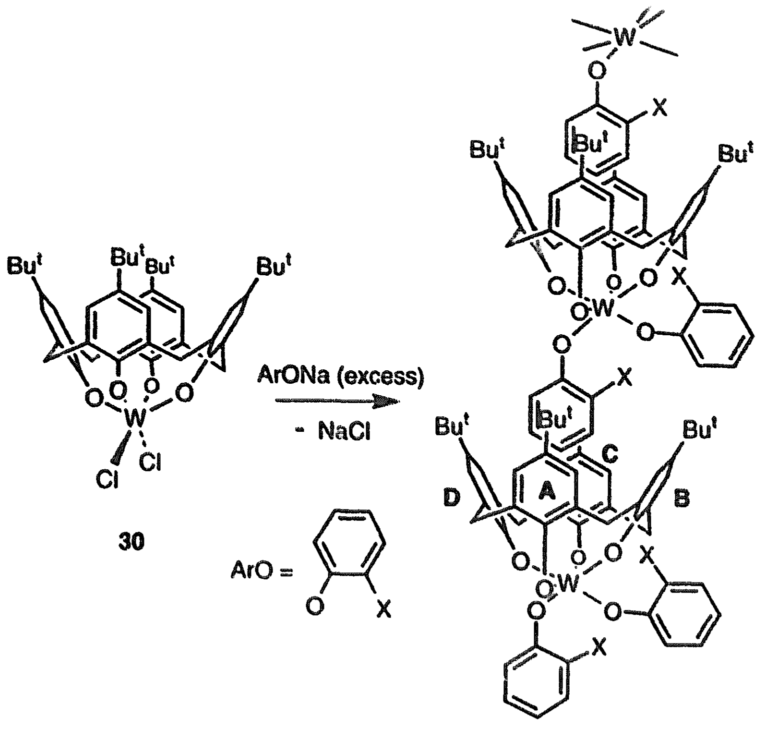


31(DMF)

Scheme 11.

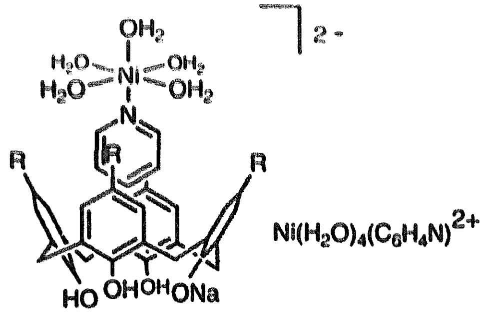
A), W–O(ring **B**) and W–O(ring **C**) bond lengths (mean value, 1.923(5) Å) are similar to the W–O bond lengths found in **27** [84]. The W–O(ring **D**) distance is significantly shorter, indicating some degree of double bond character. This observation is in keeping with an almost linear W–O–C_{ipso}(ring **D**) angle (176.9(5)°). The question whether the polymeric structure is maintained in solution remains open. It should be mentioned here that the possibility that a calixarene cavity may function as a ligand towards a transition metal-bonded aryl ring has previously been observed in $[(H_2O)_5Ni(NC_5H_5)]_2(Na)$[calix[4]arene sulphonate]·$3.5H_2O$ (**35**) and $[(H_2O)_4Cu(NC_5H_5)_2](H_3O)_3$[calix[4]arene sulphonate]·$9H_2O$ (**36**) which were reported in 1991 by Atwood et al. [85].

One of the most promising aspects of calixarenes still remaining to be explored is their use as assembling ligands for two or more metal centres. The synthesis of three dinuclear complexes, in which two quadruply bonded Mo centres are located above a calixarene matrix, is shown in Scheme 13. Complexes **37** and **38** were formed in good yield by reacting calix[4]arene and *p*-tert-butylcalix[4]arene respectively with two equivalents of KH and then with $[Mo_2(O_2CCF_3)_2(NCCH_3)_6][BF_4]_2$ [86]. Similarly, the reaction of *p*-tert-butylcalix[4]arene with two equivalents of KH in THF, followed by the addition of $[Mo_2(O_2CCH_3)_2(NCCH_3)_6][BF_4]_2$, resulted in the formation of complex **39** in 73% yield [87]. The recrystallization of **39** from benzene–THF gave a compound of formula **39(THF)**·C_6H_6. An X-ray structural determination was carried out for this complex. The Mo–Mo bond distance of 2.1263(6) Å and the eclipsed geometry of the Mo_2O_8 skeleton are consistent with an Mo–Mo quadruple bond. It should be noted that the Mo–Mo bond is somewhat

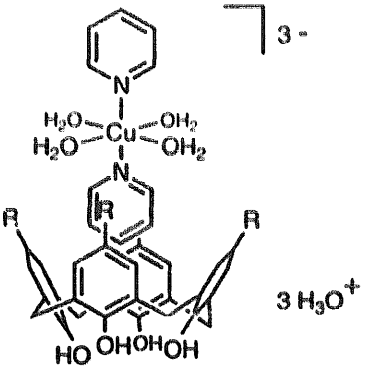


polymeric **33** X = H
polymeric **34** X = OMe

Scheme 12.

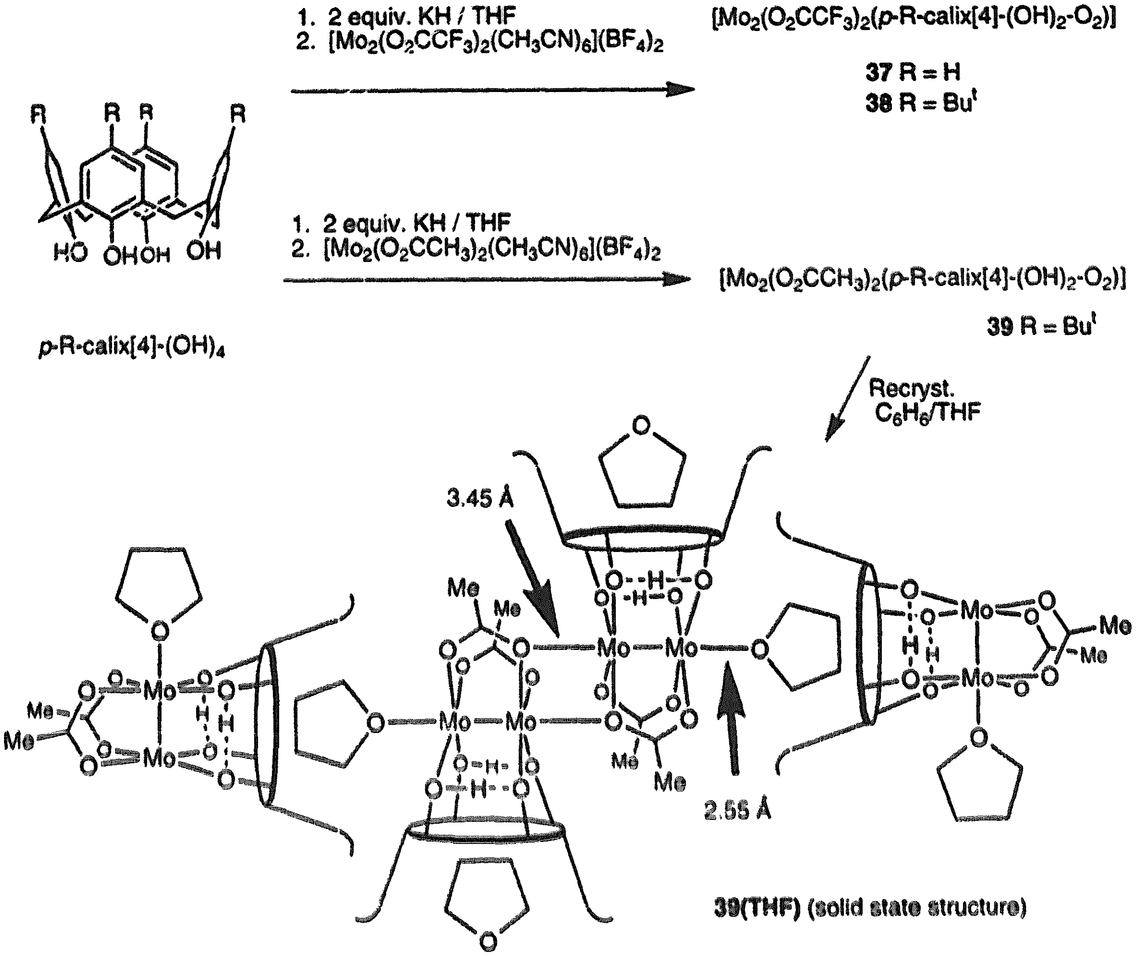


35 R = SO_3^-



36 R = SO_3^-

elongated when compared with that of [$Mo_2(OAc)_4$] (2.0934(8) Å), presumably because of the repulsive interaction between the filled pπ orbitals of the phenol and phenoxide oxygen atoms and the filled Mo–Mo δ orbitals in **39**. The OH hydrogen atoms belong to two proximal phenol groups, each OH bond lying parallel to the Mo–Mo vector and being strongly bonded to an adjacent phenoxy oxygen atom. In other quadruply bonded dimolybdenum complexes, e.g. [$Mo_2(O\text{-}Pr^i)_4(HO\text{-}Pr^i)_4$], similar strong hydrogen bonding was shown to contribute to a shortening of the metal–metal bond [88]. The axially coordinated THF molecule present in **39** is nested in the cavity of a neighbouring basket. Furthermore, each complex is weakly coordinated to the neighbouring molecules via axial Mo–O bonds with distances of 3.45 Å. This leads to an oligomeric structure in the solid state (Scheme 13).

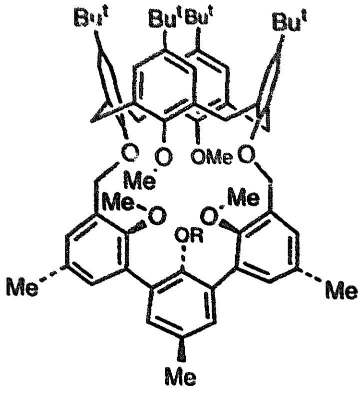


Scheme 13.

Two mononuclear silver complexes obtained from calixspherands **40** and **41** have been described by Bakker et al. [89]. On complexation, the calixarene methoxy groups undergo a high-field shift of approximately 3 ppm. Owing to the very weak silver–oxygen interactions, the thus formed complexes rapidly decompose (de-complexation half-lives: 51 and 131 h respectively) [89].

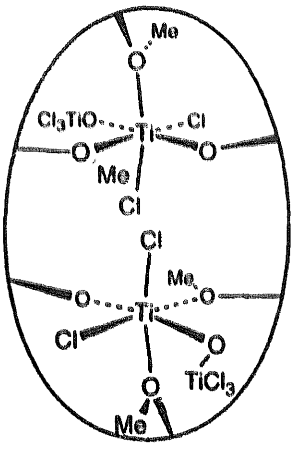
3.2. Complexes with O-bound metals derived from p-R-calix[6]arenes

The first known transition metal complex derived from *p*-tert-butylcalix[6]arene, **42**, was prepared by treating *p*-tert-butylhexamethoxycalix[6]arene with $TiCl_4$ [90]. In this reaction, attack by $TiCl_4$ forces cleavage of an O–Me bond. An X-ray structural determination established that, in the solid state, this molecule is centrosymmetric, with the calixarene adopting an elliptical cone conformation. The mole-



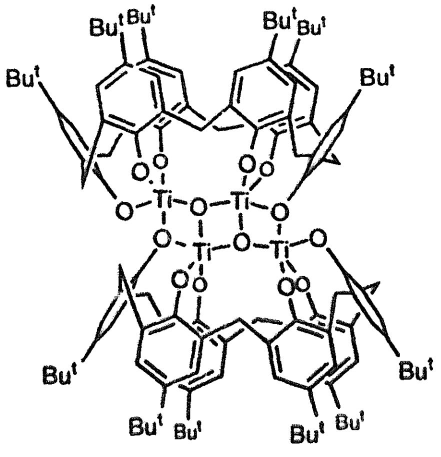
40 R = Et
41 R = Pr^i

cule contains two hexacoordinated Ti atoms (each surrounded by two chlorine atoms), two methoxy oxygen atoms (Ti–O: 2.15(2) and 2.23(2) Å), one phenoxy oxygen (with a Ti–O distance close to that of a double bond: 1.77(1) Å) and an $OTiCl_3$ fragment. The oxygen atom of the latter moiety probably originates from the clathrated water already present in the free calixarene. The Ti–O bond length (1.66(2) Å) and the three Ti–Cl bond lengths (2.17(1), 2.19(1) and 2.22(1) Å) of the tetracoordinated titanium atoms are unusually short, presumably because these Ti^{IV} atoms are coordinatively unsaturated.



p-tert-butylcalix[6]-$(OMe)_4$-$(O)_2$ $[TiCl_2(\mu\text{-}O)TiCl_3]_2$ **42**

A separate example of a titanium complex, **43**, obtained from *p*-tert-butylcalix[6]arene and Ti(OPr^i)$_4$ in boiling toluene, was reported by Andreetti et al. [91]. This complex comprises four Ti^{IV} atoms located between two cone-shaped calix[6]-arenes and two triply bridging O atoms (possibly water molecules). The X-ray structural analysis ($R = 0.199$) did not allow the O*H* atoms to be located. Interestingly, the Ti^{IV} atoms adopt a distorted trigonal bipyramidal and not the usual octahedral geometry. By comparison with the elliptical cone-shaped structure of *p*-tert-butylcalix[6]arene, the conformation of the calixarene ligands of **43** appears



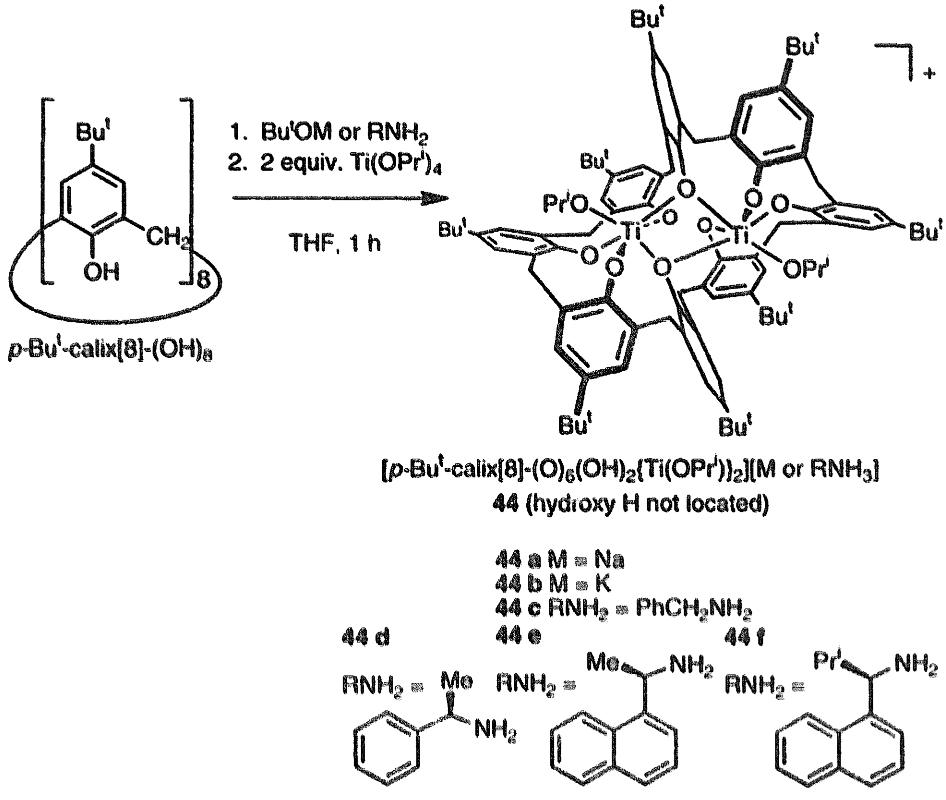
43 (O*H* atoms not located)

to be more regular because of complexation. In the solid state, a toluene molecule is guested in the apolar cavity of each calixarene unit.

3.3. *Complexes with O-bound metals derived from p-R-calix[8]arenes*

The coordination chemistry of *p*-R-calix[8]arenes towards transition metal centres has been less well investigated than that of *p*-R-calix[4]arenes, although, owing to their large size and flexibility, such macrocycles appear to be more suitable for the encapsulation of metal centres. Due to the presence of a large number of potential binding sites, such ligands also offer interesting possibilities for the preparation of multi-nuclear species.

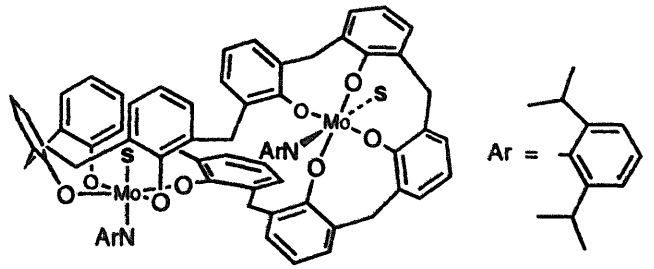
The first transition metal complex based on a *p*-R-calix[8]arene ligand was obtained by the treatment of *p*-tert-butylcalix[8]arene (*p*-Bu^t-calix[8]-(OH)$_8$) with one equivalent of a base, followed by the addition of two equivalents of Ti^{IV}(OPr^i)$_4$ (Scheme 14) [92]. This resulted in the formation of anions having the general formula $[\{p\text{-Bu}^t\text{-calix}[8]\text{-(O)}_6\text{(OH)}_2\}\{\text{Ti(OPr}^i)\}_2]^-$ (**44**), as established by fast atom bombardment mass spectrometry (FAB-MS). An X-ray structural determination was carried out for **44a**. In this complex, the lower rim annulus adopts a sort of pinched geometry with the two titanium atoms in pseudo-octahedral environments. All eight oxygen atoms of the calixarene matrix are involved in metal coordination, two behaving as bridging ligands. The remaining coordination site on each titanium is filled by an isopropoxide ligand lying inside an open cavity defined by three aryl rings. The hydroxy H atoms could not be located, but in view of their upfield shifted signal in the NMR spectrum (between 15 and 17 ppm for complexes **44a**–**44f**), it is probable that they are bonded to at least one other oxygen atom. The overall molecule is chiral. Thus when (*R*)-(+)-α-methylbenzylamine was used as the base in the reaction shown in Scheme 14, a 1 : 1 mixture of diastereomers was formed. (*R*)-(+)-1-(1-Naphthyl)-ethylamine changes the diastereomeric ratio to 3 : 1. On changing the α-methyl group in this latter amine to an isopropyl group, a 10 : 1 mixture of the diastereomers was formed. This chiral recognition probably arises from: (1) hydrogen bonding between an ammonium ion and a calixarene oxygen atom; (2) possible stacking between the aryl rings of the ligand and of the amine; (3) steric repulsion between the α-alkyl group of the amine and the metallocalixarene. When the reaction of Scheme 14 was performed with $\mathrm{Ti(OBu^t)_4}$ instead of $\mathrm{Ti(OPr^i)_4}$, an unidentified complex containing Ti was formed. From NMR measurements, it can be concluded that its structure is different from that of **44a**. However, the reaction of this unidentified material with two equivalents of isopropyl alcohol yields the same isopropoxide complex as described above.



Scheme 14.

Applying the methodology outlined in Scheme 14 to $\mathrm{Zr(OPr^i)_4(Pr^iOH)}$ and $\mathrm{V(O)(OPr^i)_3}$ leads to zirconium(isopropoxy)calix[8]arene and vanadium(oxo)-calix[8]arene complexes respectively, but no structural data were provided for these complexes [92].

The only known transition metal complex derived from calix[8]arene was obtained by reacting this ligand with two equivalents of the imido complex $\mathrm{[Mo(NAr)_2(OBu^t)_2]}$ (Ar ≡ 2,6-diisopropylphenyl) [80]. Recrystallization from $\mathrm{CH_3CN}$ afforded the bis(acetonitrile)-dimetallocalixarene complex **45**. As revealed by an X-ray structural determination, the calixarene ligand is twisted to accommodate the two bulky metal imido units. The pseudo-octahedral geometry about the Mo atoms is reminiscent of that found in **29**$\mathrm{(CH_3CN)}$, each molybdenum atom being displaced by an average distance of 0.254 Å out of the corresponding $\mathrm{O_4}$ plane towards the imido nitrogen atom.

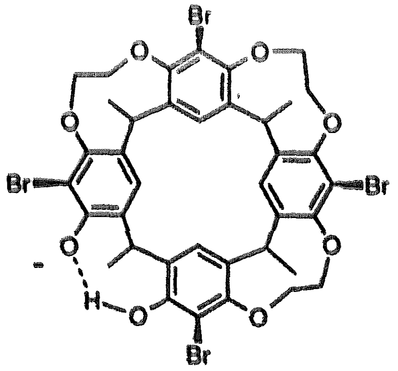


45

S = MeCN

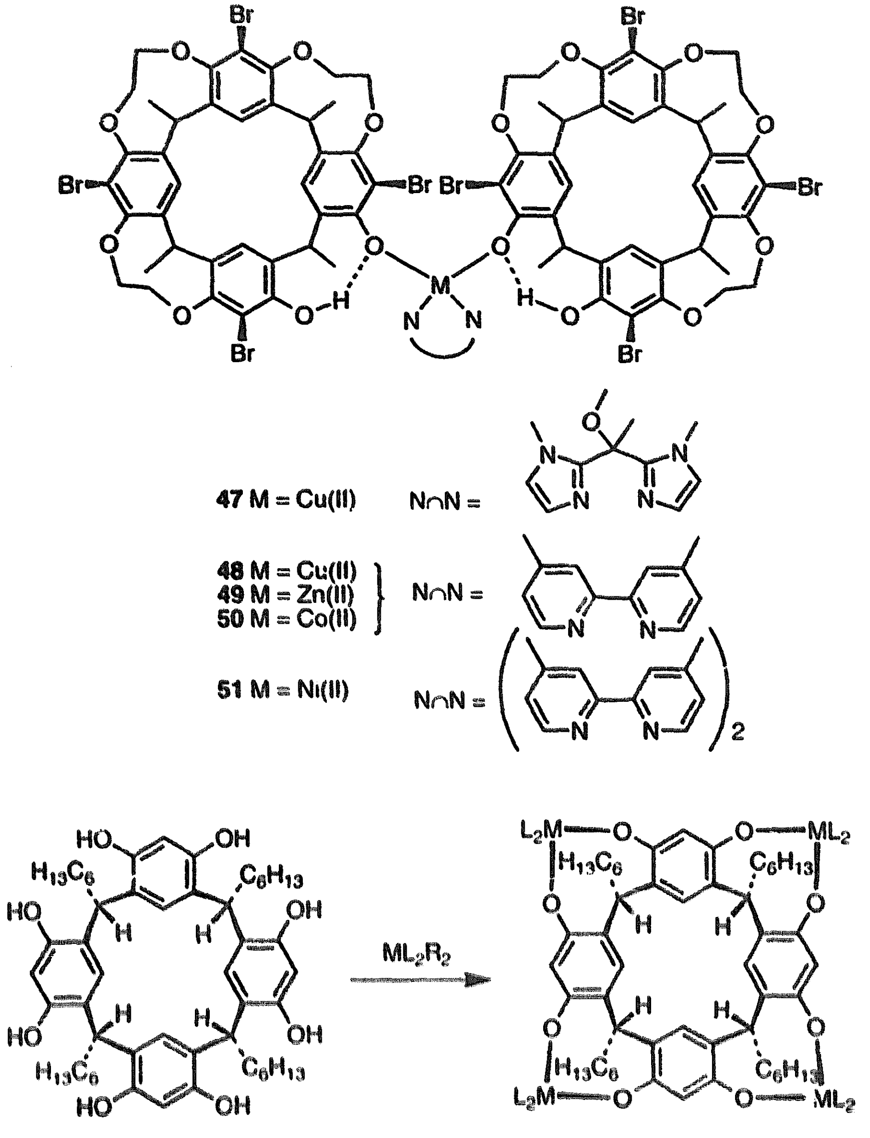
3.4. Metallation of calix[4]resorcinarenes

Treatment of the monoanionic calix[4]resorcinarene **46** with "MCl_2" units (M≡Cu, Zn, Co, Ni) in the presence of bidentate dinitrogen ligands (N∩N) gave a series of double calix[4]resorcinarene complexes (**47–51**) in which an "M(N∩N)" moiety behaves as a linker between the two cavitands [93]. It is expected that the two macrocyclic units of these molecules will be able to act cooperatively to recognize and bind potential guests. Complex **47·methanol·7 butyronitrile** has been characterized by X-ray crystallography. The geometry about the Cu^{II} centre is square planar and the two bowls adopt divergent orientations. Although in each cavitand the distance between the O(H) and the O(Cu) oxygen atoms (approximately 2.6 Å) is within the range for a hydrogen bond between phenolic oxygen atoms, this short O···O separation may simply result from the rigid structure of the cavitand framework. It should be noted that none of the solvents lie within a cavity.



46

Metallation of all the hydroxy groups of calix[4]resorcinarene **52** was achieved using $[Zr(\eta^5\text{-}C_5H_5)_2Me_2]$ and $[Fe(phen)(mes)_2]$ (see complexes **53** and **54**, Scheme 15) [94]. The result of X-ray analysis of **53** reveals that the ligand adopts the expected cone conformation and that the symmetry of the bowl is close to C_4. Interestingly, the four zirconium ions of **53** define an almost square framework with an average Zr···Zr distance of 7.763(3) Å. Complex **54** is paramagnetic, but no magnetic interaction within the tetrametallic unit could be observed. The magnetic moment per iron atom is essentially constant down to about 80 K, with a value of 5.1 μ_B, typical of Fe^{II} complexes ($J_{antiferro} = +0.4\ cm^{-1}$).



47 M = Cu(II) N∩N =

48 M = Cu(II)
49 M = Zn(II)
50 M = Co(II)

51 M = Ni(II)

52

53 M = Zr, L = C_5H_5, R = Me
54 M = Fe, L_2 = phenantroline, R = mesityl

Scheme 15.

4. The coordination chemistry of calixarenes possessing pendant binding sites

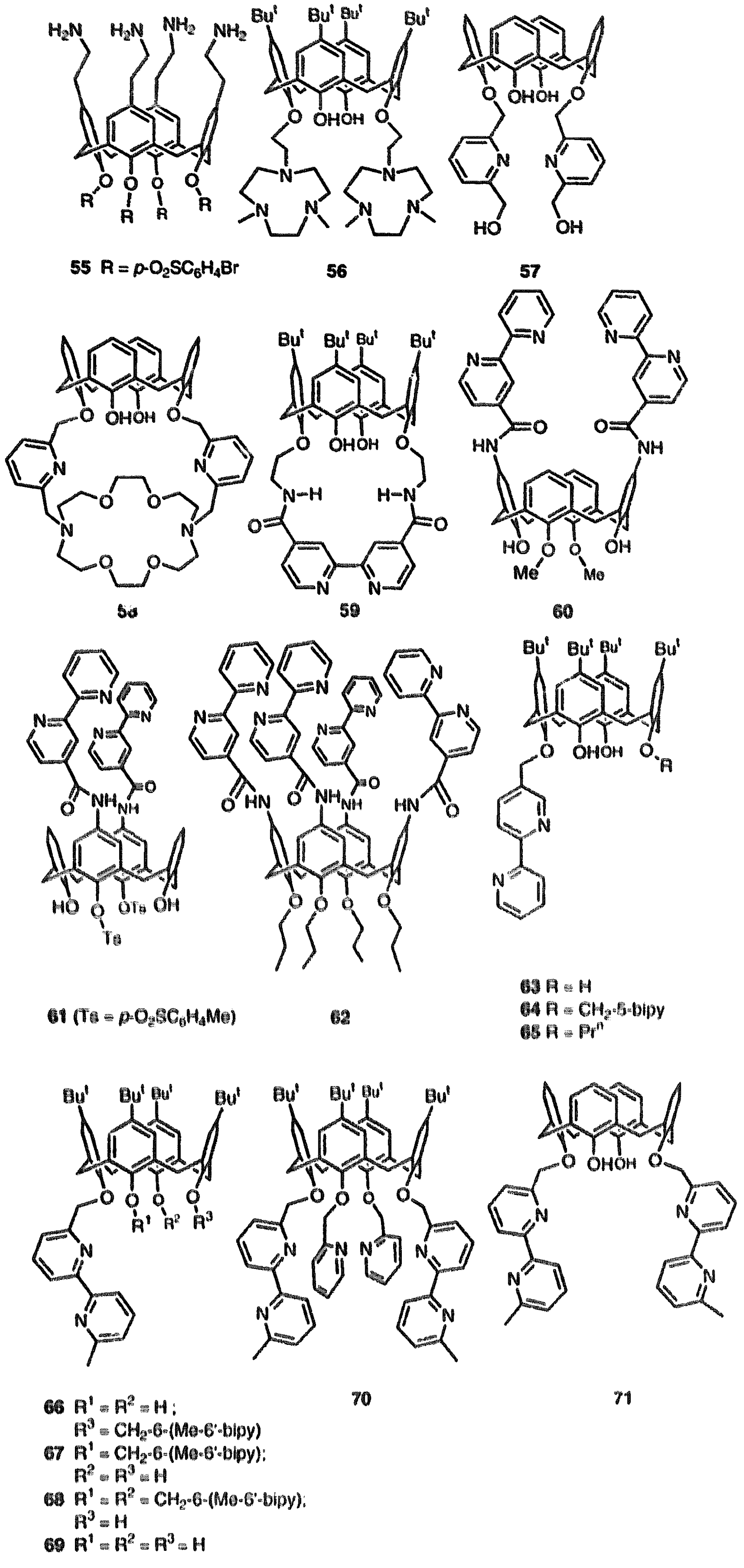
4.1. Complexes with calixarene ligands containing nitrogen donors

Functional groups containing N donor atoms have been introduced on both lower and upper rims of calixarenes. Scheme 16 gives an overview of those *p*-R-calix[4]arenes containing amine or pyridine pendant groups (compounds **55**–**71**) used for the complexation of transition metals. The first complexation study with such an amino-calixarene ligand was performed using the cone calixarene **55**, with the purpose of preparing octahedral complexes having the amino groups occupying the four equatorial sites around the metal centre [72]. In such a hypothetical system, one of the two apical sites would lie inside the calixarene cavity and would be accessible only to those molecules small enough, e.g. O_2, to pass through the annulus of the lower rim. Although it was shown that **55** is suitable for the complexation of ions such as Ni^{2+}, Cu^{2+}, Pd^{2+}, Co^{2+} and Fe^{2+} (however, no complex was fully characterized), this goal was not realized, presumably because the four mobile ethylamine arms do not allow the formation of a rigid, closed cavity.

In a recent report, Beer et al. [95] described the synthesis of the ditopic bis-(triazanonane)calix[4]arene **56** (Scheme 16). Reacting this ligand with $Ni(ClO_4)_2 \cdot 6H_2O$ and NaN_3 gave the binuclear complex **72** containing three 1,1 end-on-bonded azide bridges. As shown by an X-ray diffraction study, the two Ni atoms (Ni · · · Ni, 2.852(2) Å) are six-coordinate with a distorted octahedral environment. Complex **72** displays ferroelectromagnetic behaviour, thus contrasting with the structurally related 1,1-bridged system $[Ni(N_3)_2(tmeda)]_n$ which produces antiferromagnetic coupling [96]. The origin of this difference is unknown, but could arise either from the polymeric nature of the latter complex or from the particular values of the N–Ni–N angles which seem to be a crucial feature for magnetic coupling (average $Ni–N_{azide}–Ni$ in **72**, 86.2°).

Bipyridine units have also been attached to calixarenes in order to prepare novel types of sensor. For instance, luminescent pH sensor activity was found for complexes **73** and **74** which combine a luminophore (a trisbipyridylruthenium(II) moiety) and free phenolic units of a *p*-tert-butylcalix[4]arene fragment capable of acting as the acid–base sites [97]. The pH sensor property is based on an intramolecular photoelectron transfer (PET) process between the phenoxide ion and the Ru^{II}-trisbipy unit. For complex **73**, the distal OH is more acidic ($pK_a = 4.5$), but the phenoxide ion resulting from its deprotonation does not quench the luminescence from the metal complex. Quenching is apparent only on deprotonation of the proximal phenolic group (at pH 8.1 in 50% v/v aqueous methanol). It was proposed that, because of the better stabilization of the distal phenoxide vs. the proximal phenoxide, the oxidation potential of the distal phenoxide is too high to allow electron transfer.

As shown by an NMR study, the presence of NH(amide) functional groups in calixarenes **75** and **76** allows the binding of anions, such as halide, dihydrogenphosphate and bisulphate [98]. Titration curves for these two complexes indicate the formation of 1 ligand : $2X^-$ and 1 ligand : $1X^-$ complexes respectively. An electrochemical study revealed that, on anion complexation, it is the reduction near −1.4 V (vs. Ag/Ag^+ electrode), corresponding to the amide-substituted bipyridyl unit, which undergoes the most significant cathodic perturbation (for the bipy-centred reductions and the metal-centred oxidations, the potential variations are weak), confirming that anion recognition takes place close to the amide-bipyridine moiety. The monotopic anion receptor **76** exhibits selective recognition of $H_2PO_4^-$, even in the presence of a ten-fold excess of HSO_4^- and Cl^-. Stability constant determinations showed that the non-cyclic diamide **77** is a less efficient receptor than **76**. These



55 $R = p\text{-}O_2SC_6H_4Br$

56

57

58

59

60

61 ($Ts = p\text{-}O_2SC_6H_4Me$)

62

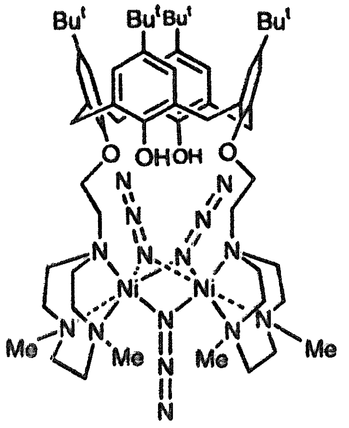
63 R = H
64 $R = CH_2\text{-}5\text{-bipy}$
65 $R = Pr^n$

66 $R^1 = R^2 = H$;
$R^3 = CH_2\text{-}6\text{-}(Me\text{-}6'\text{-bipy})$
67 $R^1 = CH_2\text{-}6\text{-}(Me\text{-}6'\text{-bipy})$;
$R^2 = R^3 = H$
68 $R^1 = R^2 = CH_2\text{-}6\text{-}(Me\text{-}6'\text{-bipy})$;
$R^3 = H$
69 $R^1 = R^2 = R^3 = H$

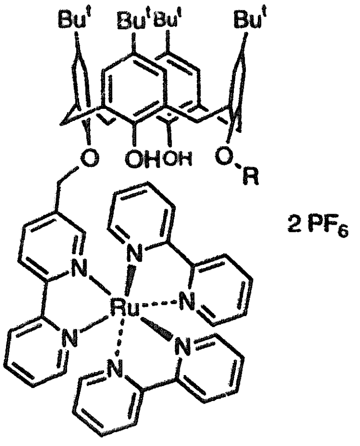
70

71

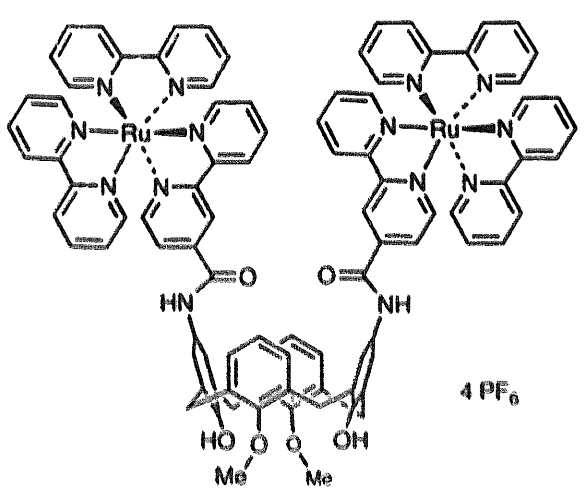
Scheme 16.



72



73 R = H
74 R = CH_2-5-bipy-$Ru^{II}(bipy)_2$•2 PF_6

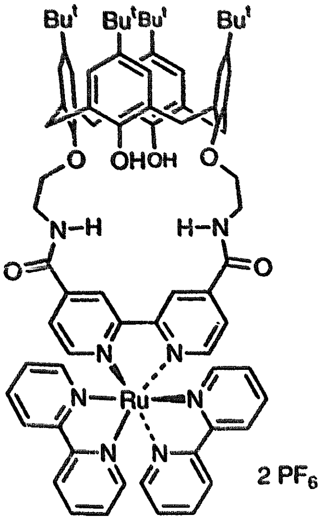


75

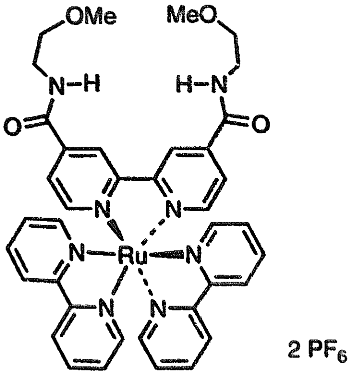
results open the way to new amperometric chemical sensors based on appropriately chosen calix-crown cavities.

A recent report mentions that the upper rim functionalized calix[4]arenes **78** and **79** bearing two and four ruthenium bipyridyl amide groups respectively also selectively sense via fluorescence emission the $H_2PO_4^-$ anion [99].

The coordinative properties of the bipyridyl-substituted ligands **66**–**69** were investigated towards copper(I) ions [100]. Ligand **69** leads to the expected double calixarene **80**. With **66** and **67**, the formation of mononuclear bis-bipyridyl copper(I) complexes, in which the two bipy arms act as a chelator, was proposed on the basis of spectroscopic data. The monomeric nature of the complexes formed, although probable, could not be confirmed by mass spectroscopy. The reaction of the mixed bis(pyridine)–bis(bipyridine) ligand **70** with $[Cu^I(CH_3CN)_4]PF_6$ resulted in the formation of the mononuclear chiral complex **81** (90% yield) [54]. The reaction of **70** with $[Cu^{II}(CF_3SO_3)_2]$ afforded the same cation, isolated as its CF_3SO_3 salt, in approximately 70% yield. The molecular structure of **81** was determined crystallo-



76



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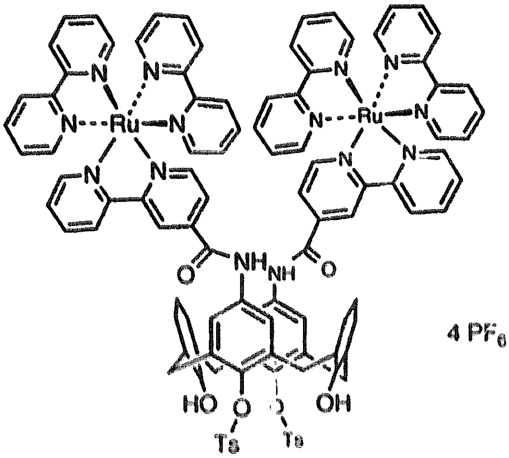
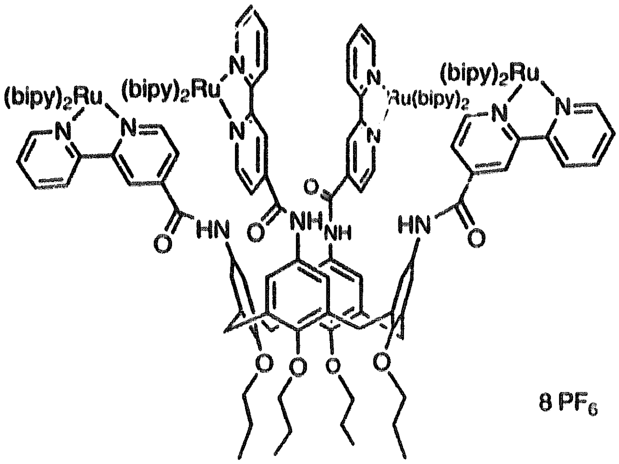
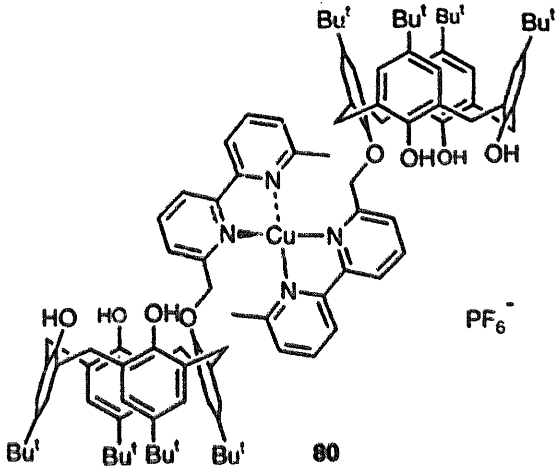


78 (Ts = p-$O_2SC_6H_4Me$)

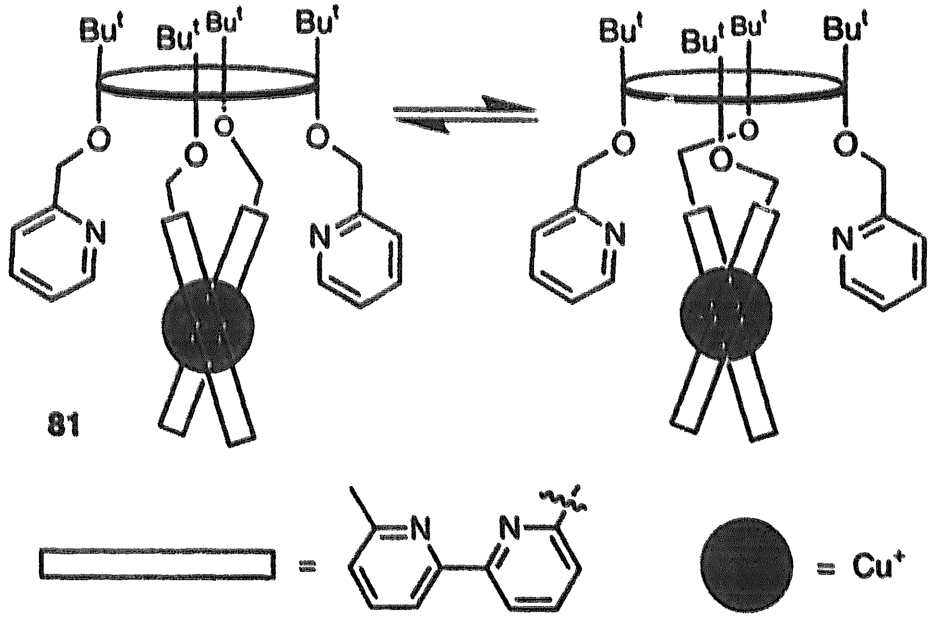


79

graphically. Coordination about the copper atom deviates from the ideal tetrahedral geometry, probably because the bipyridyl pendant arms are too short to allow the bipy units to wrap around the copper ion without strain. As shown by a careful NMR investigation, complex **81** displays dynamic behaviour in solution. This was interpreted in terms of fast exchange between the two enantiomeric forms of **81** (Scheme 17).



80



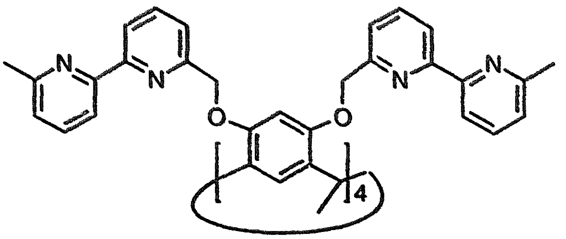
81

Scheme 17.

The octapodal, resorcarene-based bipyridyl ligand **82** was recently shown to allow the formation of the octanuclear cobalt complex **83** [101].

4.2. *Use of calixarene ligands containing phosphorus donors*

Although a large variety of phosphorus-containing calixarenes have already been synthesized, the potential of these compounds as complexing agents for transition



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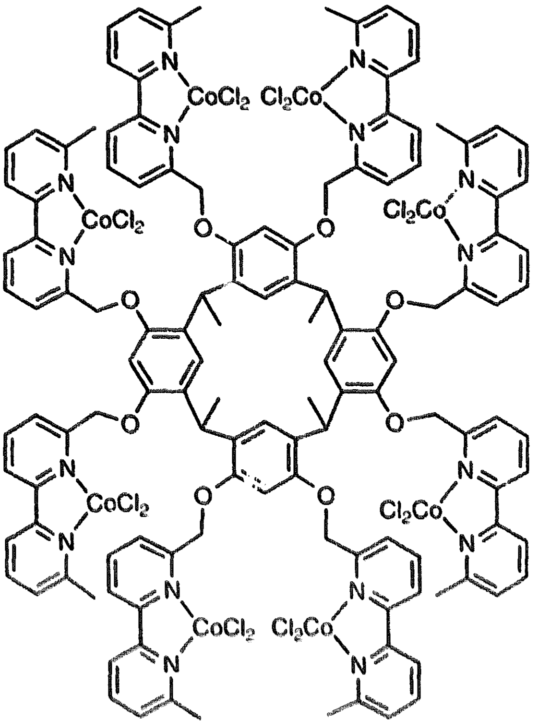


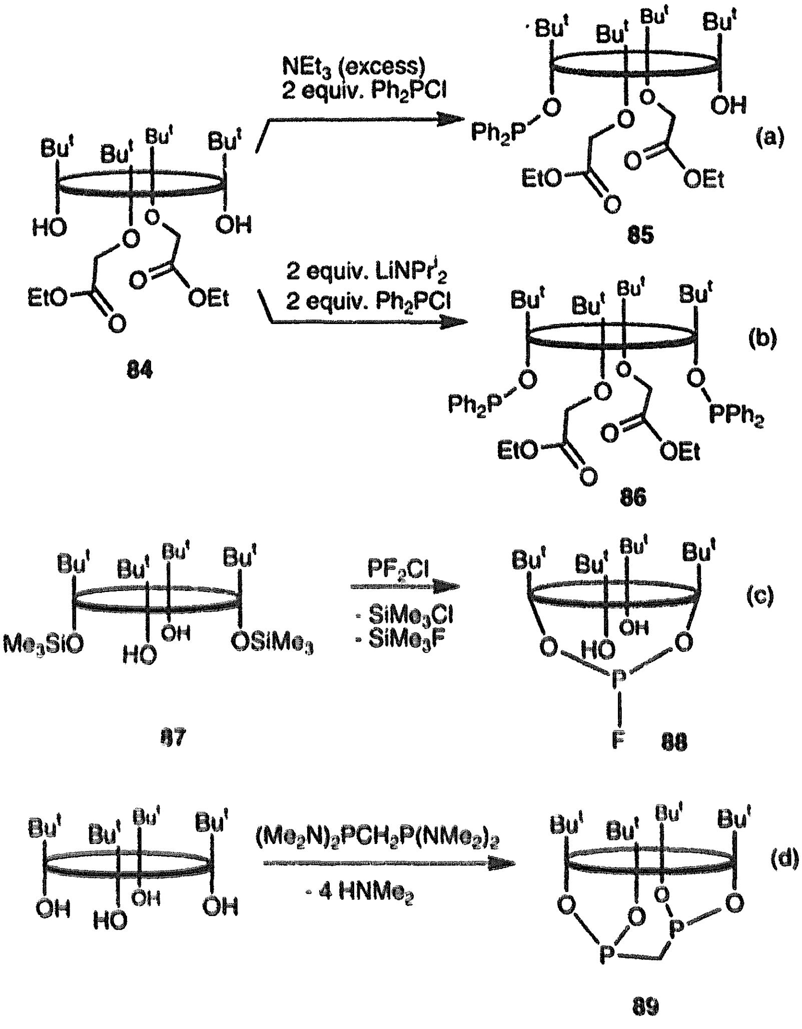
83

metals has received relatively little attention. This is rather surprising considering the versatility of P^{III} ligands in transition metal chemistry and in homogeneous catalysis. Calixarenes bearing trivalent phosphorus centres can be divided into two classes: those in which the P atom is covalently bound to a phenolic oxygen atom of a calixarene or a resorcarene and those in which the P atom belongs to a pendant group attached to the calixarene matrix.

4.2.1. Calixarenes with a phosphorus donor atom bound directly to a phenolic oxygen atom

Attachment of a P^{III} atom to a phenolic atom of a calixarene or a resorcarene may readily be achieved by treatment of the calixarene with base, followed by subsequent reaction with a halogenated P^{III} compound (Scheme 18). The number of phosphino groups which may be introduced mainly depends on the basicity of the deprotonating agent. For example, the reaction of **84** with two equivalents of Ph_2PCl in the presence of excess NEt_3 affords monophosphinite **85**, whereas using

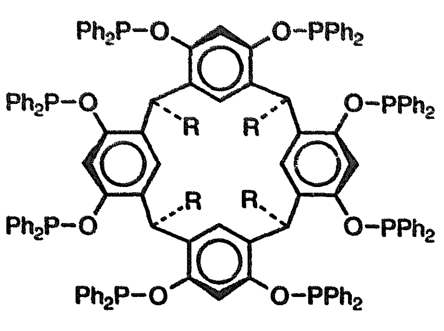
$LiNPr^i_2$ as base gives the disubstituted compound **86** (Scheme 18, (a) and (b)) [102]. An elegant alternative to this methodology concerns the reaction of a silyl derivative of the calixarene with a halophosphine. Thus the reaction of the bis-silyl compound **87** with one equivalent of PF_2Cl results in the sequential elimination of first trimethylsilylchloride and then trimethylsilylfluoride to yield the 1,3-bridged fluorophosphinite **88** (Scheme 18, (c)) [103].



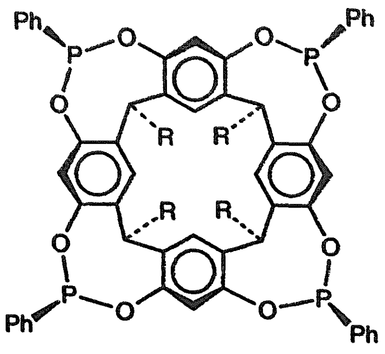
Scheme 18.

Instead of using the chlorophosphine–base route, it is sometimes advantageous to perform the phosphination with a dialkylaminophosphine. In this case, the amino group plays the role of deprotonating agent. Such a strategy employing $(Me_2N)_2PCH_2P(NMe_2)_2$ has been successfully applied for the synthesis of **89** (Scheme 18, (d)) [104].

The chlorophosphine–base strategy has also been applied to the formation of resorcarene-derived phosphites or phosphonites, such as **90** and **91** [105]. Compound **90** represents the calixarene with the highest number of phosphinito units reported to date. Its ^{31}P NMR spectrum shows two singlets of equal intensity (108 and

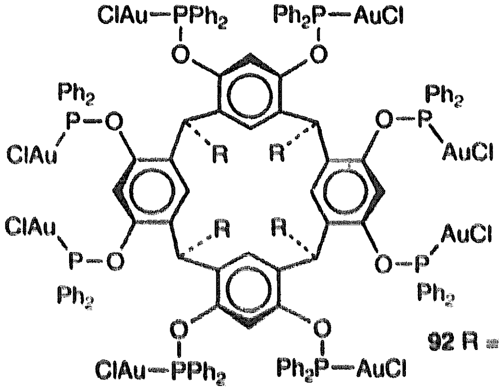


90 R = CH_2CH_2Ph



91 R = CH_2CH_2Ph

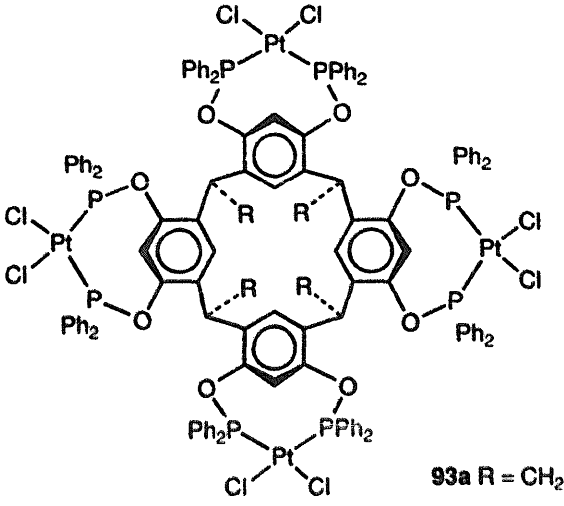
104.4 ppm in C_6D_6). Based on molecular mechanics calculations, showing that the PPh_2 groups force the bowl to become flattened, it has been suggested that the structure consists of alternating PPh_2 groups directed inwards and outwards with respect to the centre of the flattened bowl. Treating this ligand with [AuCl(SMe_2)] gives the gilded octopus molecule **92**. Interestingly, only one ^{31}P resonance was observed for the latter complex, indicating a molecule more symmetrical than the free ligand, with probably all eight AuCl groups directed towards the centre of the bowl.



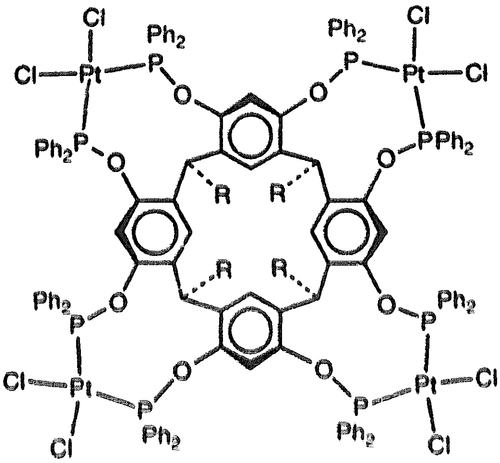
92 R = CH_2CH_2Ph

Reaction of **90** with [$PtCl_2(SMe_2)_2$] gives a tetranuclear complex in which each platinum atom is bound to two P sites arranged in a cis fashion (J(P–Pt) = 4431 Hz) [105]. Molecular mechanics calculations suggest that the resulting complex adopts structure **93a** rather than structure **93b**.

The coordinative properties of cone-shaped *p*-tert-butylcalix[4]arenes substituted at the lower rim with four identical phosphino groups have been investigated by several research groups. Four coordination modes (α–δ, Scheme 19) were found for this type of ligand. Coordination α was found in the gold complex **94** [106]. The reaction at low temperature of *p*-tert-butylcalix[4]arene-(O-PPh_2)$_4$ with two equivalents of [$Fe(CO)_3(\eta^2\text{-}C_8H_{14})_2$] in the presence of an excess of cyclooctene led to the formation of the dinuclear complex **95**, in which the calixarene ligand behaves as a double chelator (coordination mode β), each chelation involving two proximal phosphorus atoms [107]. As revealed by an X-ray diffraction study, steric crowding at the phosphorus centres prevents close interaction between the iron atoms



93a R = CH_2CH_2Ph



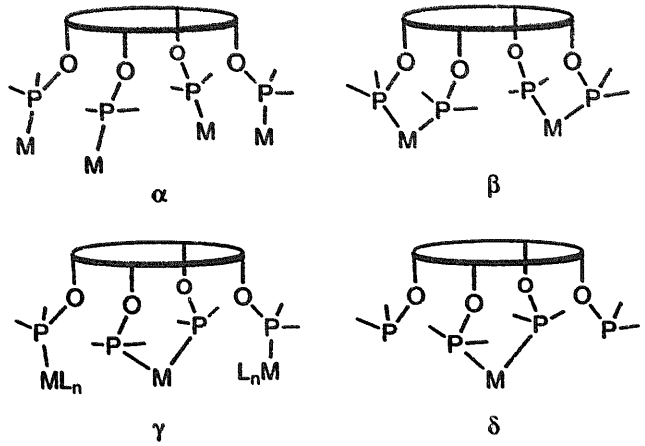
93b R = CH_2CH_2Ph

(Fe(1)···Fe(2), 7.060(2) Å). The ability of the tetraoxaphospholidone ligand **96** to act simultaneously as a chelating ligand via two distal phosphorus atoms and as a bridging ligand via the other two P atoms (coordination mode γ) was found in the copper complex **97**, obtained by reacting **96** with eight equivalents of "Cu(CO)Cl" (Scheme 20) [108]. The two terminal copper atoms adopt a linear coordination geometry; all others are trigonal.

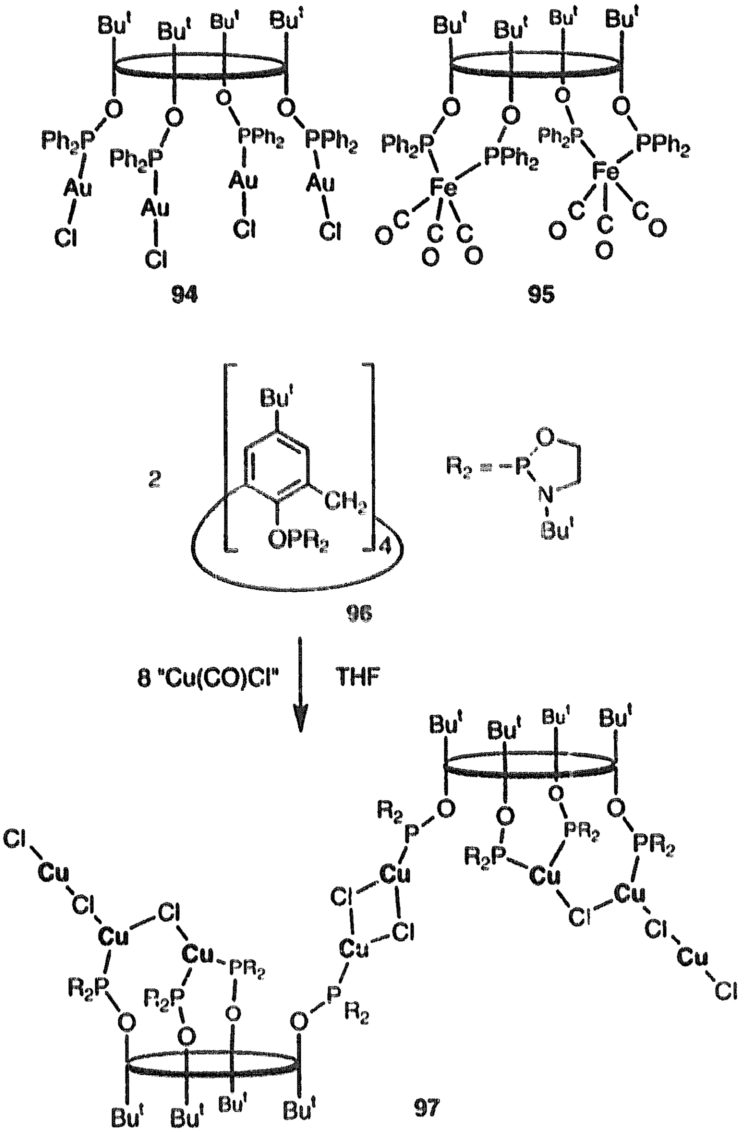
The mononuclear 1,3-chelate complex **99**, in which coordination mode δ was found, was obtained by reacting phosphinite **98** with [$PtCl_2(COD)$] (COD, 1,5-cyclooctadiene) (Scheme 21) [103]. The trans chelating behaviour of the ligand in this complex was inferred from the J(P–Pt) coupling constant of 2728 Hz. The two other phosphorus atoms remain uncoordinated.

Calixarene ligands containing less than four phosphino groups have also been investigated. The only known example of a tris(phosphinito)-calixarene complex is **100** [106]. The ^1H NMR spectrum of this compound is characterized by two distinct AB systems for the bridging methylene units and three Bu^t groups.

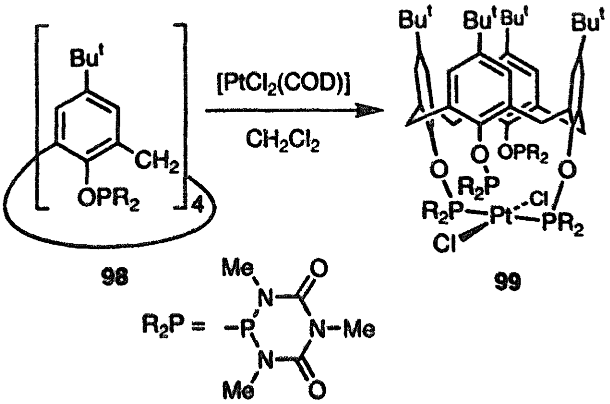
The reaction of monophosphinite **85** (L^{85}) with [$MCl_2(PhCN)_2$] (M ≡ Pd, Pt)



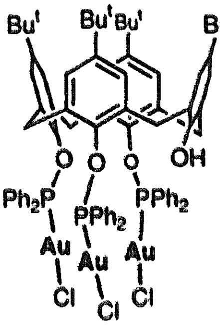
Scheme 19.



Scheme 20.

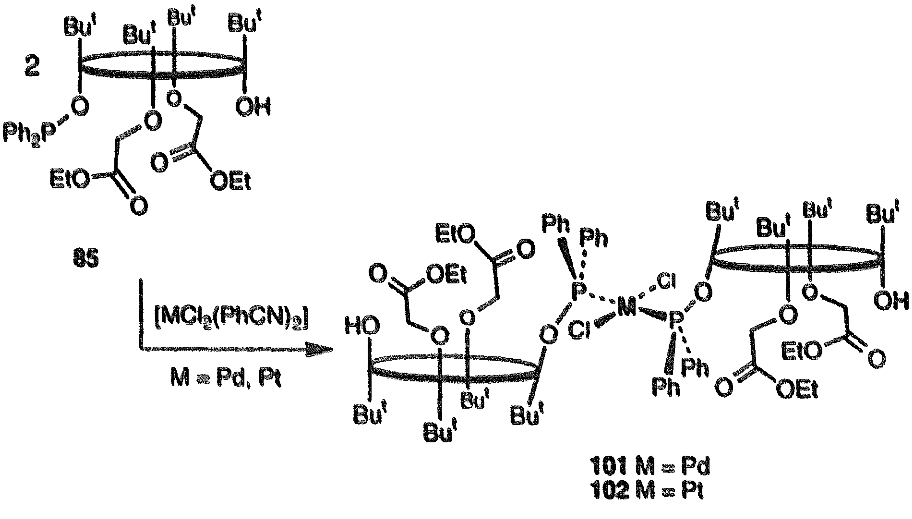


Scheme 21.



100

resulted in a high yield of formation of the corresponding *trans*-[$MCl_2 \cdot L^{85}_{2}$] complexes (**101**, M = Pd; **102**, M = Pt) (Scheme 22) [102]. The exclusive formation of the trans complexes is probably favoured by steric crowding of the phosphinite ligand. As revealed by an X-ray diffraction study (Fig. 1), the palladium complex **101** is centrosymmetric in the solid state [109]. The palladium atom lies outside the



Scheme 22.

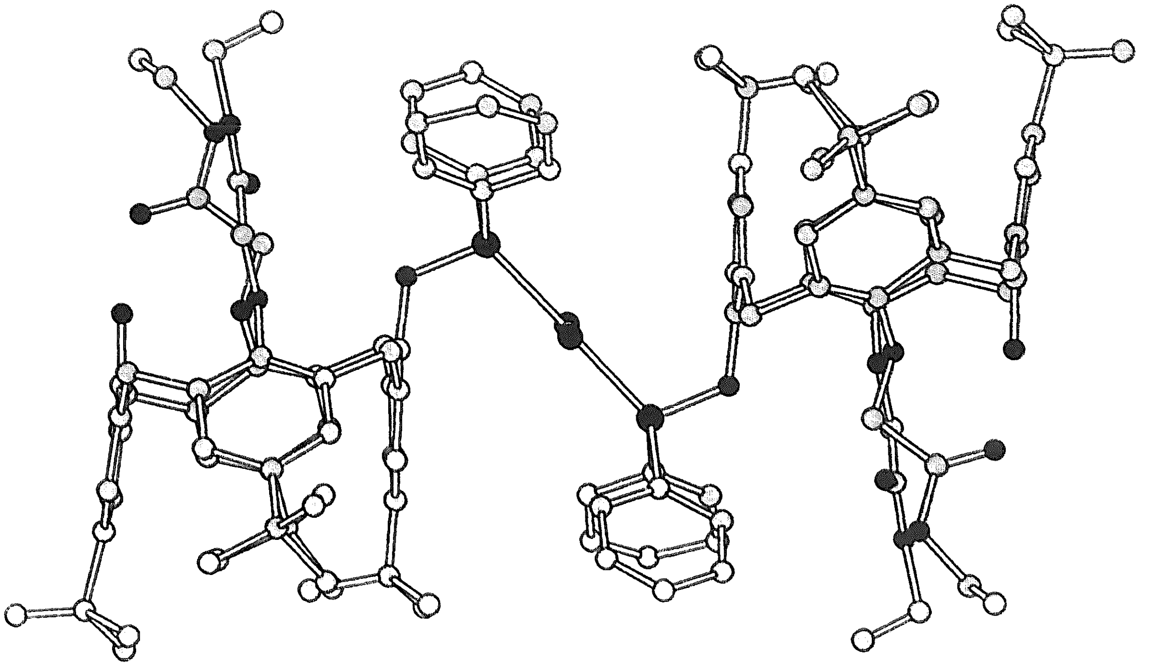
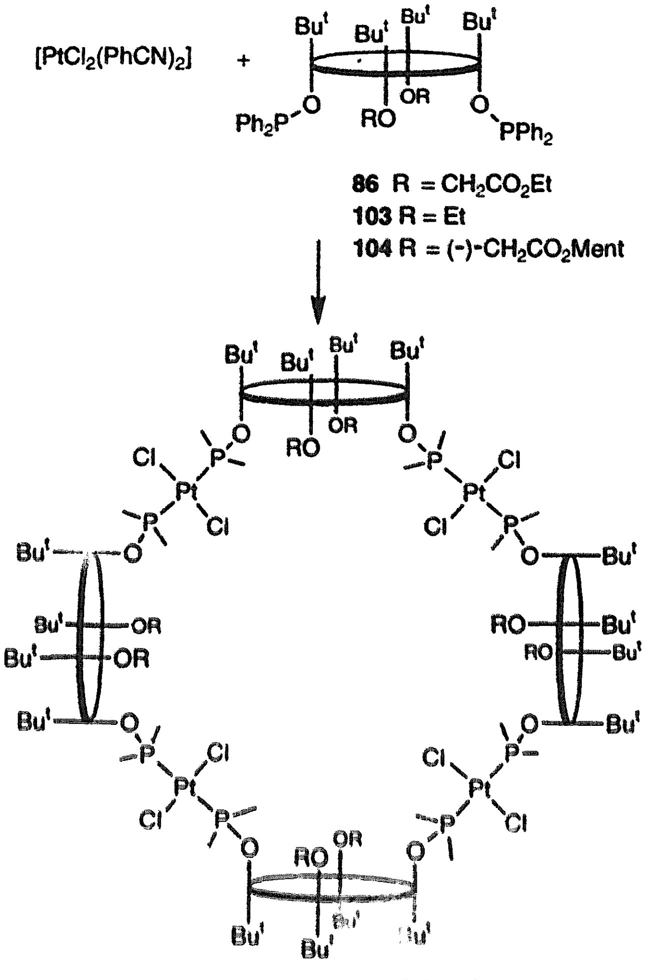


Fig. 1. Molecular structure of *trans*-$[PdCl_2L_2^{85}]$ (**101**).

calixarene cavities. Owing to steric interactions between each PPh_2 group and the aryl ring of the trans positioned macrocycle, the cone conformation of these calixarenes is somewhat distorted. Indeed, the X-ray study shows that, for each calixarene, the Bu^t group of the phosphinite unit protrudes into the cavity (see Fig. 1). This is also likely to occur in solution, since one of the Bu^t signals appears to be significantly shielded relative to the Bu^t groups of the free phosphinite.

The tendency of "MCl_2" moieties to coordinate bulky phosphinito-calixarenes in a trans P,P fashion could be exploited, in the case of 1,3-diphosphinito-calixarenes, for the build-up of oligomers [102]. Thus diphosphinites L ≡ **86**, **103** and **104** react with $[PtCl_2(PhCN)_2]$ to give soluble oligomeric species for which microanalytical data are in keeping with a formula of the type $[PtCl_2 \cdot L]_n$. The trans stereochemistry around each platinum atom was deduced from ^{31}P NMR and far-IR spectroscopy. Although no X-ray data are available for these complexes, a cyclic tetrameric structure, as shown in Scheme 23, appears to be probable in view of the osmometric weight determinations and the ^{31}P NMR spectrum showing a single peak (with platinum satellites). Interestingly, when 1,3-diphosphinito-calixarenes having distinct substituents attached at the other two facing phenolic oxygen atoms, e.g. **108** or **109**, were reacted with $[MCl_2(PhCN)_2]$ (M ≡ Pt, Pd) (Scheme 24), dimers instead of tetramers were formed (**110** and **111** respectively). This finding shows that subtle changes in the calixarene shape may induce major modifications in the structure of the oligomer formed. Despite the obvious tendency of 1,3-diphosphinito-calixarenes to behave as bridging ligands, chelating behaviour was found in at least one instance, namely **112** [102]. This observation may result, in part, from the fact that the stereochemistry about the (COD)rhodium centre requires a non-linear P–M–P arrangement. For complex **113**, reported by Cameron et al. [110], the drawn chelate structure has been proposed, but this was not corroborated by a molecular weight determination, so that a polymeric structure cannot be excluded.

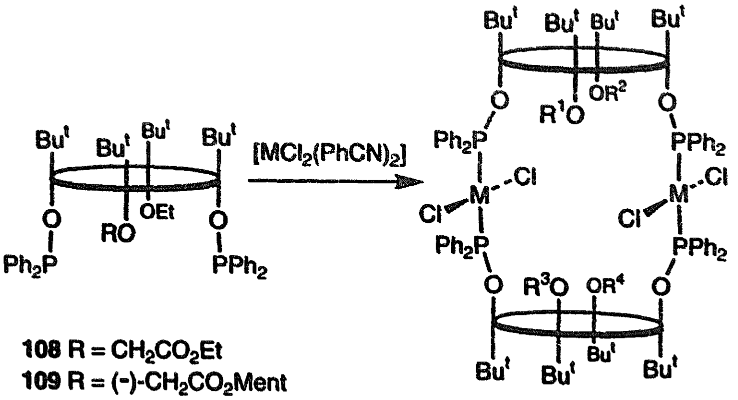


86 $R = CH_2CO_2Et$
103 $R = Et$
104 $R = (-)\text{-}CH_2CO_2Ment$

105 $R = CH_2CO_2Et$
106 $R = Et$
107 $R = (-)\text{-}CH_2CO_2Ment$

Scheme 23.

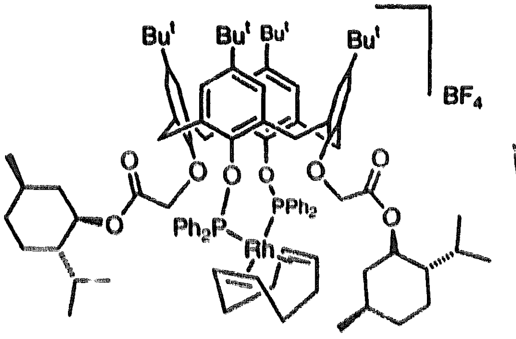
Interesting results were obtained for the resorcinarene phosphonite **91**. In principle, this ligand can adopt several conformations depending on the spatial orientation of the P-phenyl groups and the phosphorus lone pairs [105]. Molecular mechanics calculations indicate that the most preferred isomer is that having each phenyl group directed outwards from the centre of the bowl with the lone pairs pointing inside the cavity. This is consistent with the observation of a single resonance at 166.3 ppm in the ^{31}P NMR spectrum. Ligand **91** reacts with $[AuCl(SMe_2)]$ and $[PtCl_2(SMe_2)_2]$ affording complexes **114** and **115** respectively (Scheme 25) [105]. An X-ray diffraction study was undertaken for the gold complex **114**. As anticipated, all eight phenyl groups are directed away from the bowl. Three AuCl units are roughly parallel to the calixarene axis, whereas the fourth points into the cavity. A variable temperature NMR study showed that all four P-AuCl units are equivalent,



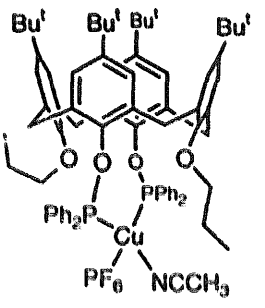
108 R = CH_2CO_2Et
109 R = (-)-CH_2CO_2Ment

110 $R^1 = CH_2CO_2Et$, $R^2 = Et$
$R^3 = R^1$ or R^2, $R^4 = R^2$ or R^1
M = Pt
111 R^1 = (-)-CH_2CO_2Ment, $R^2 = Et$
$R^3 = R^1$ or R^2, $R^4 = R^2$ or R^1
M = Pd

Scheme 24.



112

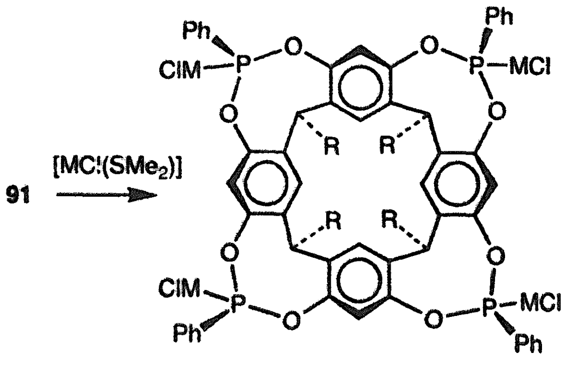


113

even at −80 °C (300 MHz spectrometer), from which it was inferred that fast motion of the four AuCl units must occur in solution, these being alternatively folded inside the bowl or located at its periphery. The possibility of the AuCl units migrating between P atoms was not considered.

Attempts to form endo-calix complexes with **114** were made using potential guests, such as PhCN, MeCN, PhCCH and HCCH, but no interaction could be demonstrated spectroscopically for these substrates [105]. However, complexation with primary amines, expected to give rise to strong Au–N interactions, was shown by NMR spectroscopy to occur in solution. The amines can lead to either inclusion complexes (e.g. with the linear amines Pr^nNH_2 and Bu^nNH_2) or, if a bulky amine is used (e.g. Pr^iNH_2), to external complexation.

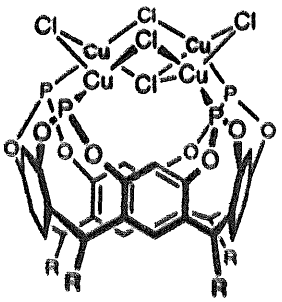
Treatment of **91** with $[(CuC{\equiv}CPh)_n]$ in the presence of pyridinium chloride yielded the unique complex **116**, in which a $Cu_4(\mu Cl)_4$ moiety bridges the bowl [111]. The



114 M = Au
115 M = PtCl(SMe$_2$)
R = CH$_2$CH$_2$Ph

Scheme 25.

main structural feature of this complex is the presence of a fifth, triply bridged Cl$^-$ anion, encapsulated within the cavity.

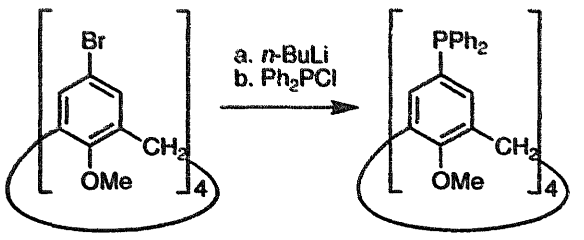


116 R = CH$_2$CH$_2$Ph (*PhP* groups not drawn)

4.2.2. *Calixarene-phosphines*

The only attempts to synthesize phosphines on the upper rim of calix[4]arenes were made by Hamada et al. [112]. On the basis of microanalytical and ^{1}H NMR data, these workers claim that the reaction shown in Scheme 26 leads to tetraphosphine **117**, obtained as a mixture of several conformers (not resolved). As expected for tertiary phosphines, this isomeric mixture was shown to display strong binding affinities for copper and nickel ions. Its interaction with Cu^{2+} results in the formation of a 1 ligand : 2 Cu^{II} complex, which was not isolated. Surprisingly, the expected reduction of Cu^{II} to Cu^{I} by phosphine complexation was not observed in this case.

A lower rim functionalized calix[4]arene with four pendant CH$_2$PPh$_2$ groups was prepared in 68% overall yield by performing the reaction sequence shown in Scheme 27 [51]. In a first step, *p*-tert-butylcalix[4]arene was treated for 3 days with NaH and Ph$_2$P(O)CH$_2$OTs (Ts = *p*-O$_2$SC$_6$H$_4$Me) in toluene. This procedure resulted in the selective formation of the cone-shaped tetraphosphine oxide **118**. Reduction of the latter compound in PhSiH$_3$ at 100 °C gave the corresponding tetraphosphine **119** in high yield. Reaction of **119** with the cyclopalladated dimer



117

Scheme 26.

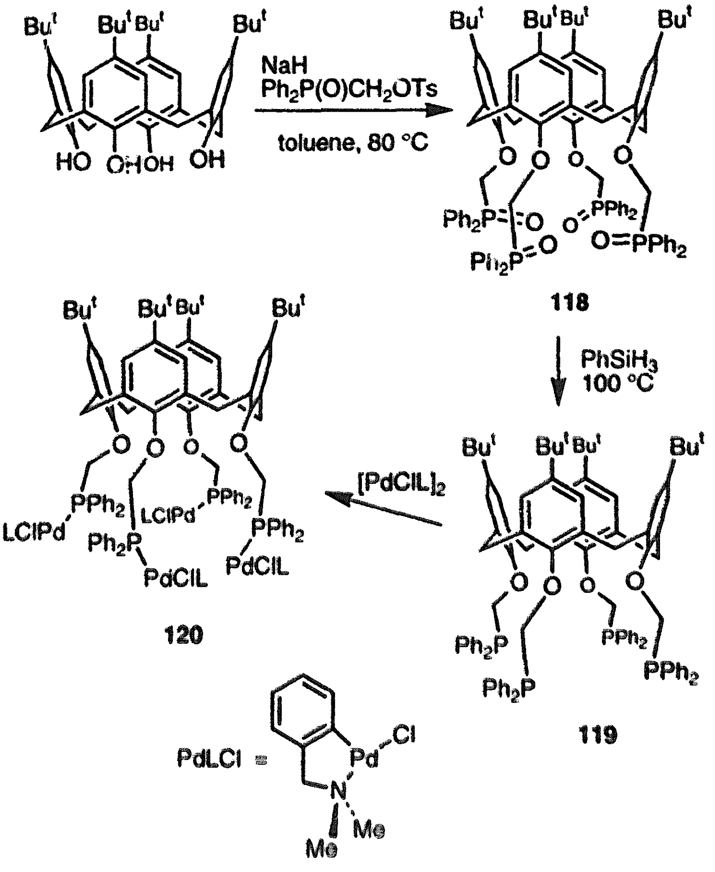
$[Pd(o\text{-}C_6H_4CH_2NMe_2)Cl]_2$ afforded the tetranuclear complex **120**. The ^1H and ^{31}P NMR spectra for **120** indicate a C_4 symmetrical structure. However, the ^1H and ^{31}P NMR signals broaden on lowering the temperature, suggesting a dynamic behaviour of the complex. It is probable that the four bulky "Ph_2PPdCl" units cannot occupy simultaneously equivalent positions, but oscillate in and out of the cavity. This interpretation is reminiscent of the alternation proposed for the tetranuclear gold complex **114** (see above). It also takes into account the observation that, in the solid state structure of the phosphine oxide **118**, one of the four P=O bonds points inside the cavity, the three others being oriented tangentially to the calixarene barrel [51]. As shown by the presence of a $^4J(P\text{–}NCH_2)$ coupling constant, the dynamics of **120** do not involve dissociation of the palladium–phosphorus bonds.

Lower rim functionalized phosphines, such as **125**–**128**, were obtained in a similar fashion [50,113] (Scheme 28). Precursors **121**–**124** were prepared using the $Ph_2P(O)CH_2OTs\text{–}Bu^tONa$ couple. The selective formation of cone conformers is obviously template controlled (the cone selectivities S_{cone} are in most cases greater than 90%). Thus, when alkylation was performed with Bu^tOK as base, partial cone conformers (in which the phosphoryl-containing aryl rings have opposite orientations) were obtained selectively, e.g. **129** and **130**. Reduction of **121**–**124** in $PhSiH_3$, used as solvent, gave the corresponding diphosphines in 100% yield.

Chelating behaviour of 1,3-di(phosphinomethyl)calixarenes towards group IX metals was found in complexes **131**–**133** [50,113,114]. The chiral rhodium(I) complex **133** operates as a hydroformylation catalyst for styrene ($CO/H_2 = 1:1$, 40 °C, 40 atm, styrene/metal = 350 : 1, solvent CH_2Cl_2–benzene), leading to phenylpropanal [113]. The branched to linear aldehyde ratio was 95 : 5, a value which is not unusual for Rh/phosphine catalysts. The reaction rate was rather slow for this process (approximately 7.5 turnovers per Rh per hour), possibly because of the partial encapsulation of the metal centre, a situation which would prevent close approach of the substrate. Under the above-mentioned conditions, no chiral induction was observed.

The use of **133** for the catalytic hydrogenation of cyclohexene ($P(H_2) = 2$ atm, 40 °C, $C_6H_{10}/Rh = 219$, solvent MeOH) gave turnovers of approximately 10 Rh^{-1} h^{-1} [115]. The hydrogenation rate of dimethyl itaconate was even slower. No chiral induction was observed for the hydrogenation of the latter substrate, suggesting that the two chiral centres are too far from the metal centre.

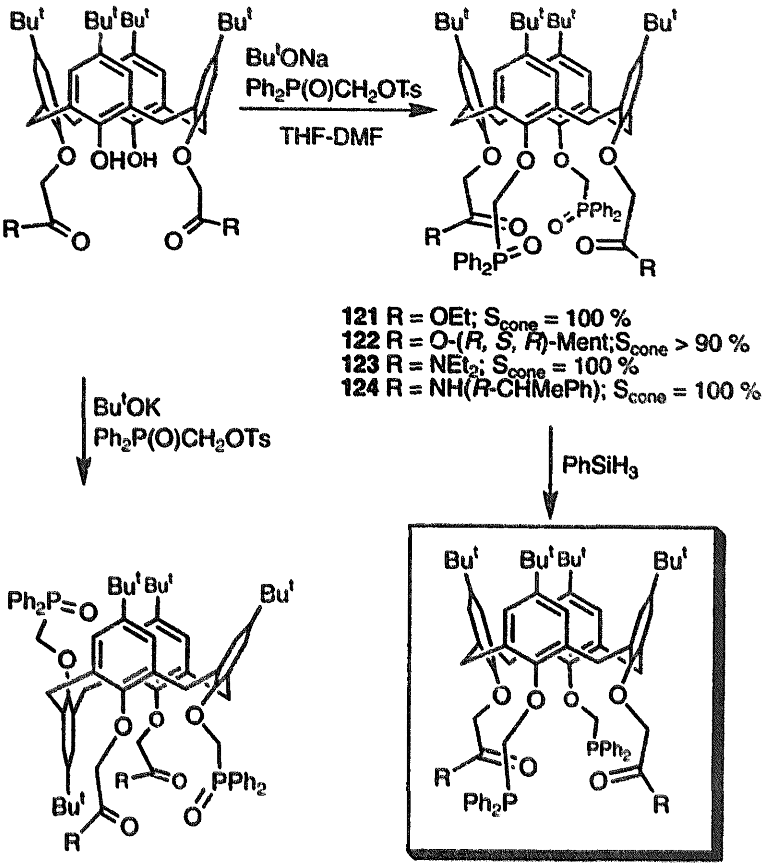
Other metallo-strapped calixarenes were obtained with the phosphine–amide



Scheme 27.

hybrid 127. Reaction of this ligand with $[PdCl_2(SEt_2)_2]$ resulted in the quantitative formation of complex **134**, in which the phosphorus atoms are held in a cis arrangement [116]. With $[PtCl_2(COD)]$, complex **135** was formed [113]. The chelating behaviour of the diphosphine in **135** was confirmed by a single X-ray diffraction study. In the solid state, the metal plane is slightly inclined with respect to the calixarene axis in order to allow minimization of the strain about the phosphorus atoms. This leads to a folding back of one of the two amides. Since all NMR data indicate a C_2 symmetrical structure, it is likely that, in solution, a fan-like motion of the metal plane occurs (Scheme 29).

The first calixarene complex engulfing a Pt–H bond, **136**, was synthesized by reaction of *trans*-$[PtHCl(PPh_3)_2]$ with **127** (Scheme 30) [117]. The trans chelating behaviour of the ligand was inferred from the J(P–Pt) value (3122 Hz) and confirmed by an X-ray diffraction study (Fig. 2). This investigation also established that, at least in the solid state, the hydride ligand of **136** is trapped within the cavity defined by the four calixarene substituents, with the Pt–H bond pointing towards the centre of the cavity. The shortest H(hydride)–O contacts (2.44 and 2.73 Å) were found for the OCH_2P oxygen atoms. In view of the ^1H and ^{31}P NMR spectra (500 MHz spectrometer), which display well-resolved signals which do not broaden on going from 30 to −80 °C, gyroscopic rotation of the Cl–Pt–H unit around the P–Pt–P axis appears to be unlikely. Directional change of the Pt–H vector was forced by

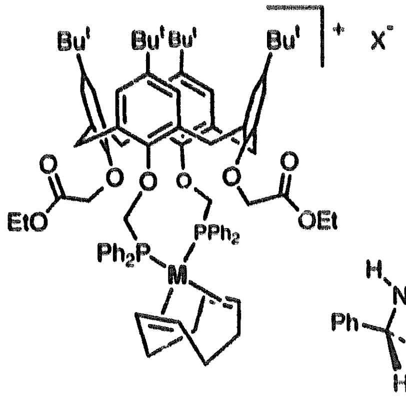


121 R = OEt; S_{cone} = 100 %
122 R = O-(*R, S, R*)-Ment; S_{cone} > 90 %
123 R = NEt_2; S_{cone} = 100 %
124 R = NH(*R*-CHMePh); S_{cone} = 100 %

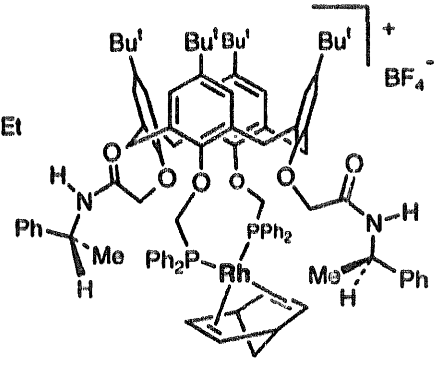
129 R = OEt
130 R = NEt_2

125 R = OEt
126 R = O-(*R, S, R*)-Ment
127 R = NEt_2
128 R = NH(*R*-CHMePh)

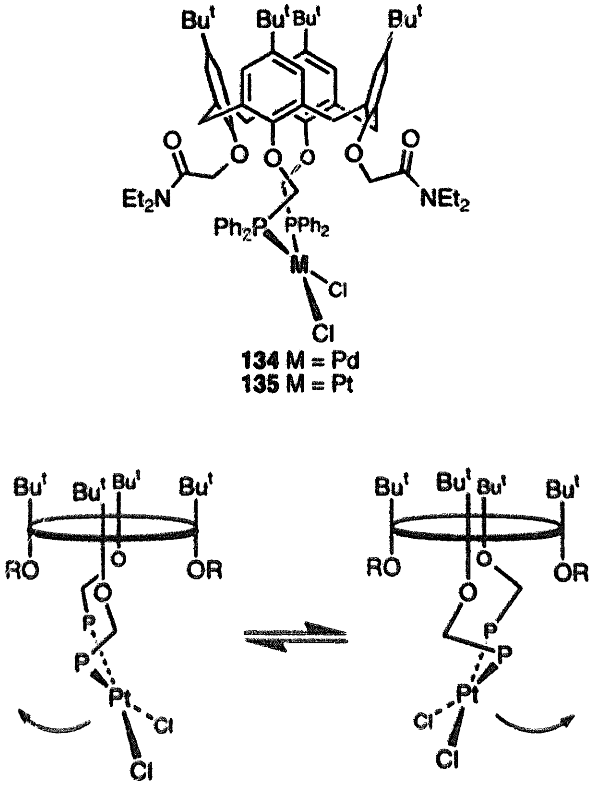
Scheme 28.



131 M = Rh; X = BF_4
132 M = Ir; X = SbF_6



133



134 M = Pd
135 M = Pt

135 (R = CH$_2$C(O)NEt$_2$)

Scheme 29.

reacting **136** with AgBF$_4$. This resulted in the formation of the cationic complex **137**, in which the calixarene behaves as a hemispherical P,O,P tridentate. Molecular models clearly show that the Pt–H bond lies approximately parallel to the calixarene reference plane and points towards the exterior of the cone.

The coordination chemistry of calixarene **138**, containing two distal diphenylphosphinoethyl groups, was investigated recently [110]. Reaction of this diphosphine with [PtCl$_2$(MeCN)$_2$] gave a complex in 41% yield in which the platinum atom is coordinated to phosphorus atoms occupying the cis positions (J(P–Pt) = 3460 Hz). The monomeric nature of this complex, leading to the formula drawn for **139**, was inferred from the presence of a peak in FAB-MS corresponding to (M + H)$^+$ (m/e = 1423.5). Reaction of **138** (L^{138}) with [Cu(CH$_3$CN)$_4$]PF$_6$ gave the complex [Cu·L^{138}·(CH$_3$CN)]PF$_6$, but its monomeric nature was not established.

An interesting calix[6]arene-derived diphosphinite, **140**, has been obtained by reacting p-tert-butylcalix[6]arene with PCl$_3$ (Scheme 31) [118]. The ligand exists in both syn and anti conformations [119], but only the syn conformer could be obtained in pure form. This latter isomer afforded complexes **141**–**145** in which the ligand behaves as a cis chelator. As shown by an X-ray study, the calixarene backbone of each phosphite moiety of **141** adopts a partial-cone conformation. The ligand bite angle is 94°. This study also established that the ligand has only non-crystallographic C_2 symmetry (there is no mirror plane). However, since the ^{1}H NMR spectrum

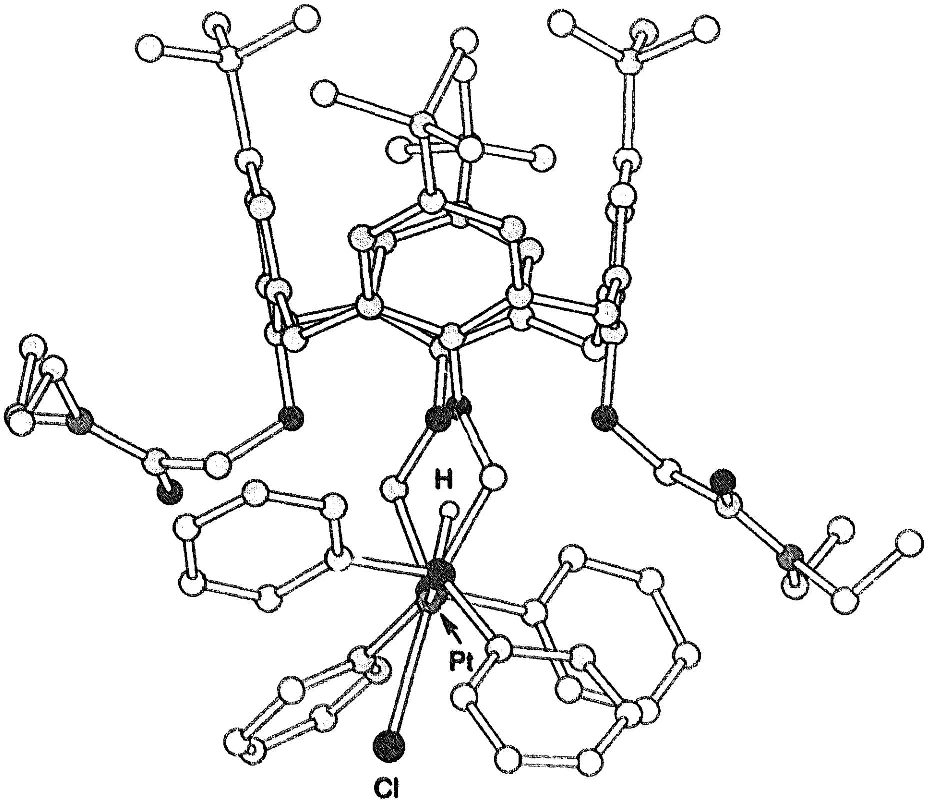
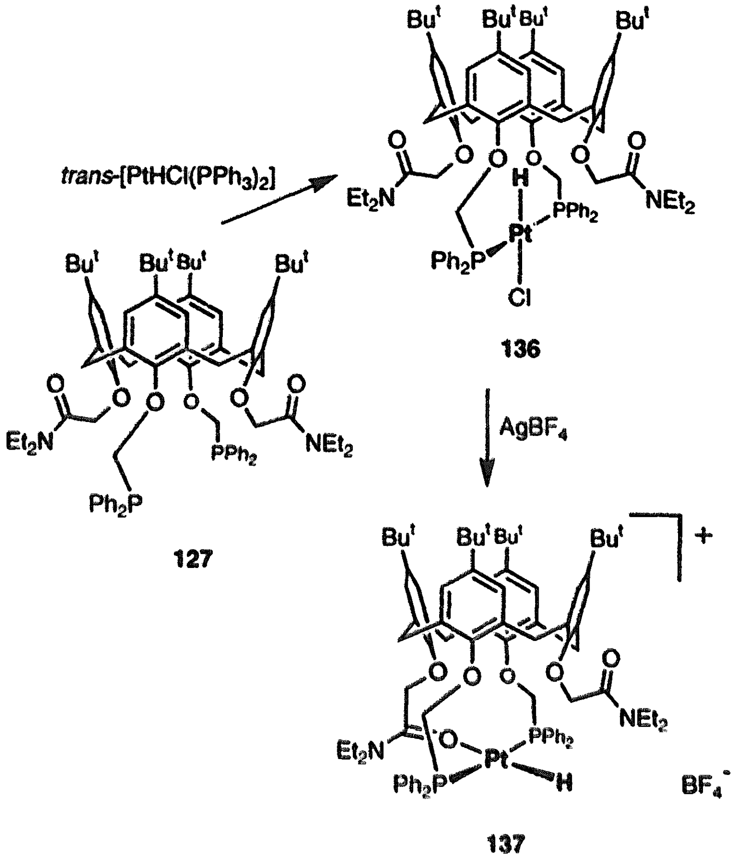


Fig. 2. Molecular structure of *trans*-[PtHClL^{127}] (**136**).

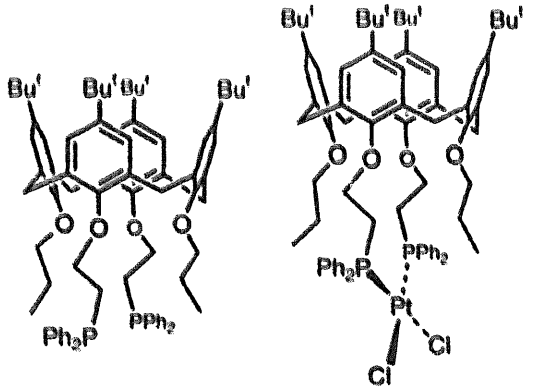
shows only two Bu^t signals in a 1 : 2 ratio and two AB systems (1 : 2 ratio) for the methylene bridges, it is probable that the ligand undergoes fluxional behaviour in solution, resulting in a fast partial-cone–partial-cone interconversion.

4.3. *Calixarene ligands with O or S donor atoms*

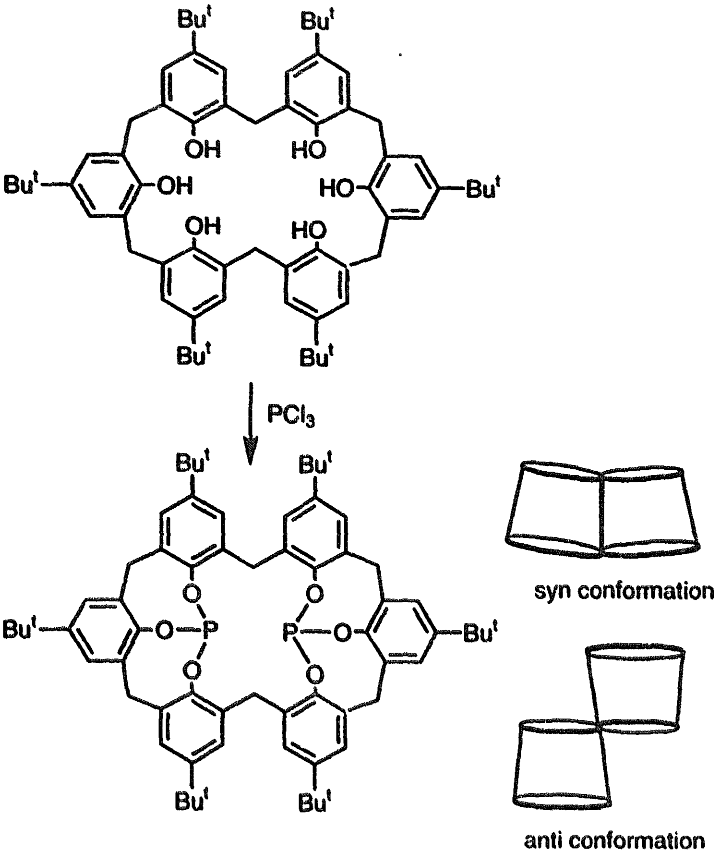
Calixarene-derived ligands containing oxygen donor atoms have found most use as complexing agents towards the oxophilic alkali metal, alkaline earth and lanthanide cations. In a recent article, Beer et al. [120] highlighted the versatile cation receptor properties of a particular ligand of this family, namely the tetraamide **146** (L^{146}). This ligand, for which the complexing properties of Li, Na and K are already known [45,46,56], was found to form comparatively stable complexes with a number of other metal ions, in particular Fe^{II}, Ni^{II}, Cu^{II} and Zn^{II}. Single crystal structural determinations were carried out for complexes with the formula $[M \cdot L^{146}][ClO_4]_2 \cdot n MeCN$ (**147**, M ≡ Fe^{II}; **148**, M ≡ Cu^{II}; **149**, M ≡ Zn^{II}; **150**, M ≡ Ni^{II}). These investigations established that, in all these complexes, the metal lies inside the cavity defined by the four $OCH_2C(O)NEt_2$ groups and that an acetonitrile molecule is located within the cone. The metal ions are not similarly bound to the eight oxygen atoms of the substituent cavity. For instance, in the Fe^{2+} and Zn^{2+} complexes, M–O bonding occurs with all eight oxygen atoms, but the M–O(amide) interaction is stronger than that with the ether oxygen atoms (average M–O(ether),



Scheme 30.

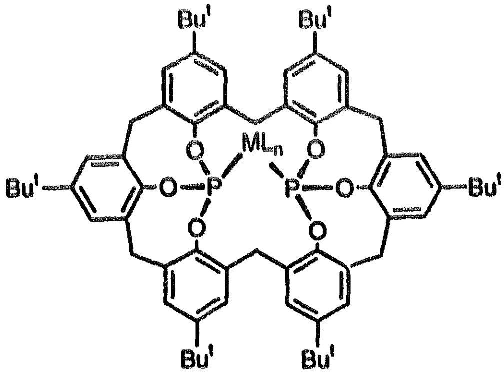


2.452 Å (Fe) and 2.579 Å (Zn); average M–O(amide), 2.170 Å (Fe), 2.080 Å (Zn)). In the copper complex, the Cu atom lies almost inside the O_4(amide) plane (average Cu–O distance, 1.910 Å) and interaction with the ether oxygen atoms is negligible (average Cu–O(ether), 2.861 Å). In the nickel complex **150**, the ligand undergoes significant rearrangement to accommodate the metal cation in a distorted octahedral environment. The characteristic features of this structure are that the nickel atom is placed significantly closer to three of the four ether oxygen atoms, and one carbonyl



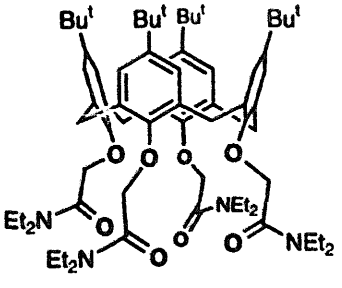
140 (syn & anti)

Scheme 31.

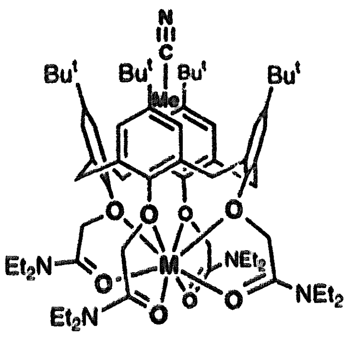


141 ML$_n$ = PdCl$_2$
142 ML$_n$ = PtCl$_2$
143 ML$_n$ = PdMeCl
144 ML$_n$ = PtMeCl
145 ML$_n$ = Re(CO)$_3$Cl

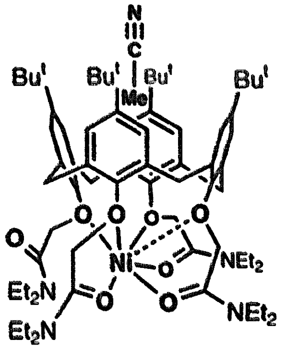
unit is twisted away from the coordination sphere. Ligand **146** is a rare example of a complexing agent capable of encapsulating metal ions of very different size and nature.



146

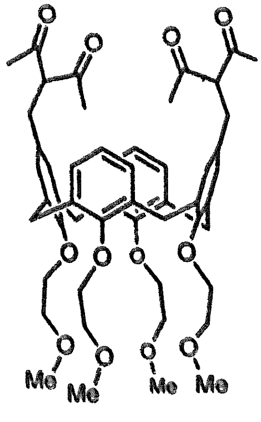


147(CH$_3$CN) M = Fe^{II}
148(CH$_3$CN) M = Cu^{II}
149(CH$_3$CN) M = Zn^{II}



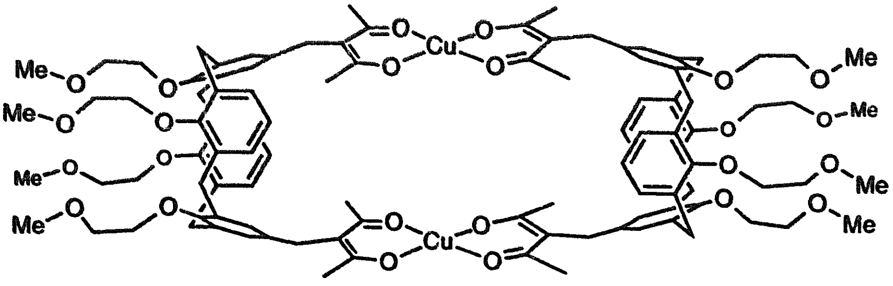
150(CH$_3$CN)

By reacting the ditopic ligand **151** with $[Cu(NH_3)_4]^{2+}$, the double calixarene **152** was formed in approximately 50% yield [121]. This dinuclear complex, containing two facing copper planes, is suitable for the formation of 1 : 1 complexes with ethylene diamine and 1,4-diazabicyclo[2.2.2]octane (DABCO). Electron spin resonance (ESR) studies suggest that, with DABCO, a 1 : 1 endo complex is formed in which the amine interacts with the two copper atoms.



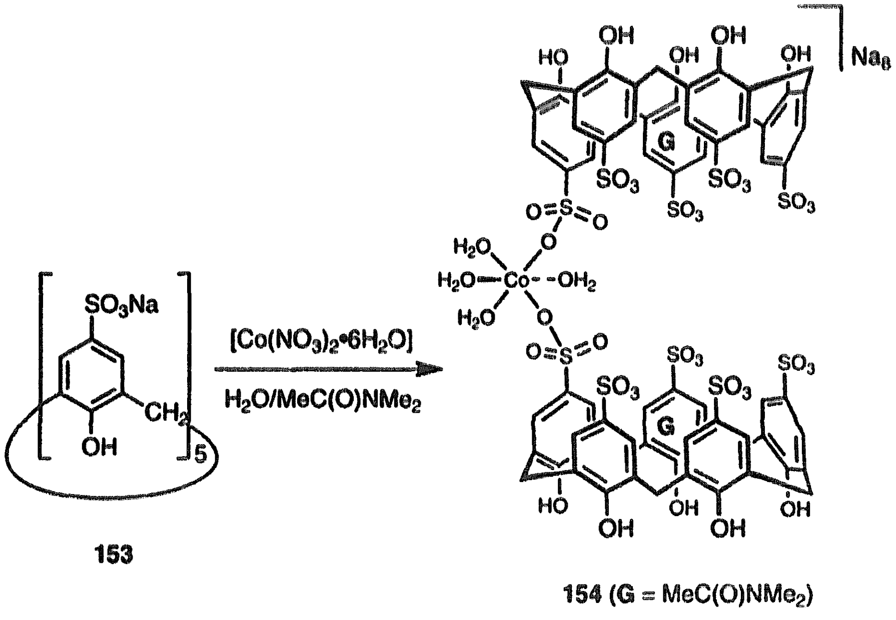
151

The interaction of a *p*-sulphonatocalixarene with transition metals has been described recently by Johnson et al. [122]. Thus reaction of the (*p*-sulphonatocalix[5]arene)$^{5-}$ anion **153** with $[Co(NO_3)_2] \cdot 6H_2O$ in the presence of



152

N,N-dimethylacetamide (DMA) afforded the double calix[5]arene **154** (Scheme 32). In this complex, the two calixarenes are linked by a "$Co(H_2O)_4$" moiety via sulphonato groups and not via phenolic oxygen atoms. An X-ray structural determination revealed a face-to-face orientation of the calixarene subunits, resulting in the formation of a "supercavity". Each calixarene incorporates a DMA guest molecule (G) deeply included inside the host. Many H_2O molecules and Na^+ ions are located between the two cavities. ^1H NMR studies suggest that, in solution (D_2O), the DMA molecules are not strongly associated with either the calixarene or the metal centre. Furthermore, it is probable that de-complexation of the metal centre occurs in solution. Reaction of **153** with $[Ni(NO_3)_2]\cdot 6H_2O$ in the presence of pyridine gave the inclusion complex $Na_8[Ni(H_2O)_4(p\text{-sulphonatocalix[5]arene})_2]\cdot 2(NC_5H_5)\cdot 38H_2O$ (**155**) (not drawn). A preliminary X-ray study suggests the presence of an octahedral Ni^{II} ion bridging between two calixarene ligands via sulphonato groups, with an uncoordinated pyridine molecule lying inside each cavity. The precise orientation of the cavities has not yet been determined. NMR studies indicate that the pyridine guests are better held within the calixarenes than DMA in **154**.



Scheme 32.

Despite the relative softness of sulphur, calixarenes containing mercapto groups have only found limited use in transition metal chemistry. The 1,3-alternate mercaptocalix[4]arene **158** was obtained in three steps (overall yield, 12%) by Gibbs and Gutsche [123] according to Scheme 33. In this synthesis, synthon **156** (1,2-alternate conformer) was first prepared by the treatment of *p*-tert-butylcalix[4]arene with NaH and *N*,*N*-dimethylthiocarbamoyl chloride in diglyme. Intermediate **157** (1,2-alternate conformer) was then prepared in 42% yield via a Newman–Kwart [124,125] rearrangement in refluxing *p*-tolyl ether. As found recently by other workers, the yield of the latter step can be increased significantly by heating **156** at 310–320 °C under argon [126]. In a final step, the reduction of **157** with $LiAlH_4$ gave **158** as a 1,3-conformer. Mixing **158** with two equivalents of mercuric acetate yielded the binuclear complex **159**, in which the 1,3-alternate conformation of the ligand is maintained [126]. An X-ray diffraction study showed linear coordination around the mercury atoms. In view of the rather short Hg–centroid(aryl) distances (3.1 Å), π interactions with the phenyl rings need to be considered. When the reaction leading to **159** was repeated using a 1 : 1 metal to ligand ratio, an intermediate 1 : 1 complex was identified, prior to its disproportionation to **159** and free ligand [126]. Under similar conditions, but using the dithiol-dihydroxy calixarene **160**, the mononuclear complex **161** could be isolated as a stable Hg complex [127]. In this complex, coordination about the Hg atom is comparable with that found for the mercury atoms of **159** (centroid–Hg distances, 3.11 and 3.07 Å).

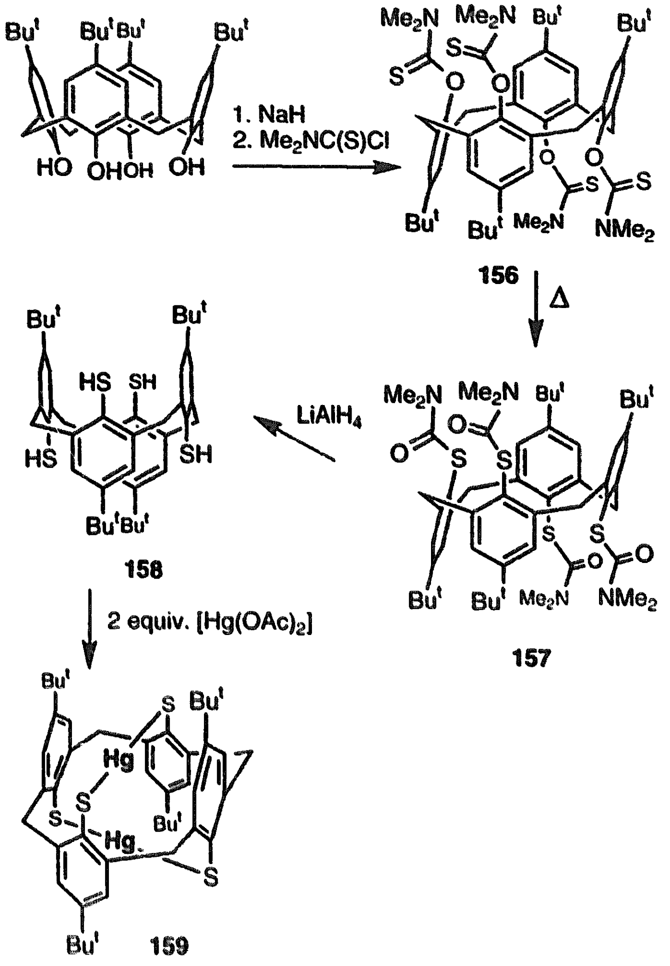
The calix[4]resorcinarenes **162**–**165**, bearing long-chain thio-alkyl groups, have been designed for anchoring to a gold surface so as to produce self-assembled monolayers [128,129]. Potential applications of such systems include receptors and sensors. Thus, for example, the layer obtained from **162** displays strong selectivity for some adsorbates, e.g. vitamin C, from dilute solutions. With the tetrasulphides **162**–**165**, monolayers obtained at room temperature are kinetically disordered, but on heating at 60 °C, a highly ordered structure with few defects can be obtained (Scheme 34). It is probable that the monolayer reorganizes after reversible Au–S bond breaking to an energetically more favourable structure having all alkyl chains held parallel. This leads to compacted monolayers of high stability which are currently being investigated for possible use as sensors.

5. Metallocalixarenes containing a metal centre bonded to an aryl ring

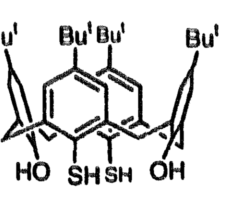
Two types of complex in which a metal is bonded to the aryl ring of a calixarene matrix have been synthesized: (1) complexes containing a σ M–aryl bond; (2) complexes with π bonding interaction. To date, the former type is limited to mercury complexes. For π complexes, we can distinguish between those having the metal lying outside the cavity and those where it is encapsulated into the void.

5.1. Complexes with σ M–aryl bonding

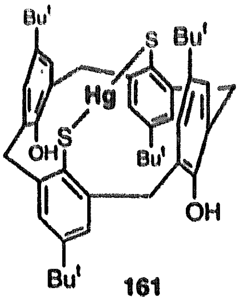
Quantitative mercuration of a series of lower rim alkylated calixarenes was achieved with mercury trifluoroacetate (Scheme 35) [130,131]. This electrophilic



Scheme 33.

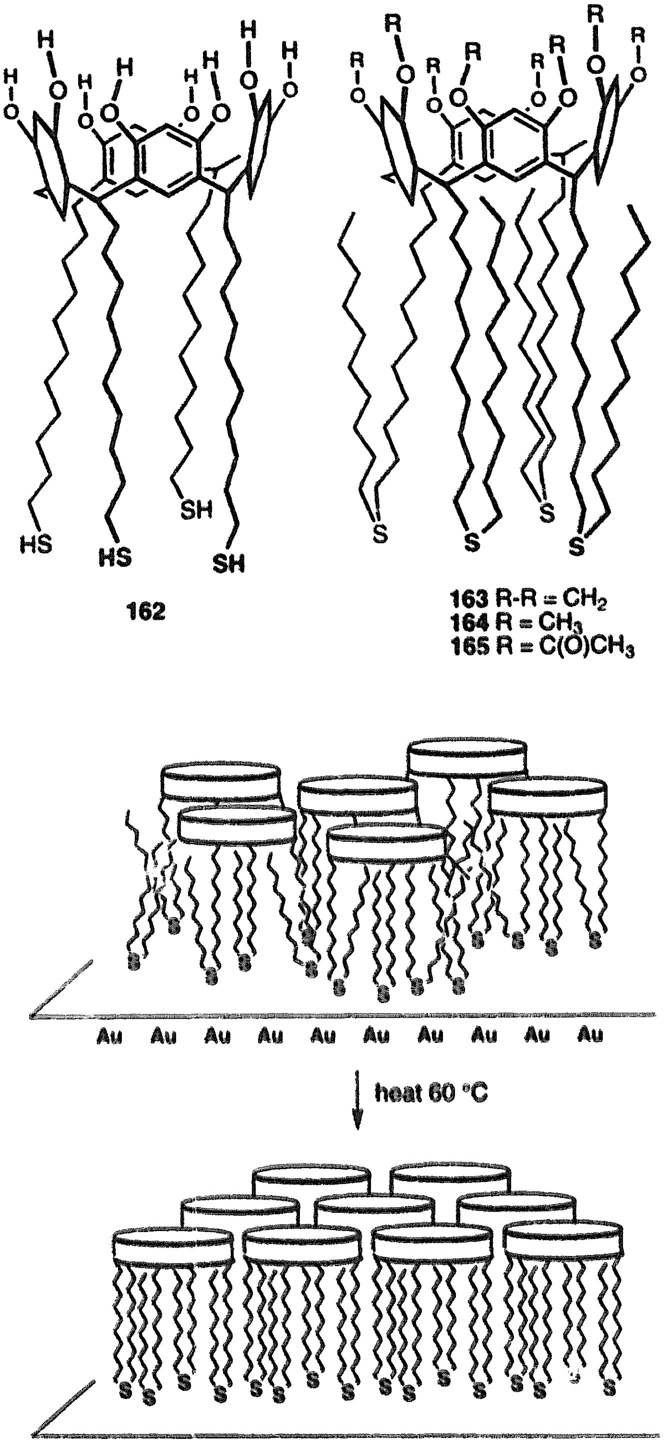


160



161

substitution proceeds selectively at the para position. It was not clearly established whether this transformation was accompanied by conformational isomerization. By introducing mercury at the para position, surfactant character was expected to be conferred to the molecules without providing appreciable water solubility. It was established that the compounds drawn in Scheme 35 do indeed form stable monolayers at the air–water interface. Surface pressure–area isotherms gave limiting areas in agreement with those predicted from Corey Pauling Koltran (CPK) models, if it was assumed that each calixarene lies at the air–water interface in a hexagonally

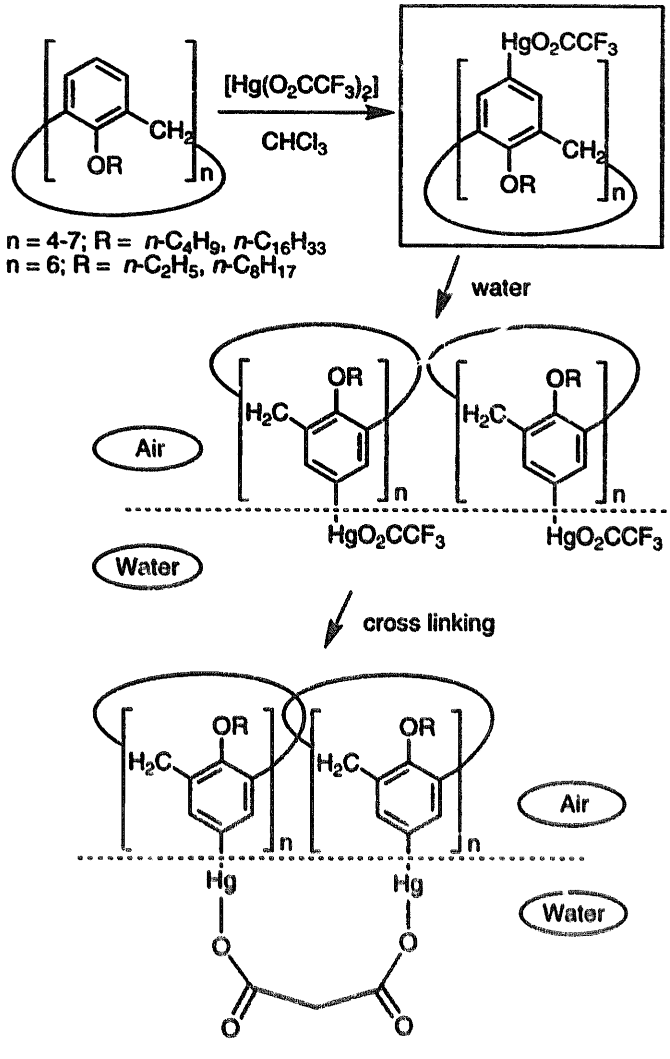


162

163 R-R = CH_2
164 R = CH_3
165 R = $C(O)CH_3$

Scheme 34.

packed array and that all Hg ions are in contact with the aqueous phase. By adding malonic acid to the latter phase, malonato bridges are formed between neighbouring calixarenes. A substantial increase in the cohesiveness of the films obtained from the calix[4–6]arene-derived surfactants is observed. These studies are relevant to the fabrication of packed monolayer assemblies with a precisely defined pore size, and hence for applications in specific "molecular filtration".

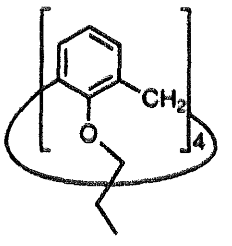


Scheme 35.

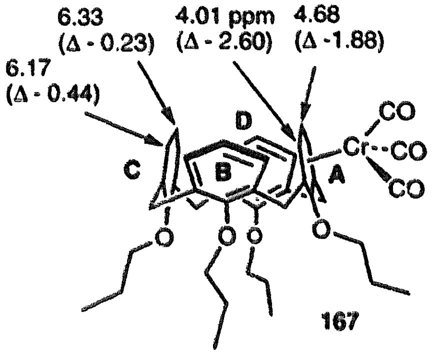
5.2. π Arene complexes

The formation of tricarbonylchromium complexes of calix[4]arenes is of strong synthetic interest. Such complexes were obtained for the first time by reacting all four possible isomers of the tetrakis(*n*-propoxy) derivative **166** (L^{166}) with $Cr(CO)_6$ [132–134]. For all conformers, 1 : 1 complexes were isolated. For the partial-cone isomer, it was found that the chromium atom coordinates to each of the three types of arene ring. A characteristic feature of these complexes is that the protons of the aryl ring interacting with $Cr(CO)_3$ appear at higher magnetic field than the uncomplexed protons [132]. The largest upfield shift was observed for the meta protons of cone isomer **167**. X-Ray structures were determined for cone-(L^{166})·$Cr(CO)_3$ (**167**), cone-(L^{166})·$2Cr(CO)_3$ (**168**) and

1,3-alternate-(L^{166})·$Cr(CO)_3$ (**169**) (for **168** two slightly different molecules are present in the unit cell) [134]. The structure of the macrocyclic matrices of **167** and **168** diverges considerably from that usually found for so-called cone conformers. The main structural feature of these two conformers concerns the chromium-bearing aryl unit (**A**) and the opposite aryl ring (**C**) which are both turned towards the exo-annulus direction. In contrast, the other two rings (**B** and **D**) are extremely flattened towards the endo-annulus direction. A careful examination of the X-ray structural data showed that this unusual geometry, termed "bis-roof" structure, probably takes place so as to relax the steric crowding around the propyl groups which interact with the neighbouring $Cr(CO)_3$ unit. In these structures, the para carbons of rings **A** and **C** approach each other (3.88(1) Å in **167** and 3.81(1) and 3.72(1) Å in **168**). The IR data clearly support the notion that these rings interact trans annularly.



166



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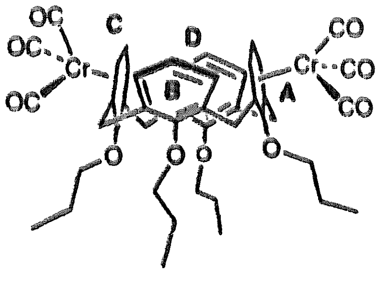
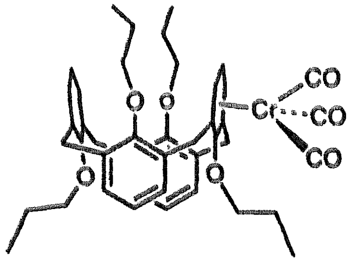


168

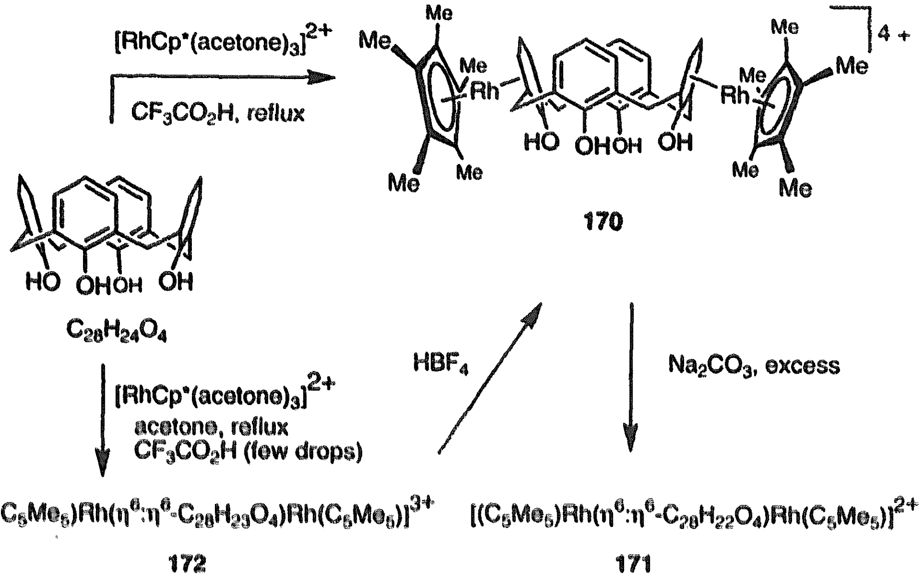


169

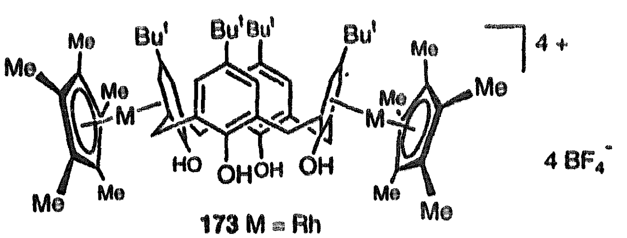
In the 1,3-alternate complex **169**, the structural change induced by $Cr(CO)_3$ complexation is relatively small. Only a slight flattening of the phenyl rings is observed in the solid state structure. This feature serves to minimize the steric crowding caused by the presence of the $Cr(CO)_3$ groups.

Attempts to obtain arene chromium complexes with *p*-tert-butylcalix[4]arenes failed.

π Complexation of the aromatic rings of calix[4]arenes could also be achieved with rhodium and iridium. Reaction in neat CF_3CO_2H of $[Rh(\eta^5\text{-}C_5Me_5)(acetone)_3][BF_4]_2$ with calix[4]arene gave the 1,3-dimetallated complex **170** in 95% yield (Scheme 36) [135]. The ^1H NMR spectrum of **170** exhibits a broad OH signal at 5.3 ppm. An excess of rhodium did not lead to further complexation. This double arene complexation facilitates deprotonation of two out of four phenolic protons. Thus the treatment of **170** with excess Na_2CO_3 resulted in the formation of dication **171**, characterized by a sharp OH signal at 10.28 ppm, a value close to that found in free calix[4]arene [7] (it should be noted that the deprotonation of the first two OH groups of calix[4]arenes requires stronger bases). It is suggested that, in **171**, each rhodium is bound to an oxocyclohexadienyl ligand. When the reaction leading to **170** was repeated in the presence of only a few drops of CF_3CO_2H, the tricationic complex **172** was formed (for which the NMR data indicate an unsymmetrical structure). The addition of HBF_4 to this complex resulted in its complete conversion to **170**. The dinuclear complex **173**, derived from the more sterically hindered *p*-tert-butylcalix[4]arene, was obtained under conditions similar to those employed for the formation of **170**.



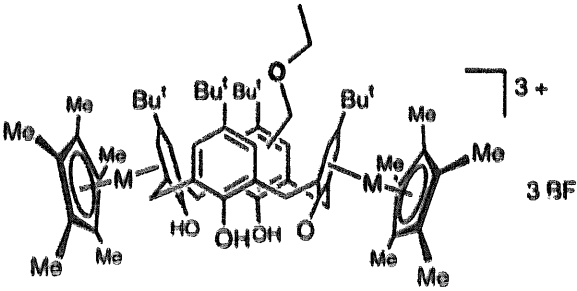
Scheme 36.



173 M = Rh
174 M = Ir

A surprising result was found by comparing the coordinative properties of *p*-tert-butylcalix[4]arene and calix[4]arene towards Ir [135]. Whereas the reaction of the former ligand with $[Ir(\eta^5\text{-}C_5Me_5)(acetone)_3]^{2+}$ in neat CF_3CO_2H afforded the dinuclear iridium complex **174**, the sterically less crowded calix[4]arene gave a tetrametallated complex of formula $[\{Ir(\eta^5\text{-}C_5Me_5)\}_4(\eta^6{:}\eta^6{:}\eta^6{:}\eta^6\text{-}C_{28}H_{22}O_4)][BF_4]_6$ (**175**, not drawn). The dinuclear Ir analogue of **170** could be obtained by performing the reaction in acetone–CF_3CO_2H instead of neat

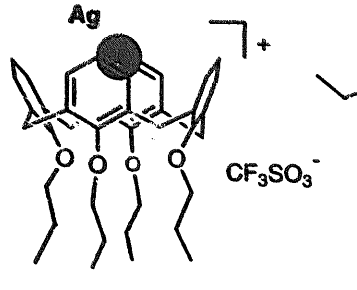
CF_3CO_2H. The spectroscopic data indicate a cone-type structure for **175** with four equivalent IrCp* units (Cp*, η^5-C_5Me_5). Slow crystallization of the dinuclear complexes **173** and **174** from CH_3NO_2–Et_2O solutions resulted in spontaneous mono-deprotonation, leading to the triply charged cationic complexes $[(\eta^5\text{-}C_5Me_5)M(\eta^6{:}\eta^6\text{-}C_{44}H_{55}O_4)M(\eta^5\text{-}C_5Me_5)][BF_4]_3$ (M≡Rh, **176**; M≡Ir, **177**). As shown by an X-ray diffraction study [135], the tricationic iridium complex **177** crystallizes with an Et_2O molecule lying inside the hydrophobic cavity and with a nitromethane molecule having no contact with the calixarene. The terminal Me group of the embedded part of the diethylether molecule is closer to the unmetallated aromatic rings (CH···Ar(centroid), 3.53 and 3.69 Å) than to the metallated rings (3.62 and 3.83 Å), indicating some CH···π hydrogen bonding with the relatively electron-rich unmetallated rings. Examination of the O···O bond distances within the lower rim leads to the conclusion that the deprotonated phenol group must be one of the two metallated rings. However, because of disorder, the corresponding two oxygen atoms could not be distinguished crystallographically. The C(aryl)–O distances of the metallated phenol rings are significantly shorter than the other two (1.30 vs. 1.37 Å), which is consistent with the oxocyclohexadienyl description proposed for such a binding site (see above).



176(Et_2O) (M = Rh)
177(Et_2O) (M = Ir)

Silver complex **178** is the first example of a cone-calix[4]arene π complex with a metal located inside the calix cavity [136]. An X-ray study shows that, in the solid state, this molecule has C_{2v} symmetry and that the silver ion is located between two (almost parallel) distal aryl rings on the line joining two para carbon atoms [136]. The other two rings are flattened and show no bonding interaction with the silver ion. The separations of Ag from the two closest *p*-C atoms of the bound aryl rings are 2.39 and 2.40 Å. These findings clearly establish that the silver cation is included in the cone-calixarene only through cation–π interactions. A similar inclusion complex was obtained from the related *p*-tert-butyl analogue **179** (not drawn). In this case, the Bu^t groups obstruct the binding to the para positions and, consistent with the ^{1}H NMR data, the Ag^+ atom is probably included deeper in the interior of the cavity.

Partial-cone **166** is also capable of binding Ag^+. A single crystal X-ray diffraction study of the resulting complex, **180**, showed that, in the solid state, the Ag^+ ion is trapped between two parallel distal aryl rings and interacts with C=C double bonds around the *p*-carbon atoms (Ag–*p*-C, 2.40 and 2.41 Å) [137]. In view of the rather



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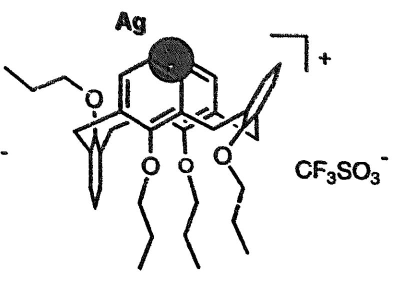
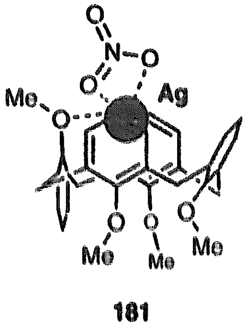


180

long distance between Ag^+ and the *p*-C atom of the third similarly oriented aryl ring (5.63 Å), π bonding cannot be invoked for this ring. Electrostatic interaction between Ag^+ and the oxygen atom of the inverted phenol ring probably occurs (Ag–O = 2.94 Å; sum of the ionic radii of Ag and O, 2.78 Å). Another partial-cone calix[4]arene silver complex, **181**, has recently been reported by Xu et al. [138]. As shown by X-ray structural analysis, the silver ion is π bonded through a $C{=}C_{para}$ edge of each of the two facing aryl groups. In contrast with **180**, the silver atom in **181** is clearly additionally stabilized by an oxygen atom, namely that of the MeO group (Ag–O, 2.517(3) Å). In this complex, the silver atom remains only weakly bonded, being easily displaced by donors such as phenylacetylenes, cyclohexene or acetonitrile.

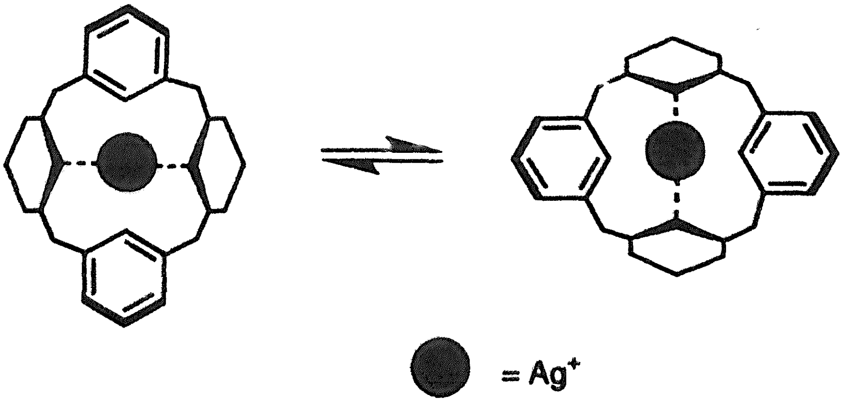


181

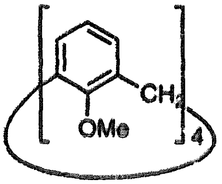
A variable temperature NMR study made with the cone complex **178** indicated a C_{2v}–C_{2v} interconversion in solution as shown in Scheme 37 [136]. This exchange implies alternate π bond formation and scission. A comparative study performed on precursor cone **166** established that a C_{2v}–C_{2v} equilibrium also exists for the free ligand; comparison of the coalescence temperatures indicates that, in the silver complex, the exchange rate is considerably slower.

Complexation of Ag^+ with the conformationally mobile tetramethoxy-calix[4]arene **182** (L^{182}), for which a partial-cone to cone equilibrium exists in solution, induced a shift in the equilibrium to the partial-cone $L^{182} \cdot Ag^+$ (**183**) [136]. This observation corroborates the results of an X-ray study [136] of the related complex **180** which shows that, in a partial-cone isomer, the two distal aryl rings involved in complexation are perfectly pre-organized for Ag^+ binding.

Complexation of Ag^+ by 1,3-alternate conformer L^{166} resulted in the formation of the mononuclear silver complex **184** having the metal atom bound to a cavity



Scheme 37.



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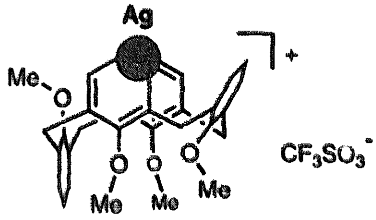
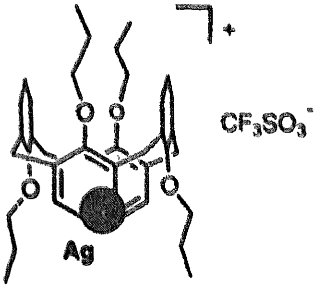


183

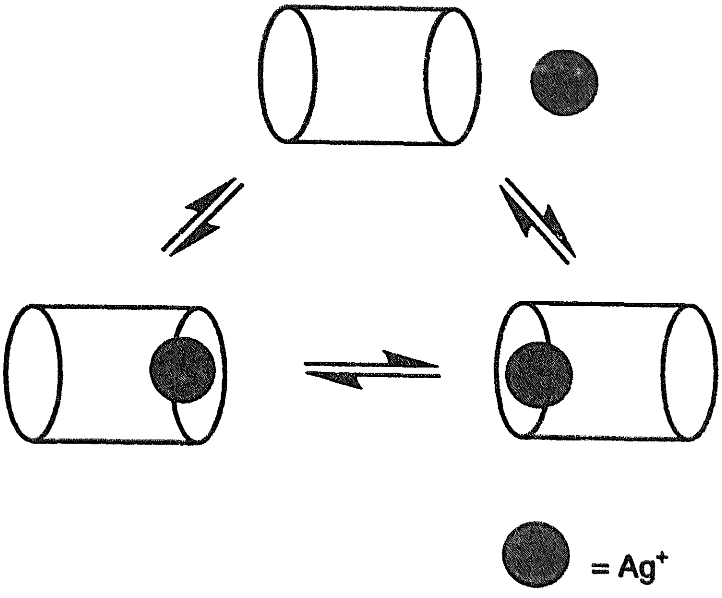
consisting of two phenolic oxygen atoms and two π basic aryl rings (this conclusion was drawn from an NMR investigation) [137]. Dynamic ^{1}H NMR studies showed that the silver ion hops from one π basic binding site to the other according to either an intermolecular or intramolecular mechanism (Scheme 38). This latter ion transfer is the first example of Ag^+ ions tunnelling across an aromatic cavity. It provides important data for the understanding of metal transport along ion channels and metal inclusion in π basic cavities. Such results are particularly relevant to furthering our understanding of ion transport in biological systems.



184

6. Calixarenes substituted with redox-active metallocenes

The incorporation of redox-active centres, such as ferrocene, into ligands of the calixarene type is aimed at the development of molecular sensory devices which

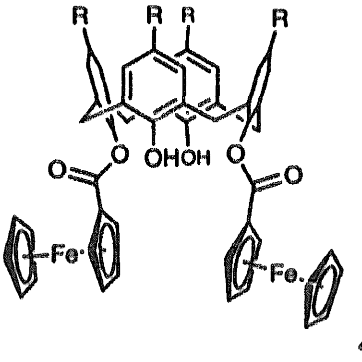


Scheme 38.

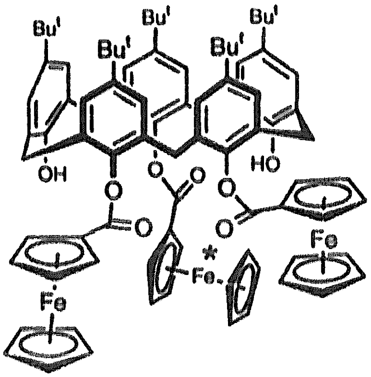
allow electrochemical recognition of trapped guests. It is also expected that these units may catalyse redox reactions on a complexed organic host. Metallocenes have been attached to the lower and upper rims of calix[4]arenes; examples of metallocene-substituted resorcinarenes have also been reported.

A straightforward method for connecting a $-C(O)(C_5H_4)M(C_5H_5)$ unit ($M \equiv Fe$, Ru) at the phenolic oxygen atoms of a *p*-R-calix[4]arene or a resorcinarene has been developed by Beer et al. [139,140]. In this methodology, a chlorocarbonyl ferrocene or ruthenocene is reacted with the phenolic substrate in the presence of excess NEt_3. With metallocenes substituted by one chlorocarbonyl group, multi-redox-active molecules, such as **185**–**188**, were isolated. The presence in **188** [141] of Lewis acid binding sites of the crown-ether type should be noted. Their presence may be helpful for combining Lewis acid catalytic activation with ferrocenyl-mediated redox reactions on small guest substrates (e.g. CO_2, CO, etc).

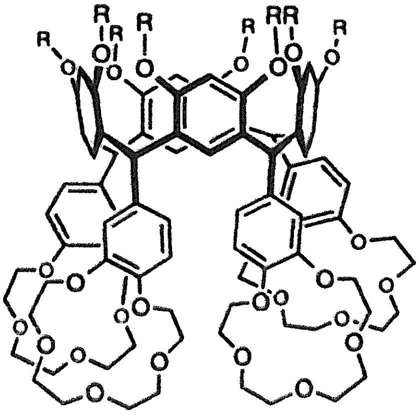
Using metallocenes substituted on both C_5 rings by a $-C(O)Cl$ functional group



185 R = H
186 R = Bu^t

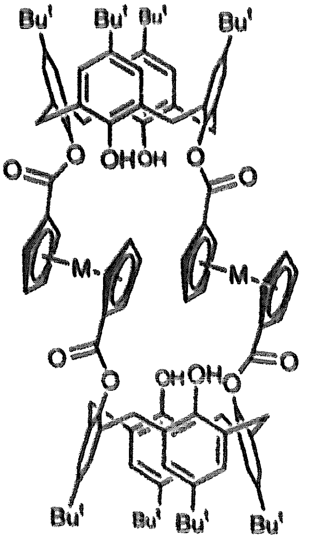


187

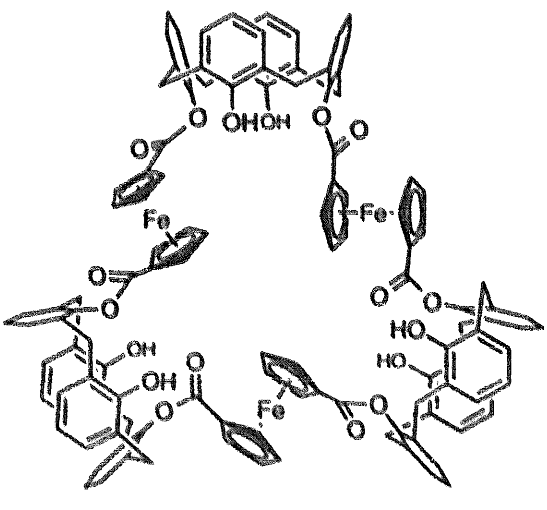


188 R = -C(O)(η^5-C_5H_4)Fe(η^5-C_5H_5)

leads to oligomeric structures, such as **189**–**191**, in which the metallocenyl unit acts as a bridge between two calixarenes [140]. Although some of these complexes were initially formulated as monomers [142], it is now clearly established that the cyclopentadienyl–cyclopentadienyl separation (3.25 Å [143]) is not compatible with transannularly bridged structures (distance between the transannular 1,3-hydroxyl groups of calix[4]arenes, approximately 2 Å). The dinuclear complex **189** was shown to be conformationally mobile [140]. The origin of this dynamic behaviour may be assigned either to a cone–partial-cone equilibrium or to intramolecular rotations of the metallocene carbonyl groups. The NMR data do not allow a distinction between these two possibilities. An electrochemical study showed that, in acetonitrile, **189** undergoes a single, reversible two-electron oxidation at 1.24 V (vs. saturated calomel electrode (SCE)), indicating that the two ferrocene units behave as non-interacting, independent moieties.



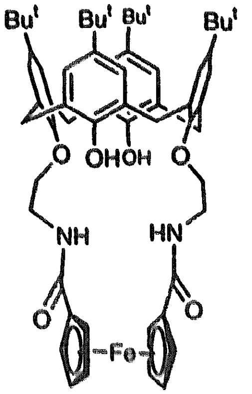
189 M = Fe
190 M = Ru



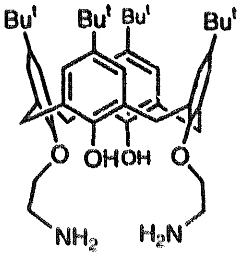
191

Interesting redox-active properties were found for the 1,3,4-trisferrocenyl-*p*-tert-butylcalix[5]arene ester molecule **187** [144]. This complex undergoes two quasi-reversible oxidations at $E_{p1} = +0.350$ V and $E_{p2} = +0.450$ V (vs. Ag/Ag$^+$). It was shown that the former process corresponds to the oxidation of a single unit, probably the $(C_5H_4)Fe^*(C_5H_5)$ unit, whereas the potential at +0.450 V corresponds to the two other ferrocenyl centres. The addition of small neutral substrates, such as *N*,*N*-dimethylformamide (DMF), dimethyl sulphoxide (DMSO) and EtOH, causes the two redox couples to merge. It is probable that the interposition of these guest molecules between the redox-active groups shields the mutual electrostatic influences between the iron centres.

The only reported example of a *p*-R-calix[4]arene having a 1,3-bridging ferrocenyl subunit is complex **192** [145]. This complex, prepared by reacting diamine **193** with $[Fe(\eta^5\text{-}C_5H_4\text{-}COCl)_2]$ in the presence of NEt_3–4-dimethylaminopyridine, is capable of electrochemically detecting the $H_2PO_4^-$ anion in the presence of a ten-fold excess of hydrogensulphate and chloride anions.



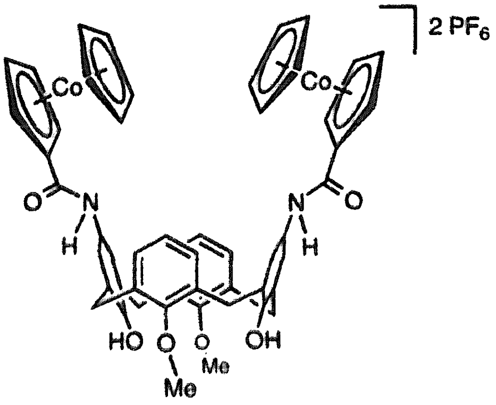
192



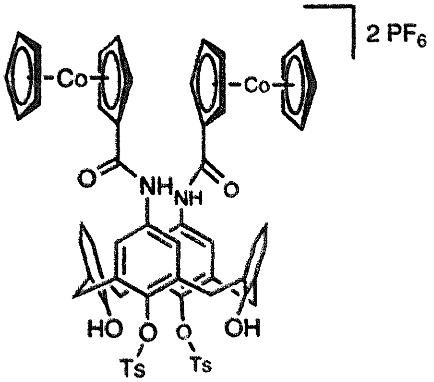
193

The idea to anchor positively charged redox-responsive units to a calix[4]arene for performing anion recognition was exploited with the ditopic bis(cobaltocenium) receptor **194** [146]. ^1H NMR titration curves show that this compound forms very stable 1 : 1 complexes with Cl$^-$, Br$^-$ and $H_2PO_4^-$ in DMSO solution and also with the adipate dianion in acetone [147]. NMR data were invoked to draw the conclusion that the anionic units probably bind in close proximity to the cobaltocenium centres. Electrochemical studies have shown that, in acetone, **194** exhibits a reversible two-electron redox reduction wave at −0.85 V (vs. Ag/Ag$^+$). The addition of anionic guest species causes substantial one-wave cathodic shifts, presumably due to stabilization of the positively charged cobaltocenium units by the complexed anions. For example, the addition of tetra-*N*-butyl adipate induced a cathodic shift of 50 mV (in acetone). Modifying the lower rim substituents of the calix[4]arene has a dramatic effect on the anion coordination properties of this type of receptor. Thus derivative **195**, containing two tosyl groups para to the amide groups, becomes much more selective for $H_2PO_4^-$ than for Cl$^-$ complexation, the reverse of **194** [99]. Presumably, the bulky tosyl groups alter the receptor shape in favour of phosphate complexation.

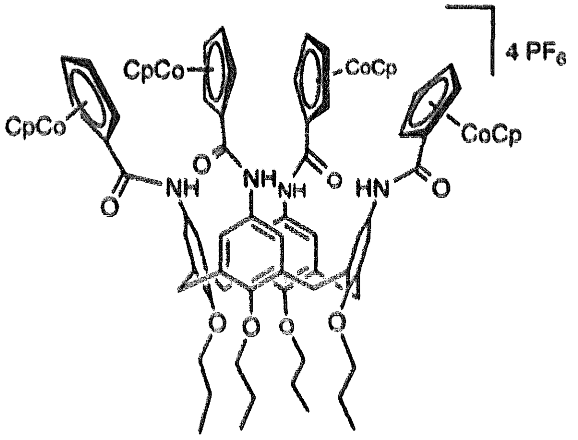
A similar selectivity preference for $H_2PO_4^-$ over Cl^- was also found for the tetrakis-(cobaltocenium) complex **196** [99]. These studies open up new perspectives for the recognition of anions by stable macrocyclic host molecules containing redox-active centres.



194

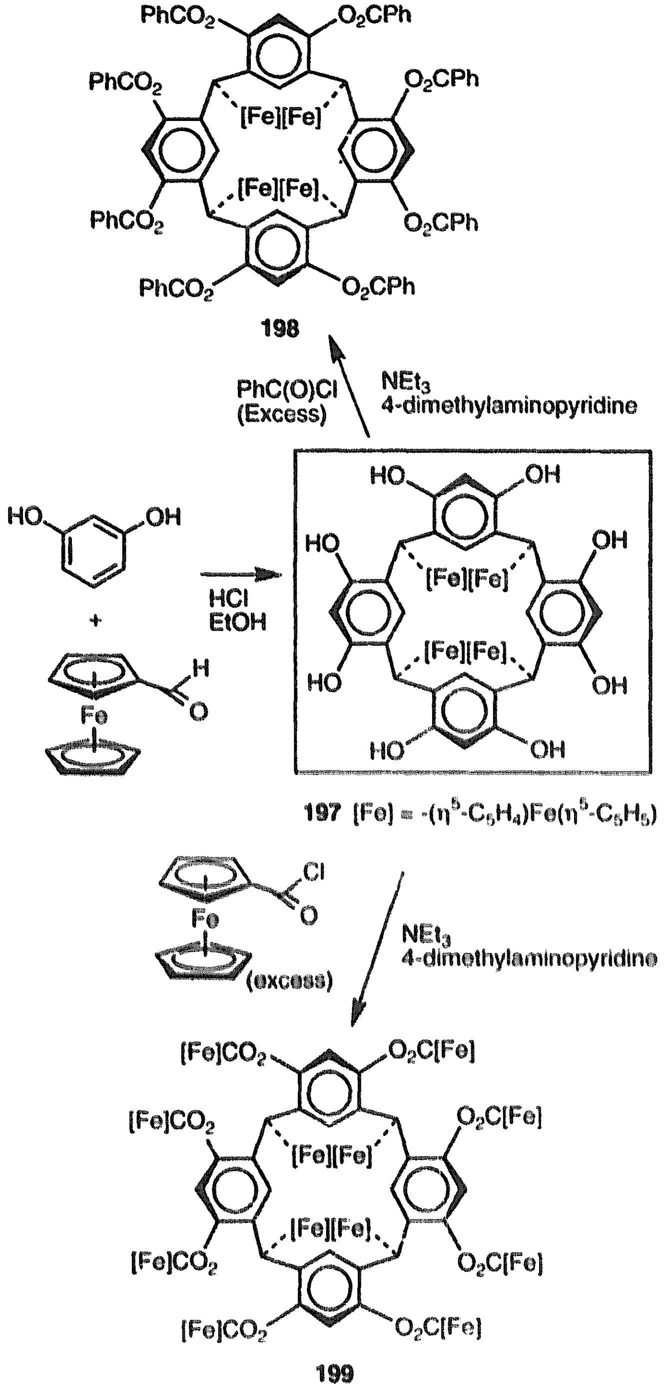


195 (Ts = p-$O_2SC_6H_4Me$)



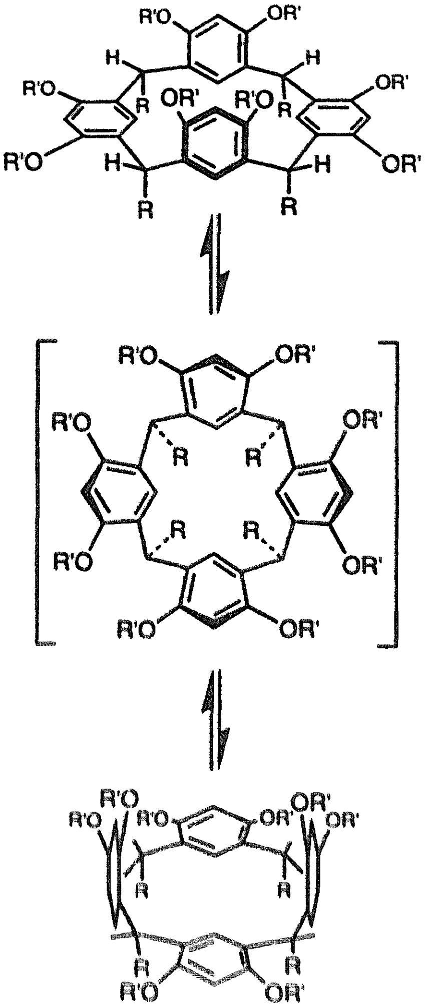
196 (Cp = C_5H_4)

Resorcinarene-derived molecules bearing multi-redox-active sites have also been described recently. The multi-ferrocenyl resorcinarene complexes **197**–**199** were obtained in high yield according to the route outlined in Scheme 39 [141,148]. In a first step, ferrocenecarbaldehyde is condensed with 1,3-dihydroxybenzene in the presence of HCl and EtOH. This reaction was performed over a heating period of 4 h to ensure the selective formation of the cis–cis–cis isomer **197**. Treatment of the insoluble material thus obtained with excess benzoyl chloride in the presence of NEt_3–4-dimethylaminopyridine gave **198**. The dodecanuclear iron complex **199** was obtained from the same intermediate with chlorocarbonylferrocene and NEt_3–4-dimethylaminopyridine. The molecular structure of complex **198** has been determined crystallographically and the expected cis–cis–cis structure was confirmed [141]. As shown by variable temperature ^1H and ^{13}C NMR studies, these cis–cis–cis isomers display dynamic behaviour in solution. Consistent with previous studies on resorcinarenes by Högberg [149,150], this motion may be rationalized in terms of an interconversion of horizontal and vertical 1,3-diacylaryl units as shown in Scheme 40. Interestingly, it was found that the interconversion occurs faster for **199** than for **198** or **188**.



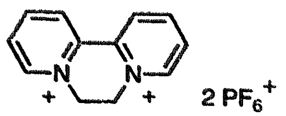
Scheme 39.

The electrochemical properties of **188** and **198** were examined carefully by cyclic voltammetry and differential pulse voltammetry. For complex **188**, containing eight

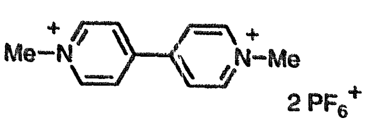


Scheme 40.

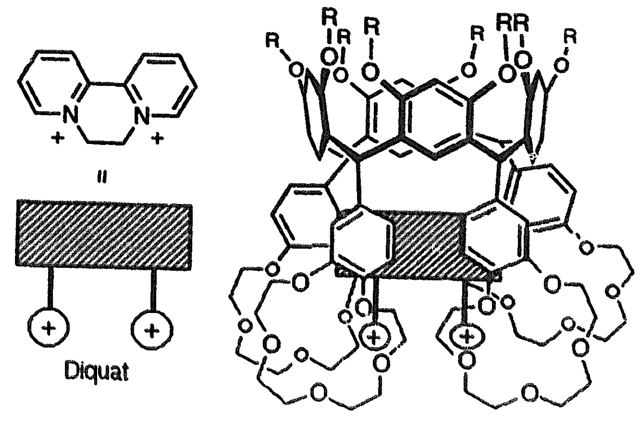
ferrocenyl units, a single, reversible, one-electron oxidation wave was observed, indicating independent one-electron transfers occurring at the same potential. For complex **198**, two reversible oxidation waves were observed at +0.58 V and +0.67 V (vs. SCE) in CH_2Cl_2, representing two reversible two-electron transfers. These two waves are in keeping with the ^1H and ^{13}C NMR spectra and the X-ray crystal structure showing two different ferrocenyl environments. As shown by ^1H NMR studies, in particular using nuclear Overhauser effect (NOE) difference spectroscopy, complex **188** forms solution complexes with diquat (**200**), involving mainly C–H · · · O hydrogen bonding between the NCH_2 protons and the oxygen atoms of the respective benzocrown ether moiety, as suggested in Scheme 41. Similar complexation in the lower box-like cavity of **188** was found for paraquat (**201**). In view of the rather long distance separating the ferrocenium centres and the bipyridinium recognition sites, it is not surprising that the diquat complexation could not be detected electrochemically. Nevertheless, introduction of metallocenes into cavity-shaped molecules remains a potentially powerful method for the detection of host–guest complexes. This area of research certainly deserves further investigation.



200 (Diquat)



201 (Paraquat)



R = $[(\eta^5\text{-}C_5H_4)Fe(\eta^5\text{-}C_5H_5)]$

Scheme 41.

7. Conclusions and perspectives

Since the first use, a decade ago, of calixarene-derived ligands for the complexation of transition metal ions, a considerable number of fundamental studies have been undertaken, demonstrating the suitability of these ligands for the construction of a large variety of mononuclear and polynuclear metal complexes. It has been shown that the presence of transition metal centres bound to calixarene matrices may seriously perturb the shape and structural properties of such macrocycles. The coordination chemists have also learned to combine the intrinsic properties of calixarenes with those of transition metal centres. This has facilitated the fabrication of promising multi-metal species, sophisticated sensors, novel anionic receptors, supercavities and highly ordered molecular materials. Many aspects of the coordination chemistry of calixarenes still remain to be explored. Calixarenes are powerful matrices for the creation of sophisticated coordination spheres; the presence of a large number of functional groups in such ligands may synergistically assist a transition metal centred reaction. Due to the suitability of calixarenes for forming inclusion complexes with organic substrates, it may be anticipated that, in the future, the potential of molecules combining a catalytic centre with a calixarene or resorcinarene cavity will be exploited for novel shape-selective catalysis and asymmetric catalysis. A further perspective offered by functional ligands derived from calixarenes, and particularly from the large calix[8]arenes, is their use for the stabilization of small cluster particles (it should be noted that C_{60} has been shown to form complexes with calix[8]arene) and their possible transformation into new metallic materials. Finally, the systematic investigation of the coordinative properties of calixarene towards transition metals will also probably lead to the discovery of interesting larger molecular systems.

Acknowledgements

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Note added in proof

In the gap since submission of this manuscript, there have been many exciting developments in the field of calixarene chemistry. We cite below the leading references which have appeared too recently to be included in the review. In particular we wish to draw attention to the fine review published by Roundhill in Progress in Inorganic Chemistry [151].

O-metallated calix[4]arenes: Nb [152], Ta [152,153], W [154,155]
Calix[4]arenes substituted with bipyridyl ligands: Co [156], Ru [156,157], Re [156], Cu [158]
Calix[4]arenes substituted with porphyrins: Fe [159]
Calixarene-related ligands containing N-donors: Co [160]
Calix[4]arenes with phosphorus ligands: Au [161], Pt [161]
Calix[4]arenes substituted with oxygen donors: Fe [162]
Calix[4]arenes substituted with thiols or thioethers: Pd [163], Au [164,165]
π-*Arene complexes of calix[4]arenes:* Ru [166]
Calix[4]arenes substituted with metallocenes: Co [167]
Calix[4]arenes substituted with alkynes: Ag [168], Au [168]
Calix[6]arenes bearing sulfonato groups: Fe [169]
Resorcinarenes complexes: Cu [170], Ag [170], Hg [170]

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