Available online at www.sciencedirect.com
SCIENCE DIRECT
Coordination Chemistry Reviews 244 (2003) 45–70
COORDINATION CHEMISTRY REVIEWS
www.elsevier.com/locate/ccr

Coordination chemistry of the larger calixarenes

Carl Redshaw *

Wolfson Materials and Catalysis Centre, School of Chemical Sciences and Pharmacy, The University of East Anglia, Norwich NR4 7TJ, UK

Received 7 October 2002; accepted 23 December 2002

Contents

Abstract . . . 45
1. Introduction . . . 46
2. Alkali metal and alkali earth metals . . . 46
3. Early transition metals . . . 50
  3.1 Titanium . . . 50
  3.2 Zirconium . . . 51
  3.3 Vanadium . . . 52
  3.4 Niobium . . . 52
  3.5 Molybdenum . . . 53
  3.6 Tungsten . . . 54
  3.7 Rhenium . . . 56
4. Late transition metals . . . 57
  4.1 Iron . . . 57
  4.2 Ruthenium . . . 57
  4.3 Cobalt and nickel . . . 57
  4.4 Iridium . . . 58
  4.5 Palladium and platinum . . . 59
  4.6 Copper . . . 59
  4.7 Zinc . . . 61
  4.8 Mercury . . . 62
5. Main group elements . . . 62
  5.1 Aluminium . . . 62
  5.2 Carbon . . . 62
  5.3 Silicon . . . 64
  5.4 Tin . . . 64
  5.5 Nitrogen . . . 64
  5.6 Phosphorus . . . 65
6. Lathanides and actinides . . . 67
7. Concluding remarks . . . 69
Acknowledgements . . . 69
References . . . 69

Abstract

This article presents a systematic review of the coordination chemistry of the calix[n]arenes, where $n \geq 5$. Particular attention is given to the variety of synthetic methods that have been employed, together with structural data that has been assembled.

Keywords: Calixarenes; Complexes; Synthesis; Structures

---

* Tel.: +44-1603-593-137; fax: +44-1603-592-003.
E-mail address: carl.redshaw@uea.ac.uk (C. Redshaw).

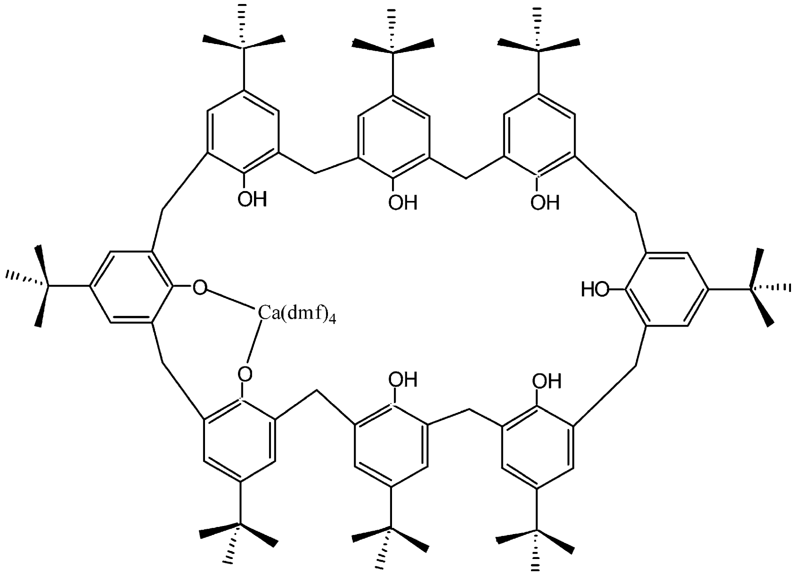
0010-8545/03/$ - see front matter © 2003 Elsevier B.V. All rights reserved.
doi:10.1016/S0010-8545(03)00099-7

1. Introduction

The coordination chemistry of the simplest of the calix[*n*]arenes, the calix[4]arene, is now relatively well developed as highlighted by a number of recent reviews [1]. The vast majority of these metallocalix[4]arene derivatives exist as either mono or binuclear complexes, retaining a cone-like conformation for the parent ligand. By contrast, metal compounds containing the larger ring systems ($n \geq 5$) are still quite rare despite the conformational variations offered by the increased flexibility of the larger number of polyphenolic rings. An additional attractive feature of the latter is their ability to simultaneously coordinate more than one metal centre. In this context, we herein review the coordination chemistry for calix[*n*]arene complexes, where $n \geq 5$, paying particular attention to both the degree of 'metallation' of the ring and the conformations adopted.

2. Alkali metal and alkali earth metals

Interest in calixarenes of Group I stems from the observation that they effect the transport of ions of this group through water/organic solvent/water membranes [2]. Further to this, it has been postulated that the larger calix[*n*]arenes, by virtue of their increased flexibility, may transport more than one metal at a time [3]. Surprisingly though, structural information on such systems is scant. Harrowfield et al. have isolated the calcium complex [Ca(*p*-*tert*-butylcalix[8]areneH$_6$)(dmf)$_4$] (**1**) (dmf = dimethylformamide) in about 30% yield from the reaction of the parent calix[8]arene with [Ca(ClO$_4$)$_2$·6DMSO] (DMSO = dimethylsufoxide) in the presence of a base (Et$_3$N) [4]. The calcium center is six-coordinate with the calix[8]arene acting as a bidentate chelate; the remaining coordination sites are occupied by the solvent (dmf).

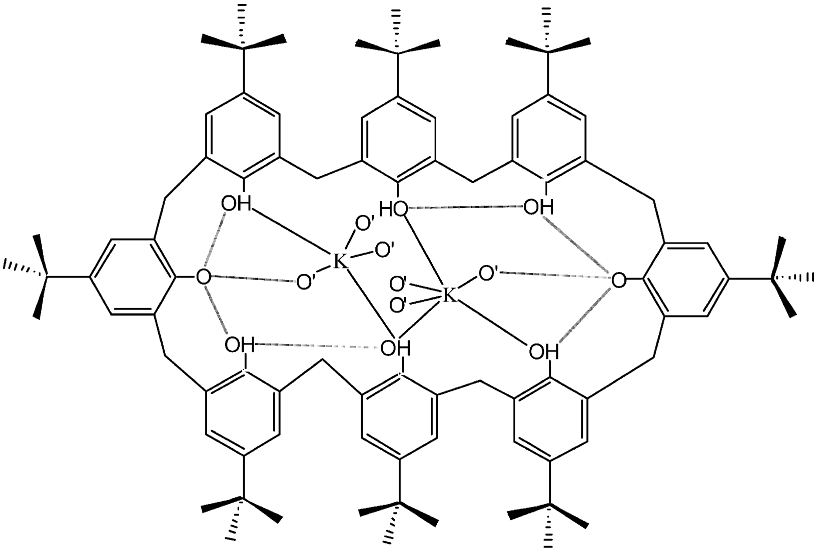


1

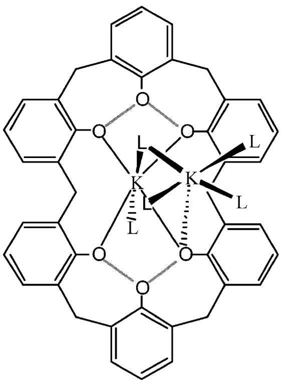
The same group have also characterised the dipotassium salt [K$_2$(*p*-*tert*-butylcalix[8]areneH$_6$]·3MeCN·H$_2$O (**2**) from the reaction of K$_2$CO$_3$ and the parent *p*-*tert*-butylcalix[8]areneH$_8$ (yield ~ 50%).

Recently, Clague et al. reacted *p*-*tert*-butylcalix[8]areneH$_8$ with 8 equivalents of base (either KOH or KOBu^t) in an ethanol/diethylcarbonate solvent system, obtaining on prolonged standing (72 h) at ambient temperature, colourless crystals of the dipotassium complex **3** [5]. Spectroscopic data was not reported, however, a crystal structure analysis revealed a molecule lying on a crystallographic inversion centre with the K$^+$ ions lying above and below the cavity of the doubly deprotonated calix[8]arene. The latter adopting a pinched conformation with two ArOH groups bridging the K$^+$ ions at the pinch.

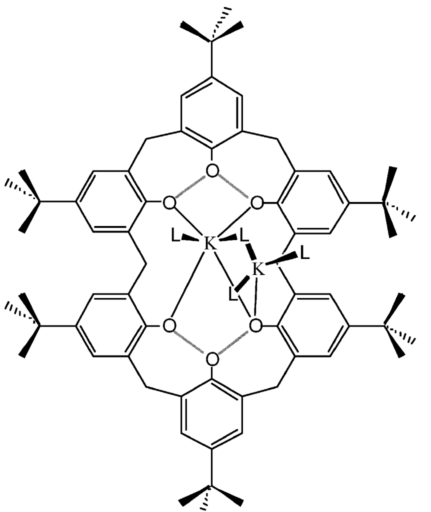
The same group at Hull has also reported mixed lithium–strontium complexes derived from *p*-R-calix[8]areneH$_8$ (R = ^{i}Pr (**4**), Bu^t (**5**)) [6]. The syntheses involved interaction of the parent calix[8]arene with



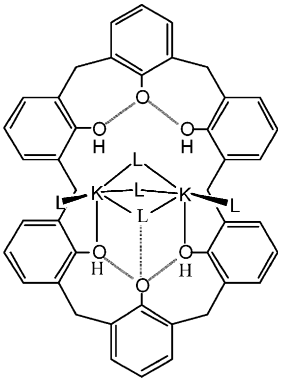
3 (O' = oxygen of diethylcarbonate or ethanol)



6 L = MeOH

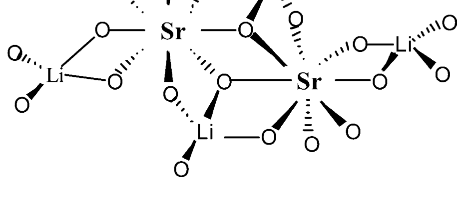


7 L = MeOH

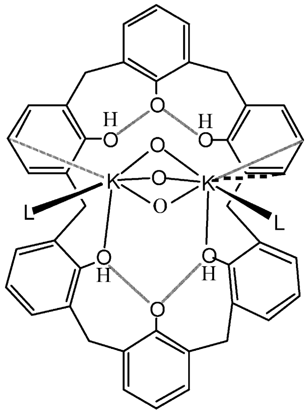


8 L = H_2O

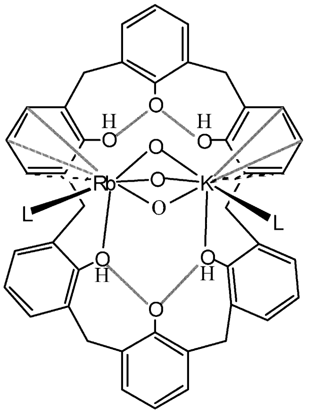
^{n}BuLi (8 equivalents) under argon and subsequent reaction with $SrBr_2$ (8 equivalents). The reaction is also thought to involve adventitious oxidation to account for the presence of pentanaoate ligands. The overall yield is low (< 5%), however, despite this crystals suitable for X-ray analysis (using Synchrotron radiation) were obtained. The inorganic core is shown below—each strontium centre is eight coordinate with a distorted square antiprismatic geometry. Overall the complex has crystallographic inversion symmetry and to balance the charges two of the phenolic groups remain protonated.



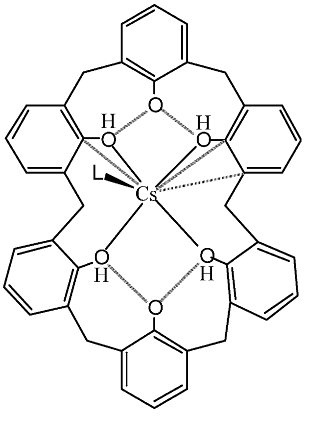
The crystal structures of three potassium calix[6]arene complexes, **6**–**8**, have been reported by Murayama and Aotei [7]. In all three complexes, the two K^+ ions are bound to a doubly deprotonated calix[6]areneH_4 (*p*-*tert*-butyl derivative in **7**) ligand. The presence of cation π interactions for all structures are inferred from the close K^+-phenyl ring contact distances [3.28(2)–3.68(2) Å for **6**, 3.30(3)–3.65(3) for **7** and 3.168(6)–3.582(6) Å in **8**]. In complex **7**, the missing methanol ligand (c.f. **6**) allows a hydroxyl group of an adjacent molecule (not shown below) to bind and results in a one-dimensional polymeric structure. The synthesis of **6**–**8** involves mixing the parent calix[6]arene with excess KOH (KOH and NaOH for **8**) in a water/methanol mixture with a pH of ca. 10. No yields or spectroscopic data were given.



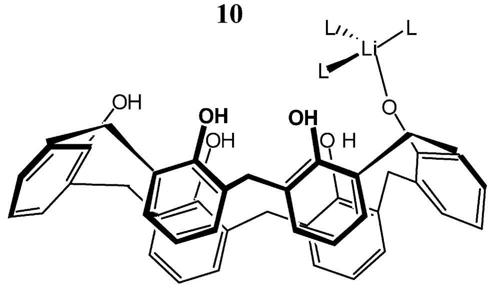
9



10



11



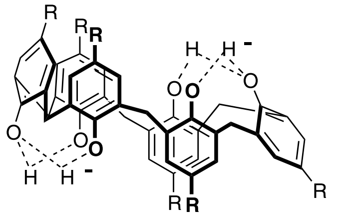
12

L = Me_2CO

Both calix[6]areneH_6 and *p*-*tert*-butylcalix[6]areneH_6 form dianions such as **9** in high yield (70–90%) when treated with one equivalent of M_2CO_3 (M = K, Rb, Cs) in acetonitrile or acetone. Interestingly, treatment of calix[6]areneH_6 with one equivalent each of K_2CO_3 and Rb_2CO_3 yields the bimetallic product **10**. A change in reaction stoichiometry of 2:1 for calix[6]arene:base results in the formation of monoanions, for example **11**, in high yield (70–100%). Monoanions such as **12** are also readily available using $MOBu^t$ as base (M = Li, Na) in either tetrahydrofuran or acetonitrle under a nitrogen atmosphere. Related monanions of calix[8]arenes are obtainable using $MOSiMe_3$ (M = Li, Na, K) or MOH (M = Rb, Cs). Solution NMR studies indicate that the monoanionic calix[6]arene systems are more conformationally flexible than are those of the dianionic calix[6]arene counterparts. The latter can be assigned a 1,2,3-alternate conformation on the basis of their ^1H-NMR spectra. A crystal structure determination for complex **9** reveals that one of the K^+ centres is involved in intermolecular bonding with a phenolic oxygen of a neighbouring molecule to afford an infinite one-dimentional chain [8]. The crystal structure of **11** shows that it possesses a 1,2,3-alternate conformation, whilst that for **12** reveals a cone conformation. All three structures contain cation π-arene intercations.

In 1995, Steed, Atwood, Clark et al. reported the synthesis of the water-soluble inclusion complexes Na_5[*p*-sulfonatocalix[5]arene]·H_2O (**13**) and Na_7[*p*-sulfonatocalix[5]arene]·$8H_2O$ (**14**) [9], formed on addition of concentrated sulfuric acid to *p*-*tert*-butylcalix[5]areneH_5, followed by quenching with either NaCl or Na_2CO_3, respectively. Neutralisation of **13** (pH 7) with Na_2CO_3 yielded the hydrate Na_7[*p*-sulfonatocalix[5]arene]·$18H_2O$ (**15**), whilst further reaction of **14** with $Zn(NO_3)_2 \cdot H_2O$ in the presence of pyridine *N*-oxide afforded Na_5[*p*-sulfonatocalix[5]arene]·pyridine*N*-oxide·$8^1/_2H_2O$ (**16**). Crystal structure determinations revealed that the large bowl-shaped cavity of **15** contained three water molecules, whilst the presence of seven sodium ions in the crystal lattice confirmed the heptaanionic nature of the calix[5]arene. The crystal structure of **16** revealed that the included molecule of pyridine *N*-oxide makes a short contact [2.56(1) Å] with a protonated sulfonate group via H-bonding. Also reported were the crystal structures of the products resulting from interaction of **13** with the lanthanide species $M(NO_2)_3 \cdot H_2O$ [M = Ln, Gd, Eu and Tb] in the presence of pyridine *N*-oxide—see Section 6.

A year later, Atwood, Steed et al. reported the crystal structure of the dimeric hydrate Na_{10}[*p*-sulfonatocalix[5]arene]$_2$·$33^1/_2H_2O$ (**17**) [10], which readily forms complexes with Co(II) and Ni(II)—see Section 4.3. The related calix[6]arene complex Na_8[calix[6]arenesulfonate]·$20^1/_2H_2O$ (**18**) has been shown to adopt a double partial cone conformation, the stability of which is thought to be due to the presence of intramolecular hydrogen bonding—as shown below [11].



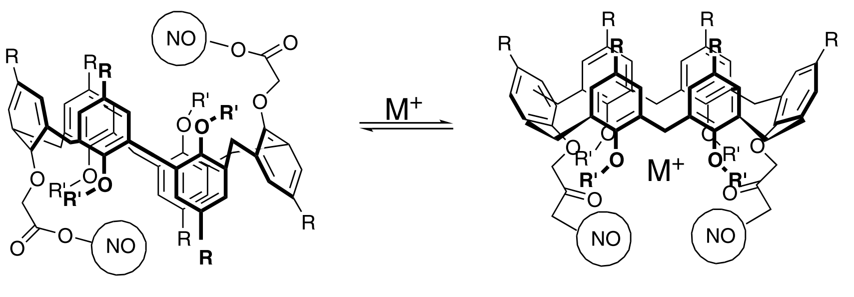
(**18**, R = SO_3^-)

The stereochemical isomers of calix[6]arene bis-crown-4, **19** (1,2,3-alternate) and **20** (cone), form 1:1 complexes with alkali metals (Cs, Rb, K, Na, Li) showing a preference (greatest for **20**) for the larger caesium ion [12].

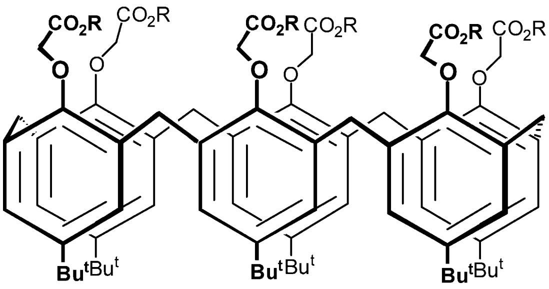
Lithium ion selectivity can be achieved using a 1,3-4,5-double diamide bridged calix[6]arene, whilst a preference for the larger ions is achieved using *p*-*tert*-butylcalix[6]-1,4-2,6-dioxo-diaza-crown-4 (diagrams not shown) [13].

Shinkai and co-workers have reported the synthesis of the *o*-alkylated calix[6]arenes **21**, **22** and **23**. The extraction of alkali metal picrates with these ligands showed selectivity for K^+ and Cs^+ over Li^+ and to a lesser extent Na^+ [14].

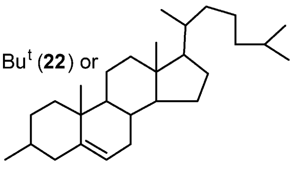
Related calix[5 and 6]arene ketones and thioamides **24** were reported by McKervey and co-workers [15]. X-ray crystal structure determinations for the Na^+ and Rb^+ complexes thereof revealed that the cations to be



1,2,3-alternate (**26**) R = Bu^t, R' = CH_2COOEt Cone (**27**)

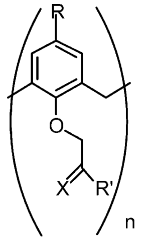


R = Et (**21**), Bu^t (**22**) or



(**23**)

encapsulated by the ethereal and carbonyl oxygen atoms; the degree of complexation being dependant on the bulk of the alkyl residues adjacent the ketonic carbonyl.



R = H, Bu^t
X = O, n = 5, R' = Me, Bu^t, OH, Cl
n = 6, R' = Me, Bu^t

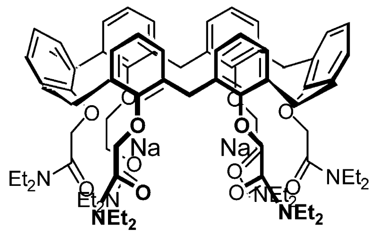
R = Bu^t
X = S, n = 5, R' = NPr^n_2
n = 6, R' = $N[(CH_2)_4]_2$

24

The same group has also investigated the calix[6]arene esters **25** (R′ = OEt, OBu^t, NEt_2 in structure above) which adopt a 1,2,3-alternate conformation in the ‘free’ state (similar to that observed for **19**). For R = ^{t}Bu, NMR data is indicative of a cone conformer when complexed with K^+ or Cs^+, whereas for R = Et the situation is more complex and for K^+ a lozenger-shaped ligand has been proposed. For Cs^+ and R = Et, interconversion of pinched cones (each with C_{3v} symmetry) is proposed.

Calix[6]arene esters have also been reacted with $NO^\bullet$ radicals and subsequently treated with alkali metal cations [16]. Interestingly, EPR measurements reveal that in the 1,2,3-alternate conformer **26**, the radicals were too far apart to interact with one another (triplet seen in EPR). However, the addition of the metal cation resulted in adoption of the cone conformer **27**, for which the radicals are in closer proximity (unsymmetrical quintet observed in EPR). The greatest effect was observed for the Rb^+ cation.

Shinkai and co-workers have also utilised 1,5:3,7-doubly bridged calix[8]arenes **28** (no diagram) in which the oxygen atoms are arranged in both a square-planar and tetrahedral arrangement. These ligands showed a high affinity for Cs^+ over other alkali metal cations [17].



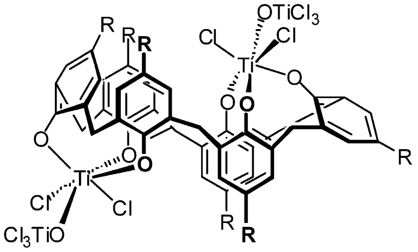
29

The calix[6]arene amide **29**, prepared via interaction of α-chloro-*N*,*N*-diethylacetamide on the parent calix[6]areneH_6, has been complexed with Na^+, K^+ and Cs^+ (picrate salts). On the basis of ^{1}H-NMR, the ligand in 1:2 complex with Na^+ was assumed to adopt a cone conformation. A 1:1 complex with guanidinium salts was also reported [18].

3. Early transition metals

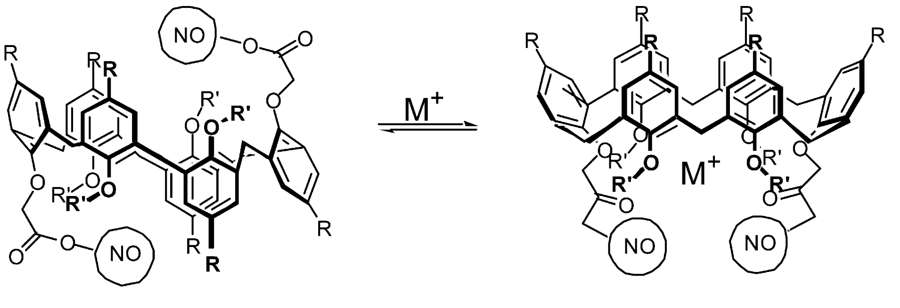
3.1. Titanium

One of the earliest reports of a transition metal calixarene complex was that of Atwood in 1986 who reacted hexamethoxycalix[6]arene with 4 equivalents of $TiCl_4$ isolating a centrosymmetric complex **30** which contained two bimetallic units of the form [Cl_3TiO-$TiCl_2$], the calix[6]arene ligand adopting an eliptical cone conformation [19]. The reaction is thought to proceed via cleavage of an O–Me bond and ultimately the loss of CH_3Cl molecules.

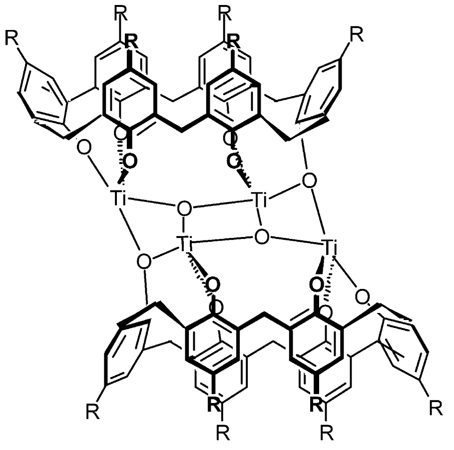


30 R = Bu^t

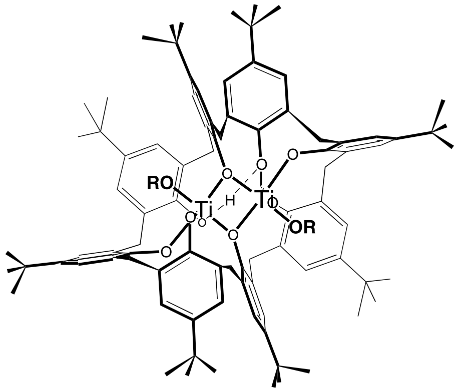
The tetrametallic complex **31**, obtained from the



1,2,3-alternate (**26**) R = Bu^t, R' = CH_2COOEt Cone (**27**) reaction of $TiCl_4$ with *p-tert*-butylcalix[6]areneH_6, was crystallographically characterised by Calestani, Ungaro and co-workers [20]. The quality of the data makes detailed geometric discussions ambiquous, however, the general identity and connectivity is clear. Four distorted pyramidal titanium centres are bound (two to each) to two calix[6]arene ligands, the latter adopting elliptical cone conformations. Two triply bridging oxo groups complete the coordination sphere at titanium.

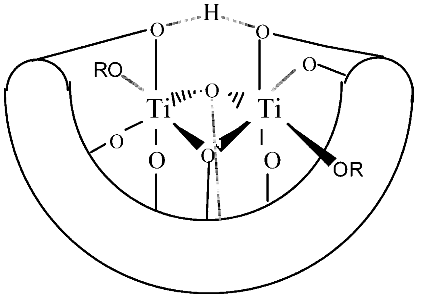


31 R = Bu^t



32

Pedersen has utilised the tetrakis-alkoxide $[Ti(OPr^i)_4]$ or better still $[Ti(OBu^t)_4]$ in combination with *p-tert*-butylcalix[8]areneH_8 and a base in a one-pot procedure to generate salts of the dimetallocalix[8]arene **32** (see also zirconium and vanadium) [21]. The alkoxide ligands (OR) on the metal reside in cavities formed by 3 of the phenol sub-units of the saddle-shaped calix[8]arene ring. This produces upfield shifts for these groups in the proton NMR. The remaining phenolic proton is found at about 16 ppm and its position in the structure was verified by other NMR experiments.

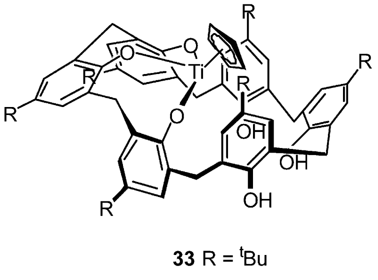


Petrella et al. have recently isolated the mono and binuclear cyclopentadienyl complexes (Cp) **33** and **34**. Both are obtained in high yields (~ 90%) via reaction of the parent calix[6]arene and potassium metal (2 equivalents for **33** and 4 equivalents for **34**), followed by subsequent treatment with 1 or 2 equivalents of $[TiCp_2Cl_2]$, respectively. In the resulting metal complexes, the *p-tert*-butylcalix[6]arene ligand adopts an inverted double cone conformation with a Cp group in one of the cavities [22].

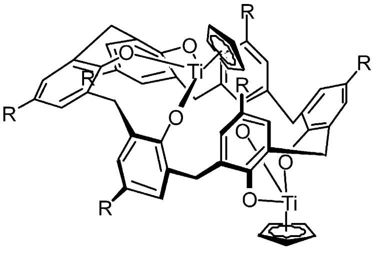
3.2. Zirconium

As noted above, Pedersen has isolated a zirconium complex **35** analogous to **32** utilising $Zr(OPr^i)_4/Pr^iOH$ as starting material [21].

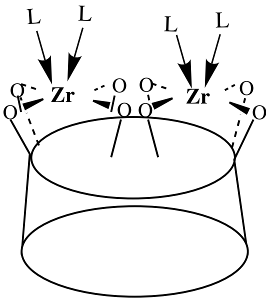
The only other zirconium containing calix[8]arene we are aware of results from the interaction of excess $[Zr(NMe_2)_4]$ with the parent calix[8]arene producing on work-up (extraction with acetonitrile) the tetra-amidine complex **36** [23].



33 R = ^tBu



34 R = ^tBu



36 L = NHC(Me)NMe_2

3.3. Vanadium

The interaction of the oxoalkoxide $[VO(OPr^i)_3]$ (2 equivalents) with *p*-*tert*-butylcalix[8]areneH_8 in the presence of a base affords the black crystalline salt {*p*-*tert*-butylcalix[8]areneH$[V(O)]_2$} (**37**) $[M^1$ or $R^1NH_3]$ $[M^1 = $ Li, Na, K; $R^1 = (\pm)$-2-methyl-1-(1-napthyl)-propyl- or (R)-1-(1-napthyl)ethyl-)] [21].

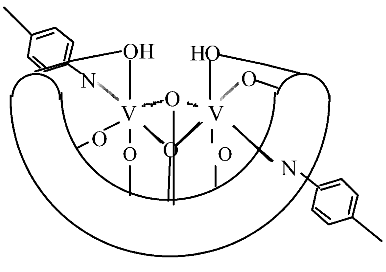
Two other vanadium containing calix[6 or 8]arenes have been characterised [24]. Reaction of the parent calix[8]areneH_8 with $[V(N$*p*-tolyl)$(OBu^t)_3]$ (tolyl = *p*-$CH_3C_6H_4$) yielded, via the loss of six *tert*-butanol molecules, the dimetallocalix[8]areneH_2 complex **38** in good yield (about 70%). The central core of this complex has a local confacial bioctahedral environment with asymmetric 'phenoxide' bridges about two vanadium centres. The V–V internuclear distance (3.334 Å) is clearly too long for any bonding interaction between the two vanadium centres. The calixarene conformation is similar to that observed for Na[(*p*-*tert*-butylcalix[8]arene){Ti(OPr^i)}$_2$] [21]. In the presence of either Me_2AlCl or methylaluminoxane (MAO), **38** polymerises ethylene at room temperature with activities up to 50 gmmol^{-1} h^{-1} bar^{-1}.

The reaction of *p*-*tert*-butylcalix[6]areneH_6 with $[V(NBu^t)(OBu^t)_3]$ led to the yellow/brown trimetallated complex **39** in poor yield. A central pseudo octahedral vanadium centre is linked via μ_2-oxo bridges to two tetrahedral vanadyl centres. Both the V=O groups and the near-linear imido group are all above the plane of the calix[6]arene ring and point approximately in the same direction. The oxo groups are involved in H-bonding to a $[Bu^tNH_3]$ cation. A thf or Bu^tOH molecule binds to the central vanadium in preference to the reaction solvent (MeCN). As one would expect, the ^{1}H-NMR spectrum is complex, however, six distinct CH_2 signals are evident. Strong stretches are observed in the infra-red (970 cm^{-1}) and are assignable to v(V=O).

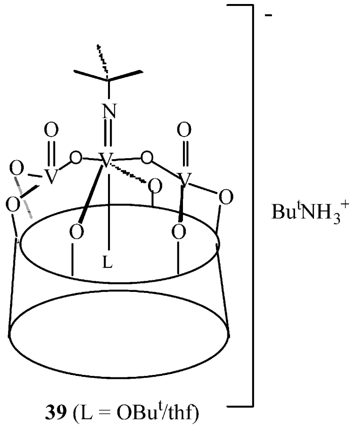
3.4. Niobium

Niobium calix[4]arene chemistry is relatively well developed [25]. For the larger ring systems though there are no reports in the literature. However, in our laboratory we have recently synthesised a number of derivatives of the *p*-*tert*-butylcalix[6 and 8]arenes [26].

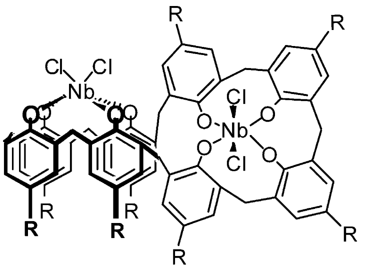
Interaction of the oxytrichloride complex $[NbOCl_3]$ (2 equivalents) with *p*-*tert*-butylcalix[8]areneH_8 in refluxing toluene afforded, after work-up, orange prisms of the tetrachloride complex $[(NbCl_2)_2$*p*-*tert*-butylcalix[8]arene$H_2]$ (**40**) in moderate yield (ca. 40%). Stoichiometrically **40** forms via the loss of one water molecule and one molecule of HCl per niobium centre. The calix[8]arene ring twists considerably to accommodate the two *cis*-Cl_2Nb fragments, the latter existing in local distorted octahedral environments. There is no incorporation of metal bound solvent presumably because each niobium has already attained the favoured octahedral geometry. This product is also readily available from the reaction of the pentachloride $NbCl_5$ with the parent calix[8]areneH_8.



38

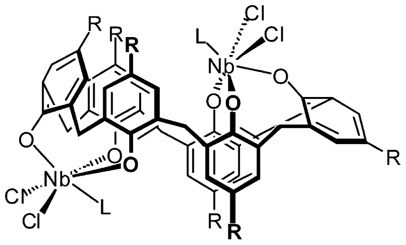


39 (L = OBu^t/thf)



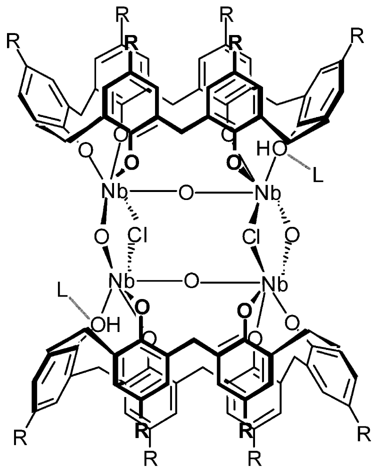
40 (R = Bu^t)

Excess $NbCl_5$ reacts with *p*-*tert*-butylcalix[6]arene to afford, after work-up, the orange acetonitrile solvate {$[NbCl_2(NCMe)]_2$*p*-*tert*-butylcalix[6]arene} (**41**) in moderate yields (55–60%). Two facially coordinated pseudo octahedral niobium centres bind, one above and one below, to the calix[6]arene ring. The coordination geometry about each niobium is completed by *cis*-chlorines and a solvent bound molecule. One of these acetonitrile molecules is located in one of two small cups, the latter being a consequence of the twist of the ring.



41 R = Bu^t, L = MeCN

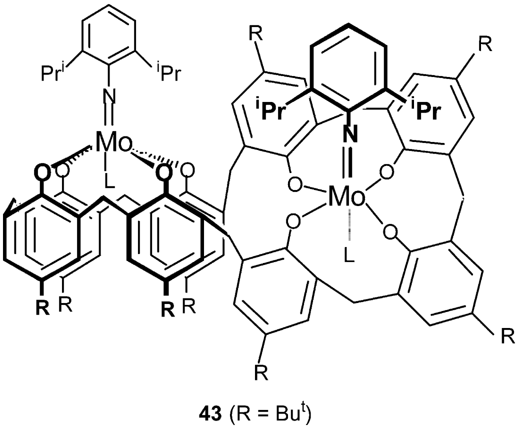
Applying the methodology outlined for **40**, but using *p*-*tert*-butylcalix[6]areneH_6 and 2 equivalents of $[NbOCl_3]$ affords yellow needles of **42** in about 30% yield. Overall **42** is the result of the loss of 10 molecules of HCl from 4 equivalents of $[NbOCl_3]$. The molecule is dimeric and consists of two *p*-*tert*-butylcalix[6]areneH ligands each coordinated by two pseudo octahedral niobium centres which share a linear Nb–O–Nb bond. The two halves of the molecule are linked by μ_2 oxo and chloro ligands. Each calix[6]arene ligand adopts a large cone conformation reminiscent of the situation found in the titanium complex **31**. The phenolic protons here are each involved in H-bonding to a solvent (MeCN) molecule.



42 R = Bu^t, L = MeCN

3.5. Molybdenum

The first molybdenum complex derived from a large calixarene, **43**, was readily prepared from the imido-alkoxide complex $[Mo(NAr)_2(OBu^t)_2]$ (Ar = 2,6-$^iPr_2C_6H_3$) via alkoxide and imide displacement reactions. Intermediate species were not observed [27].

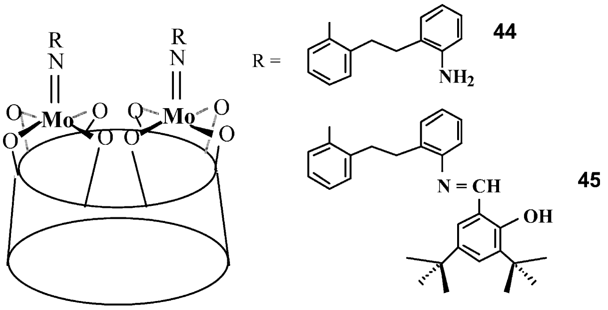


43 (R = Bu^t)

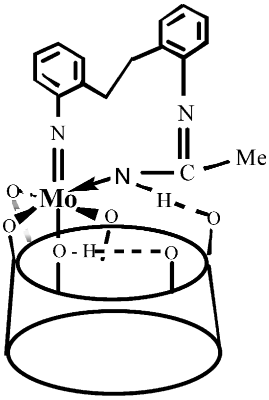
An X-ray crystal structure revealed how the calixarene ligand twisted to accommodate the two bulky near-linear organoimido groups. An acetonitrile molecule (solvent of crystallisation) occupied the position *trans* to each imido group.

This methodology was extended to include the related *ansa*-bis(imido) derivative $[Mo(OBu^t)_2\{[2,2'-(N)-C_6H_4]_2(CH_2CH_2)\}]$ [28]. For the latter, a ring-opening reaction occurred whereby as well as the loss of four *tert*-butanol molecules (per two Mo), two protons were transferred each to one of the nitrogens of a chelate ligand to release two pendant amino groups. The conformation of the calix[8]arene ring in **44** is such that each organoimido group is encapsulated by 3 calixarene-phenolate subunits—a double cup.

The pendant amino groups of **44** can be exploited for the synthesis of bulky imine-type complexes [29]. For example, reaction of **44** with 3,5-di-*tert*-butylsalicylaldehyde (2 equivalents) in refluxing ethanol readily affords, in ca. 70% yield, the bis(salicylaldimine) complex {[Mo(2-$NC_6H_4CH_2CH_2C_6H_4N$-2-CHC_6H_2-2′-(OH)-3″, 5″-Bu^t_2]$_2$(p-*tert*-butylcalix[8]arene)} (**45**). An X-ray study revealed how the ring twisted to adopt an edge-shared bioctahedron about the molybdenum centres. This 'pinched' conformation is similar to that observed for the complex Na{*p*-*tert*-butylcalix[8]arene[Ti(OPr^i)]$_2$} [21].



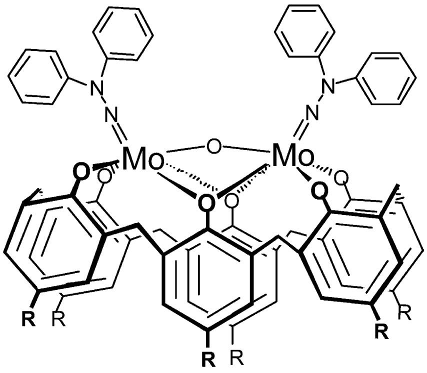
Applying the methodology outlined for **44** to *p*-*tert*-butylcalix[6]areneH$_6$ leads to a calix[6]arene supported 11-membered metallocyclic ring complex **46** formed on intramolecular insertion of the pendant amino group into a molybdenum–acetonitrile bond [30].



46

The amidine (imine) to Mo bond length [2.162(8) Å] is indicative of a dative bond, indicating a formal +VI oxidation state for the molybdenum centre. The calix[6]arene ring adopts a severely twisted 'hump-like' or partial cone (up–up–out) conformation, only previously seen for the palladium(II) chloride diphosphite complex **72**—see Section 4.5 [46].

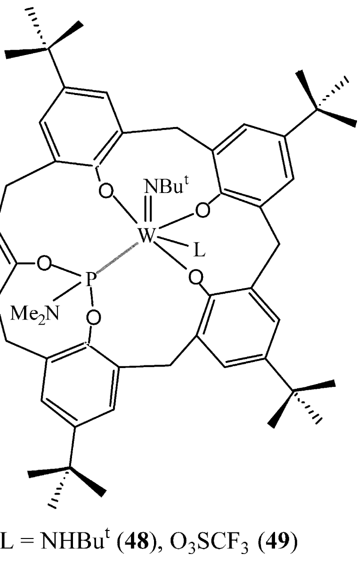
One other molybdenum complex derived from *p*-*tert*-butylcalix[6]areneH$_6$ has been reported [31]. Reaction of [Mo($NNPh_2$)(OBu^t)$_3$] and the parent calix[6]arene in toluene/thf affords in ca. 60% yield the brown hydrazido(2−) complex {[Mo($NNPh_2$)]$_2$(μ-O)*p*-*tert*-butylcalix[6]arene] (**47**). The ligand adopts a unique conformation in which two opposite bridging phenolic rings support a distorted confacial bioctahedral structure; the third bridging oxygen atom is believed to arise by abstraction from the ether solvent.



47 R = Bu^t

3.6. Tungsten

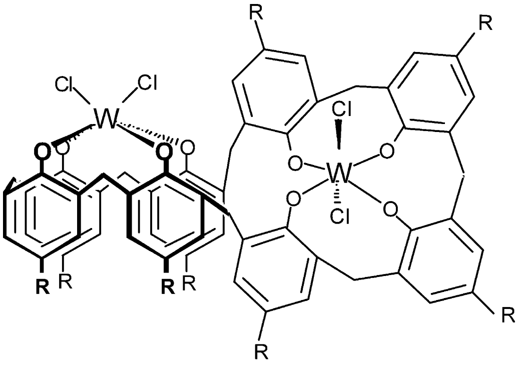
Lattman has demonstrated the ability of the calix[5]arene ligand to accommodate both a main group ligand, here Me_2NP, as well as a functionalised transition metal, [W(NBu^t)L] (L = $NHBu^t$ **48**, SO_3CF_3 **49**) [32]. The metal containing complexes are generated from a ligand synthesised from the reaction of the parent calix[5]arene and tris(dimethylamino)phosphine—see Section 5.5 Phosphorus. This ligand then readily reacts with [W(NBu^t)$_2$($NHBu^t$)$_2$], via loss of two molecules of *tert*-butylamine, to afford yellow **48** in ca. 80% yield. For **48**, the ^{31}P-NMR spectrum contains a signal at δ 116, which shows only a small $^1J_{PW}$ coupling (43 Hz). Similarly, the crystal structure reveals a long W–P 'bond' distance (3.15 Å). The calix[5]arene ligand exhibits a flattened conformation.



L = $NHBu^t$ (**48**), O_3SCF_3 (**49**)

Treatment of **48** with trifluoromethanesulfonic (triflic) acid, CF_3SO_3H in refluxing toluene (3 days) swaps the amide group on tungsten for a triflate group yielding a red complex **49** in about 60% yield. This complex is air and moisture stable. Interestingly, this change in the electronics at the metal centre has a dramatic effect on the W–P bond strength as indicated by both the size of $^1J_{PW}$ (352 Hz) and the W–P bond length (2.74 Å). The calix[5]arene ligand of **49** adopts more of a cone conformation.

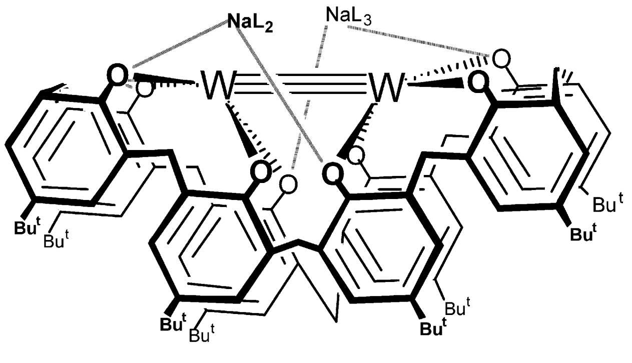
The reaction of *p*-*tert*-butylcalix[8]areneH$_8$ with WCl_6 (1.98 equivalents) in toluene readily gives multigramme quantities of $\{[WCl_2]_2$*p*-*tert*-butylcalix[8]arene$\}$ (**50**) [33]. NMR data were complex and suggestive of the presence of *cis* and *trans* isomers. Successive extractions and recrystallisations from acetonitrile eventually yielding a sample of the pure *cis*,*trans*-$\{[WCl_2]_2$*p*-*tert*-butylcalix[8]arene$\}$. The conformational twist of the ring resembles that of the molybdenum imido complex **43**, i.e. each WCl_2 fragment is encapsulated by three phenolate sub-units.



50 (R = Bu^t)

The sensitivity of the system was also problematic as indicated by the isolation of oxo species of the form $\{[WO][WCl_2]$*p*-*tert*-butylcalix[8]arene$\}$ (**51**).

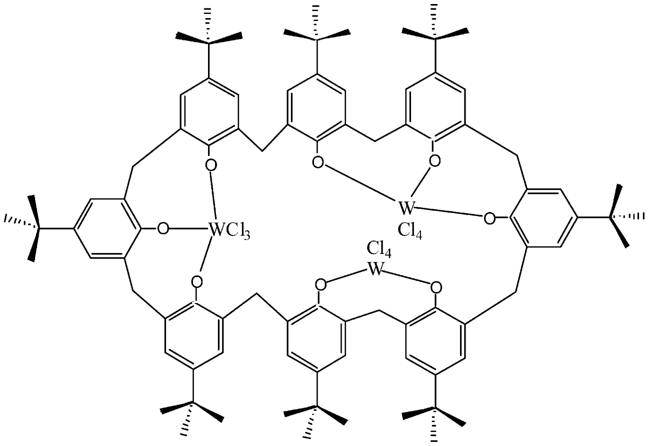
Reduction of **50** with sodium amalgam in toluene yields the first example of a metal–metal triple bond supported by a large calixarene ligand. The conformation of the latter adopted in the complex **52** is best described as two back-to-back cups, each comprising three phenoxide sub-units. The four phenoxide oxygens bound to each tungsten are somewhat staggered, resulting in a cleft.



52

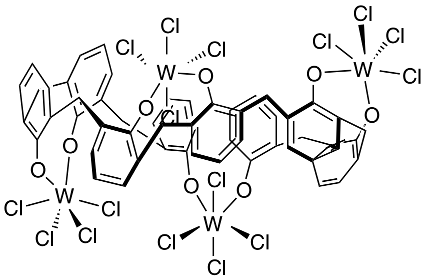
The geometry at both of the five-coordinate tungsten centres can best be described as square-based pyramidal with the triple bond at the apex. Bridging sodium atoms and associated solvent molecules (MeCN) create a system reminiscent of that observed for the sodium/pyridine moieties of the calix[4]arene derivative reported by Floriani and co-workers [34]. The tungsten–tungsten distance is 3.13(1) Å in the latter calix[4]arene complex and this compares favourably with that in found **52** [2.2976(6) Å].

The use of excess of WCl_6 (3 equivalents) in this system results in the isolation of two highly metallated species. A dark purple trimetallated complex **53** is formed in ca. 55% yield on recrystallisation from acetonitrile and contains two facially coordinated tungsten centres, whilst the third tungsten centre has a *cis*-O_2Cl_4 geometry. As expected, the calix[8]arene ring has to twist considerably to accommodate the three large tungsten centres; there are local ‘3 phenolate’ cups at both WCl_3 moieties.



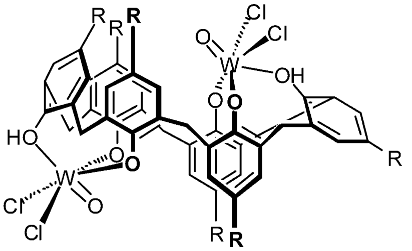
53 L=MeCN

A blue tetrametallated complex **54** is formed in somewhat lower yields (about 15%) on extraction with 1,2-dichloroethane. Here, each of the four WCl_4O_2 units is bound to the calix[8]arene framework via *cis*-oxygens, two above and two below the plane of the ring.



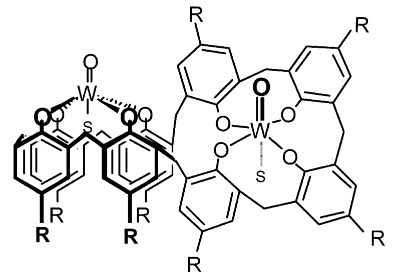
54 (Bu^t groups removed for clarity)

For the smaller calix[*n*]arenes (*n* = 3 and 4), metal oxo species have attracted interest due to their tendency to self-assemble into columnar structures and when multiple dodecyloxy groups are present liquid crystalline phases form [35]. To-date, for the larger ring systems investigations are scant and only discrete molecules have been derived from the *p*-*tert*-butylcalix[6 and 8]areneH$_{6,8}$ ligands [21]. Reaction of 2 equivalents of $WOCl_4$ with *p*-*tert*-butylcalix[6]areneH$_6$ in toluene affords, via the loss of two molecules of HCl per tungsten, the purple/red complex **55**. The ligand remains doubly protonated and adopts a pinched conformation to accommodate the two facially coordinated metal centres. The geometry about each tungsten centre is best described as pseudo octahedral with the oxo ligand lying *trans* to an elongated W–O bond [2.332(8) Å]. In the IR, there is a strong band at 941 cm^{-1} assigned to the v(W=O) grouping [36].



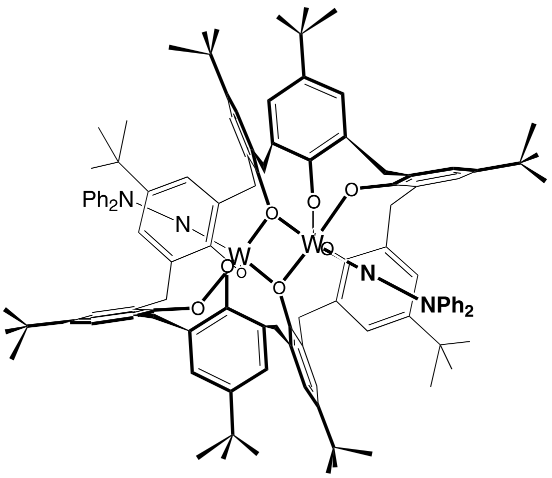
55

A similar procedure using *p*-*tert*-butylcalix[8]areneH$_8$ and 2 equivalents of $WOCl_4$ gave the expected bis(oxo) product **56**, formed via loss of four molecules of HCl per tungsten. The ring here in **56** twists to accommodate the two [W=O] fragments in a manner similar to that observed for the organoimido complex **43**. A molecule of the solvent (MeCN) binds to each tungsten centre *trans* to the oxo function and each is encapsulated by three calixarene sub-units. The IR has a strong band at v 969 cm^{-1} assigned to the W=O moiety. The W=O bond lengths in both **55** and **56** average about 1.70 Å which is typical of those observed in other tungsten(VI) oxo complexes [37].



56 R = Bu^t, S = MeCN

One other tungsten complex of *p*-*tert*-butylcalix[8]areneH$_8$ is known—treatment of the ligand with the hydrazido-tetraalkoxide [W(NNPh$_2$)(OBu^t)$_4$] (2 equivalents) results in elimination of eight molecules of Bu^{t}OH and formation of orange/red **57** in about 50% yield [31]. Again the presence of the bulky metal bound substituents forces the calix[8]arene ring to twist substantially with each hydrazido fragment being capped by three linked phenoxide groups. The tungsten centres are displaced by an average 0.253 Å out of the plane of the calixarene oxygens towards N$_\alpha$ of each hydrazido(2−) ligand. There is no metal bound solvent.

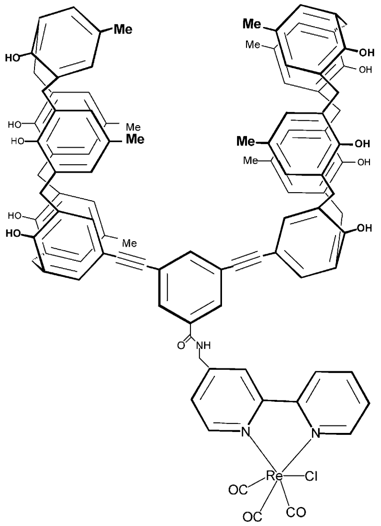


57

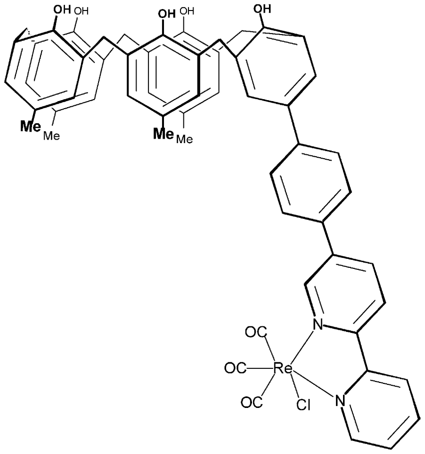
3.7. Rhenium

Fukazawa and co-workers have recently reported Fullerene sensors based on calix[5]arene rhenium carbonyl complexes of the form **58** and **59** [38]. The double calix[5]arene **58** is prepared from an iodocalix[5]arene precursor using Palladium-catalysed Sonogashira methodology, whilst **59** is formed from a bromopyridine under Suzuki conditions. Both species exhibit luminescence, which is quenched by the addition of either C_{60} or C_{70}.

van Leeuwen et al. have isolated the octahedral rhenium carbonyl complex [Re(CO)$_3$Cl(*syn*-**112**)] **60** (for ligand system see Section 5.5), in which the two



58



59

phosphorus atoms of the calix[6]arene diphosphite are *trans* to the chloride (^{31}P-NMR—one signal). The *facial* arrangement for the CO ligands is confirmed by IR spectroscopy [30].

4. Late transition metals

4.1. Iron

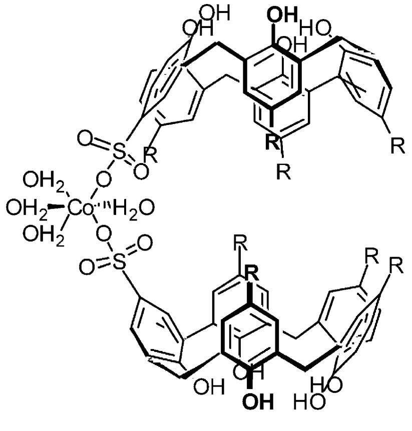
A violet, water-soluble complex of iron(III) is formed on interaction of a solution generated from iron(III) perchlorate with calix[6]arene-*p*-sulfonic acid [$H_{12}CS$] over the pH range 2.5–5.5 [40]. Studies of the acid–base properties of such ligands have found that at $pH < 11$ only two of the hydroxyl protons are readily disociated, whilst the six sulfonic groups possess high acidity. In the present reaction, potentiometric and spectrophotometric studies are suggestive of the formula $\{[Fe(OH)_2]_2H_6CS\}^{2-}$ (**61**).

4.2. Ruthenium

Inoue and co-workers have utilised a calix[6]arene ligand functionalised at the lower-rim with bipyridyl containing arms to form the tetrakis(ruthenium)tris(bipyridine) calix[6]arene **62** in good diastereomeric purity (racemic **62** has also been prepared) [41].

4.3. Cobalt and nickel

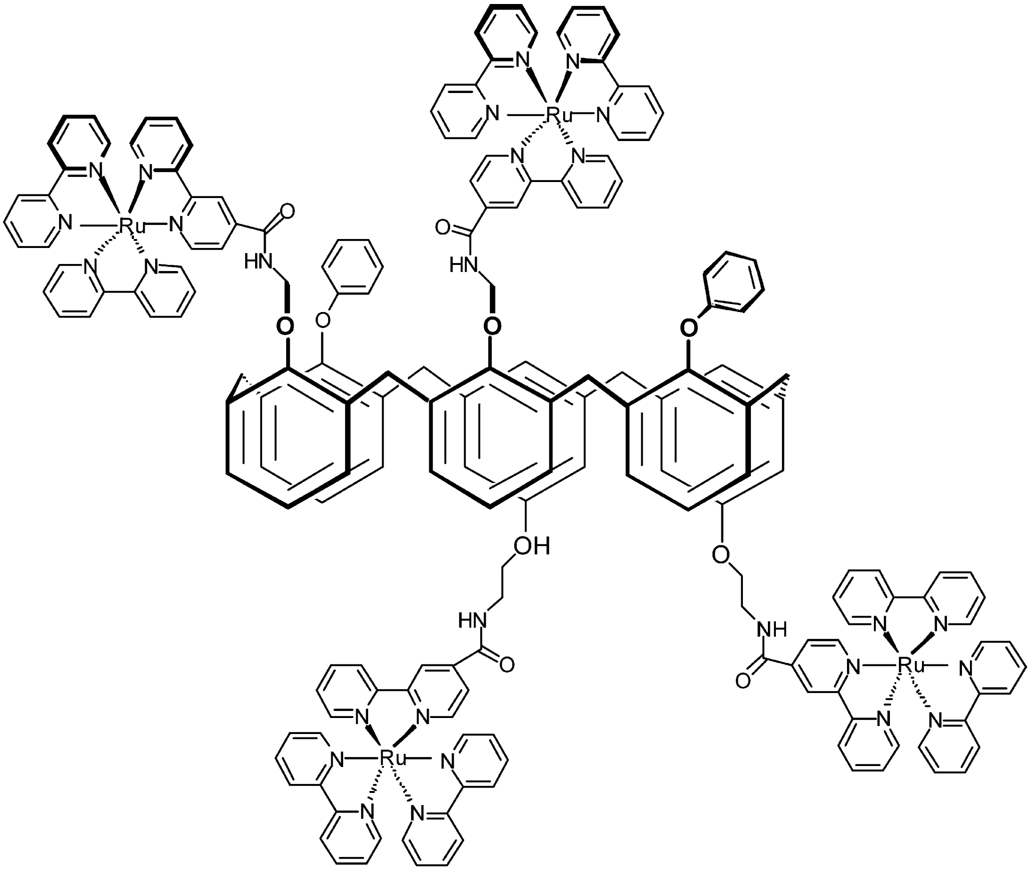
Reaction of pentasodium *p*-sulfonatocalix[5]arene (**17**) with [$Co(NO_3)_2 \cdot 6H_2O$] in the presence of *N*,*N*-dimethylacetamide in water yielded the pink bis(calix[5]arene) complex **63** in 40% yield [10]. The bridging of the two calixarenes by the $Co(H_2O)_4^{2+}$ fragment, which resides on a crystallographic mirror plane, results in what is best described as a 'super-cavity'. An amide ligand is loosely held (as evidenced by NMR: δ ~free ligand) in each calixarene cavity and is involved in bridging to two Na^+ ions. Overall the structure consists of alternating hydrophilic and hydrophobic layers and is similar to that observed for **17**.



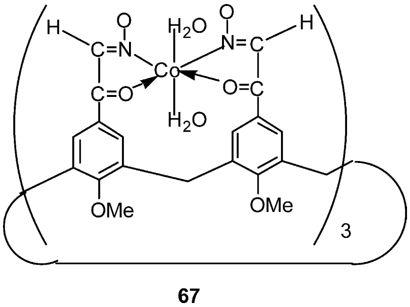
63 R = SO_3

The related nickel complex $\{Na_8[Ni(H_2O)_4(p\text{-sulfonatocalix[5]arene})_2] \cdot 2\text{pyridine} \cdot 38H_2O\}$ (**64**) is formed on interaction of [$Ni(NO_3)_2 \cdot 6H_2O$] with pentasodium *p*-sulfonatocalix[5]arene in a similar fashion to **63**. On the basis of NMR spectroscopy and a unit cell determination it is proposed the structure of **64** closely resembles that of **63**. Chemical shift values also suggest the pyridine molecules here are more deeply embedded in the calix[6]arene cavities than are the amides in **63**. 1,10-Phenanthroline bridged (A,D) calix[6]arene derivatives of cobalt(II) **65** and nickel(II) **66** (2:1 complexes) have also been reported (for ligand see Section 4.5) [42].

An octahedral green cobalt complex **67** is formed on reaction of a keto-oxime calix[6]arene with $CoCl_2 \cdot 2H_2O$ in excellent yield (95%) [43].



62

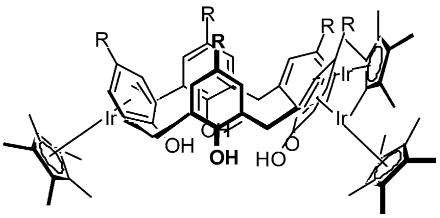


67

The related *vic*-dioxime ligands reacts in a similar manner with $CuCl_2 \cdot 2H_2O$, $NiCl_2 \cdot 6H_2O$ or $CoCl_2 \cdot 6H_2O$ forming square-planar [Cu **68** and Ni **69**] and octahedral [Co] **70** species, respectively [43].

4.4. Iridium

Atwood and co-workers reported anion inclusion for a π-metalated *p*-*tert*-butylcalix[5]arene complex of iridium [44]. Treatment of excess $[\{Ir(Cp^*)Cl(\mu\text{-}Cl)\}_2]$ with $AgBF_4$ in acetone and subsequent reaction with *p*-*tert*-butylcalix[5]areneH$_5$ yielded (71%) the triiridium π-metalated complex $[\{IrCp^*\}_3$(*p*-*tert*-butylcalix[5]areneH)]$[BF_4]_5 \cdot 0.5CH_3NO_2 \cdot \sim 2Et_2O$ (**71**). In **71**, two adjacent arene rings and the distil ring are bound to Cp*Ir moieties. The crystal structure reveals the deep inclusion of one of the BF_4 anions within the bowl-shaped cavity formed by the calix[5]areneH ring, the anion lying close to the two adjacent metalated rings. The disorder associated with this anion is thought to be due to the increased size of the cavity compared to that found in the related calix[4]arene complex [{Ru(*p*-cymene)}$_4$calix[4]areneH$_2$]$[BF_4]_6$ [45].



71

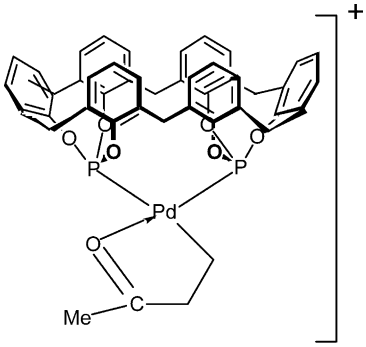
4.5. Palladium and platinum

The calixarene diphosphite *syn*-**127** (see Section 5.6) reacts in either CH_2Cl_2 or thf with MCl_2(COD) (COD = cyclooctadiene) to afford [(*syn*-**127**)MCl_2] M = Pd **72**, Pt **73** [39,46]. The ^{31}P-NMR of **73** shows only one signal (δ 49.7 ppm) with a large $^{1}J_{Pt-P}$ (5800 Hz) indicative of a *cis* complex. The bite angle for **72** was established by X-ray diffraction to be about 90°. Similar reaction of *syn*-**127** with (COD)M(Me)Cl affords [(*syn*-**127**)M(Me)Cl] M = Pd **74**, Pt **75**. Both these species display an AB pattern in their ^{31}P-NMR spectra due to the non-equivalence of the phosphorus atoms.

Reaction of *syn*-**127** (2 equivalents) with $Pd(dba)_2$ (dba = dibenzylideneacetone) affords a yellow solution from which Pd(*syn*-**127**)$_2$ can be isolated in 68% yield.

Complex **74** can be converted to the unstable acetyl complex [(*syn*-**127**)PdC(O)MeCl] (**76**) by treatment with CO for several minutes in CH_2Cl_2. The complex can be spectroscopically characterised, but not isolated.

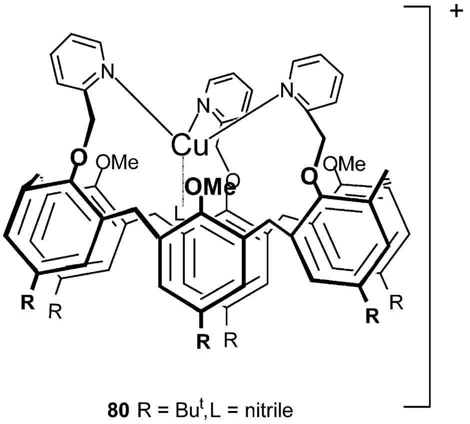
However, reaction of **74** with silver triflate, AgOTf in CH_2Cl_2/MeCN yielded the cationic species [(*syn*-**127**)Pd(Me)(MeCN)](OTf) (**77**). NMR data suggests the acetonitrile is *cis* to the methyl ligand. This cationic derivative shows good activity for the copolymerisation of carbon monoxide and ethene. Treatment of **77** with CO led to the acetyl complex [(*syn*-**127**)PdC(O)Me(MeCN)](OTf) (**78**). Further reaction of **78** with ethene yielded the stable five-membered ring species **79**.



79

4.6. Copper

Methoxy calix[6]arene ligands functionalised at the lower-rim with pyridyl-containing arms (an N_3 donor set) have been successfully employed by Reinaud and co-workers for the synthesis of copper(I) complexes [47]. Such species mimic the type II site of monocopper proteins. The first such complex was synthesised on an NMR scale from the addition of 1.1 equivalents of $[Cu(MeCN)_4]PF_6$ to *p*-*tert*-butylcalix[6]arene(OMe)$_3$(pic)$_3$ (pic = picolyl) affording the mononuclear complex **80**. This preparation initially involved acetonitrile as L, but this can be readily exchanged for other non-bulky nitriles. Indeed, crystals suitable for an X-ray study were obtained for the propionitrile derivative. Here, the copper(I) centre is tetrahedral with near C_{3v} symmetry. The copper-bound nitrile ligand resides well inside the calix[6]arene cone, the latter having dimensions at each end of 7.91 and 11.28 Å. The helical shape adopted by the three pyridine groups results in chirality at copper. Interestingly, the complex



80 R = Bu^t,L = nitrile

remains unaffected by oxygen.

When the same ligand, calix[6]pic$_3$, is reacted with CuCl, the complex [Cu(calix[6]pic$_3$)Cl] (**81**) is formed in excellent yields (~ 90%). The chloride ligand is now embedded in the calix[6]arene cavity. As for **80**, this complex exhibits C_3 symmetry, chirality (at low temperature), and is resistant to oxygen [48].

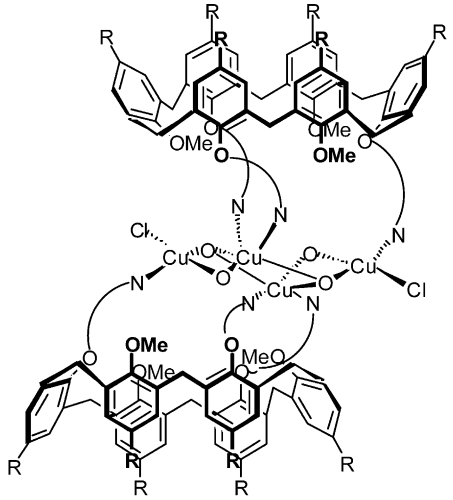
The family of ligands was extended to include a number of tris(imidazole) derivatives bearing methyl or ethyl substituents on both the imidazole ring and oxygens on the lower-rim of the calix[6]arene. On reaction with $[Cu(MeCN)_4]PF_6$, the expected complexes [Cu(S)*p*-*tert*-butylcalix[6]arene(OR)$_3$(imidazoleR^1)$_3$] [R = R^1 = Me (**82**); R = Me, R^1 = Et (**83**); R = Et, R^1 = Me (**84**); R = R^1 = Et (**85**); S = solvent] were produced, which possessed rather broad and uninformative NMR spectra. However, on treatment with CO, the spectra sharpened up considerably consistent with the formation of the cuprous species [Cu(CO)*p*-*tert*-butylcalix[6]arene(OR)$_3$(imidazoleR^1)$_3$] [R = R^1 = Me (**86**);

$R = Me$, $R^1 = Et$ (**87**); $R = Et$, $R^1 = Me$ (**88**); $R = R^1 = Et$ (**89**)]. The conformation adopted by the calixarene in such complexes was highly dependant on the particular alkyloxyether substituent present on the lower-rim of the calix[6]arene. For example, the ethyloxyether derivative maintained C_3 symmetry on cooling as evidenced by its ^{1}H-NMR (such a symmetry is unaffected by the interconversion of the two enantiomeric helices); the conformation is such that the *tert*-butyl groups point alternately in and out of the cavity of the flattened cone. By contrast, for the methoxyether the whole NMR spectrum was seen to broaden on cooling and at −70 °C it was concluded from exchange experiments that the complex exhibited only pseudo C_3 symmetry resulting from fast internal *tert*-butyl exchange. In other words, the symmetry is broken by the partial inclusion of one *tert*-butyl group and the system fluctuates between three equivalent conformations [49].

These ligands can be made water soluble by the attachment of hydrophilic sulfonate groups bound to the upper-rim of the calix[6]arene. This work has led to the water soluble (and air stable) copper complex **90** and its carbon monoxide adduct **91** (neither shown here). Both contain a calix[6]arene ligand which adopts a cone conformation with a well-defined hydrophobic cavity [50].

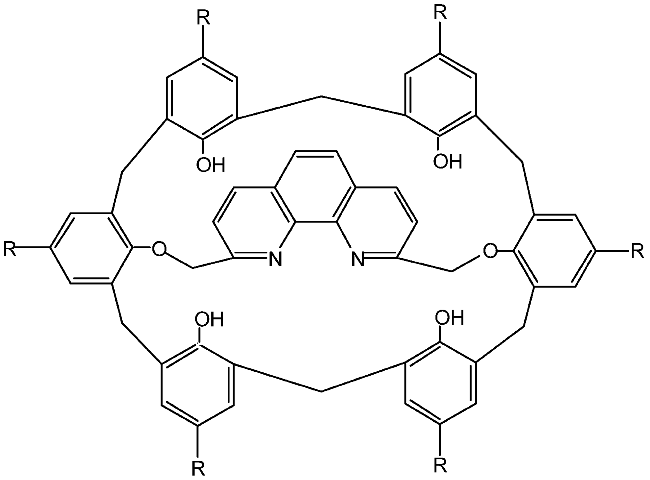
For the ligand $R = R^1 = Me$, a number of copper(II) complexes have also been isolated [51]. Reaction with either copper(II) perchlorate or triflate yields mononuclear dicationic species of the form $[Cu(H_2O)_2calix[6]imidazole]^{2+}$ [$L = ClO_4$ (**92**), O_3SCF_3 (**93**)], which each contain a square-based pyramidal copper(II) centre as evidenced by EPR data. The water molecule contained within the calix[6]arene cavity is readily displaced by non-bulky nitriles. A crystal structure of $[Cu(H_2O)_2calix[6]imidazole(NCMe)]^{2-}$ revealed a distorted tetragonal copper center bound via the imidazole groups to a calix[6]arene with ca. C_3 symmetry. One of the imidazole groups (that occupying the apical site of the square-based pyramid) is somewhat more loosely held that the remaining two [$Cu{-}N = 2.189(3)$ c.f. 2.008(3) and 2.030(3) Å].

A blue tetranuclear complex **94** is formed in good yield (> 60%) on reaction of **81** with one equivalent of $[Cu(MeCN)_4]PF_6$ under a dioxygen atmosphere in tetrahydrofuran [52]. A crystal structure determination revealed a stepped-cubane core $[Cu_2(OH)_2]$, sandwiched between two imidazolyl-containing calix[6]arene ligands ($R = R^1 = Me$). The latter adopt cone conformations and have an imidazole arm folded into their cavity. Magnetic susceptibility measurements are consistent with strong antiferromagnetic coupling in each of the $Cu(OH)_2Cu$ fragments. The resemblence of this dicopper core to type 3 copper proteins, catachol oxidase, sparked investigations into the oxidation catalysis of 3,5-di*tert*-butylcatechol. It was found that **91** readily dehydrogenated the catechol, but was slow to regenerate via O_2 autooxidation. Electrochemical studies showed that **94** could be reversibly oxidised to mixed valence species $Cu^{II}_3Cu^{III}$ and $Cu^{II}_2Cu^{III}_2$.



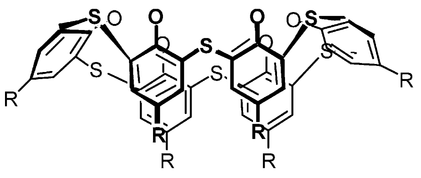
94 R = Bu^t

Calix[6]arenes bridged by 1,10-phananthroline in an A,D fashion (see **95**), which are readily available from the parent calix[6]arene and bis(bromomethyl)-1,10-phenanthroline in the presence of ^{t}BuOK, have been used by Lüning and co-workers to prepare 2.1 complexes of Cu^{2+}, Co^{2+} and Ni^{2+} and with Cu^+ a 1:1 complex. Such species have been used in the copper(I) catalysed cyclopropanation of alkenes (both cyclic and acyclic) with diazoacetates; an unusual *syn* selective cyclopropanation was observed [42].

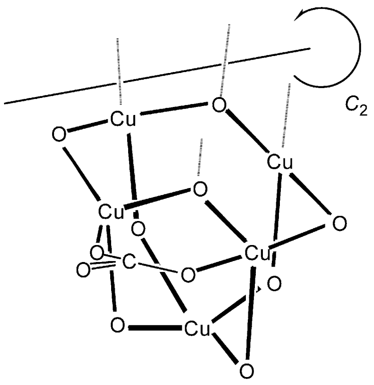


95

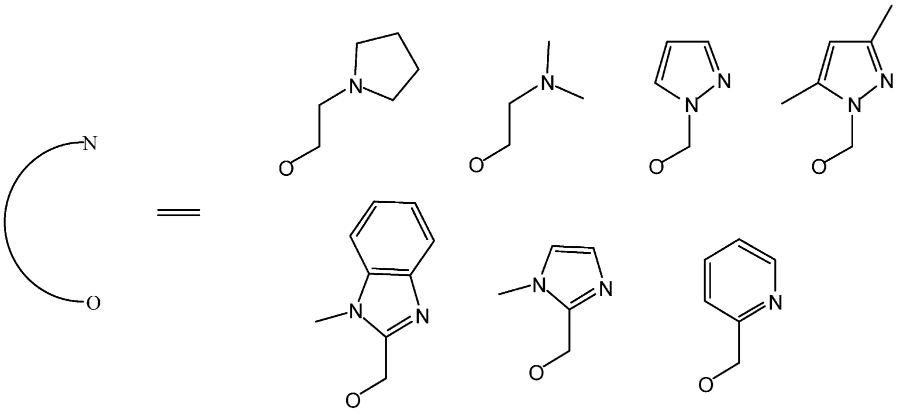
Interestingly, a ferromagnetic decacopper(II) cluster supported by two *p*-*tert*-butylthiacalix[6]arene ligands is available on reaction of the parent thiacalix[6]areneH_6 (H_6L) with $Cu(OAc)_2$ [53]. This red complex $[Cu_{10}L_2(\mu_3\text{-}O)_2(\mu_3\text{-}OH)(\mu\text{-}AcO)]\cdot 8dmf\cdot 6H_2O$ (**96**) is best viewed as



The hexaanionic thiacalix[6]arene of **96** (R = Bu^t)



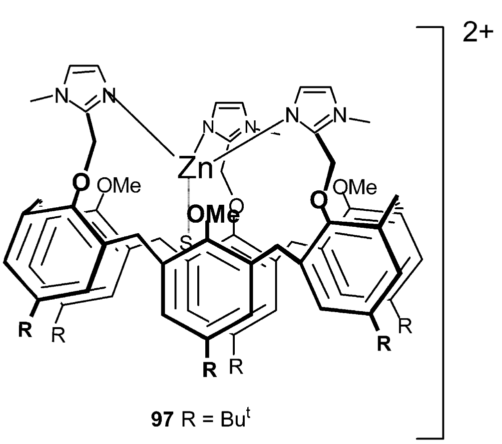
One of the two pentacopper(II) units of **96**



consisting of two pentacopper(II) clusters (see above), each of which resides in a large channel formed by the pinched-cone conformation of each thiacalix[6]arene ligand. Four of the phenoxy oxygens are aligned in a square-planar arrangement, at the center of which resides a copper(II) ion. Above this are four other copper centers forming part of a square with hydroxy, oxo, acetate and the two remaining phenoxy oxygen atoms.

4.7. Zinc

Ligands similar to those used in Section 4.4 where utilised to mimic the active site of zinc enzymes by providing a tris(imidazole) environment with a cone cavity. Thus reaction of $[Zn(ClO_4)_2(H_2O)_6]$ with *p-tert*-butylcalix[6]arene$(OMe)_3(Imme)_3$ (Imme = 2-methylene-1-methyl-1*H*-imidazole) yields **97**. The water molecule resides within a hydrophobic pocket and is readily exchanged for other neutral molecules such as amines, amides and nitriles [54].



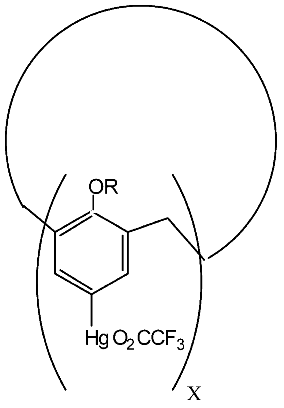
97 R = Bu^t

S = acetonitrile, ethanol, propionitrile, n-propanol, isopropanol, dimethylsulfoxide, acetic acid, 1-aminoheptane, acetamide, propionaldehyde, 2-methylbutylamine, *N*,*N*-dimethylformamide, *N*-methylacetamide.

Crystal structure analyses reveal that H-bonding and CH/π interactions (between guest and calix[6]arene ligand) play a key role in stabilization. The ligand class was readily extended to include ligands derived from a number of tertiary amines, pyrazoles and benzimidazole groups—shown below [55].

4.8. Mercury

Treatment of O-alkylated calix[5, 6 or 7]arenes with mercury trifluoroacetate afforded the respective mercurated (at the *para* position) calix[5, 6 or 7]arenes **98** in quantitative yield.



98

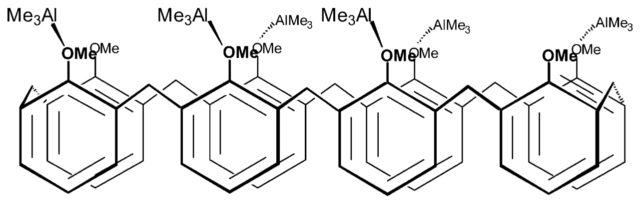
R = Et, ^{n}Bu, n-C_8H_{17}, n-$C_{16}H_{12}$
X = 5, 6, 7

These species behave as surfactants forming monolayers at the air–water interface. The cohesiveness is substantially increased by the addition of malonic acid [56].

5. Main group elements

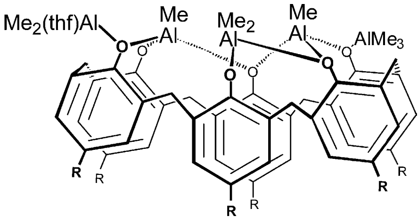
5.1. Aluminium

Atwood and co-workers reacted the methyl-ethers of calix[8]arene and *p-tert*-butylcalix[8]arene with trimethylaluminium (8 equivalents) obtaining in each case colourless crystals of the hexaaluminium species **99** and **100**, respectively [57]. The absence of bulky *tert*-butyl groups in **99** allows all six Me_3Al groups to point outward away from the centre of the calixarene ring; in **100** (not shown) two of these Me_3Al groups are more inwardly directed. The crystal packing of each complex highlights differences in their inclusion behaviour. For **99**, the solvent molecules (two toluenes per unit cell) lie between sheets of calixarene molecules to form an intercalated system. For **100**, there are four benzene molecules per unit cell and these fit rather nicely into tunnels formed by groups of four calixarene molecules.



99

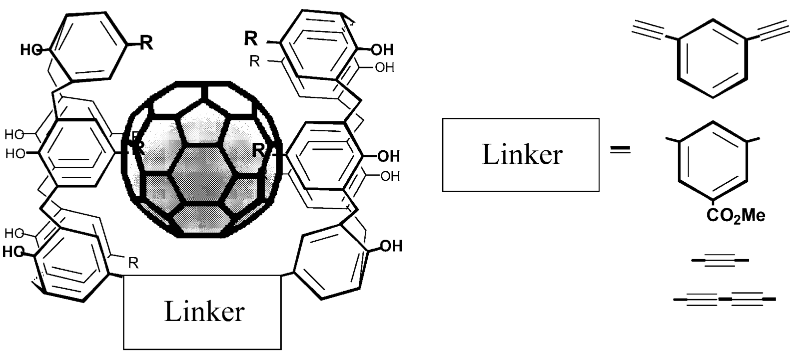
About 10 years later, Bott and Smith reacted *p-tert*-butylcalix[6]areneH$_6$ with 4 equivalents of trimethylaluminium isolating on work-up, the colourless pentaaluminium complex **101** [58]. The calixarene ring here adopts a conformation such that all six oxygen atoms are almost coplanar (maximum deviation from the plane is 0.2 Å) and a channel is formed. There is a Me_2Al group residing within this channel and one result of this is that one of the methyl groups is in close proximity to a couple of aromatic rings as evidenced by an upfield shift in the proton NMR (δ −2.10). Other organoaluminium moieties present include $Me_2Al(thf)$, Me_3Al, MeAl as well as a fully demethylated aluminium center. The ^{27}Al-NMR, however, only exhibits a single broad resonance at δ 135–150.



101 R = Bu^t

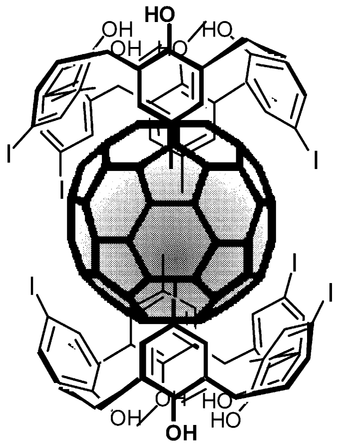
5.2. Carbon

About 10 years ago, Verhoeven and Williams showed that calix[8]arenes bearing sulfonate groups at the lower-rim were powerful tools for the extraction of C_{60} from toluene into water [59]. A couple of years later, the groups of Atwood and Shinkai noted that C_{60} could be selectively complexed by *p-tert*-butylcalix[8]areneH$_8$ in 99.8 wt.% purity from carbon soot [60]. This 1:1 complex **102** was thought to consist of a trimeric aggregate of C_{60} encapsulated by three calix[8]arenes, each with a double-cone conformation. Unfortunately, spectroscopic characterisation of this trimeric aggregate was hampered by a breakdown of the structure in solution. The C_{60} was readily released by the addition of chloroform. Similar results were observed by Verhoeven and co-workers in carbon disulfide [61]. This group also investigated the solid-state ^{13}C-NMR, observing an upfield shift of 1.4 ppm with concommitent line sharpening upon addition of fullerene. The structure can also accommodate one C_{70} by isomorphous replacement of a C_{60} [62]. Further studies on the selectivities of



104 R = Me

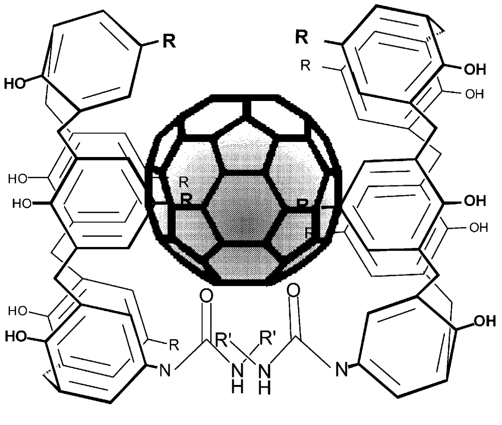
a series of para-substituted calix[8]arenes (where the para group = H, Me, Et, Pr^n, Bu^n, Bu^s, Bu^t, amyl, Oct, Ph) towards C_{60} and C_{70} suggested that the *tert*-butyl group was the para group of choice for such inclusion chemistry [63]. The retention behaviour of calix[6 and 8]arenes with various C_{60} bonded silica phases in microcolumn liquid chromatography has been investigated. The bowl shaped cavity of *p*-*tert*-butylcalix[8]areneH$_8$ was seen to be beneficial for retention [64].



103

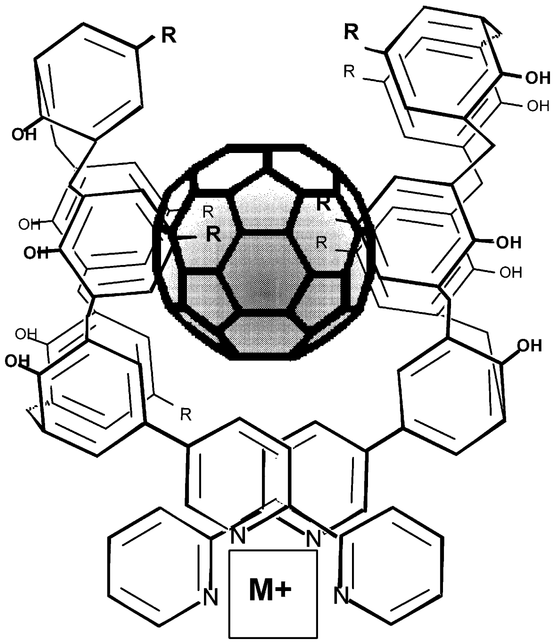
Both C_{60} and C_{70} form isostructural 2:1 complexes with calix[6]arene as shown by X-ray diffraction studies. The fullerenes reside in cavities of the double-cone conformation of the calix[6]arene. [65] Fukazawa and co-workers examined the inclusion of C_{60} in toluene, benzene, o-dichlorobenzene and CS_2 by *p*-Xcalix[5]areneH$_5$ (X = Me, H, I) **103** [66]. The initial purple solution rapidly turned yellow on addition of the calix[5]arene; the largest association constant observed (as determined by the Benesi–Hildebrand method) was $2.1 \pm 0.1 \times 10^3$ dm^3 mol^{-1}. The latter was dependant upon the solubility of the fullerene in the solvent such that the more weakly it was solvated the more tightly it was bound. An X-ray diffraction study of a sample of the iodocalix[5]arene with an equimolar amount of guest was obtained by slow diffusion of a CS_2 solution. Surprisingly, in contrast to the solution studies observed above, the structure revealed that the C_{60} was encapsulated within a pocket formed by two calix[5]arenes, i.e. a 2:1 complex. Strong binding of the guest was inferred from the numerous (144) short (< 4.0 Å) contacts between the carbons of the fullerene and those of the calix[5]arene. This result prompted the Fukazawa group to rationally synthesise '2:1' complexes by utilising a bridged calix[5]arene system **104** (c.f. rhenium section). The well-defined cavity size led to huge association constants for both C_{60} and C_{70} [67]. Thermodynamic studies indicated that such complex formation in chloroform is associated with a negative entropy change, whilst in toluene there is tight solvation of the guest (i.e. a positive entropy change) [68].

Because the guest molecule is now strongly held, it proved difficult to separate out guest from host. A related system which was capable of both binding and releasing the fullerene was based on the calix[5]arene urea derivative **105**. Here, the fullerene could be readily released on addition of a protic acid [69].



105 R = Me, R' =$(CH_2)_6CH_3$

More recent advances have made use of metal assisted self-assembly. Two bipyridyl-containing calix[5]arenes can be fixed in position by complexation with a silver cation, such that a tetrahedral bis(bipyridyl) silver complex **106** is formed. Complex formation with fullerene (C_{60} or C_{70}) was verified by electrospray mass spectrometry [70]. Similar metal-induced fullerene complexation is possible in the presence of tetrahedral Cu^+ complexation [71].



106 R = Me

5.3. Silicon

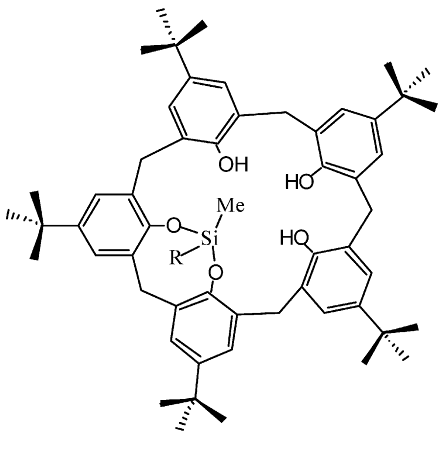
The mono and di-substituted silyl calix[5]arenes **107** and **108** are readily available in good yields (>70%) from the reaction of the parent *p-tert*-butylcalix[5]areneH$_5$ and RMeSi(NMe$_2$)$_2$ (R = Me, Ph). The synthesis of **107** requires the use of excess *p-tert*-butylcalix[5]areneH$_5$ (optimsed conditions are silane/calixarene 0.35:1), whilst **108** is prepared stoichiometrically. Solid-state structures of the products approximate to the four idealised conformations of calix[5]arenes, viz. cone, partial cone, 1,2- and 1,3-alternate [72].

5.4. Tin

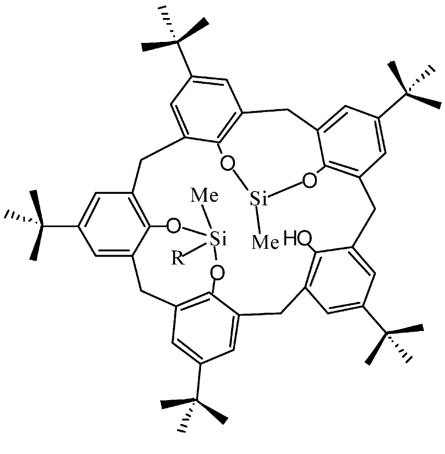
Prepared by Pedersen using either Sn(OPr^i)$_4$/^{i}PrOH or Sn(OPr^i)$_3$(^{n}Bu) yielding {[*p-tert*-butylcalix[8]arene(SnY)$_2$]K} [Y = OPr^i (**109**), ^{n}Bu (**110**)], in which the calix[8]arene ligand adopts a 'propeller-like' conformation [21].

5.5. Nitrogen

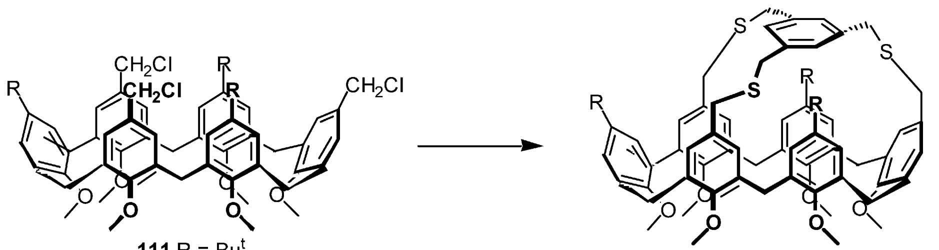
The larger calixarenes can act as receptors for quaternary ammonium cations. In order that this can take place it is necessary to 'freeze-out' the cone conformation. From their observations, Shinkai et al. reasoned that the calix[6]arene would provide the most favourable cone conformation for π/cation interactions [73]. The flexibility of calix[6]arenes can be greatly reduced by either functionalisation at the upper or lower-rim. Here, we shall consider one example of each. Use of 1,3,5-tris(mercaptomethyl)benzene under high dilution conditions with the tris(chloromethyl)calix[6]arene (**111**) produces the upper-rim capped C_3-



107 R = Me, Ph



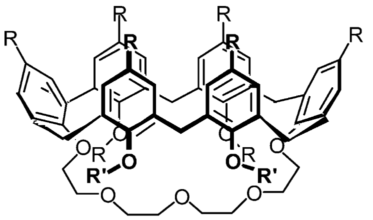
108 R = Me, Ph



111 R = Bu^t

112 R = Bu^t

symmetric calix[6]arene **112** in 28% yield. NMR experiments with trimethylanilinium iodide ($PhNMe_3I$) indicated that complexation/decomplexation was slower than the NMR timescale (separate signals were observed from those of free $PhNMe_3I$). Similar studies with the parent *p-tert*-butylcalix[6]areneH_6 failed to show any separate signals, though an upfield shift was observed [74]. Lower-rim functionalisation to reduce conformational flexibility can be achieved via selective 1,4-bridging with polyether chains followed by alkylation with either methyl iodide or α-chloro-*N*,*N*-diethylacetamide to afford either the tetramethoxy derivative **113** or the tetramide **114**, respectively. An X-ray study of **114** confirmed the cone conformation. NMR experiments with tetramethylammonium acetate revealed a 1:1 complex for which the exchange was slow on the NMR timescale [75].

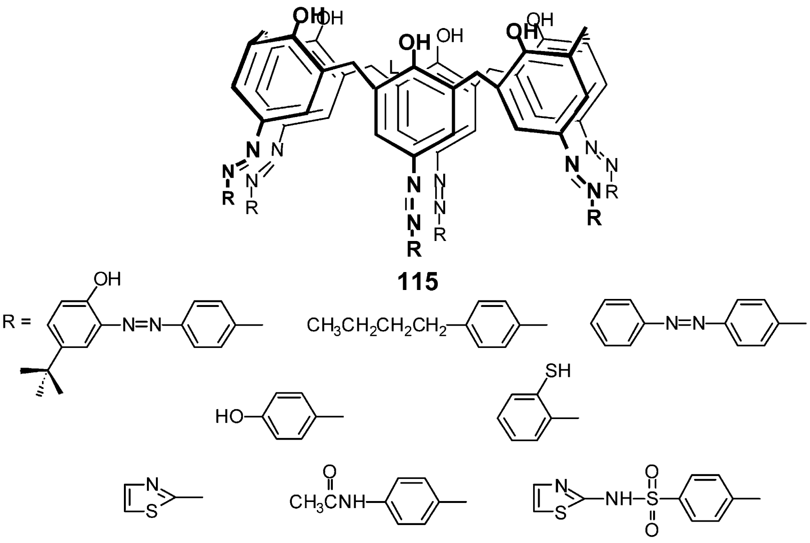


R = Bu^t; R '= Me (**113**), CH_2CONEt_2 (**114**)

The azo ligands **115**, shown below, have been examined as transfer agents (aqueous phase to organic phase) for the cations Na^+, K^+, Sr^+, Ag^+, Hg^+, Hg^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Al^{3+}, Fe^{3+}, Cr^{3+} and La^{3+} [76].

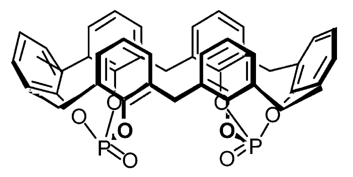
5.6. Phosphorus

The diphosphate **116** is available from the parent calix[6]arene in about 50% yield on treatment with $ClPO(OEt)_2$ [77]. The ^{31}P-NMR spectrum consists of a singlet at δ −22.4, whilst in the ^1H-NMR at 250 K, six



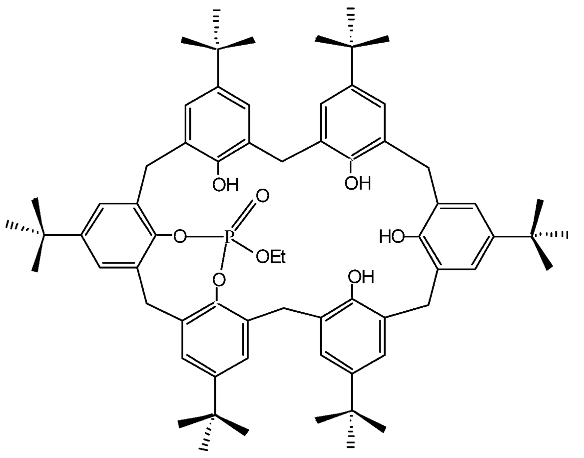
115

sharp doublets (CH_2) and three sharp singlets (^tBu) are observed. X-ray diffraction of a sample recrystallised from acetonitrile reveals a conformation of ca. C_2 symmetry consistent with *syn* sub-groups (defined as the rings resulting from three phenolic oxygens and a bridging phosphorus). The orientation of the P=O group was exclusively *exo*.

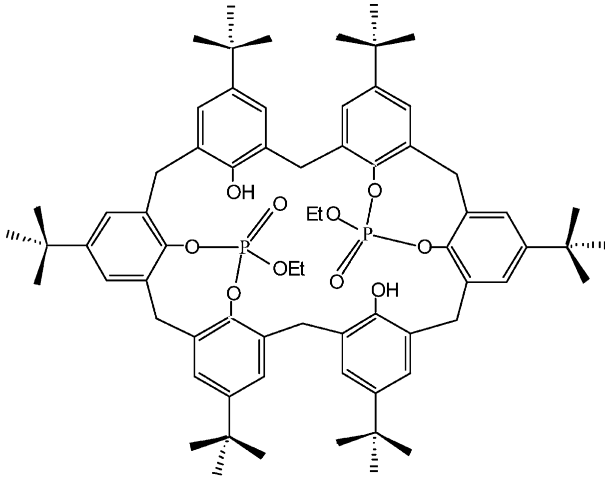


Syn **116**

A single phosphate group can be attached to two adjacent oxygens of the calix[6]arene framework (see **117**) by reacting caesium fluoride (base) followed by ethyldichlorophosphate (one equivalent) with the parent calix[6]arene [78].



117



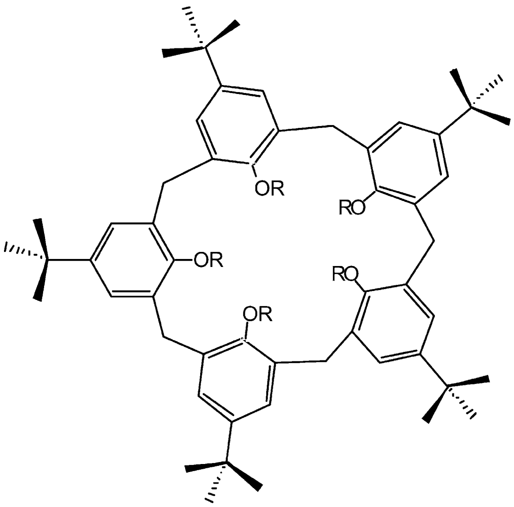
118

The use of potassium hydride as base here and 2 equivalents of ethyldichlorophosphate results in the isolation of the species **118**. The structure of the latter is established by ^{1}H-NMR data, which eliminates the possibility that adjacent pairs of oxygens might bind to phosphorus.

A number of thiophosphorylated calix[6]arenes have been prepared from *p-tert*-butylcalix[6]areneH$_6$ and diethoxythiophosphoryl chloride under phase transfer conditions [79]. The mono(thiophosphate) **119** and the 1,3-bis(thiophosphate) **120** (neither shown) are each obtained in about 25% yield when the reaction is carried out in a basic dichloromethane solution at ambient temperature for 1 h. Both were shown by NMR studies to adopt a dynamic *syn* conformation with a pinched calix[6]arene framework.

A pentakis(thiophosphate) **121** is the only product after 10 h (32% yield). A large excess of diethoxythiophosphoryl chloride in combination with 50% aqueous NaOH in refluxing dichloromethane yields, in 68% yield, the 1,4-bis(thiophosphate) **122**. The latter reacts with dimethylsulphate/Cs_2CO_3 in refluxing acetonitrile to afford a tetramethylether-1,4-bis(thiophosphate) (**123**) (yield 42%); the thio groups adopt an *anti* orientation. Two other methylether derivatives **124** with C_{3v} symmetry (37% yield) and **125** (81% yield) have been obtained from 1,3,5-trimethylether-*p-tert*-butylcalix[6]areneH$_3$ and 1,2-dimethylether-*p-tert*-butylcalix[6]areneH$_4$, respectively on reaction with diethoxythiophosphoryl chloride.

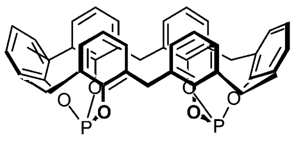
By a procedure similar to that used for **121**, but using diisopropylchlorophosphate and *p-tert*-butylcalix[5]areneH$_5$, the penta(diisopropoxyphosphonoxy) ligand **126** is formed in good yield (73%) [80].



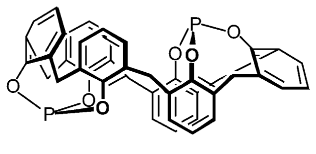
$R = PO(OPr^i)_2$

126

The diphosphite **127** is available in 20–40% yield from the reaction of PCl_3, the

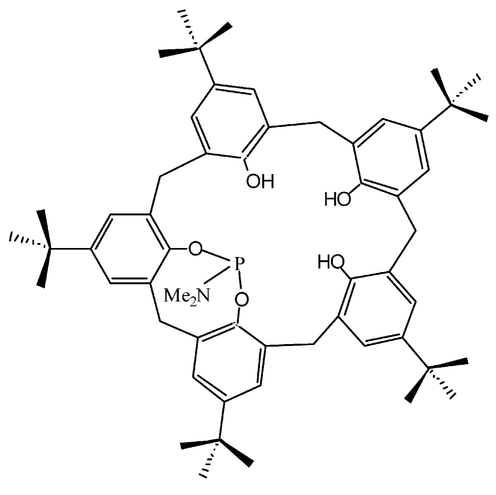


Syn **127**



anti **127**

parent calix[6]arene and a base. The low yields were attributed to problems associated with purification. Spectroscopy indicated the presence of two non-interconvertible conformations, for which the phosphite moieties are either *syn* (major component) or *anti* (minor component) with respect to the cavity of the calixarene backbone. This diphosphite has been complexed to a number of metals including Platinum and palladium, doing so in a *cis* fashion. The bite angle for the [(*syn*-**127**)PdCl$_2$] complex was extablished, by X-ray diffraction, to be about 90°. The cationic palladium(II) derivative shows good catalytic activity for the copolymerisation of carbon monoxide and ethene [46].



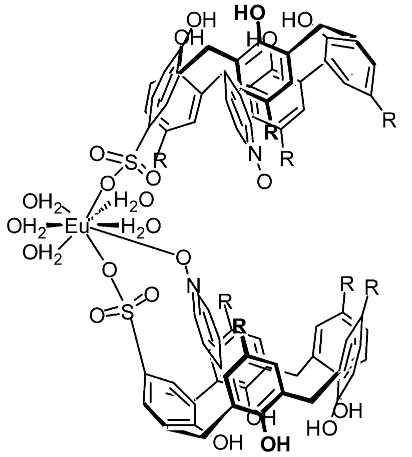
128

Treatment of *p*-*tert*-butylcalix[5]areneH$_5$ in toluene with tris(dimethylamino)phosphine, (Me$_2$N)$_3$P affords the white air-stable solid **128** in 86% yield. The Me$_2$NP moiety binds to two adjacent (deprotonated) phenolic groups of the calix[5]arene ring as evidenced by the ^{1}H-NMR [three singlets (Bu^t) and six doublets (CH$_2$—non-equivalent hydrogens)] [32]. This new ligand system has the ability to also accommodate transition metal centers—see Section 3.6 (tungsten).

6. Lathanides and actinides

Calixarenes complexes of both the actinides and Lanthanides have been comprehensively reviewed very recently [1g]. We will therefore only discuss here one or two highlights.

The *p*-sulfonatocalix[5]arene **13** reacts with La(NO$_3$)$_3$·H$_2$O in water in the presence of pyridine *N*-oxide to afford Na$_2$[La(H$_2$O)$_9$][*p*-sulfonatocalix[5]arene]·pyridine *N*-oxide·10H$_2$O (**129**) [9]. The La(III) centre is not directly bound to the calix[5]arene ligand, preferring instead to hydrogen bond via its aqua ligands. A disordered pyridine *N*-oxide molecule occupies the calix[5]arene cavity. The extended structure is best described as a bi-layer similar to that found for **15**. Similar treatment of **13** with Gd(NO$_3$)$_3$·H$_2$O and pyridine *N*-oxide yielded Na$_7$[Gd(H$_2$O)$_6$][*p*-sulfonatocalix[5]arene]·2pyridine *N*-oxide·34H$_2$O (**130**), in which a dodecahedral Gd centre bridges two calix[5]arene ligands via Gd–O(sulfonate) bonding. The bowl-shaped cavities here each contain an 'edge-on' pyridine *N*-oxide molecule. The structural differences between **129** and **130** are attributed to the large size of La^{3+}. Europium on the other hand is similar in size (ionic radii) to gadolinium and hence the analogous reaction with Eu(NO$_3$)$_3$·H$_2$O yields the complex Na[Eu(H$_2$O)$_9$][Eu(pyridine *N*-oxide)(H$_2$O)$_5$(*p*-sulfonatocalix-[5]arene)$_2$]·pyridine *N*-oxide·$17^1/_2$H$_2$O (**131**), containing an eight coordinate Eu^{3+} centre bridging the two calix[5]arene ligands. It should also be noted that one of the pyridine *N*-oxide molecules now also binds to the bridging Eu(III) centre.

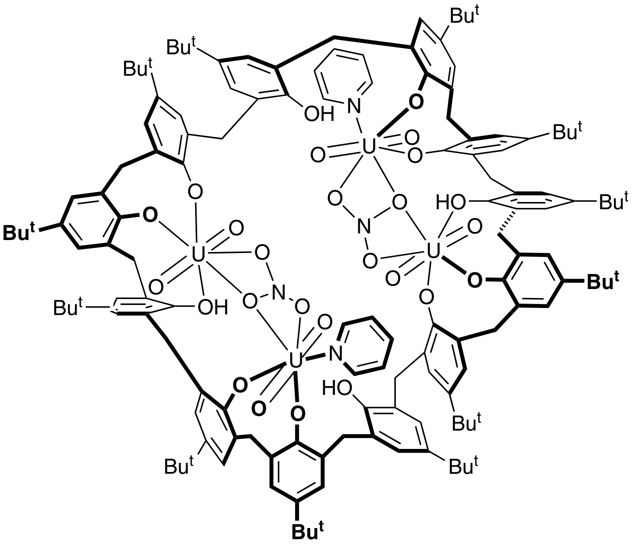


core of **131** R = SO$_3$

One conclusion that can be drawn from the discussion of the structures **129**–**131** and also that of the *p*-sulfonatocalix[6]arene **18**, is that under these aqueous conditions, *p*-sulfonatocalix[5 and 6]arenes preferentially bind to Lanthanide ions via their sulfonato groups as opposed to the phenolic complexation suggested a decade earlier for the uranyl ion by Shinkai et al. [81].

The complexes we have met thus far are derivatives of calix[*n*]arenes, where $n = 5$–8. The coordination chemistry of calixarenes with $n > 8$ is rather scant. Recently, however, a small number of lanthanides and actinide complexes of either calix[9 or 12]arene have been reported. Levard et al. reacted UO$_2$(NO$_3$)$_2$·6H$_2$O with *p*-*tert*-butylcalix[12]areneH$_{12}$ in pyridine in the presense of Et$_3$N, isolating red **132** in 46% yield [82]. Crystals suitable for X-ray diffraction were grown over 180 days! Four pentagonal uranyl cations form two symmetry related bimetallic units bound to the calix[12]arene through five oxygens (only four of which are deprotonated); a tridentate nitrate is bound between two metal cations of each half of the molecule.

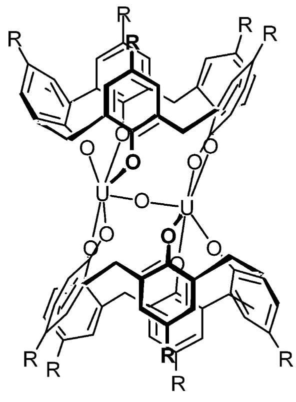
The conformation of the macrocycle is best described as alternating loops and cones.



132

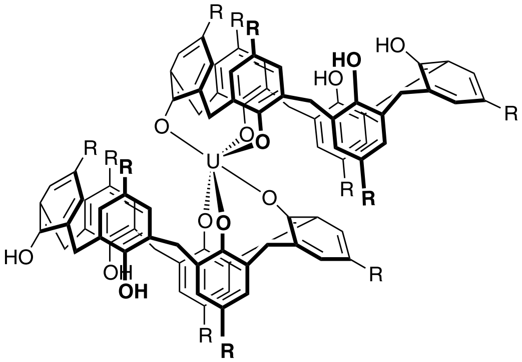
Reaction of uranyl nitrate hexahydrate, [$UO_2(NO_3)_2 \cdot 6H_2O$] with *p*-benzylcalix[7]areneH_7 in the presence of 1,4-diazabicyclo[2.2.2]octane (DABCO) yielded the complex [$(UO_2)_6$(*p*-benzylcalix[7]arene)$_2(O)_2$(DABCOH)$_6$]$\cdot$3MeCN$\cdot$$CHCl_3$$\cdot$5MeOH$\cdot$3$H_2O$ (**133**), as revealed by X-ray crystallography [83]. A hexanuclear uranium(VI) cluster (shown below) is sandwiched between two symmetry related calix[7]arene ligands, each of which is bound to two of the UO_2^{2+} cations. The two remaining UO_2^{2+} cations are part of a near-planar U_4O_2 core and are involved in μ_3-oxo bridging. The basis complex [$(UO_2)_6$(*p*-benzylcalix[7]arene)$_2(O)_2$] has an overall charge of -6, which is balanced by the presence of six protonated DABCO molecules. The conformation adopted by each calix[7]arene ligand in **134** has undergone what is best described as a flipping of the phenolic rings in the 1 and 4 positions when compared to that observed in the free ligands *p*-Rcalix[7]areneH_7 (R = ethyl or *tert*-butyl—this latter complex is a pyridine adduct) [84].

The first non-uranyl complexes containing large calixarene ligands have been prepared via the interaction of UCl_4 with *p*-*tert*-butylcalix[5 and 6]arenes in wet pyridine [85]. In the case of *p*-*tert*-butylcalix[5]areneH_5, a dinuclear red complex **135** has been structurally characterised. Here, a μ_2-oxo bridge sits on a centre of inversion and links two distorted octahedral uranium centres. Each cone-shaped calix[5]arene acts as a tridentate ligand to one uranium center and a bidentate ligand to the other. A pyridinium cation in each cavity suggests that the complex is based on uranium(V) and broad NMR resonances provide further evidence that this is indeed the case. In pyridine/acetone solution, **135** is readily oxidised to the corrsponding uranium(VI) complex {[U(*p*-*tert*-butylcalix[5]arene)]$_2$O} (**136**).



136 R = Bu^t

For *p*-*tert*-butylcalix[6]areneH_6, treatment with UCl_4 followed by exposure to air yields the red uranium(VI) complex [U(*p*-*tert*-butylcalix[6]areneH_3)]$_2$ (**137**). This complex can be viewed as a novel homoleptic U(OR)$_6$ species in which the distorted octahedral uranium cation lies on a centre of inversion and is bound to two calix[6]arene ligands, each binding via three phenolate oxygen atoms. The two partial cones of each 1,2,3-alternate calix[6]arene contain a pyridine molecule (in the solid-state).



137 R = Bu^t

7. Concluding remarks

This review highlights the significant progress that has been made in the development of the coordination chemistry of the larger calixarene ring systems. In a short period of time since the discovery of the first metallocalixarene in the mid 1980s', this exciting area has revealed a variety of structural motifs and there is doubtless much rich chemistry yet to be discovered.

Acknowledgements

The author wishes to acknowledge The Royal Society, The Leverhulme Trust, The EPSRC and Professor V.C. Gibson (Imperial College) for past financial support and the continuing superb crystallographic efforts of Dr Mark R.J. Elsegood (University of Loughborough).

References

[1] (a) C.D. Gutsche, Calixarenes, Royal Society of Chemistry, Cambridge, 1989.;
(b) D.M. Roundhill, Prog. Inorg. Chem. 43 (1995) 553;
(c) C. Wieser, C.B. Dielman, D. Matt, Coord. Chem. Rev. 165 (1997) 93;
(d) A. Ikeda, S. Shinkai, Chem. Rev. 97 (1997) 1713;
(e) C.D. Gutsche, Calixarenes Revisited, Royal Society of Chemistry, Letchworth, 1988.;
(f) J.L. Atwood, L.J. Barbour, M.J. Hardie, C.L. Raston, Coord. Chem. Rev. 222 (2001) 3;
(g) Z. Asfari, V. Böhmer, J. Harrowfield, J. Vicens (Eds.), Calixarenes 2001, Kluwer, Dordrecht, 2001;
(h) W. Sliwa, Croatica Chem. Acta 75 (2002) 131;
(i) P.D. Harvey, Coord. Chem. Rev. 233/234 (2002) 289.

[2] M.A. McKervey, M.J. Schwing-Weill, F. Arnaud-Neu, in: G.W. Gokel (Ed.), Comprehensive Supramolecular Chemistry, Pergamon, Elsevier Science Ltd, Oxford, 1996.

[3] S.R. Izatt, R.T. Hawkins, J.J. Christensen, R.M. Izatt, J. Am. Chem. Soc. 107 (1985) 63.

[4] J.M. Harrowfield, M.I. Ogden, W.R. Richmond, A.H. White, Dalton Trans. (1991) 2153.

[5] N.P. Clague, W. Clegg, S.J. Coles, J.D. Crane, D.J. Moreton, E. Sinn, S.J. Teat, N.A. Young, Chem. Commun. (1999) 379.

[6] N.P. Clague, W. Clegg, J.D. Crane, D.J. Moreton, E. Sinn, S.J. Teat, N.A. Young, Dalton Trans. (1999) 3535.

[7] K. Murayama, K. Aoki, Inorg. Chim. Acta 281 (1998) 36.

[8] T.A. Hanna, L. Liu, A.M. Angeles-Boza, X. Kou, C.D. Gutsche, K. Ejsmont, W.H. Watson, L.N. Zakharov, C.D. Incarvito, A.L. Rheingold, J. Am. Chem. Soc. 125 (2003) in press.

[9] J.W. Steed, C.P. Johnson, C.L. Barnes, R.K. Juneja, J.L. Atwood, S. Reilly, R.L. Hollis, P.H. Smith, D.L. Clark, J. Am. Chem. Soc. 117 (1995) 11426.

[10] C.P. Johnson, J.L. Atwood, J.W. Steed, C.B. Bauer, R.D. Rogers, Inorg. Chem. 35 (1996) 2602.

[11] J.L. Atwood, D.L. Clark, R.K. Juneja, G.W. Orr, K.D. Robinson, R.L. Vincent, J. Am. Chem. Soc. 114 (1992) 7558.

[12] M.T. Blanda, D.B. Farmer, J.S. Brodbelt, B.J. Goolsby, J. Am. Chem. Soc. 122 (2000) 1486.

[13] (a) Y.K. Chen, Y.Y. Chen, Org. Lett. 2 (2000) 743;
(b) Y.K. Chen, Y.Y. Chen, Tetrahedron Lett. 41 (2000) 9079.

[14] H. Otsuka, K. Araki, S. Shinkai, Tetrahedron 51 (1995) 8757.

[15] (a) S.E. Bell, J.K. Browne, V. McKee, M.A. MeKervey, J.F. Malone, M.A. O'Leary, A. Walker, F. Arnaud-Neu, O. Boulangeot, O. Mauprivez, Schwing-Weill, J. Org. Chem. 63 (1998) 489.;
(b) F. Arnaud-Neu, G. Barrett, D. Corry, S. Cremin, G. Ferguson, J.F. Gallagher, S.J. Harris, M.A. McKervey, M.-J. Schwing-Weill, Perkin Trans. 2 (1997) 575.

[16] K. Araki, R. Nakamura, H. Otsuka, S. Shinkai, Chem. Commun. (1995) 2121.

[17] A. Ikeda, Y. Suzuki, K. Akoa, S. Shinkai, Chem. Lett. (1996) 963.

[18] A. Casnati, P. Minari, A. Pochini, R. Ungaro, W.F. Nuenhuis, F. de Fong, D.N. Reinhoudt, Isreal J. Chem. 32 (1992) 79.

[19] S.G. Bott, A.W. Coleman, J.L. Atwood, Chem. Commun. (1986) 610.

[20] G.D. Andreetti, G. Calestani, F. Ugozzoli, A. Arduini, E. Ghidini, A. Pochini, R. Ungaro, J. Inclusion Phenom. 5 (1987) 123.

[21] (a) G.E. Hofmeister, F. Ekkehardt, S.F. Pedersen, J. Am. Chem. Soc. 111 (1989) 2318;
(b) G.E. Hofmeister, E. Alvarado, J.A. Leary, D.I. Yoon, S.F. Pedersen, J. Am. Chem. Soc. 112 (1990) 8843.

[22] A.J. Petrella, N.K. Roberts, D.C. Craig, C.L. Raston, R.N. Lamb, Chem. Commun. (2003) 1014.

[23] V.C. Gibson, C. Redshaw, M.R.J. Elsegood, unpublished work.

[24] V.C. Gibson, C. Redshaw, M.R.J. Elsegood, Dalton Trans. (2001) 767.

[25] C. Floriani, Floriani-Moro, in: Z. Asfari, V. Böhmer, J. Harrowfield, J. Vicens (Eds.), Calixarenes 2001, Kluwer, Dordrecht 29 (2001) 536.

[26] C. Redshaw, M.R.J. Elsegood, unpublished results.

[27] V.C. Gibson, C. Redshaw, W. Clegg, M.R.J. Elsegood, Chem. Commun. (1995) 2371.

[28] V.C. Gibson, C. Redshaw, W. Clegg, M.R.J. Elsegood, U. Siemeling, T. Türk, Dalton Trans. (1996) 4513.

[29] V.C. Gibson, C. Redshaw, M.R.J. Elsegood, New J. Chem. 26 (2002) 16.

[30] C. Redshaw, M.R.J. Elsegood, Polyhedron 19 (2000) 2657.

[31] C. Redshaw, M.R.J. Elsegood, Inorg. Chem. 39 (2000) 5164.

[32] M. Fan, H. Zhang, M. Lattman, Chem. Commun. (1998) 99.

[33] V.C. Gibson, C. Redshaw, M.R.J. Elsegood, Chem. Commun. (2002) 1200.

[34] L. Giannini, E. Solari, A. Zanotti-Gerosa, C. Floriani, A. Chiesi-Villa, C. Rizzoli, Angew. Chem. Int. Ed. Engl. 36 (1997) 753.

[35] (a) M. Aoki, K. Murata, S. Shinkai, Chem. Lett. (1991) 1715;
(b) M. Aoki, K. Nakashima, H. Kawabata, S. Tsutsui, S. Shinkai, Perkin Trans. 2 (1993) 347.

[36] C. Redshaw, M.R.J. Elsegood, Eur. J. Inorg. Chem. (2003) in press.

[37] W. Clegg, R.J. Errington, P. Kraxner, C. Redshaw, Dalton Trans. (1992) 1431.

[38] T. Haino, H. Araki, Y. Fujiwara, Y. Tanimoto, Y. Fukazawa, Chem. Commun. (2002) 2148.

[39] F.J. Parlevliet, A. Olivier, W.G.J. de Lange, P.C.J. Kamer, H. Kooijman, A.L. Spek, P.W.N.M. van Leeuwen, Chem. Commun. (1996) 583.

[40] J.-P. Scharff, M. Mahjoubi, R. Perrin, New J. Chem. 17 (1993) 793.

[41] D. Hesek, Y. Inoue, S.R.L. Everitt, M. Kunieda, H. Ishida, M.G.B. Drew, Tetrahedron Asymmetry 9 (1998) 4089.

[42] F. Löffler, U. Lüning, G. Gohar, New J. Chem. 24 (2000) 935.

[43] H. Deligöz, M. Yilmaz, Synth. React. Inorg. Met. Org. Chem. 26 (1996) 943.

[44] J.W. Steed, C.P. Johnson, R.K. Jueja, J.L. Atwood, R.S. Burkhalter, Supramol. Chem. 6 (1996) 235.

[45] J.W. Steed, R.K. Juneja, J.L. Atwood, Angew. Chem.

[46] F.J. Parlevliet, M.A. Zuideveld, C. Kiener, H. Kooijman, A.L. Spek, P.C.J. Kamer, P.W.N.M. van Leeuwen, Organometallics 18 (1999) 3394.
[47] S. Blanchard, L. Le Clainche, M.-N. Rager, B. Chansou, J.-P. Tuchagues, A.F. Duprat, Y. le Mest, O. Reinaud, Angew. Chem. Int. Ed. 37 (1998) 2732.
[48] S. Blanchard, M.-N. Rager, A.F. Duprat, O. Reinaud, New J. Chem. (1998) 1143.
[49] Y. Rondelez, O. Sénèque, M.-N. Rager, A.F. Duprat, O. Reinaud, Chem Eur. J. 6 (2000) 4218.
[50] Y. Rondelez, G. Bertho, O. Reinaud, Angew. Chem. Int. Ed. 41 (2002) 1044.
[51] L. Le Clainche, M. Giorgi, O. Reinand, Inorg. Chem. 39 (2000) 3436.
[52] O. Sénèque, M. Campion, B. Douziech, M. Giorgi, E. Rivière, Y. Journaux, Y. Le Mest, O. Reinaud, Eur. J. Inorg. Chem. 1 (2002) 2007.
[53] T. Kajiwara, N. Kon, S. Yokozawa, T. Ito, N. Iki, S. Miyano, J. Am. Chem. Soc. (2002) in-press.
[54] O. Sénèque, M.-N. Rager, M. Giorgi, O. Reinaud, J. Am. Chem. Soc. 122 (2000) 6183.
[55] (a) O. Sénèque, M. Giorgi, O. Reinaud, Chem. Commun. (2002) 984;
(b) O. Sénèque, Y. Rondelz, L. Le Clainche, C. Inisan, M.-N. Rager, M. Giorgi, O. Reinaud, Eur. J. Inorg. Chem. (2001) 2597.
[56] (a) M.A. Markowitz, R. Bielski, S.L. Regen, J. Am. Chem. Soc. 110 (1998) 7545;
(b) M.A. Markowitz, V. Janout, D.G. Castner, S.L. Regen, J. Am. Chem. Soc. 111 (1989) 8192.
[57] A.W. Coleman, S.G. Bott, J.L. Atwood, J. Inclusion Phenom. 5 (1987) 581.
[58] J.M. Smith, S.G. Bott, Chem. Commun. (1996) 377.
[59] R.M. Williams, J.W. Verhoeven, Recl. Trav. Chim. Pays-Bas. 111 (1992) 531.
[60] (a) J.L. Atwood, G.A. Koutsantonis, C.L. Raston, Nature 368 (1994) 229;
(b) T. Suzuki, K. Nakashima, S. Shinkai, Chem. Lett. (1994) 699.
[61] R.M. Williams, J.M. Zwier, J.W Verhoeven, G.H. Nachtegaal, A.P.M. Kentgens, J. Am. Chem. Soc. 116 (1994) 6965.
[62] C.L. Raston, J.L. Atwood, P.J. Nichols, I.B.N. Sudna, Chem. Commun. 1 (1996) 2615.
[63] T. Suzuki, K. Nakashima, S. Shinkai, Tetrahedron Lett. 36 (1995) 249.
[64] K. Jinno, K. Tanabe, Y. Saito, H. Nagashima, R.D. Trengove, Anal. Comm. 34 (1997) 175.
[65] J.L. Atwood, J.B. Leonard, C.L. Raston, I.B.N. Sudria, Angew. Chem. Int. Ed. Engl. 37 (1998) 981.
[66] T. Haino, M. Yanase, Y. Fukazawa, Angew. Chem. Int. Ed. Engl. 36 (1997) 259.
[67] T. Haino, M. Yanase, Fukazawa, Angew. Chem. Int. Ed. Engl. 37 (1998) 997.
[68] M. Yanase, M. Matsuoka, M. Suzuki, H. Iwamoto, T. Haino, Y. Fukazawa, Tetrahedron Lett. 41 (2000) 493.
[69] M. Yanase, T. Haino, Y. Fukazawa, Tetrahedron Lett. 40 (1999) 2781.
[70] T. Haino, H. Araki, Y. Yamanaka, Y. Fukazawa, Tetrahedron Lett. 42 (2001) 3203.
[71] T. Haino, Y. Yamanaka, H. Araki, Y. Fukazawa, Chem. Commun. (2002) 402.
[72] P. Sood, H. Zhang, M. Lattman, Organometallics (2002) in press.
[73] (a) S. Shinkai, Tetrahedron 49 (1993) 8933;
(b) K. Araki, H. Shimizu, S. Shinkai, Chem. Lett. (1993) 205.
[74] M. Taleshita, S. Nishio, S. Shinkai, J. Org. Chem. 59 (1994) 4032.
[75] A. Casnati, P. Jacopozzi, A. Pochini, F. Ugozzoli, R. Cacciapaglia, L. Mandolini, R. Ungaro, Tetrahedron 51 (1995) 591.
[76] A. Akdogan, M. Deniz, S. Cebecioglu, A. Sen, Deligöz, Separation Sci. Technol. 37 (2002) 973.
[77] F. Grynszpan, O. Aleksiuk, S.E. Biali, Chem. Commun. (1993) 13.
[78] D.M. Roundhill, E. Georgiev, A. Yordanov, J. Incl. Phenom. Mol. Recog. Chem. 19 (1994) 101.
[79] W. Wróblewski, Z. Brzózka, R.G. Janssen, W. Verboom, D.N. Reinhoudt, New J. Chem. 20 (1996) 419.
[80] O. Aleksiuk, F. Grynspan, S.E. Biali, J. Incl. Phenom. Mol. Recog. Chem. 19 (1994) 237.
[81] (a) S. Shinkai, H. Koreishi, K. Ueda, T. Arimura, Manabe, J. Am. Chem. Soc. 109 (1987) 6371.;
(b) S. Shinkai, Y. Shiramama, H. Satoh, O. Manabe, T. Arimura, K. Fujimoto, T. Matsuda, Perkin Trans. II (1989) 1167.
[82] P.C. Leverd, I. Dumazet-Bonnamour, R. Lamrtine, M. Nierlich, Chem. Commun. (2000) 493.
[83] P. Thuéry, M. Nierlich, B. Souley, Z. Asfari, J. Vicens, Dalton Trans. (1999) 2589.
[84] (a) M. Perrin, S. Lecocq, Z. Asfari, C.R. Acad. Sci. Paris 310 (1990) 515;
(b) G.D. Andreetti, F. Ugozzoli, J. Inclusion Phenom. 10 (1991) 241.
[85] P.C. Leverd, M. Nierlich, Eur. J. Inorg. Chem. (2000) 1733.