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The Inside of Metal Calixarene Chemistry

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Calixarene molecules are often associated with their ability to form inclusion complexes with organic or inorganic guests. These complexes are usually formed due to the guest molecule interactions with the calixarene aromatic cavity and/or substituents attached to it. The present mini-review discusses a different type of calixarene inclusion complexes, where the inclusion event occurs due to the coordination of an organic or inorganic ligand to a metal centre attached to the lower rim of calix[4]arene. Structural and chemical properties of such complexes of 'uninvited' guests are discussed.

Keywords: Calixarene; Metal complexes; Inclusion chemistry; Coordination compounds

INTRODUCTION

Calixarene inclusion complexes, with organic guest molecules penetrating the hydrophobic cavity, have been known for more than two decades [1]. In fact, the simplest calixarene that is often used as a starting material for a variety of synthetic transformations—*p*-*t*-Bu-calix[4]arene—includes a toluene molecule in its structure and is available commercially as a toluene adduct [2]. In most cases, the inclusion process is guided by the interactions between the guest molecule and the hydrophobic cavity of the calixarene host (Fig. 1a). Since such interactions are weak, the host–guest complexation involving simple neutral molecules is generally observed only in the solid state [3]. Alternatively, the host–guest complexation can be achieved by placing the appropriate substituents at the carbon atoms of the upper (aromatic) rim [4]. When a metal, particularly a transition metal, centre is coordinated to the lower rim oxygen atoms, there are new possibilities for the host–guest interactions that must be taken into account. Metal coordination to the phenolic oxygens increases the partial negative charge on these atoms. This 'excess of electron density' created at the calixarene lower rim allows for the second metal centre coordination to the oxygen atoms from the inside of the calixarene cavity (Figure 1b) [5]. The second metal ion or even metal centre bearing additional ligands becomes incorporated inside the hydrophobic part of the calixarene ligand as a result of the first metal coordination on the top of the calixarene lower rim. While included inside the calixarene, the new guests may begin interacting with the cavity; however, the distinction can be made from the typical host–guest chemistry since the guests in the metal calixarene complexes have not been 'invited' by the organic host. An excellent review of bimetallic calixarene inclusion complexes has recently appeared in the literature [6].

When a metal centre is coordinatively unsaturated, it is also capable of the direct complexation of neutral organic or inorganic donor molecules. In sterically crowded metal complexes, the donor ligand can only approach the metal from the inside of the calixarene cavity. Since this type of complexation arises from the tendency of a metal centre to increase its coordination number when a suitable two-electron donor is present, the ligand is 'included' into the calixarene cavity without typical, if any, 'host–guest' interactions with the calixarene host (Fig. 1c). Unlike the previous example where the calixarene oxygen atoms and aromatic rings are involved in the complexation, there is formally no attractive interaction at all between the neutral 'guest' and 'host', metal centre being fully responsible for the ligand incorporation inside the cavity. In many instances, the same metal calixarene complexes can coordinate either organic ligands or metal ions inside the calixarene cone. The purpose of this mini-review is to discuss the structural and chemical properties of these special types of inclusion complexes, where the guest inclusion is associated with the metal centre coordinated at the lower rim of a calix[4]arene molecule. As not comprehensive, this review will

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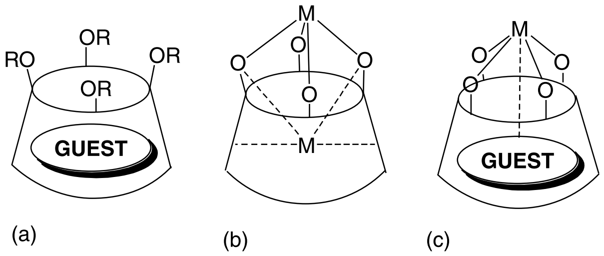


FIGURE 1 Possible inclusion complexes of calix[4]arenes.

only cover metal calixarene complexes where the guest inclusion was unambiguously established.

Examples of transition metal calixarene complexes started to appear in the literature in the mid-1980s of the last century [7]. In 1991, Floriani *et al*. [8] reported that the reaction of a tungsten(VI) oxo chloro precursor with *t*-Bu-calix[4]arene gave the tungsten-capped calixarene complex **1**, which can coordinate a donor molecule inside the calixarene cavity (Scheme 1). The X-ray structure of one such complex **1a** with an organic ligand, acetic acid, coordinated to the metal centre was presented. The coordinative unsaturation of the tungsten centre was essential for this type of complexation, since in similar hexacoordinate W(VI) complexes no ligand inclusion was observed. Since then, many examples of ligand complexation to the metal centre from the inside of the calixarene scaffold were reported. These reports will now be reviewed according to the metals' place in the periodic table.

MAIN-GROUP METAL COMPLEXES

There are few examples of neutral ligands incorporated inside the calixarene cavity due to the complexation to a main-group metal centre. Walther *et al.* [9] reported the formation of several alkaline metal complexes of an unsubstituted calixarene ligand. The complexes contained several metal ions held together by two calixarene units. One of the sodium complexes has been crystallized with dimethylformamide (DMF) molecules coordinated to the metal from the inside of the cavity. The ligand is coordinated via the carbonyl oxygen atom; however, the bonding distances could not be established due to the poor quality of the crystal structure.

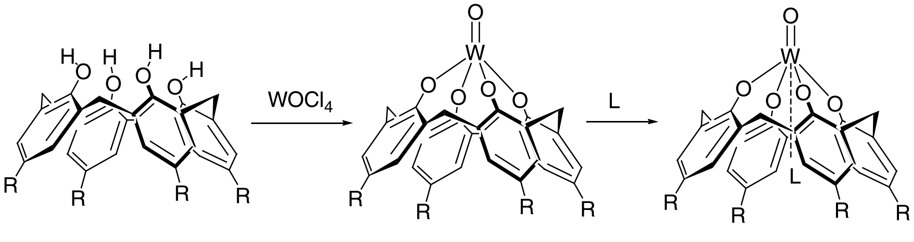
While the majority of the inclusion complexes involves typical labile two electron donors, usually solvents, a less common ligand coordination type in metal calixarene inclusion complexes was reported by Raston *et al.* The authors demonstrated that the reduction of the aluminium chloride calixarene complex with NaH in THF produces the aluminium hydride complex **2**, with the hydride pointing inside the calixarene cavity (Scheme 2) [10]. This endo-cavity hydride complex could alternatively be prepared by treating its exo-isomer with H_3AlNMe_3 under reflux. The comparative reactivity studies showed that the endo-isomer is more resistant towards hydrolysis than its exo-isomer.

GROUP IV METAL COMPLEXES

The Floriani group reported the synthesis and characterization of several titanium calixarene complexes in various oxidation states. In particular, they reported a Ti(III) complex **3** with a coordinated benzonitrile molecule that penetrates the calixarene cavity (Scheme 3) [11]. The IR spectrum of this complex showed the substantial shift of the coordinated nitrile group to $2260\,\text{cm}^{-1}$, when compared with $2228\,\text{cm}^{-1}$ for the non-coordinated ligand. Interestingly, although Ti(IV) derivatives by far dominate the titanium calixarene chemistry [12], their inclusion complexes with neutral ligands have not been reported, further indicating the importance of the coordinative unsaturation for the formation of such complexes.

GROUP V METAL COMPLEXES

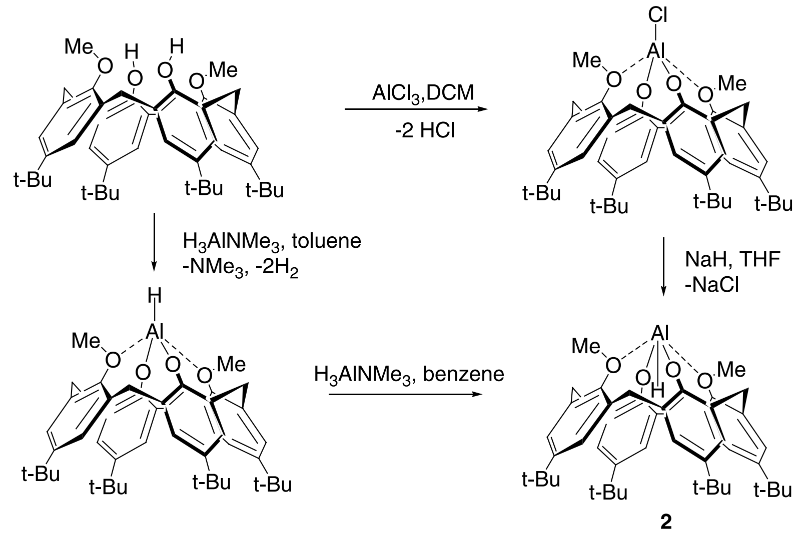
A dimeric vanadium(III) complex **4** was produced in the reaction of the mono-methylether of *t*-Bu-calix[4]arene with $V(Mes)_3$-THF. This unsaturated d^2 complex is capable of coordinating isonitrile and nitrile molecules inside the cavity (Scheme 4) [13]. The X-ray structure of its *t*-BuNC adduct has



1

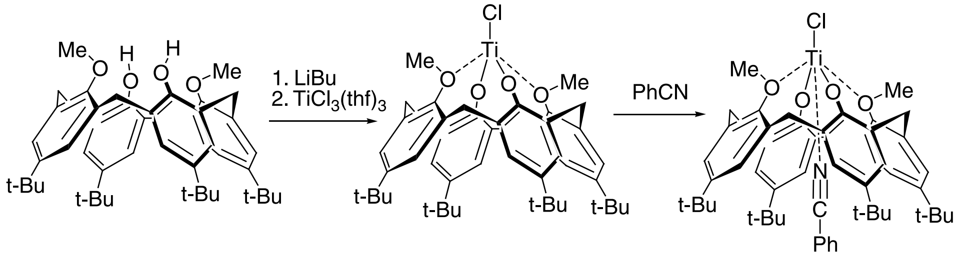
1a : L = CH_3COOH
1b : L = H_2O

SCHEME 1 Synthesis of the first metal calixarene inclusion complex.



2

SCHEME 2 Preparation of complex **2**.

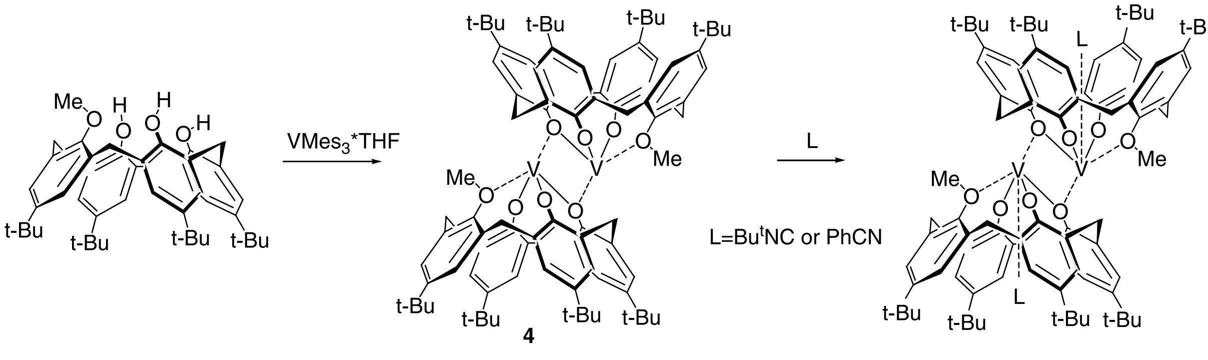


3

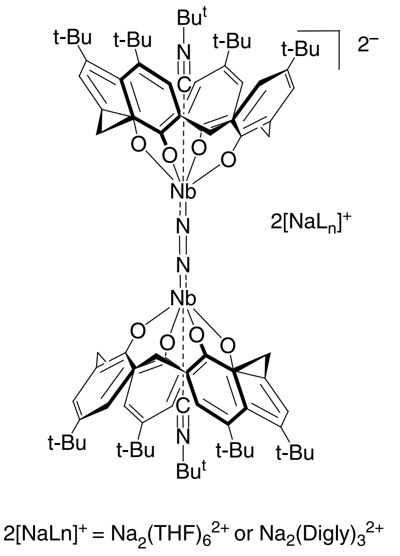
SCHEME 3 Synthesis of the Ti(III) inclusion complex **3**.

revealed significantly longer vanadium—oxygen bonds, compared with similar V–calixarene complexes, as a result of the coordination of the strong isonitrile σ-donor. The vanadium–isonitrile distance is 2.157(14) Å and is rather unremarkable. The corresponding benzonitrile complex was similarly obtained upon the addition of PhCN to **4**. No X-ray structure has been reported; however, the IR spectrum clearly shows the coordinated nitrile molecule due to characteristic band at 2274 cm^{-1}. Interestingly, the addition of pyridine or 4,4-dipyridyl to **4** did not lead to the inclusion complexes. Instead, cleavage of the dimeric structure was observed.

Dimeric Nb(V) complexes **5** with a bridging-reduced dinitrogen ligand were prepared by Floriani *et al.* (Fig. 2) [14]. Complexation of *t*-BuNC inside the cavity of each of the calixarene molecules gave saturated niobium complexes with the strongly coordinated guest ligand. This strong coordination



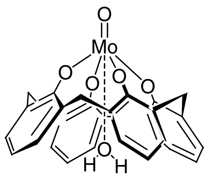
SCHEME 4 Synthesis of the dimeric V(III) inclusion complexes.



5

FIGURE 2 Schematic presentation of the dimeric Nb complex **5**.

is manifested in the significant increase in the C—N stretching frequency to 2206 cm^{-1} due to high acidity of the metal centres. The crystal structure obtained for one of the complexes was of low quality, precluding the discussion of the relevant bond distances.



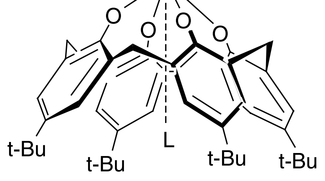
7

FIGURE 4 Schematic presentation of complex **7**.

Lippard *et al.* prepared Ta(V) complexes **6**, where the tantalum centre is coordinated to 4-phenoxide ligands of the calixarene lower rim and pentamethyl cyclopentadienyl (Cp*) ligand on the top of it (Fig. 3) [15]. Coordination of H_2O and CH_3CN molecules to the metal from the inside of calixarene cavity was confirmed by both X-ray crystallography and solution NMR analysis. The Ta—$NCCH_3$ coordination is also clearly observed in the IR spectrum due to an approximately 50 cm^{-1} shift of the nitrile group signal to a higher frequency upon complexation to a metal centre. The Ta—H_2O distance of 2.188(3) Å is significantly shorter than the metal–water distances in other calixarene complexes (cf. Mo—H_2O distances longer than 2.34 Å, *vide infra*), although no other structure of a metal–water complex with the Cp* group *trans* to the H_2O ligand has been reported. Interestingly, the ^{1}H NMR signal of the coordinated water molecule appears downfield from that of the free H_2O (2.23 versus 1.56 ppm in $CDCl_3$). Since ligand incorporation into the calixarene cavity usually results in significant upfield shifts due to the aromatic ring's shielding effect (which was indeed found for the CH_3CN ligand) [16], this observation suggests that complexation to the metal increases the acidity of the water protons that compensates for the aromatic shielding.

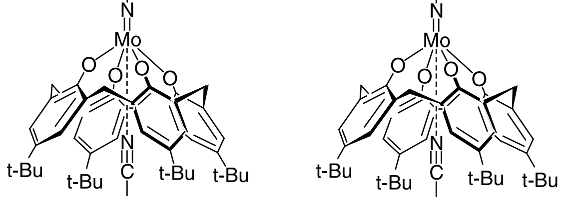
GROUP VI METAL COMPLEXES

Most of the examples of metal calixarene complexes with neutral ligands coordinated inside the hydrophobic cavity have been reported with group VI metals. The monomeric molybdenum oxo complex **7** containing a water molecule inside the calixarene was prepared by Hanna *et al.* (Fig. 4) [17]. The X-ray structure of this complex showed metal–oxygen distance of 2.340(2) Å. Two monomeric Mo complexes **8**, with an imido group as an exohedral ligand, were reported by Radius *et al.* The complexes have additional acetonitrile molecules coordinated to the metal centre inside the cavity, with the Mo—N distances of 2.343(9) and 2.303(3) Å for the *t*-BuC═N— and ArylC═N—*trans*-ligands, respectively (Fig. 5) [18]. The Gibson group reported both mono- and bimetallic molybdenum arylimido complexes (**9** and **10**, respectively) having acetonitrile molecule inside the cavity (Figs. 6 and 7) [19]. Each of the complexes was characterized by X-ray analysis. Similar to a previous example [18], the bimetallic aryl imide complex exhibited a bonding distance of



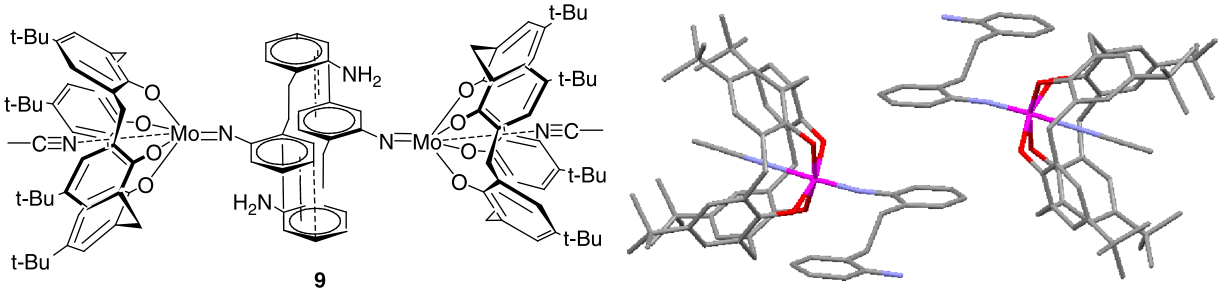
6a = H_2O, **6b** = CH_3CN

FIGURE 3 Schematic presentation of complexes **6a,b**.



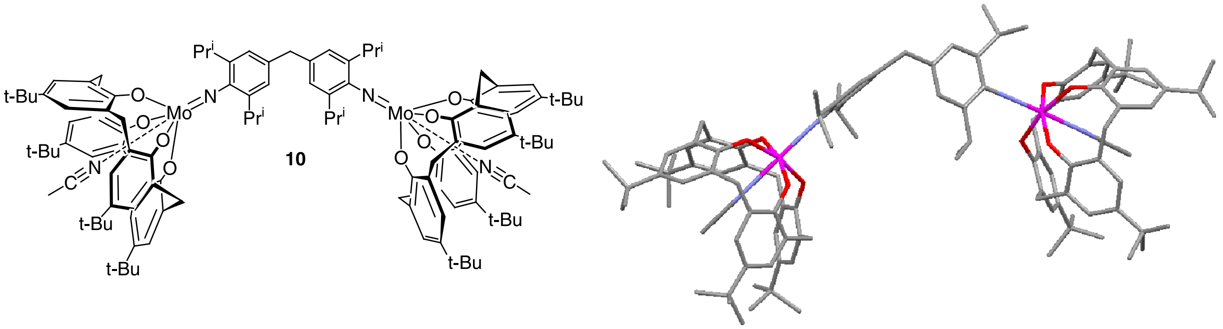
8a **8b**

FIGURE 5 Schematic presentation of complexes **8a,b**.



9

FIGURE 6 Schematic and structural presentation of complex **9**.



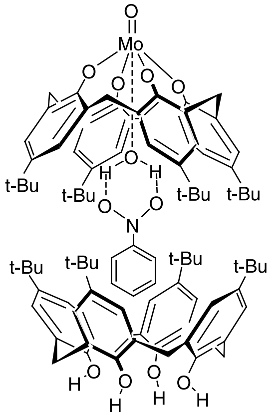
10

FIGURE 7 Schematic and structural presentation of complex **10**.

2.304(6) Å, while the monometallic one showed the Mo—NCCH$_3$ distance of 2.326(2) Å. The bond lengthening in the latter can possibly be explained by the packing of the monomeric complex, which shows strong π-stacking interactions of the arylimido group that can influence the distance of the Mo—N bond *trans* to it.

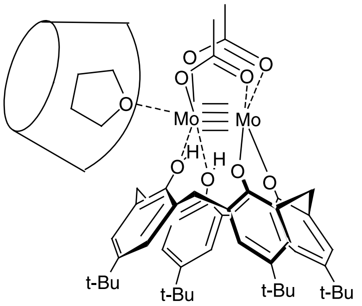
Unusual molybdenum(IV) olefin complexes were prepared by Floriani *et al*. and shown to coordinate acetonitrile inside the calixarene cavity [20]. The same group also reported a rare molybdenum calixarene complex **11** with a water molecule coordinated to the metal as an endo-ligand. This ligand, in turn, is involved in hydrogen bonding interactions with a molecule of nitrobenzene encapsulated in another (metal-free) calixarene molecule (Fig. 8) [21]. These weak interactions result in some elongation of the Mo—O distance to 2.408(16) Å in comparison with the monomeric aqua complex—2.340(2) Å [17]. An interesting example of a bimetallic Mo complex **12** having Mo—Mo quadruple bond was reported by the Lippard group. The X-ray structure of **12** showed that one of the metal centres is coordinated to a THF molecule, which, in turn, is located inside the calixarene cavity of another metal calixarene complex (Fig. 9) [22].

A variety of tungsten calixarene complexes containing endohedral ligand molecules have been reported. In addition to the already mentioned tungsten–oxo complex with the coordinated acetic



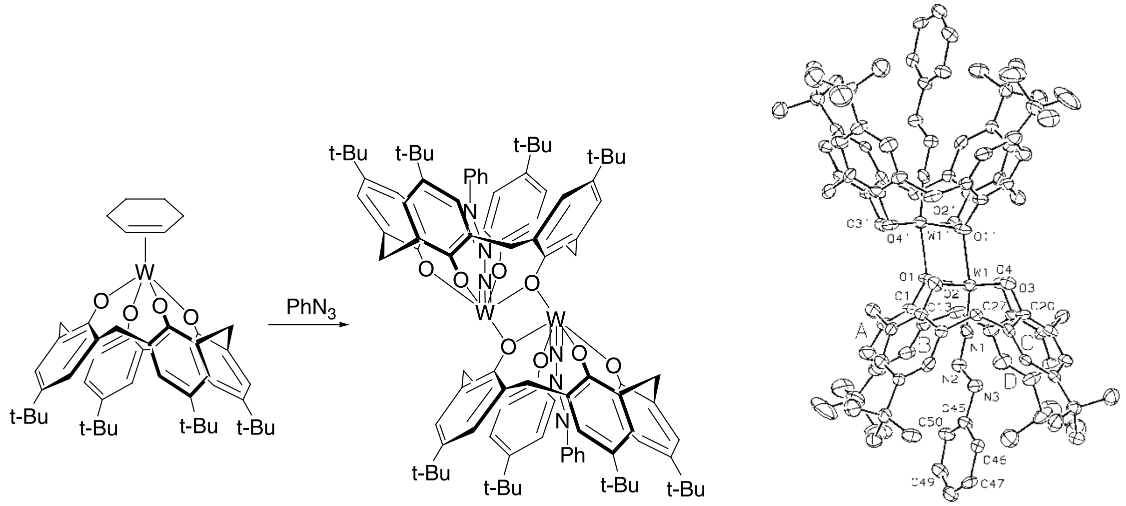
11

FIGURE 8 Schematic presentation of complex **11**.



12

FIGURE 9 Schematic presentation of complex **12**.



13

SCHEME 5 Synthesis and X-ray structure of the dimeric W complex **13** is reprinted with permission from (*23*), Copyright 2001 American Chemical Society.

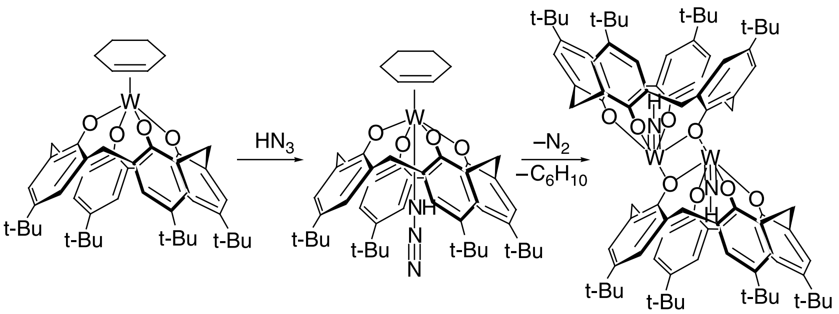
acid molecule [8], the Floriani group prepared a variety of calixarene complexes with different substituents at the tungsten centre, some of them also having organic and inorganic guests coordinated to the metal. The W(IV) alkene complex reacted with phenyl azide to give the triazenido inclusion complex **13** (Scheme 5), while performing the same reaction with bulkier azides resulted in the olefin displacement reaction.

When HN_3 was used in place of PhN_3, the initial coordination of the acid inside the calixarene cavity was proposed, followed by the dinitrogen release and formation of the imido inclusion complex **14** (Scheme 6) [23]. The same alkene complex was also prepared with the acetonitrile ligand inside the cavity [24].

The Floriani group also reported dimeric W complexes **15** having multiple metal–metal bonds with organic donors incorporated inside the calixarene. The *t*-BuNC adduct, with the isonitrile ligands coordinated to each of the tungsten centres, was characterized by X-ray crystallography, showing the W—C distance of 2.188(11) Å (Scheme 7) [25]. The dimeric complexes could also be obtained from the corresponding monomeric carbene complexes of W—calixarenes, which were also capable of ligand coordination inside the cavity. The studies of PhCHO and *t*-BuNC inclusion complexes **16** have been reported (Scheme 8) [26].

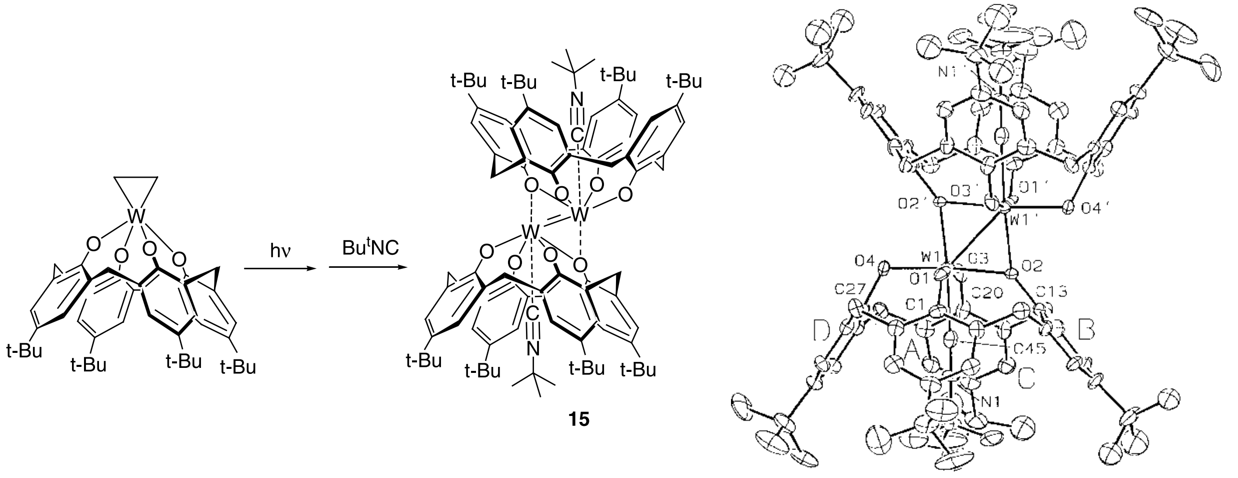
Radius and Attner reported several X-ray structures of tungsten(VI) imide complexes with donor molecules incorporated inside the calixarene ligand [18]. In particular, the acetonitrile and *t*-Bu-isonitrile ligands are interesting for comparison with other inclusion complexes (Fig. 10). For example, the acetonitrile complex **17a** showed the W—N distance of 2.314(3) Å, which is longer than 2.2610(18) Å reported for the otherwise identical tungsten complex **18**, that has the hydrazido group as the exohedral ligand, reported by Redshaw and Elsegood [27] (Fig. 10). These data suggest a stronger *trans*-influence of the hydrazide compared with the imide ligand. On the other hand, the same M—$NCCH_3$ distance showed negligible changes when Mo was used instead of W, with the Mo—$NCCH_3$ distance being 2.303(3) Å in the otherwise analogous complex.

More dramatic differences in the metal–ligand distance is observed when the metal centres are



14

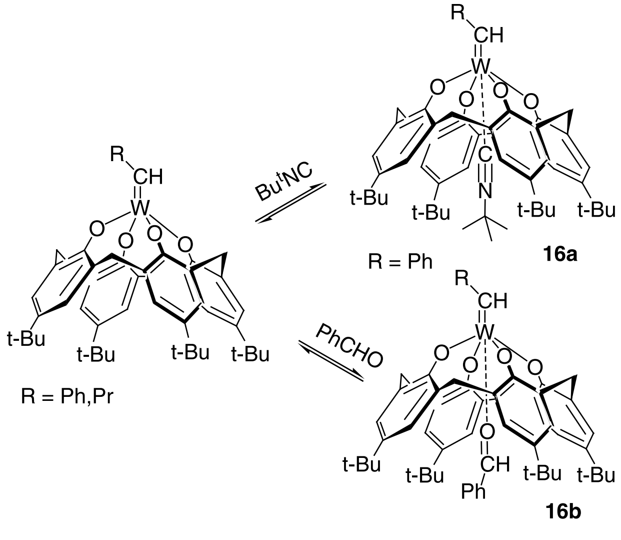
SCHEME 6 Synthesis of **14**.



SCHEME 7 Synthesis and X-ray structure of **15** is reprinted with permission from (*25*), Copyright 1999 American Chemical Society.

in different oxidation states. While the W(VI) centre showed the W—C bond length of 2.417(13) Å in its *t*-Bu-isonitrile complex **17b**, the same distance in the W(IV) complex **15** was significantly shorter—2.188(11) Å [25]. This difference points to significant back-bonding in the latter, expected for a metal centre in a lower oxidation state.

Other tungsten–oxo calixarene complexes were used to complex various organic and inorganic molecules. The Swager group reported the synthesis of a series of bithiophene-substituted W(VI) calixarene complexes **19** containing water, DMSO or substituted formamide ligands inside the calixarene cavity (Scheme 9) [28]. The DMSO complex **19a** has been crystallized and showed the W—O bonding distance of 2.319(7) Å. This complex represents a rare example of a DMSO molecule coordination to a metal centre inside the calixarene cavity [29]. The guest complexation was also studied by the ^{1}H NMR spectroscopy. Large upfield shifts (about 5 ppm) from the signals of free ligands were observed upon the complexation of several substituted formamides inside the calixarene cavity.



SCHEME 8 Synthesis of complexes **16a,b**.

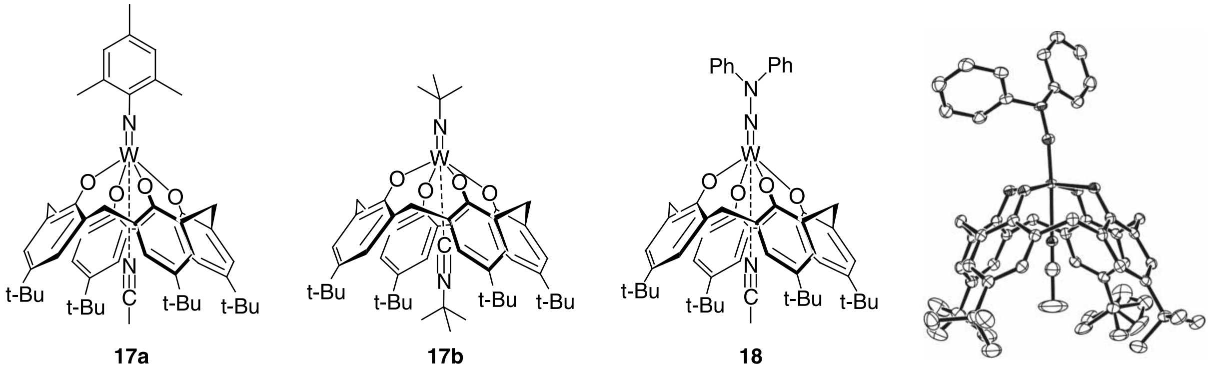
Upon the electropolymerization, conducting polymeric films were obtained which showed the conductivity dependence on the guest organic molecule. For example, polymeric films of mono-*N*-substituted formamide complexes showed significantly higher conductivity values than complexes with di-*N*-substituted formamides (Scheme 10) [28]. This dependence on the ligand steric bulk can be explored further in the design of chemosensors for neutral organic molecules.

In continuation of this approach, Ugozzoli *et al.* very recently reported several W(VI) oxo calixarene complexes with a number of neutral guests inside the cavity. The latter included CH_3CN, DMF and H_2O. Interestingly, with water as a guest, ethyl acetate molecule was observed in the X-ray structure in the second coordination sphere to tungsten [20]. The carbonyl oxygen of the ester showed strong interactions with both hydrogen atoms of the water molecule (Fig. 11) [30].

Finally, the 'original' Floriani W=O complex of *t*-Bu-calixarene with the water molecule inside the cavity **1b** was crystallized [31]. The reported crystal structure showed the W—H_2O distance of 2.37(1) Å, which is only slightly longer than the metal—H_2O distance in a similar molybdenum complex [17].

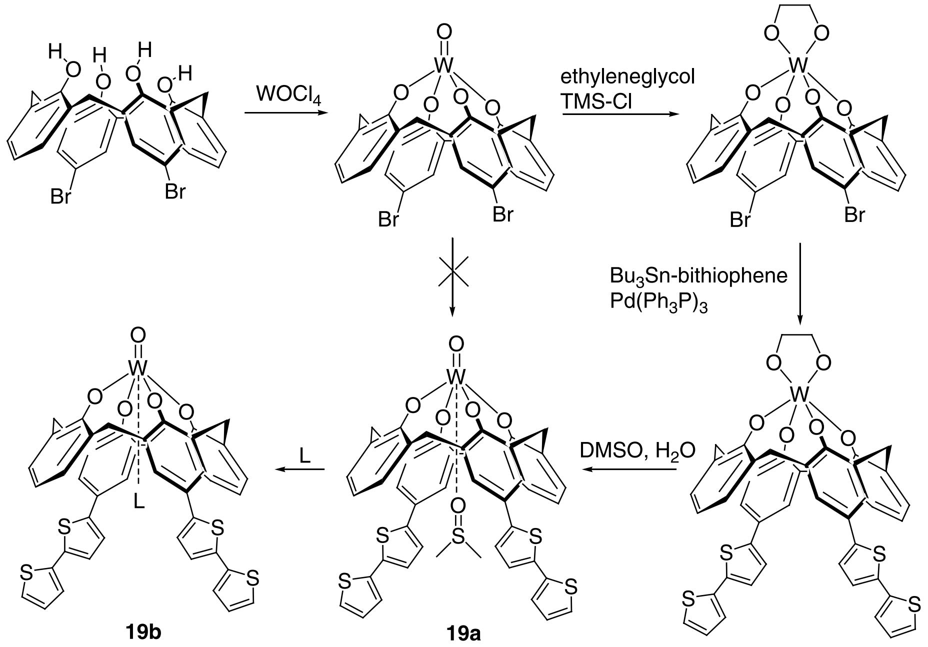
GROUP VII METAL COMPLEXES AND LATE TRANSITION METAL COMPLEXES

The Ishii group reported the synthesis and X-ray structure of a Re calixarene complex capable of coordinating a Pd(II) organometallic fragment endohedrally to the oxygen atoms of the lower rim to give a bimetallic Re–Pd inclusion complex [32]. To the best of our knowledge, this represents the



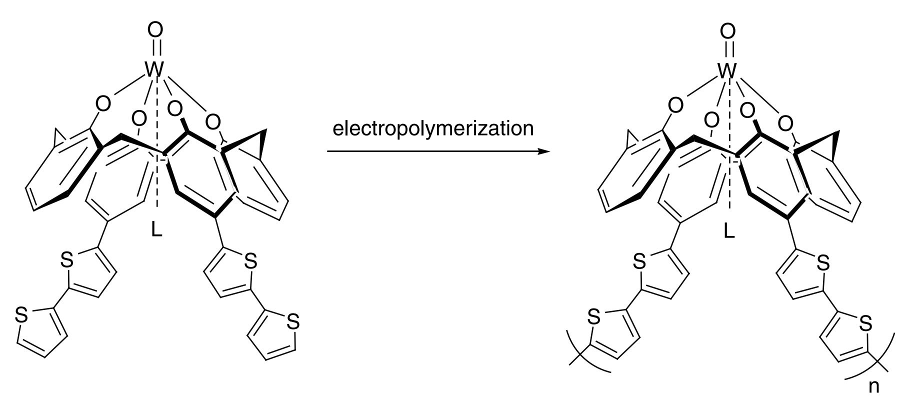
17a **17b** **18**

FIGURE 10 Complexes **17a,b** are reprinted with permission from (27), Copyright 2000 American Chemical Society.



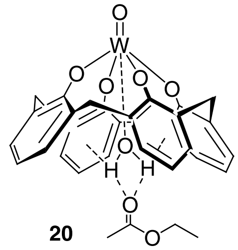
L = H_2O, PhNHCHO, $PhCH_2NHCHO$,
NH_2CHO, Me_2NCHO, N-Bu_2NCHO, DMSO

SCHEME 9 Synthesis of the Tungsten(VI) precursors for electropolymerization.



L = RNHCOH - more conductive
L = R_2NCOH - less conductive

SCHEME 10 Preparation of the conducting host–guest polymers.



20

FIGURE 11 Schematic presentation of complex **20**.

only example of fully characterized group VII metal complex reported in the literature [33]. Thus, there are no examples of group VII metal calixarene complexes crystallized with a donor ligand coordinated to the metal centre inside the calixarene cavity. The same is true for the platinum triad metals, where only few complexes with the calixarene ligands directly bound to the metal centre have been reported [34]. Not being sufficiently oxophilic, such metals have a general tendency of coordinating to the aromatic rings of the calixarene rather than the lower rim [35]. However, if the coordinative unsaturation is created, nothing should prevent donor ligands from coordinating to the metal centre and we will probably see the inclusion complexes of late transition metals in the future. We are also unaware of structurally characterized calixarene complexes of the coinage metals, where the metal is bound to the calixarene lower rim. Considering the low affinity of these metals to oxygen donors and lower coordination numbers than in other transition metal complexes, this comes as no surprise [36].

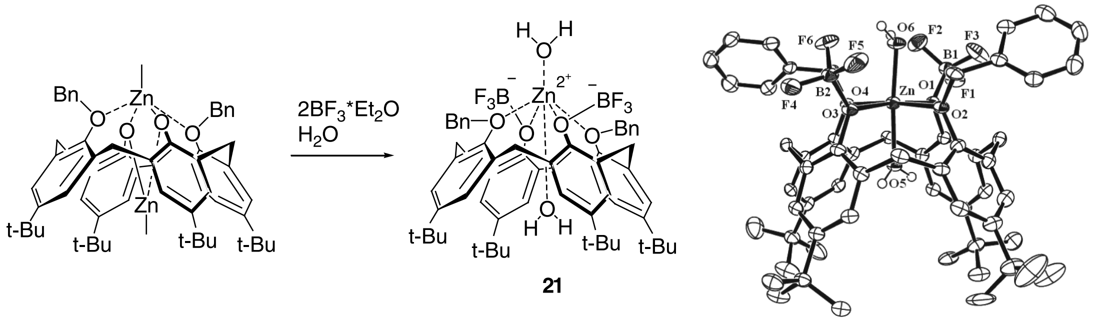
GROUP XII METAL COMPLEXES

We recently demonstrated that the reaction of the bimetallic methylzinc complexes of 1,3-*O*-dibenzylcalixarene [37] with wet BF_3 results in an unusual cationic Zn complex **21**, where the counterions are formed by BF_3 attack at the phenoxide oxygen atoms. The complex has two water molecules coordinated to the zinc centre, one of them entering the calixarene cavity (Scheme 11) [38]. The Zn—O distances in the coordinated water ligands differ significantly: 2.123(2) Å for the 'guest' water molecule versus 2.018(2) Å for the exo-water molecules.

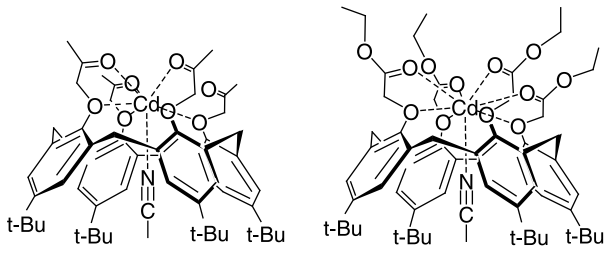
Cadmium calixarene complexes **22** have been reported for the calixarene tetraesters. The crystal structures of these complexes showed acetonitrile coordination to the cadmium atom through the hydrophobic cavity (Figure 12) [39]. Depending on the bulkiness of the substituent, eight- and nine-coordinated Cd complexes were observed and the Cd—$NCCH_3$ distances were shown to be dependent on the metal coordination number. The eight-coordinated complex **22a** showed a shorter Cd—nitrogen bond of 2.428(2) versus 2.465(3) Å in the nine-coordinate complex **22b**. Interestingly, the isostructural lead(II) complexes showed no CH_3CN coordination to the metal, even though the guest acetonitrile molecule was observed in the X-ray structures of those complexes. Similar lack of coordination of the 'included' acetonitrile molecule was also reported for other metal complexes [40], which show different, 'non-coordinating' orientation of the acetonitrile guest [41].

SUMMARY AND PROSPECTS

As this mini-review demonstrates, the inclusion chemistry of metal calixarene complexes can be very rich. In addition to neutral donors, metal ions or organometallic fragments can also be 'included' inside the calixarene cone and can even influence the properties of the host molecule [6, 42]. Due to lack of space, these compounds have not been discussed here. Although most inclusion complexes of metal calixarenes reported to date were investigated primarily from the structural point of view, one can see the potential of such complexes in a variety of applications. One such application would be the design of chemosensors based on ligand coordination to the metal centre from inside the calixarene. Various neutral donors, which are otherwise difficult to detect due to weak interactions with most of the



SCHEME 11 Synthesis and X-ray structure of **21**.



22a **22b**

FIGURE 12 Schematic presentation of complexes **22a,b**.

receptors, can be observed in their metal complexes [28]. Since the cavity can easily be modified, it can be fine-tuned to specific organic analytes. This might also include the detection of enantiomeric compounds by chirally shaped calixarene cones. As ligand complexation to a metal centre is generally a straightforward reaction, proper amplification of this binding event might result in versatile chemosensory materials.

Another application which is worthy of particular attention is the use of intra-cavity coordination to affect the catalytic activity of the metal calixarene complexes. Although calixarene molecules have the general features of ligands used in most popular catalytic transformations, their use in catalysis is relatively scarce [43]. It is well established that the catalytic activities of several commonly used catalysts is often dependent on the presence of an extra ligand that can trigger the catalytic reaction [44]. Calixarene cavity is naturally shaped to accommodate some and reject other donor molecules, and, thus, the possibility of using the external coordination in metal calixarene complexes to activate the metal centre towards catalysis should be seriously considered.

Although beyond the scope of this mini-review, two elegant systems where the metal centre complexation provided novel calixarene inclusion complexes will be mentioned. Both systems utilized pendant ligands to attach the metal centre above the lower rim of a calixarene molecule. Matt *et al*. [45] prepared a series of phosphine and phosphite-substituted calixarene molecules, capable of coordinating a late transition metal centre. Complexation to the phosphorus donors, placed either at the lower or upper rim, results in a ligand inclusion inside the calixarene cavity. Carbon monoxide, hydride or aromatic donors can thus be introduced as 'guests' of the calixarene ligand [46]. This type of complexation can potentially lead to a new type of catalytic reaction where the organic molecule bound to the metal centre inside the calixarene cone serves as a substrate. Similar approaches using the resorcinarene or cyclodextrin cavities have been reported [47]. It is also yet to be seen whether metals directly coordinated to the calixarene lower rim can perform catalytic reactions inside the calixarene cone.

Reinaud *et al*. used 1,3,5-trisubstituted amine or imine linkers to chelate copper, zinc or late transition metal ions above the lower rim of a calix[6]arene derivative. These complexes are capable of coordinating either an organic or inorganic ligand inside the calix[6]arene cavity. In addition to interesting structural properties, the new complexes mimic the active sites of several metalloenzymes and show reactivity that makes them suitable for studies of biologically relevant transformations at a metal centre in biomimetic systems [48]. The corresponding derivatives of the calix[4]arene were also prepared; however, the cavity appears to be too small to show a similar type of reactivity [49].

References

[1] For general reviews on calixarenes see: (a) Bohmer, V. *Angew. Chem., Int. Ed. Engl*. **1995**, *34*, 713. (b) Ikeda, A.; Shinkai, S. *Chem. Rev*. **1997**, *97*, 1713. (c) Ludwig, R. *Fresenius J. Anal. Chem*. **2000**, *367*, 103. (d) *Calixarenes Revisited*; Gutsche, C.D. Ed.; Springer: New York, 1998

[2] This complex was first reported in: Andreetti, G.D.; Ungaro, R.; Pochini, A.J. *Chem. Soc., Chem. Commun*. **1979**, 1005

[3] Brouwer, E. B.; Enright, G. D.; Ratcliffe, C. I.; Facey, G. A.; Ripmeester, J. A. *J. Phys. Chem. B* **1999**, *103*, 10604, (b) Leon, S.; Leigh, D.A.; Zerbetto, F. *Chem. Eur. J*. **2002**, *8*, 4854.

[4] Bott, S. G.; Coleman, A. W.; Atwood, J. L. *J. Am. Chem. Soc*. **1988**, *110*, 610, (b) Barbour, L.J.; Damon, A.K.; Orr, G.W.; Atwood, J.L. *Supramol. Chem*. **1996**, *7*, 209. (c) Shinkai, S.; Araki, K.; Matsuda, T.; Nishiyama, N.; Ikeda, H.; Takasu, I.; Iwamoto, M.J. *Am. Chem. Soc*. **1990**, *112*, 9053.

[5] Dubberley, S. R.; Blake, A. J.; Mountford, P. *J. Chem. Soc., Dalton Trans*. **2003**, (b) Dubberley, S.R.; Blake, A.J.; Mountford, P. *Chem. Commun*. **1997**, 1603. (c) Guillemot, G.; Solari, E.; Rizzoli, C.; Floriani, C. *Chem. Eur. J*. **2002**, *8*, 2072. (c) Petrella, A.J.; Roberts, N.K.; Raston, C.L.; Craig, D.C.; Thornton-Pett, M.; Lamb, R.N. *Eur. J. Inorg. Chem*. **2003**, 4153. (d) Caselli, A.; Solari, E.; Scopelliti, R.; Floriani, C.; Re, N.; Rizzoli, C.; Chiesi-Villa, A.J. *Am. Chem. Soc*. **2000**, *122*, 3652. (e) Zanotti-Gerosa, A.; Solari, E.; Giannini, L.; Floriani, C.; Chiesi-Villa, A.; Rizzoli, C. *Chem. Commun*. **1997**, 183. (f) Gibson, V.C.; Redshaw, C.; Clegg, W.; Elsegood, M.R.J. *Chem. Commun*. **1997**, 1605.

[6] Petrella, A. J.; Raston, C. L. *J. Organomet. Chem*. **2004**, *689*, 4125.

[7] For first transition metal calixarene complexes see: (a) Olmstead, M.M.; Sigel, G.; Hope, H.; Xu, X.; Power, P.P.*J. Am. Chem. Soc*. **1985**, *107*, 8087. For recent reviews on transition metal calixarene chemistry see: (b) Sliwa, W. *Croat. Chem. Acta* **2002**, *75*, 131. (c) Wieser, C.; Dieleman, C.B.; Matt, D. *Coord. Chem. Rev*. **1997**, *165*, 93. (d) Harvey, P.D. *Coord. Chem. Rev*. **2002**, *233*, 289

[8] Corazza, F.; Floriani, C.; Chiesi-Villa, A.; Rizzoli, C. *Inorg. Chem*. **1991**, *30*, 4465.

[9] Fischer, R.; Gorls, H.; Walther, D. *Eur. J. Inorg. Chem*. **2004**, 1243.

[10] Gardiner, M. G.; Koutsantonis, G. A.; Lawrence, S. M.; Nichols, P. J.; Raston, C. L. *Chem. Commun*. **1996**, 2035.

[11] Zanotti-Gerosa, A.; Solari, E.; Giannini, L.; Floriani, C.; Re, N.; Chiesi-Villa, A.; Rizzoli, C. *Inorg. Chim*. **1998**, *270*, 298.

[12] Petrella, A. J.; Craig, D. C.; Lamb, R. N.; Raston, C. L.; Roberts, N. K. *Dalton Trans*. **2003**, 4590, (b) Petrella, A.J.; Roberts, N.K.; Raston, C.L.; Craig, D.C.; Thornton-Pett, M.; Lamb, R.N. *Eur. J. Inorg. Chem*. **2003**, 4153. (c) Cotton, F.A.; Dikarev, E.V.; Murillo, C.A.; Petrukhina, M.A. *Inorg. Chim. Acta* **2002**, *332*, 41. (d) Delaigue, X.; Hosseini, M.W.; Leize, E.; Kieffer, S.; van Dorsselaer, A. *Tetrahedron Lett*. **1993**, *34*, 7561. (e) Lattman, M. *ACS Symposium Series* **2006**, *917*, 237.

[13] Castellano, B.; Solari, E.; Floriani, C.; Scopelliti, R.; Re, N. *Inorg. Chem*. **1999**, *38*, 3406.

[14] Caselli, A.; Solari, E.; Scopelliti, R.; Floriani, C.; Re, N.; Rizzoli, C.; Chiesi-Villa, A. *J. Am. Chem. Soc.* **2000**, *122*, 3652.

[15] Acho, J. A.; Doerrer, L. H.; Lippard, S. *J. Inorg. Chem.* **1995**, *34*, 2542.

[16] Arena, G.; Contino, A.; Gulino, F. G.; Magrì, A.; Sciotto, D.; Ungaro, R. *Tetrahedron Lett.* **2000**, *41*, 9327.

[17] Liu, L.; Zakharov, L. N.; Golen, J. A.; Rheingold, A. L.; Watson, W. H.; Hanna, T. A. *Inorg. Chem.* **2006**, *45*, 4247.

[18] Radius, U.; Attner, J. *Eur. J. Inorg. Chem.* **1999**, 2221, (b) Radius, U.Z. *Anorg. Allg. Chem.* **2004**, *630*, 957.

[19] Gibson, V. C.; Redshaw, C.; Clegg, W.; Elsegood, M. R. J. *Chem. Commun.* **1998**, 1969, (b) Gibson, V.C.; Redshaw, C.; Clegg, W.; Elsegood, M.R.J.J. *Chem. Soc., Chem. Commun.* **1995**, 2371.

[20] Guillemot, G.; Solari, E.; Scopelliti, R.; Floriani, C. *Organometallics* **2001**, *20*, 2446.

[21] Corazza, F.; Floriani, C.; Chiesi-Villa, A.; Guastini, C. *J. Chem. Soc., Chem. Commun.* **1990**, 640.

[22] Acho, J. A.; Lippard, S. *J. Inorg. Chim. Acta* **1995**, *229*, 5.

[23] Guillemot, G.; Solari, E.; Floriani, C.; Rizzoli, C. *Organometallics* **2001**, *20*, 607.

[24] Giannini, L.; Solari, E.; Floriani, C.; Chiesi-Villa, A.; Rizzoli, C. *J. Am. Chem. Soc.* **1998**, *120*, 823.

[25] Giannini, L.; Solari, E.; Floriani, C.; Re, N.; Chiesi-Villa, A.; Rizzoli, C. *Inorg. Chem.* **1999**, *38*, 1438.

[26] Giannini, L.; Solari, E.; Dovesi, S.; Floriani, C.; Re, N.; Chiesi-Villa, A.; Rizzoli, C. *J. Am. Chem. Soc.* **1999**, *121*, 2784.

[27] Redshaw, C.; Elsegood, M. R. J. *Inorg. Chem.* **2000**, *39*, 5164.

[28] Vigalok, A.; Swager, T. M. *Adv. Mater.* **2002**, *14*, 368.

[29] For a review see: Calligaris, M.; Carugo, O. *Coord. Chem. Rev.* **1996**, *153*, 83

[30] Arduini, A.; Massera, C.; Pochini, A.; Secchi, A.; Ugozzoli, F. *New J. Chem.* **2006**, *30*, 952.

[31] Jablonski, C.; Brown, M. *Can. J. Chem.* **2001**, *79*, 463.

[32] Iwasa, K.; Kochi, T.; Ishii, Y. *Angew. Chem. Int. Ed.* **2003**, *42*, 3658.

[33] Manganese calixarene complexes were mentioned in: Floriani, C.; Floriani-Moro, R. *Adv. Organomet. Chem.* **2001**, *47*, 167 and ref. 18

[34] Esposito, V.; Solari, E.; Floriani, C.; Re, N.; Rizzoli, C.; Chiesi-Villa, A. *Inorg. Chem.* **2000**, *39*, 2604, (b) Giusti, M.; Solari, E.; Giannini, L.; Floriani, C.; Chiesi-Villa, A.; Rizzoli, C. *Organometallics* **1997**, *16*, 5610. (c) Ishii, Y.; Onaka, K.; Hirakawa, H.; Shiramizu, K. *Chem. Commun.* **2002**, 1150 (d) Kotzen, N.; Goldberg, I.; Lipstman, S.; Vigalok, A. *Inorg. Chem.* **2006**, *45*, 5266.

[35] Steed, J. W.; Juneja, R. K.; Burkhalter, R. S.; Atwood, J. L. *Chem. Soc., Chem. Commun.* **1994**, 2205, (b) The complexes also support anion coordination inside the cavity: Staffilani, M.; Hancock, K.S.B.; Steed, J.W.; Holman, K.T.; Atwood, J.L.; Juneja, R.K.; Burkhalter, R.S. *J. Am. Chem. Soc.* **1997**, *119*, 6324.

[36] Akrivos, P. D.; Katsikis, H. J.; Koumoutsi, A. *Coord. Chem. Rev.* **1997**, *167*, 95.

[37] Bukhaltsev, E.; Goldberg, I.; Vigalok, A. *Organometallics* **2004**, *23*, 4540, (b) Bukhaltsev, E.; Goldberg, I.; Vigalok, A. *Organometallics* **2005**, *24*, 5732.

[38] Kotzen, N.; Goldberg, I.; Vigalok, A. *Inorg. Chem. Commun.* **2005**, *8*, 1028.

[39] De Namor, A. F. D.; Chahine, S.; Kowalska, D.; Castellano, E. E.; Piro, O. E. *J. Am. Chem. Soc.* **2002**, *124*, 12824.

[40] De Namor, A. F. D.; Piro, O. E.; Salazar, L. E. P.; Aguilar-Cornejo, A. F.; Al-Rawi, N.; Castellano, E. E.; Velarde, F. J. S. *J. Chem. Soc., Farad. Trans.* **1998**, *94*, 3097.

[41] Xu, W.; Puddephatt, R. J.; Manojlovic-Muir, L.; Muir, K. W.; Frampton, C. S. *J. Incl. Phenom.* **1994**, *19*, 277.

[42] Gibson, V. C.; Redshaw, C.; Clegg, W.; Elsegood, M. R. J. *Chem. Commun.* **1997**, 1605.

[43] Soriente, A.; Fruilo, M.; Gregoli, L.; Neri, P. *Tetrahedron Lett.* **2003**, *44*, 6195, (b) Ozerov, O.V.; Ladipo, F.T.; Patrick, B.O.J. *Am. Chem. Soc.* **1999**, *121*, 7941. (c) Ozerov, O.V.; Brock, C.P.; Carr, S.D.; Ladipo, F.T. *Organometallics* **2000**, *19*, 5016. (d) Bukhaltsev, E.; Frish, L.; Cohen, Y.; Vigalok, A. *Org. Letters* **2005**, *7*, 5123. (e) Morohashi, N.; Yokomakura, K.; Hattori, T.; Miyano, S. *Tetrahedron Lett*. **2006**, *47*, 1157. (f) Notestein, J.M.; Iglesia, E.; Katz, A.J. *Am. Chem. Soc*. **2004**, *126*, 16478. (g) Redshaw, C.; Rowan, M.A.; Warford, L.; Homden, D.M.; Arbaoui, A.; Elsegood, M.R.J.; Dale, S.H.; Yamato, T.; Casas, C.P.; Matsui, S.; Matsuura, S. *Chem. Eur. J.* **2007**, *13*, 1090.

[44] Jacobsen, E. N. *Acc. Chem. Res.* **2000**, *33*, 421, (b) Aida, T.; Inoue, S. *Acc. Chem. Res.* **1996**, *29*, 39.

[45] Jeunesse, C.; Armspach, D.; Matt, D. *Chem. Commun.* **2005**, 5603, (b) Steyer, S.; Jeunesse, C.; Armspach, D.; Matt, D.; Harrowfield, J. *Calixarenes 2001*; Asfari, Z., *et al.*, Eds.; Kluwer Academic: Dordrecht, The Netherlands, **2001**; 513.

[46] Lejeune, M.; Jeunesse, C.; Matt, D.; Kyritsakas, N.; Welter, R.; Kintzinger, J. J. *Chem. Soc., Dalton Trans.* **2002**, 1642, (b) Wieser-Jeunesse, C.; Matt, D.; De Cian, A. *Angew. Chem., Int. Ed*. **1998**, *37*, 2861. (c) Wieser, C.; Matt, D.; Fischer, J.; Harriman, A.J. *Chem. Soc., Dalton Trans.* **1997**, 2391.

[47] Engeldinger, E.; Armspach, D.; Matt, D. *Chem. Rev.* **2003**, *103*, 4147, (b) Purse, B.W.; Rebek, J. Jr. *Proc. Nat. Acad. Sci*. **2005**, *102*, 10777.

[48] Le Poul, N.; Campion, M.; Douziech, B.; Rondelez, Y.; Le Clainche, L.; Reinaud, O.; Le Mest, Y. *J. Am. Chem. Soc.* **2007**, *129*, 8801, (b) Darbost, U.; Seneque, O.; Li, Y.; Bertho, G.; Marrot, J.; Rager, M.-N.; Reinaud, O.; Jabin, I. *Chem. Eur. J.* **2007**, *13*, 2078. (c) Izzet, G.; Zeng, X.; Akdas, H.; Marrot, J.; Reinaud, O. *Chem. Commun*. **2007**, 810. (d) Seneque, O.; Rager, M.-N.; Giorgi, M.; Prange, T.; Tomas, A.; Reinaud, O.J. *Am. Chem. Soc*. **2005**, *127*, 14833. (e) Darbost, U.; Rager, M.-N.; Petit, S.; Jabin, I.; Reinaud, O.J. *Am. Chem. Soc*. **2005**, *127*, 8517.

[49] Abidi, R.; Oueslati, I.; Amri, H.; Thuéry, P.; Nierlich, M.; Asfari, Z.; Vicens, J. *Tetrahedron Lett.* **2001**, *42*, 1685, (b) Tuntulani, T.; Thavornyutikarn, P.; Poompradub, S.; Jaiboon, N.; Ruangpornvisuti, V.; Chaichit, N.; Asfari, Z.; Vicens, J. *Tetrahedron* **2002**, *58*, 10277.