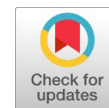


Review of Calixarene-Derivatives in Transition Metal Chemistry



Nasser Thallaj

Abstract: The survey depicts the combination of large-scale monodentate phosphites in response to PCl_3/NEt_3 with *p*-tert-butyl calix[4]-(OH)3-OR, where R contains an oxygen-containing substituent ($R = CH_2P(O)Ph_2$, $-CH_2CO_2Et$, $-CH_2C(O)NEt_2$, $-CH_2CH_2OMe$). These funnel-shaped calixarenes have a phosphorus particle bridging three phenolic oxygen atoms, and are incredibly steady in NaOH-aqueous arrangement due to the cone point being more noteworthy than 180° . Upon response with transition metal particles, these phosphites shape either P monodentate complexes or expansive P,O chelate complexes including the oxygen atom of the R group. The reactivity of four different ligands in the rhodium-catalyzed hydroformylation of octene was examined. The general trend is that a bulkier phosphite ligand leads to a slower reaction rate. The ligand-to-base ratios ranged from 1.4 to 3.6, and the highest straight aldehyde selectivity was observed when the carboxylate group was CH_2CO_2Et .

Keywords: Calixarene, Transition metals, Phosphite, Phosphinite, Hydroformylation, Calix-quinone.

I. INTRODUCTION

Calix[n]arenes are polyphenolic macrocycles composed of n phenolic units connected by methylene bridges.[1] Although these polyphenols have been known since the 1940s, it was not until the pioneering work of American Gutsche at the end of the 1970s that reliable syntheses enabling their preparation in large quantities was developed. Gutsche demonstrated that the most successful way to obtain such a compound was to condense a para-substituted phenol with formaldehyde in the presence of suitable catalytic amounts. The control of several parameters, including the base/phenol ratio and the nature of the base-bound cation, determines the number of aromatic rings forming the calix[n]arene structure [figure 1](#).

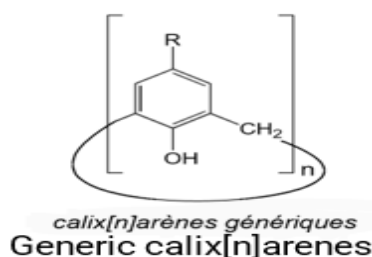


Figure 1

Manuscript received on 05 April 2022 | Revised Manuscript received on 12 April 2022 | Manuscript Accepted on 15 April 2022 | Manuscript published on 30 April 2022.

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Two primary factors were responsible for the remarkable development of macrocyclic compounds: (a) the receptor properties of certain conformers that form complex compounds with multiple substrates; b) the possibility of using calixarenes as scaffolds to anchor a range of merging ligands, allowing the fabrication of highly complex coordination structures. This second aspect has been highlighted in this study, which is specifically devoted to the expedited synthesis of phosphorus-containing cal[4]arene. One of the particular motivations for this research was the utilization of the calix[4]arene framework for the assembly of novel high-footprint P(III) compounds, such as phosphites and phosphines, for use in olefin hydroformylation. The calix[4]arenes possess four unique conformations, including cone, partial cone, 1,2-alternate, and 1,3-alternate. Generally, calix[4]arenes in the cone conformation can form inclusion complexes. It should be noted that most cone conformations demonstrate an energetic behavior in structure, characterized by a fast facilitated vibration of the aromatic rings around the equilibrium position. As a result, when two cores approach the calixarene center, the other two move away from it. [figure 2](#)

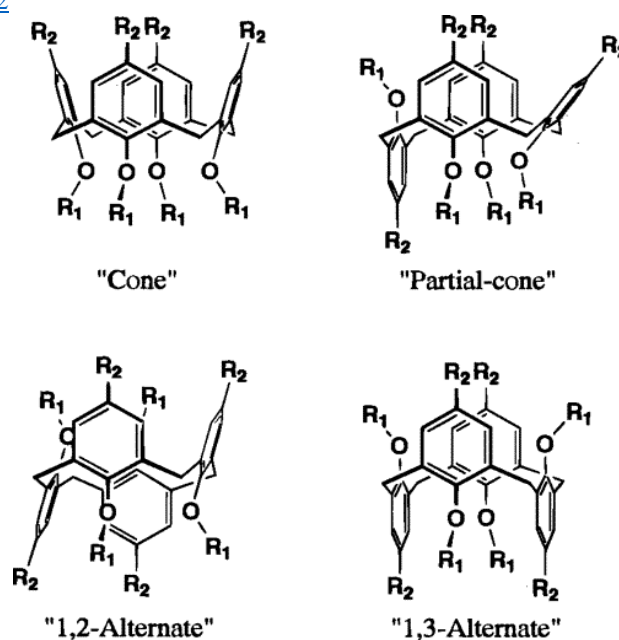


Figure 2

The chemist typically uses observational rules based on the chemical shifts of the carbon atoms in the CH₂ bridging groups to distinguish between different conformations. Thus, for a CH₂ bridge between two aromatic rings arranged in the same direction (syn), the displacement of ¹³C is between roughly 29 and 33 ppm.



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In contrast, when the relative orientation is anti, the chemical shift of HC2 is greater than 37 ppm. The difference, $\Delta\delta$, between the chemical shifts of the axial hydrogen H and the equatorial H of the same CH₂ group also provides helpful

information. Generally, for two syn-oriented aromatics, $\Delta\delta$ is greater than 0.7 ppm, while for anti-oriented aromatics, $\Delta\delta$ is less than 0.6 ppm. [figure 3](#)

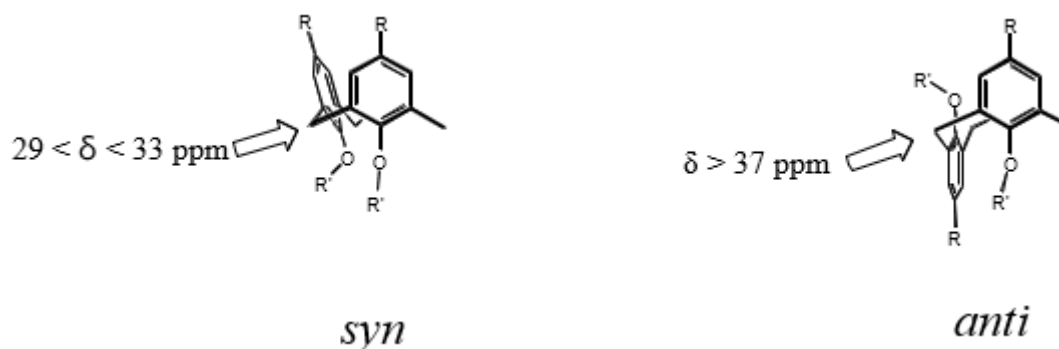


Figure 3

We remind the reader of a simplified scheme of olefin hydroformylation with monodentate phosphines. [figure 4](#)

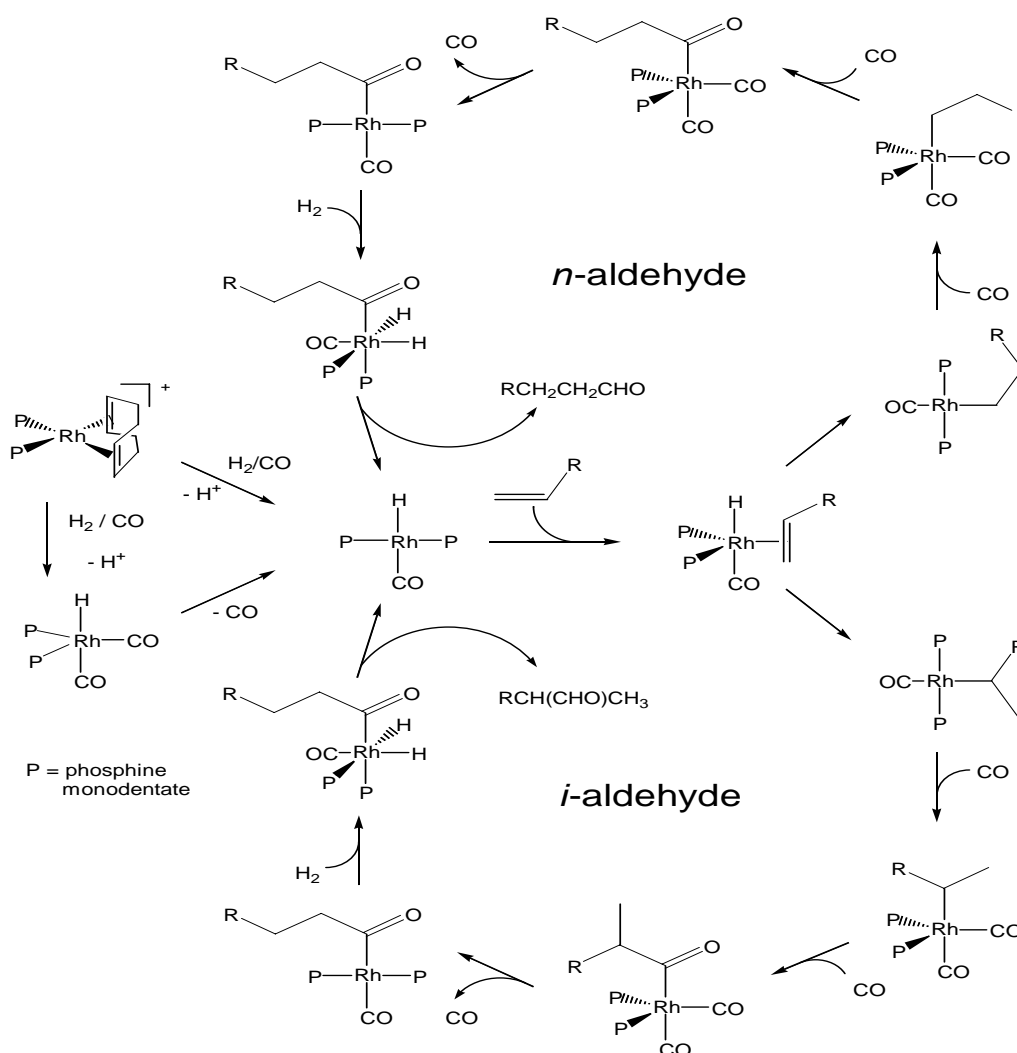


Figure 4: Simplified scheme of olefin hydroformylation

Calixarenes [1] provide unique platforms not only for the assembly of specific polydentate monotopic ligands for transition metal complexes, but also for polytopic ligands capable of supporting multiple distinct metal ions in close proximity. Such homo- or heteropolymetallic architectures provide important opportunities for exploring reactions based on metal-metal interactions or metal migration within the framework. Subsequent research has focused on the use of calixarenes in homogeneous catalysis, and cone-shaped calixarenes have been found to be ideal for the production of novel chelating ligands with unusual bite angles, an essential attribute for selectivity in catalysis. Utilizing the calixarene scaffold to host a catalytic center is another promising application. These metal cavitators offer the ability to select substrates based on their size and may act as shape-selective catalysts. These concepts are discussed in more depth in the article "Calixarenes 2001". [2] Other potential applications of catalysis involve the use of chiral chelators derived from chiral calixarenes. [3] A previously established application is the use of calixarenes as analogs of oxide catalyst surfaces. Applications of functionalized calixarene transition metal complexes in fields other than catalysis are also discussed elsewhere. [2] The basis for the content of this chapter has been outlined in a previous review. [4]

II. COMPLEXES WITH O-BOUND METALS DERIVED FROM P-RCALIX[N]ARENES

2.1 Complexes having the metal centre bound to phenolic oxygen atoms

The synthesis of p-tert-butyl calix[4]arene tetraanions has enabled remarkable chemistry, such as the stepwise reduction of dinitrogen to the [5,6]-niobium nitride complex. This is evidenced by treatments of $[\text{Mo}(\text{NAr})(\text{CHCMe}_2\text{Ph})(\text{O}_3\text{SCF}_3)_2(\text{dme})]$ and $[\text{Cr}(\text{NBut})_2(\text{OBut})_2]$ with p-But-calix[4]-(OK)₄ in tetrahydrofuran - resulting in the formation of dimeric complex $[\text{Mo}(\text{NAr})(\text{L})(\text{K})_2(\text{NCMe})_3\text{O}]_2$ and complex 2 respectively. In both cases, two oxygen atoms were present, likely originating from the solvent, which produced a ladder pattern in the complex structures. Furthermore, the calixarene units displayed remarkable affinity towards lithium and potassium ions, capturing them through π -bonding with two phenoxy rings. The reaction of $[\text{Cr}(\text{NBut})_2(\text{OBut})_2]$ with p-but-calix[4]arene yielded complex 2, in which two calixarenes that have been oxidatively bound to the chromium atom are present. Additionally, a calixarene unit is capable of binding to lithium ions [figure 5. \[7\]](#)

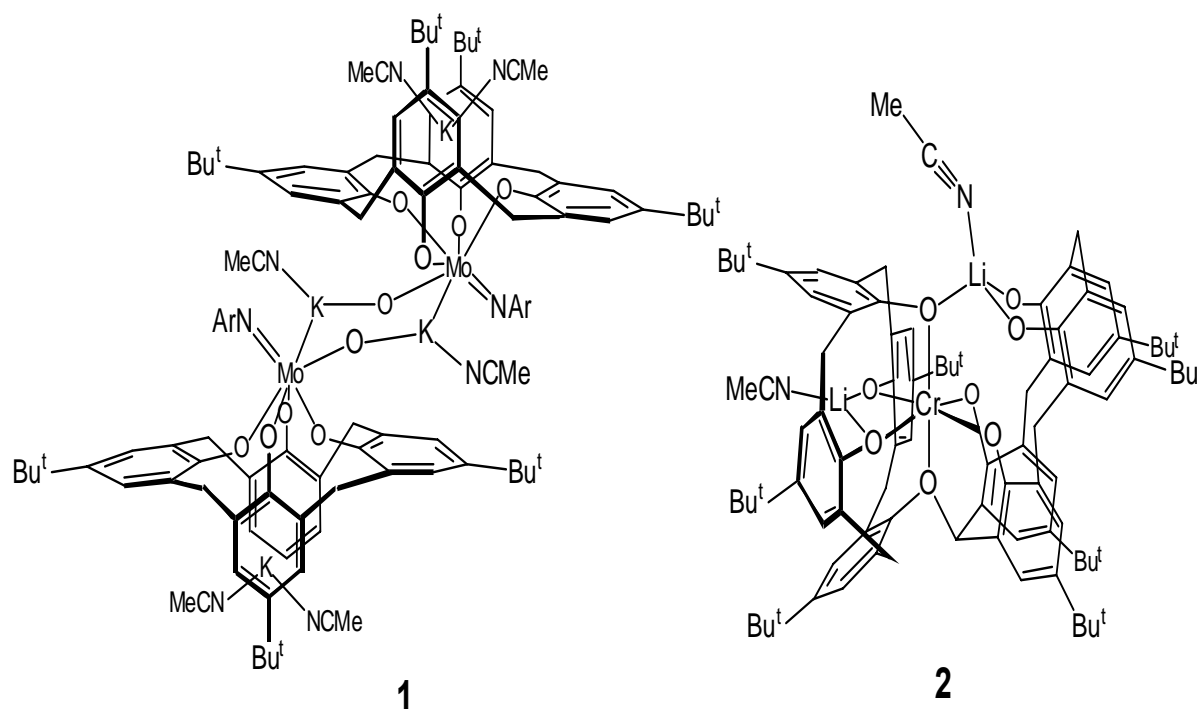
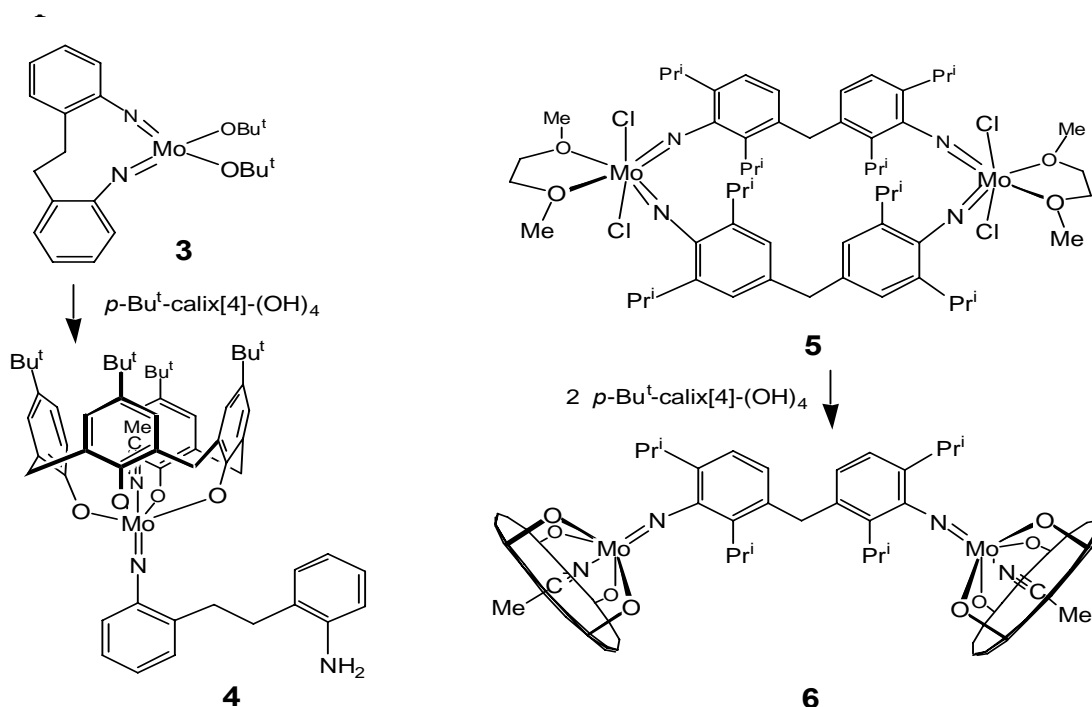


Figure 5

The diimido complex 3 underwent a ring-opening reaction when exposed to p-But-calix[4]-(OH)₄, resulting in deprotonation of the four phenolic units to yield imido complex 4 (Scheme 1) [8]. Similarly, using a bridging diimide caused the same reaction in the dinuclear complex 6.



Scheme 1.

The reaction of *p*-But-calix[4]-(OH)₄ with the mixed imido/amino complexes [M(NBu)₂(NHBut)₂] (M = Cobalt, Tungsten) yielded calissarenes 7 and 8,[9] while its reaction with [M(NMes)₂Cl₂(dme)] (Mes = 2,4,6-Me₃-C₆H₂) gave rise to the respective calissarenes 9 and 10. The calissarenes 7-10 were observed to contain particles such as CH₃CN, CNBu^t, or H₂O. Coordination of acetonitrile was found to cause an upshift of the methyl flag by approximately 2 ppm, which is indicative of its shielding effect. Notable upfield shifts were also observed in the case of CNBu^t upon coordination [figure 6](#).

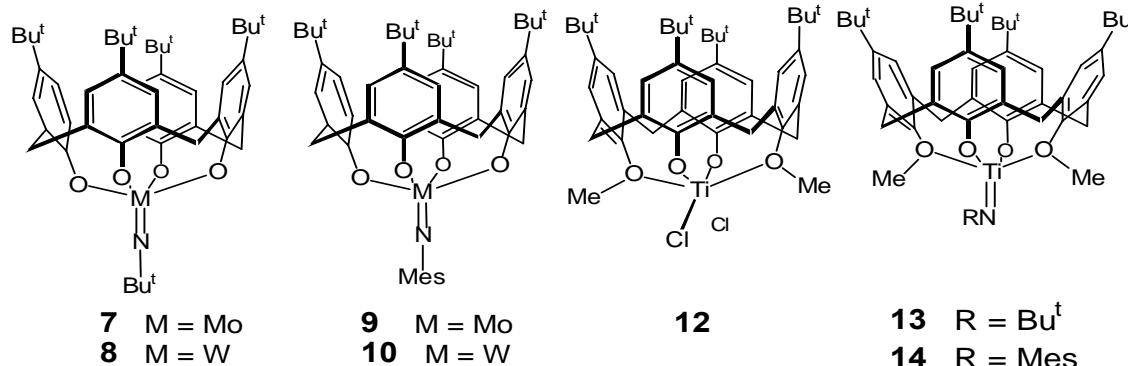


Figure 6

The reaction of 12, a *p*-Sed-calyx[4](OMe)₂(OH)₂, with TiCl₄(THF)₂, two equivalents of LiNHBut or LiNHMes (Mes = 2,4,6 trimethylphenyl) yield mononuclear titaniumimide complexes stabilized by the *p*-Sed-calyx[4](OMe)₂(O)₂-dianion[10]. The Ti center of 14 has a distorted trigonal bipyramidal geometry, with ether oxygen atoms in the apical positions, two phenoxide oxygen atoms and an imide nitrogen atom in the equatorial plane. A reaction of TiCl₄ with 1,2-substituted calissarene 15 results in the formation of a 1,2-TiCl₂-bridged complex 16, with one Ti center bound to two oxygen atoms of the calissarene.[11] At 80 °C in C₆D₆, with an abundance of sodium present, the shape of 16 catalyzes the cyclotrimerization of terminal acetylenes to the 1,2,4-trisubstituted benzenes at great yields with regioselectivity of 95% or higher. Alkylation of 16 with MgR₂ (R = Me; CH₂Ph) created complexes 17 and 18, of which the first one quickly disintegrated.[12] The use of [Ph₃C][B{3,5-(CF₃)₂C₆H₃}₄] in the presence of CH₃CN led to the formation of cationic complexes 19 and 20, which are relatively stable in solution. Further, the application of [Ph₃C]CF₃SO₃ to remove the chloride ions, gave rise to the formation of compounds 21 and 22. Upon reaction of 22 with Na[B{3,5-(CF₃)₂C₆H₃}₄] in the presence of CH₃CN, complex 20 was observed whereas decomposition was observed with 21 [figure 7](#).

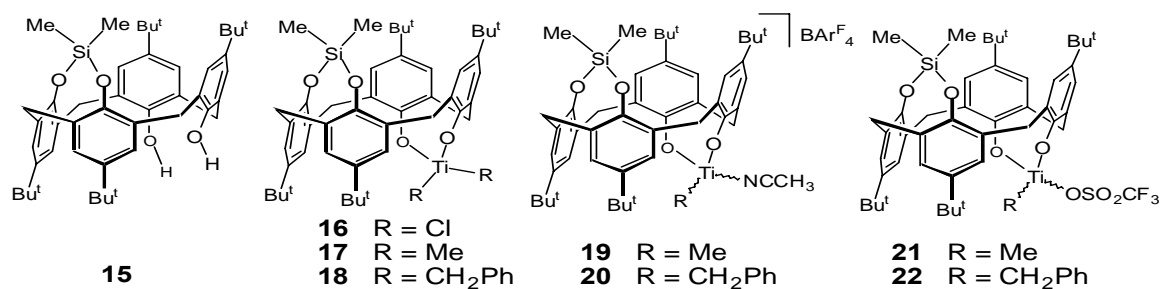
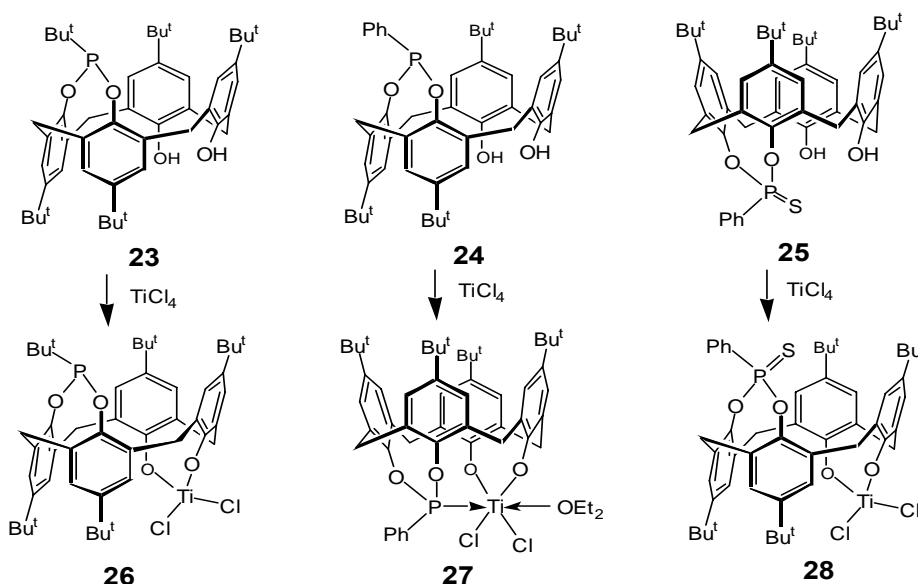


Figure 7

Mono-Ti calixarene complexes with metal bridging at adjacent positions have been synthesized by the reaction of TiCl₄ with 23, 24, and 25 (Scheme 2) to give 26-28. [12] In 26, the 1,2-alternate structure is maintained, whereas the structure of 27 involves a conformational change. The [13]P NMR of 27 reveals that the phosphorus lone pair is interacting with the Ti center. Complex 28 exists in solution as an equilibrium mixture of cone and 1,2-alternate conformers. Within the temperature range 298-348 K, the equilibrium is in favor of the 1,2-alternate isomer. When methylaluminoxane was used as the activator, complexes 16–22 and 23–28 exhibited moderate ethylene polymerization activity.



Scheme 2.

The abundance response of TiCl₄ with p-Sed-calix[4]-(OH)₄ yields a dimeric complex, [Ti₂(μ₃-O)Cl₂(p-Sed-calix[4]-O₄)₂] 29, which is centrosymmetric and consists of four TiIV atoms and two triply bridging O atoms forming a planar stepping stool structure analogous to the calix[6]arene-Ti complex [14] figure 8.

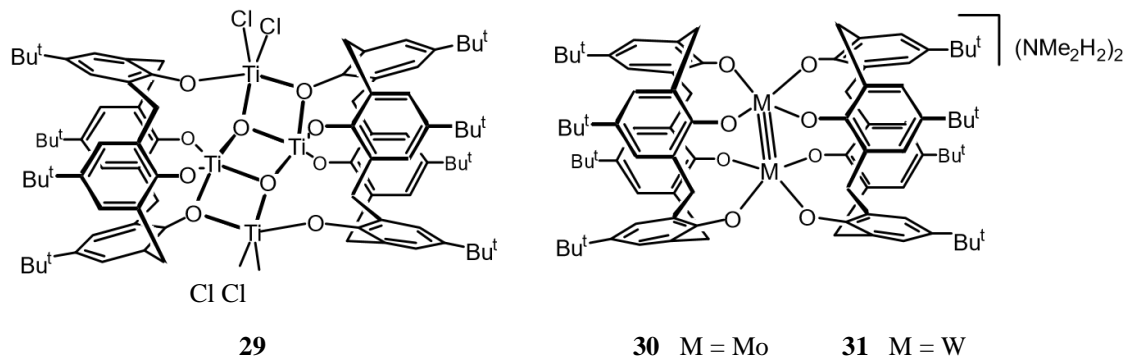
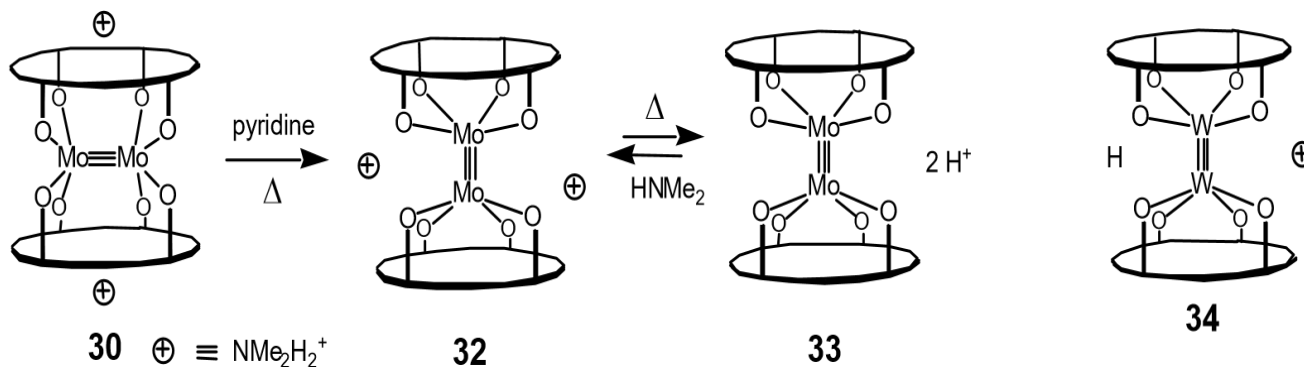


Figure 8

The reaction of p-Sed-calix[4]-(OH)₄ with [M₂(NMe₂)₆] (M = Mn, W) hydrocarbon solvents yielded dianionic complexes 30 and 31, with metal-metal interactions being reinforced by two bridging calixarenes which function as tetraanionic species. [15, 16] Calixarenes usually have a cone-like structure and a metal-metal bond, comparable to triple bonds. Reaction of 30 with

hot pyridine gave complex 32 (Figure 3), with both calixarene units coordinating the pyridine molecule.[17] This reaction involves a significant conformational change, as each calixarene in this complex acts as a terminal ligand. The hydrogen-bonding of an oxygen atom present in each calixarene ligand to an H_2NMe_2 cation was observed when the pyridine solvate was heated under a vacuum for 3 days, which yielded complex 33. This complex was also obtained by coordination of p-But-calyx[4]-(OH) with $[\text{Mo}(\text{O}i\text{Bu})_6]$. Analogous reactions were seen in tungsten complexes 32 and 33, which reacted in benzene to form complex 34, characterized by a metal-metal bond between the H_2NMe_2 cation and the phenolic oxygen atom, as well as a proton bound to two other oxygen atoms. Layered structures akin to complexes 29-34 were observed in p-But-tetrathiacalixarene complexes with transition metals.[18]



Scheme 3.

The formation of multimetallic complexes through the phenolic oxygen atoms of calix[4]resorcinarenes was observed upon reaction of $[\text{MoTp}(\text{NO})\text{I}_2]$ (Tp = hydrotris(pyrazol-1-yl)borate) with tetrahexylcalix[4]resorcinarene 35 (resH4). This reaction yielded a mixture of metal macrocycles, which could be isolated as $[\{\text{MoTp}(\text{NO})\}_2(\text{resH}_4)]$ 36, $[\{\text{MoTp}(\text{NO})\}_3(\text{resH}_2)]$ 37, and $[\{\text{MoTp}(\text{NO})\}_4(\text{res})]$ 38 [figure 9].[19]

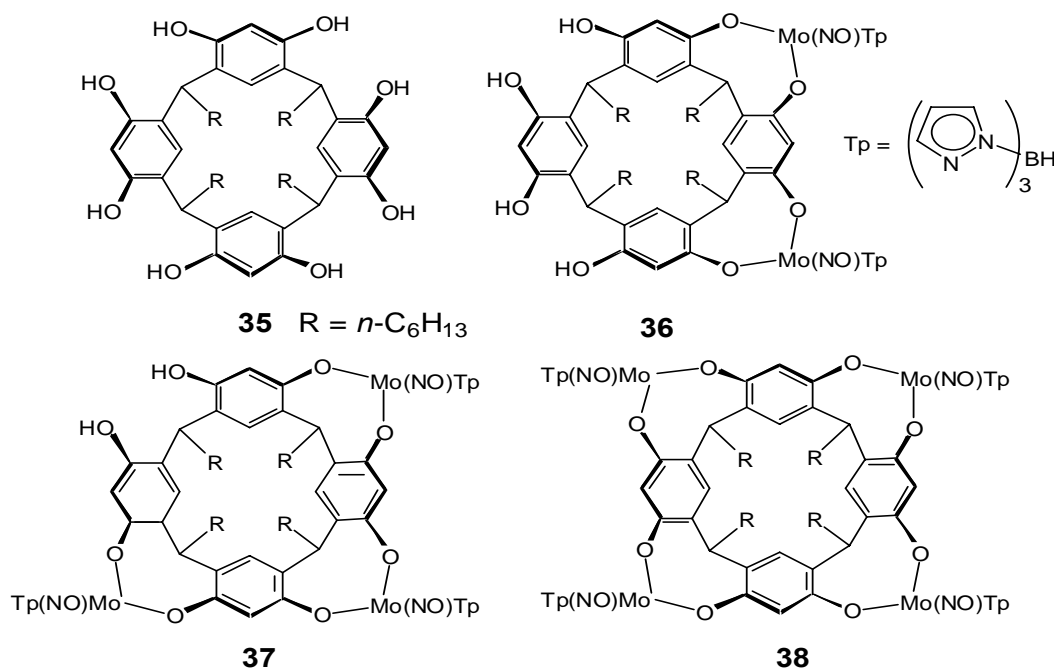


Figure 9

2.2 Complexes having a metal centre bound to oxygen or sulfur atoms belonging to pendent functional groups

A metal receptor with the ability to bind a metal at its entrance is the upper edge functionalized calix[4]arene 39. Upon reaction with $[\text{Pd}(\text{MeCN})_4](\text{BF}_4)_2$, the palladium complex 40 is formed. Analysis of the ^1H NMR spectrum indicates that the methyl group is located within the palladium depth. When the acetonitrile atom is replaced with 4-phenylpyridine, complex 41 is generated. The binding of the β -aryl ring into the receptor is further evidenced by the upshift of the p-H and m-H protons at 3.90 and 2.78 ppm, respectively.[20]

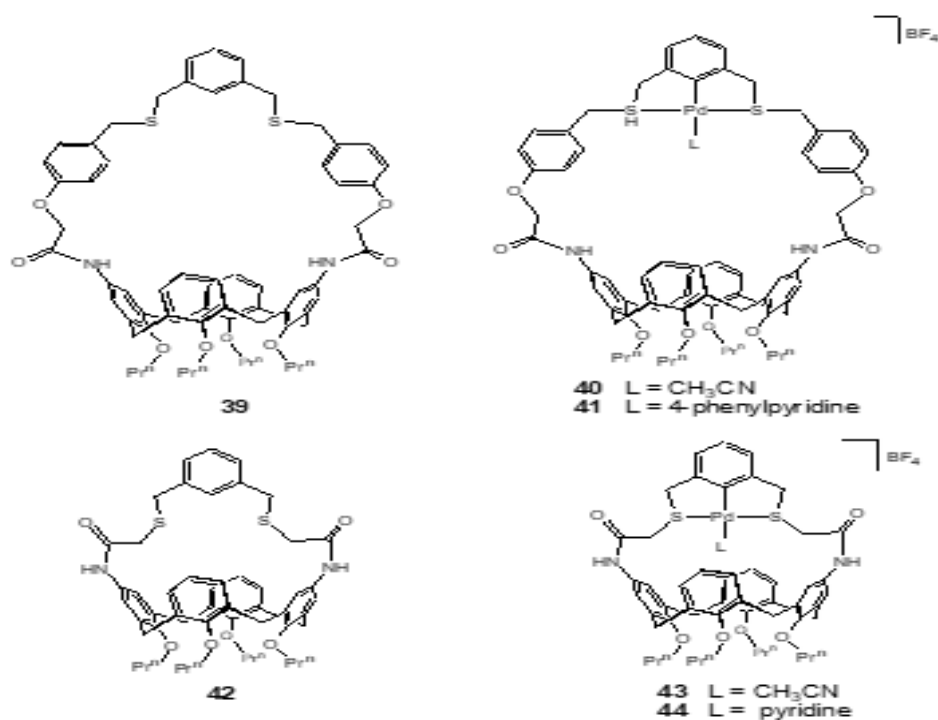


Figure 10

The obtained compound 43 was quickly derived from calixarene 42 containing a shorter dithio head. The activated acetonitrile was efficiently removed by pyridine to yield compound 44. NMR spectroscopy revealed an altered structure (the two m-H of the phenoxy rings bearing the amide groups are unequal), possibly since the pyridine is too large to fit into the receptor cavity and thus lies outside. The asymmetry disappears with increasing temperature, suggesting a dynamic process where pyridine likely moves across the cavity from one side "out of the cavity" to the opposite side. The selectivity of Complex 40 towards 4-phenylpyridine and 3-phenylpyridine has been found to be notable due to its conformational compatibility with the receptor figure 10. [21,22] Calixarenes with oxygen-containing pendant groups have been extensively used in solvent extraction. The coordination properties of such units have been extensively studied. Consequently, the copper (II) particle within the tetraamide complex 45 was found to be located in the O8 environment. The X-ray study indicated that the particle had fourfold symmetry in the solid state, with the copper being closer to the four carbonyl oxygen atoms (Cu...O 1.926 (6) Å) as opposed to the ether oxygen atoms (2.963 (6) Å). In complex 46, the press particle is linked to six oxygen molecules, with the shortest bond being with the O molecules of phenol (Fe...O 1.802(8) and 1.830(7) Å) followed by the bond with the oxygen particle of the carbonyl oxygen (2.058(7) and 2.031(7) Å), and the longest being to the oxygen atoms of the ether (2.230(7) and 2.312(7) Å) figure 11. [23]

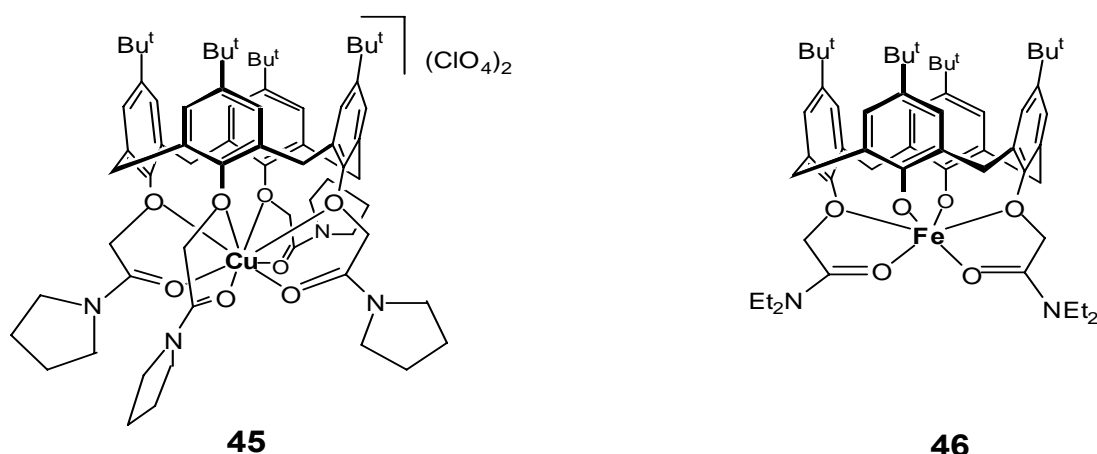


Figure 11

III. CALIXARENE COMPLEXES WITH METALS BOUND TO N DONOR ATOMS

3.1 Attempts to prepare metallo-enzyme models

Metallocalixarene 47, featuring two distal Zn(II) centres connected by bis(aminomethyl)pyridyl ligands, is the first example of a dinuclear complex with both strong binding to a phosphate diester substrate and high catalytic hydrolysis activity.[24] This results in a 23,000-fold increase in the rate of catalytic cyclisation of the model RNA substrate 2-(hydroxypropyl)-p-nitrophenylphosphate 48 when the presence of 47 is present.

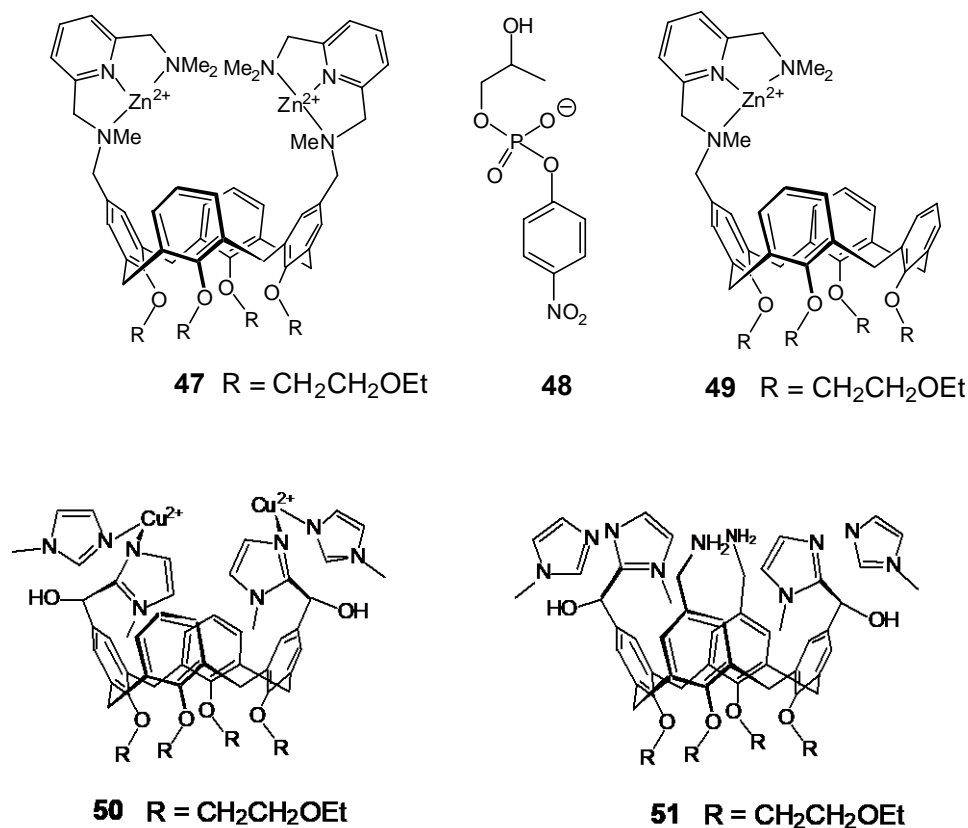
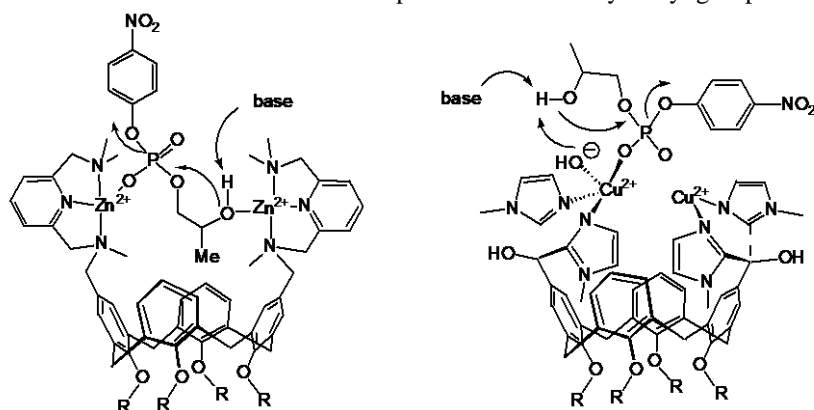


Figure 12

This would enable the monozinc complex 47 to accomplish a higher activity than the monozinc complex 49, since it may require the nearness of two zinc particles to create the best condition for the deprotonation of the hydroxyl bunch. Comparative studies between the monozinc complex 49, which has a much lower activity than monozinc complex 47, suggest that the two zinc centers in 47 may work synergistically [figure 12](#)

. It is conceivable that one of the Zn atoms functions as a Lewis acid catalyst to activate the P-O bond, while the other activates the hydroxyl group, aiding its deprotonation (Plot 4). This could explain the higher activity of monozinc complex 47, as two zinc atoms are required to create the best conditions for the deprotonation of the hydroxyl group.



Scheme 4.

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Comparative studies with the monozinc complex 49 (which has approximately 50-fold lower activity) suggest that the two Zn centers in 47 act synergistically. It is proposed that one Zn ion functions as a Lewis acid activator of the P-O bond, while the other activates the hydroxyl group, facilitating its deprotonation (Figure 4). Subsequent to this work, another dinuclear complex was designed, namely the Ku(II) complex 50 in which the metal ions are complexed with a bis(methylimidazolyl) chelator.[25] The use of this complex to transesterify 48 results in a rate of 10^4 , which is lower than that of the Zn(II) complex 47. The mechanism of catalysis of copper complex 50 differs from that of zinc complex 47. In this case, both Cu(II) ions activate the phosphate simultaneously, as depicted in Figure 4, while the hydroxyl group bound to one copper molecule facilitates the activation of the adjacent β -hydroxyl group (bifunctional catalysis).[26] Significant trinuclear involvement has been observed with 52-mimicking phosphodiesterases (which cleave RNA dinucleotides 53a).[27] The accelerated rate compared to the uncatalyzed response is around 104-105 and remarkable differences in rates were observed for various nucleobases of the dinucleotides: GpG>>UpU>>ApA. The trinuclear complex is 10, 19, and 160 times more active than the binuclear complex 47 when cleaving CpC, UpU, and GpG, respectively. The increased activity is likely due to the favourable substrate binding and catalytic contribution of all three Zn(II) ions. [figure 13](#)

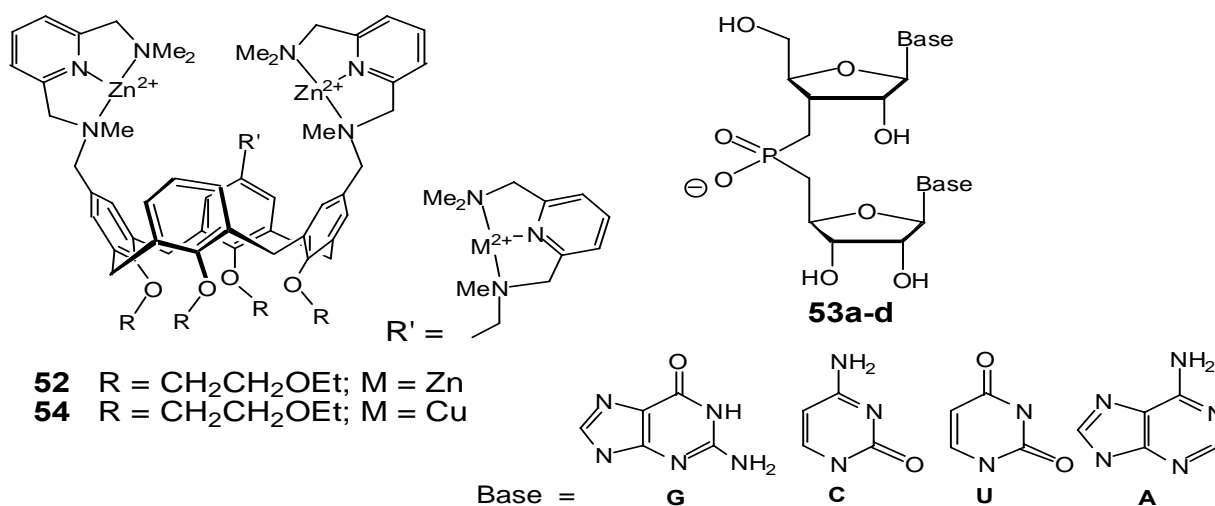
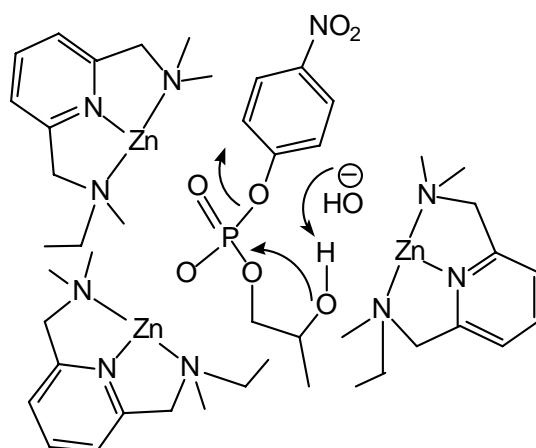


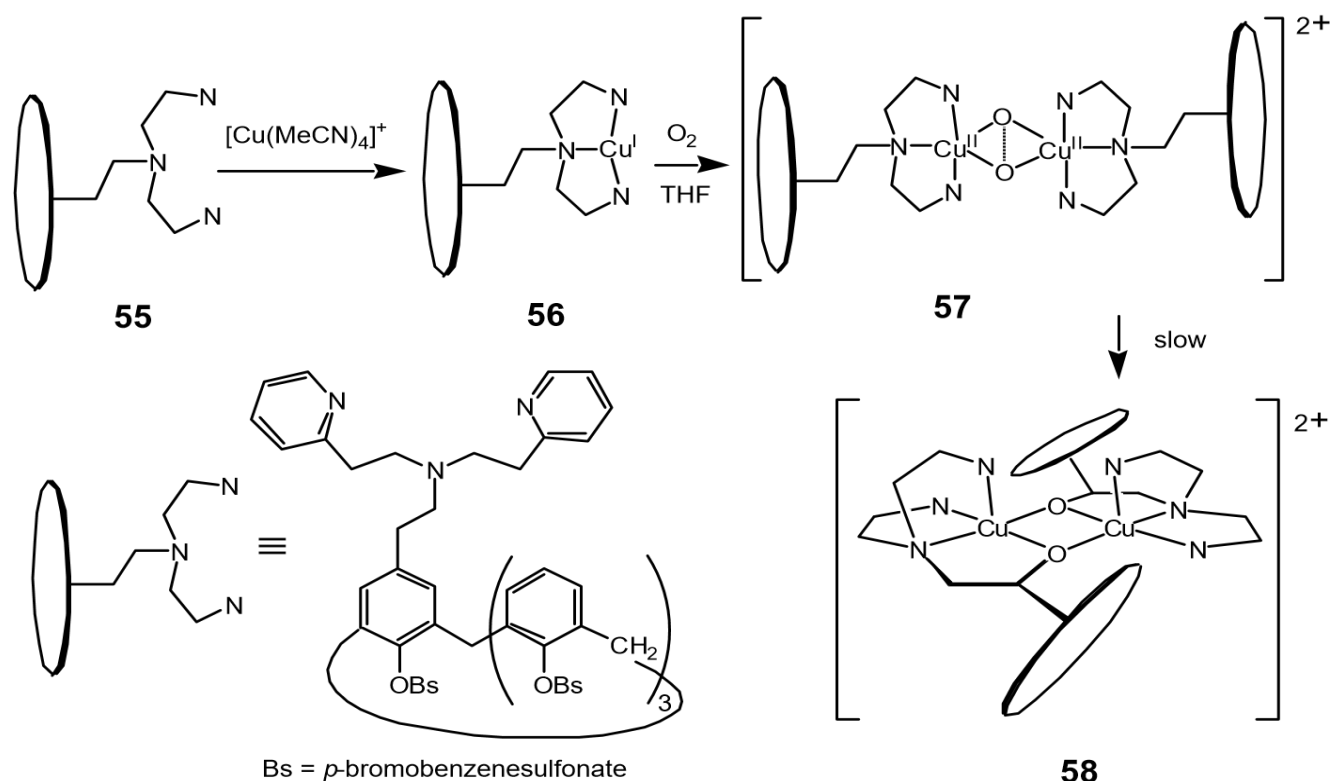
Figure 13

The heterotrinnuclear metallophosphoesterase 54 was found to be more dynamic than previously thought. The catalytic cleavage of substrate 48 by the trinuclear complex was similarly investigated. Under conditions similar to the transesterification of compound 48 to 47, the enzyme 52 exhibited a rapid increase of the reaction rate to 32,000.[28] The proposed structure involves two Zn centres that activate the phosphoryl group, while the third activates the β -hydroxyl group (Scheme 5).



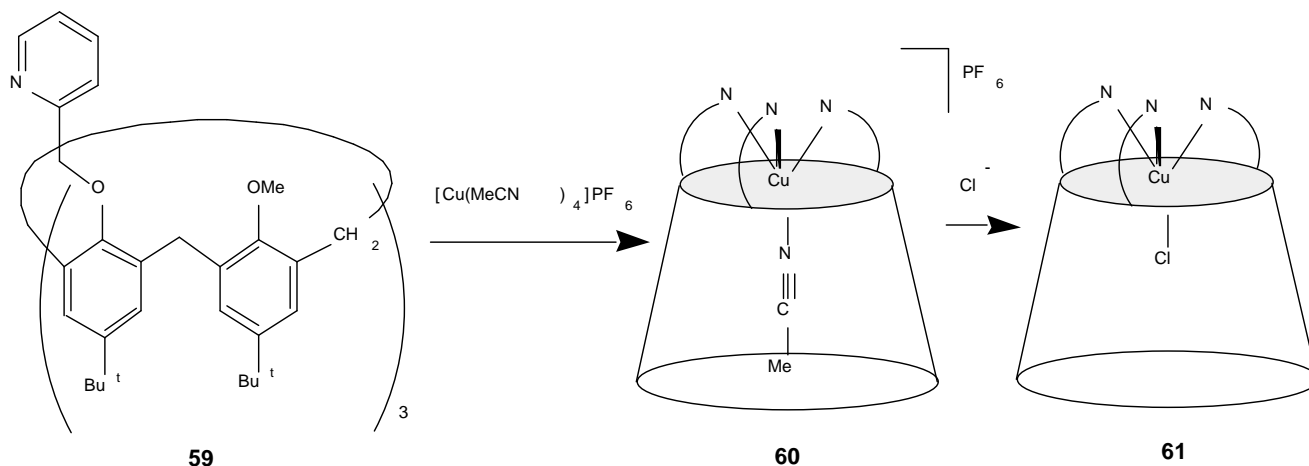
Scheme 5. Possible mechanism for the cleavage of 48 by 52

Receptors such as amino-dipyridyl calixarene 55 have been utilized in the development of dinuclear oxidation catalysts [29]. Combination of 55 with [Cu(CH₃CN)₄] resulted in 56, which reacted with oxygen to create complex 57 with the expected structure (Scheme 6). 57 eventually converts to 58, which relates to the oxidation of the benzyl carbon of the branches that connect the N3 ligands and the calixarene unit.



Scheme 6.

The calix[6]arene scaffold was used to generate a Cu(I) complex in the monometallic protein display 60 (Figure 7).[30] The metal center is attached to three pyridine units of ligand 59, with the fourth ligand being an acetonitrile molecule situated within the cavity. Exchange of the acetonitrile can effectively be interchanged with other aliphatic nitriles. Replacement with chloride dianion yielded complex 61.[31,32] In solution, it exists as two distinct helical enantiomers. As revealed by NMR spectroscopy in the presence of a chiral shift reagent, chirality is imparted to the calixarene framework at low temperature, creating a chiral environment around one coordination site.



Scheme 7.

3.2 Complexes formed from resorcinarenes containing pendant nitrogen ligands

The tetragonal planar cations of the $[M(dppp)]$ type ($M = Pd, Pt$; $dppp = Ph_2P(CH_2)_3PPh_2$) can be used to form capsules of suitably functionalized calixarenes. Reaction of tetrafunctionalized resorcinarenes 62 and 63 with $[Pd(dppp)](CF_3SO_3)_2$ (stoichiometry 2L:4M) and $[Pt(dppp)](CF_3SO_3)_2$, respectively, yielded cage compounds 64 and 66. Nuclear magnetic resonance spectroscopy revealed the capsules possess D_{4h} symmetry and the highest peaks observed in the electrospray ionization-mass spectrometry range correspond to $[M-2 CF_3SO_3]$ cations. The presence of the CF_3SO_3 anion inside the capsule was suggested from the ^{19}F nuclear magnetic resonance range ($\delta = -81.5$ ppm for 64 versus -78.2 ppm for external anions) and confirmed by X-ray crystallography [figure 14](#).

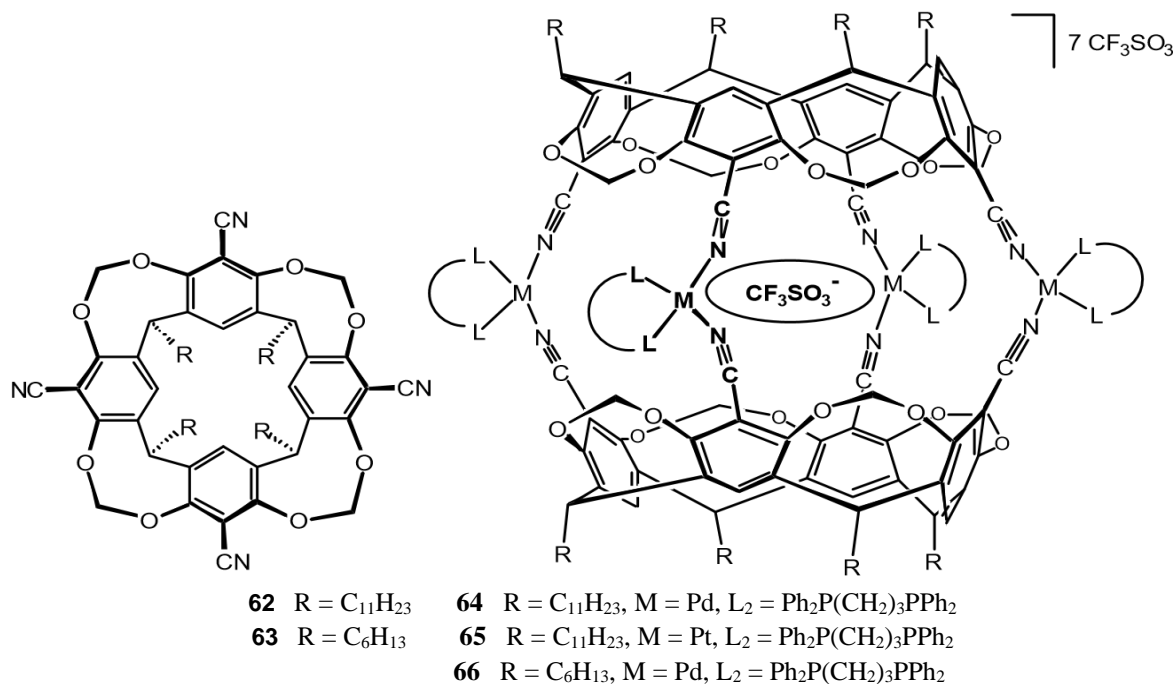


Figure 14

The paramagnetic Fe(II) cage complex **67** was formed as a result of the reaction between an iminodiacetic acid-functionalized resorcinarene precursor and FeCl₂ in an aqueous medium of pH 5. [33,34] X-ray crystallographic analysis revealed that the iminodiacetate ligands are arranged in an N,N-cis orientation; N,N trans coordination would not lead to the formation of a cage structure. When **67** forms in water, it contains six water molecules in its cavity. The addition of bromobenzene to the reaction mixture yielded the inclusion of that molecule within the capsule. NMR studies have indicated that the cavity is capable of forming host-guest complexes with molecules that do not contain metal-binding groups, such as pentane, cyclohexane, benzene, and fluorobenzene [figure 15](#).

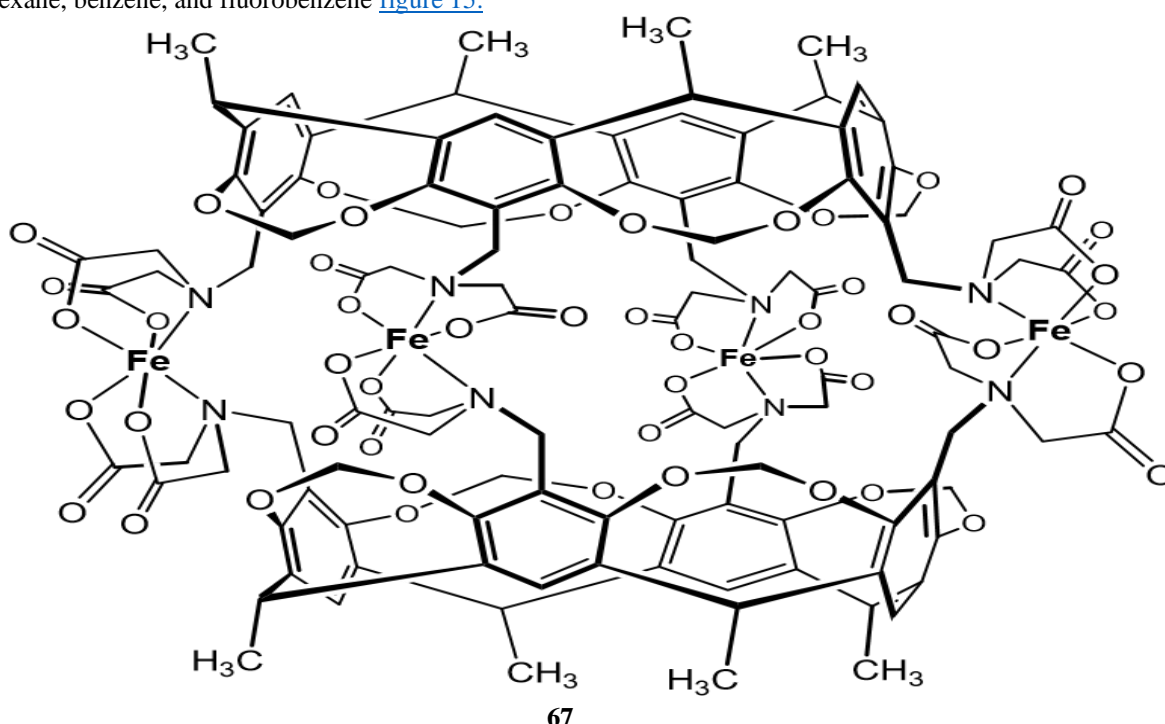
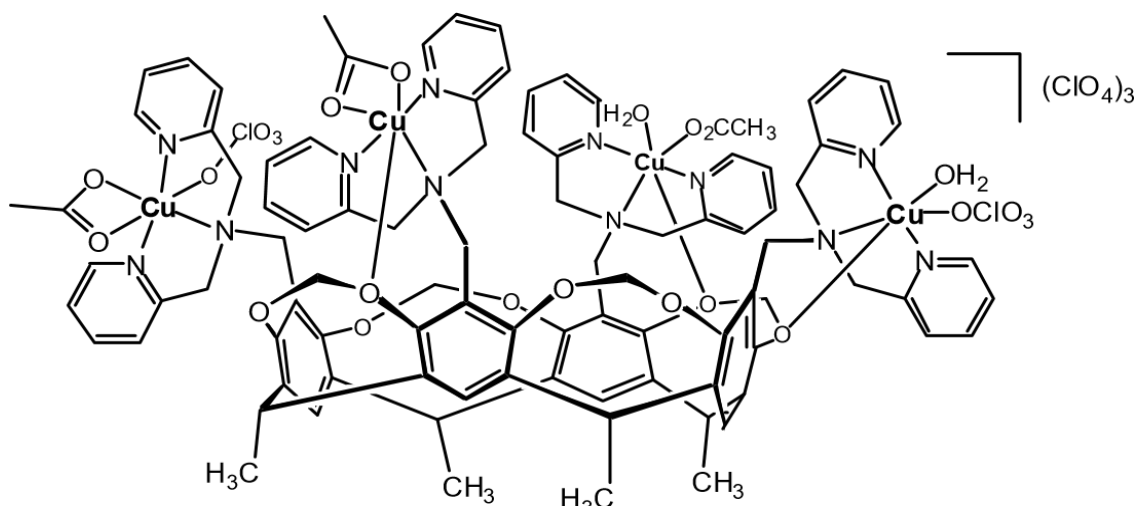


Figure 15

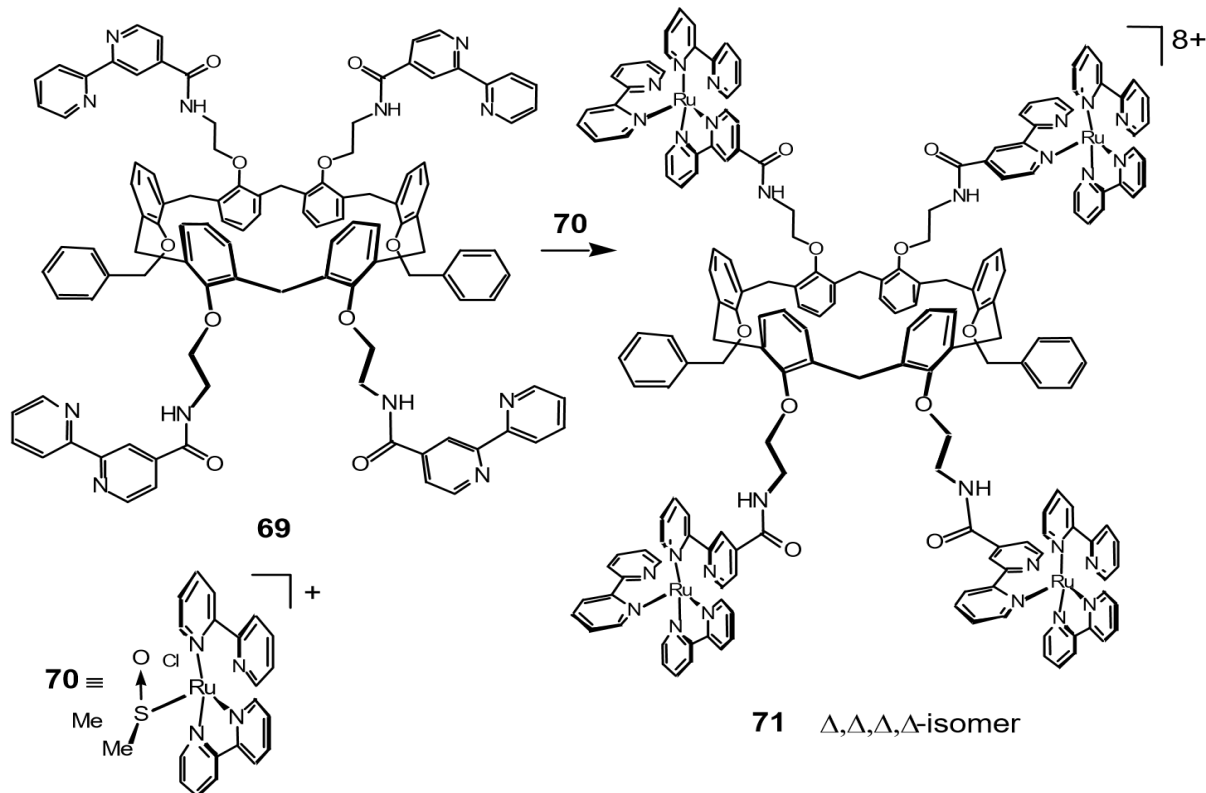
The tetranuclear complex **68** was synthesized by combining the [Cu₄(resorcinarene)(CH₃CO₂)₃(ClO₄)₂(H₂O)₂](ClO₄)₃ in 74% yield [31-35]. This complex is composed of four separate Cu centers, all of which are surrounded by a southern N₃ environment. The Cu centers operate as magnetically autonomous units [figure 16](#).



68
Figure 16

3.3 Other complexes obtained from calix[n]arenes substituted by nitrogen-containing ligands

Over the past decade, there has been an increasing interest in the use of calixarenes for the fabrication of electrochemiluminescent or electrochemical sensors for detecting anions or cations. To prevent the development of intricate mixtures of isomers, the tetra-Ru complex 71 was synthesized by the reaction of the tetrapyridine precursor 69 with the pure precursor $\text{cis-}\Delta\text{-[Ru(bpy)}_2\text{(DMSO)Cl]PF}_6$ 70 (98.6 %). It was not possible to determine the exact yield of the product $\Delta,\Delta,\Delta,\Delta$, however, it was approximated to be around 90 %, based on CD spectroscopy and HPLC (Scheme 8). The reaction of the cone conformer of the homooxalix[3]arene-derived trispyridine compound 72 [34,35,36] with $[\text{Pd}(\text{dppp})](\text{CF}_3\text{SO}_3)_2$ gave complex 73 in a high yield when the 2calix:3Pd stoichiometry was precisely utilized. The Nuclear Magnetic Resonance (NMR) spectra, which demonstrate the symmetrical D_{3h} structure, indicate that the phenyl units are more planar than in the original compound. Osmometry was used to infer the formation of the $[\text{Pd}_3(\text{calix})_2](\text{CF}_3\text{SO}_3)_6$ compound. Mass spectrometry studies demonstrate that the cage is capable of holding two CD_2Cl_2 molecules. [37]



Scheme 8.

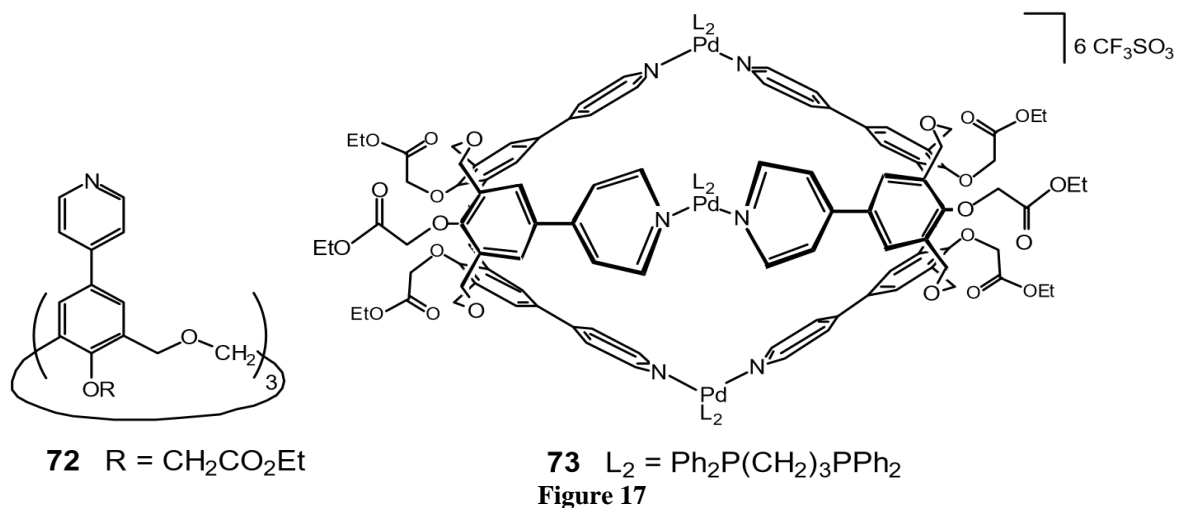


Figure 17

The slow diffusion of a tetranitrile solution in AgAsF₆ solution enabled the assembly of a functionalized 1,2-substituted calixarene, resulting in a complex whose polymeric solid structure was identified by X-ray diffraction [figure 17](#). The structure consists of stacked calixarene units connected by tetrahedral silver ions with two pairs of nitrile ligands (C-N-Ag 144°) [figure 18](#).[\[38\]](#)

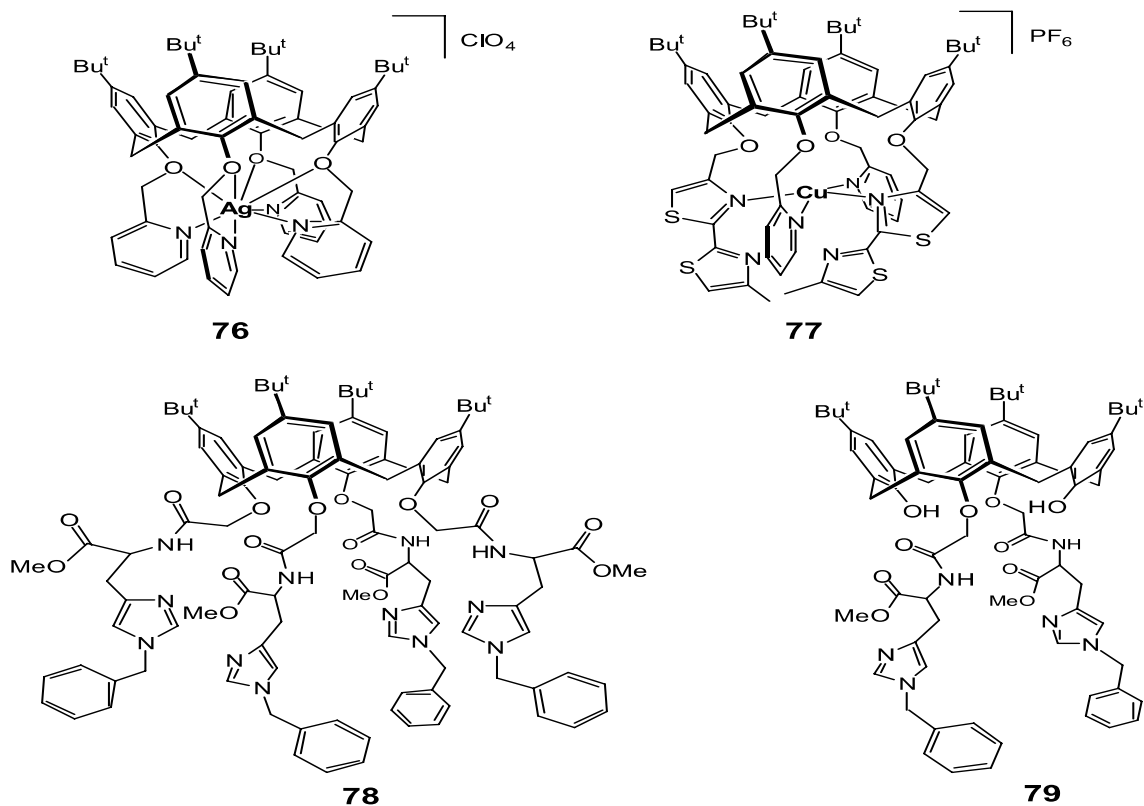
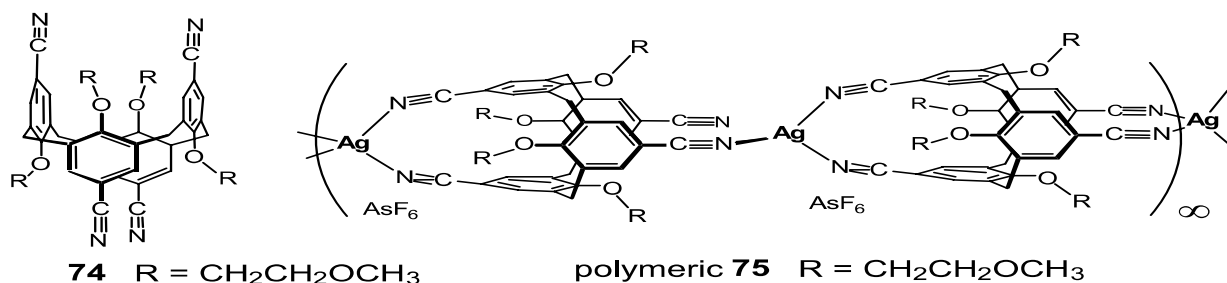


Figure 18

The Ag(I) cation is found in an N4O4 environment within complex 76, which has a highly symmetric cone structure, leading to the confinement of the acetonitrile molecule in a hydrophobic pocket. The silver ion is situated in the center of the square antiprism (Ag...O: 2.923 (3); Ag...N: 2.483 (5) Å). Cu(I) is encapsulated by a hybrid bis(pyridine)-bis(thiazole)calix[4]arene complex 77, as suggested by ¹⁵N NMR spectroscopy. [39] Studies of two histidyl pollands 78 and 79 also showed that they could bind one (paramagnetic) CoCl₂ unit; however, the exact structure of the resulting complexes could not be determined due to the lack of crystals suitable for X-ray diffraction analysis.[40]

IV. CALIXARENE COMPLEXES OBTAINED FROM PHOSPHORUS LIGANDS

4.1. Complexes from calixarenes with phosphorus atoms tethered to the lower rim

The reaction of monophosphinite 80 with [MCl₂(PhCN)₂] (M = Pd, Pt) yielded isomorphous MCl₂L₂ complexes 82 and 83.[41] This selectivity in the formation of trans compounds is likely due to the size of the ligands. In the solid state, the phosphine groups are situated in such a way that minimizes steric disorder in the calixarene units while the two calixarene moieties adopt a distinct spatial matrix. Each phosphinate aryl ring is pushed towards the center of the cavity, with the C...C separation between the p-carbon atoms of the phenol ring and the phosphinate atom being 4.64 Å. Diphosphinide 81 reacted with [PtCl₂(PhCN)₂] gave off a poorly soluble oligomeric material. This is congruous with the formation of tetrameric structures previously observed for soluble forms of 81 [figure 19](#).[42]

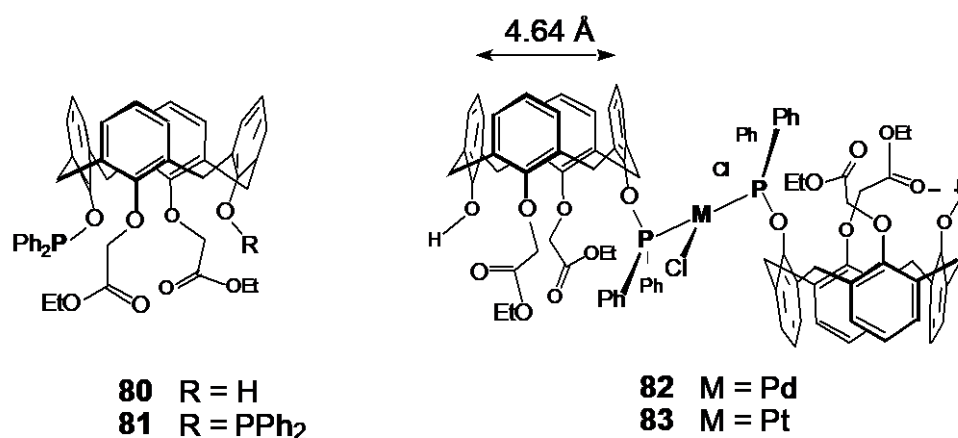


figure 19

The formation of chelate complexes involving proximal phosphinides by ligands 84 and 85 has been demonstrated. [43] Reaction of the corresponding [MCl₂(COD)] precursors (M = Pd, Pt, COD = cycloocta1,5-diene) with 84 yielded homometallic complexes 86 and 87 in high yield. Additionally, dirhodium complex 88 was obtained from [Rh(CO)2Cl]₂; however, the precise relative stereochemistry of the two metal centers is unknown. Analyses of these metallocrocyclic units revealed a downfield shift for the endo-ArCH proton, a result that is similar to what was observed for slightly larger metal macrocycles [figure 20](#). [44]

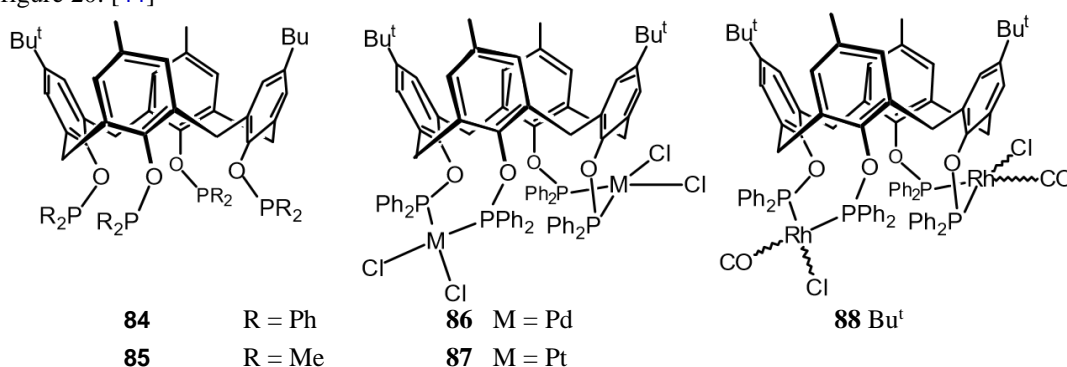
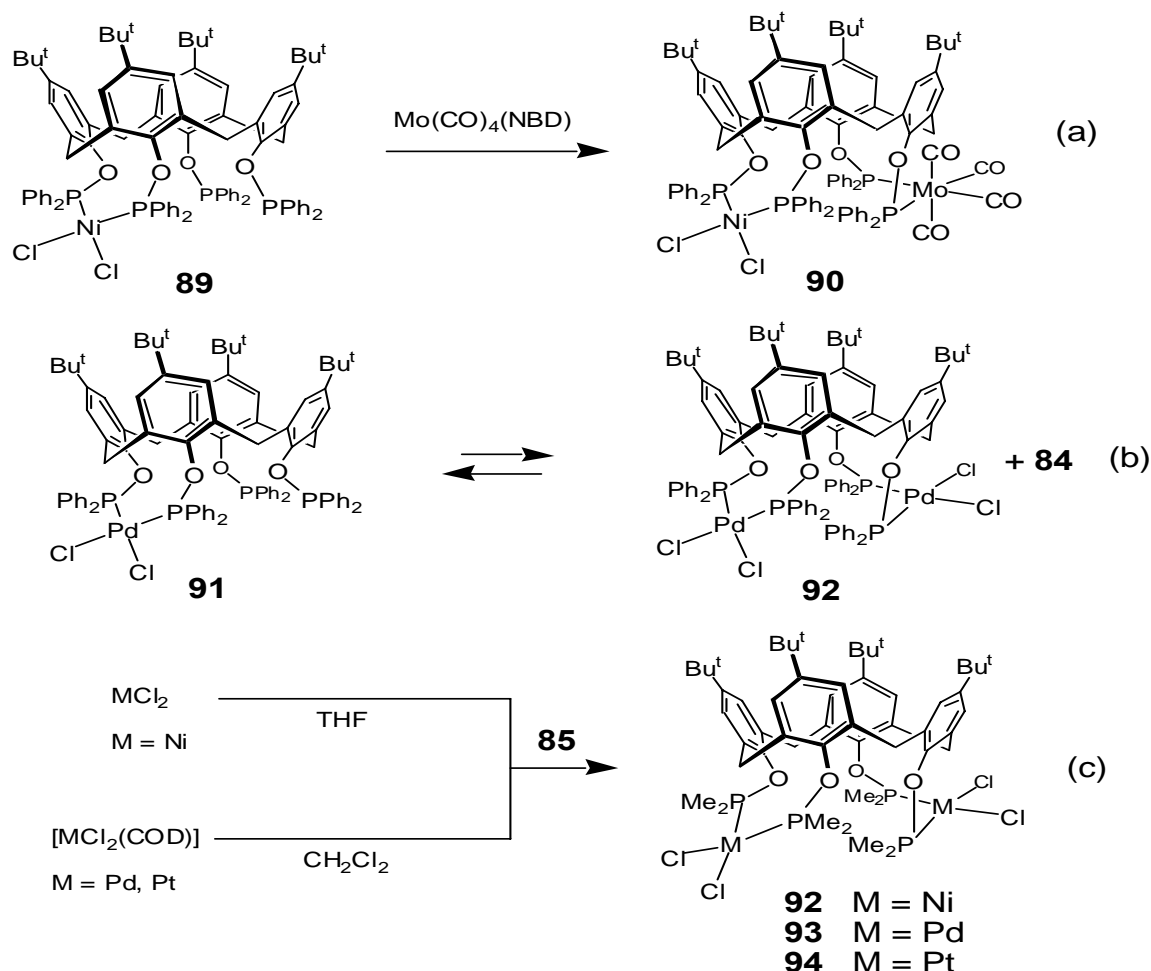


Figure 20

The reaction between 84 and NiCl₂ yielded the monometallic chelate complex 89.[43] This provides a useful method for the synthesis of heterobimetallic systems like Ni-Mo complex 90 (Scheme 9a). Additionally, the monometallic palladium complex 91 can be obtained from [PdCl₂(COD)] using a 1Pd:1L ratio; however, the complex undergoes slow disproportionation to 84 and the corresponding dipalladium complex 86 (Scheme 9b).



Scheme 9.

The sterically less demanding and more basic tetraphosphinide **85** (Figure 9c) was quickly converted into bichelate complexes (M = Ni, Pd, Pt).^[43] X-ray diffraction studies of complexes **93** and **94** demonstrated that the PM bonds are situated away from the cavity, despite the long distance between the two adjacent phosphorus centers. Reaction of **85** with $[\text{PtCl}_2(\text{PhCN})_2]$ yielded the bischelate complex **96** in high yield, while the use of $[\text{PdCl}_2(\text{PhCN})_2]$ as the starting material resulted in the corresponding dipalladium complex **97** in 91% yield, along with some oligomeric material.^[45] The catalytic activity of complex **96** in the vicinity of SnCl_2 facilitates the hydroformylation of styrene, however its catalytic capacity is lower than that of standard $\text{PtCl}(\text{SnCl}_3)$ (diffus) catalysts. Nevertheless, a marginally higher regioselectivity (10%) was observed for the branched/aldehyde. Additionally, the action of $[\text{RhCl}_2(\text{NBD})]_2/\mathbf{95}$ and $[\text{RhCl}_2(\text{NBD})]_2/\mathbf{98}$ blends in the hydroalkoxycarbonylation of styrene ($\text{PhCH}=\text{CH}_2\text{CO}/\text{ROH}$, 130 °C, 140 bar) is poor due to alcoholization of the PO bonds.^[45] The catalytic performance of these complexes in the hydroformylation of styrene is lower than that of conventional Rh/phosphine systems, yet aldehyde selectivity is comparable to the most efficient rhodium catalysts figure 21.^[45]

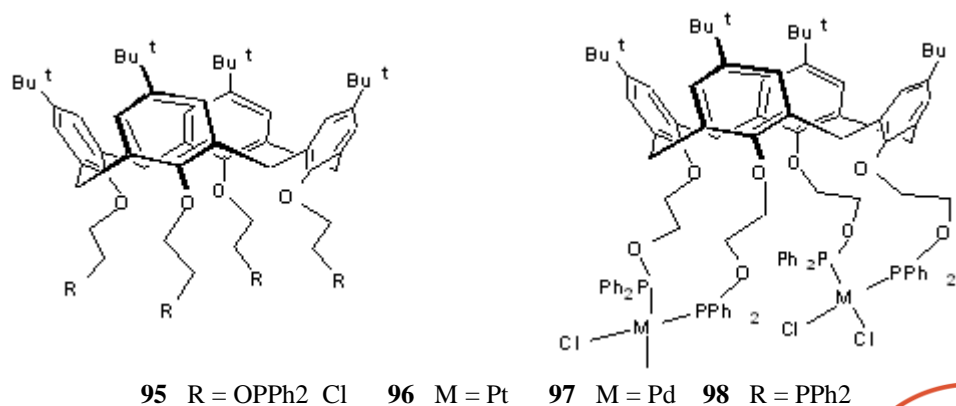
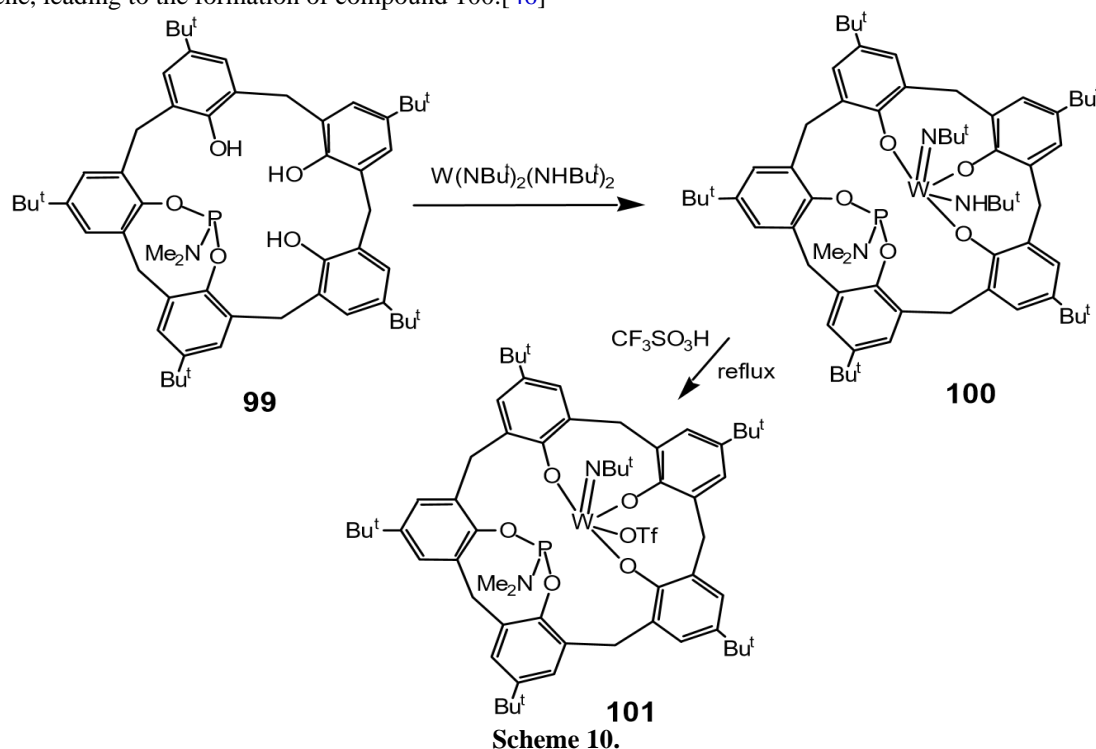


Figure 21

Review of Calixarene-Derivatives in Transition Metal Chemistry.

The $[W(NBu^t)_2(NHBU^t)_2]$ reacted with aminophosphide 99 in the presence of a tungsten block situated at the entry of a calix[5]arene, leading to the formation of compound 100.[46]



The tungsten ion features a square pyramidal arrangement, while the calixarene molecular structure is very flat. The phosphorus single bond is directed to the 6th coordination position with a P...W distance of 3.15 Å, which is located beyond the normal P-W bond length. Nevertheless, the two atoms are close enough to cause a slight shift of the 43 Hz mode in the NMR range. The replacement of the butyl amide ligand with OTf resulted in the formation of complex 101. The change in electron density at the metal center triggers a considerable decrease in the P-W bond length (2.74 Å in 101), and the imido ligand now resides within the calcium shell [figure 22](#).

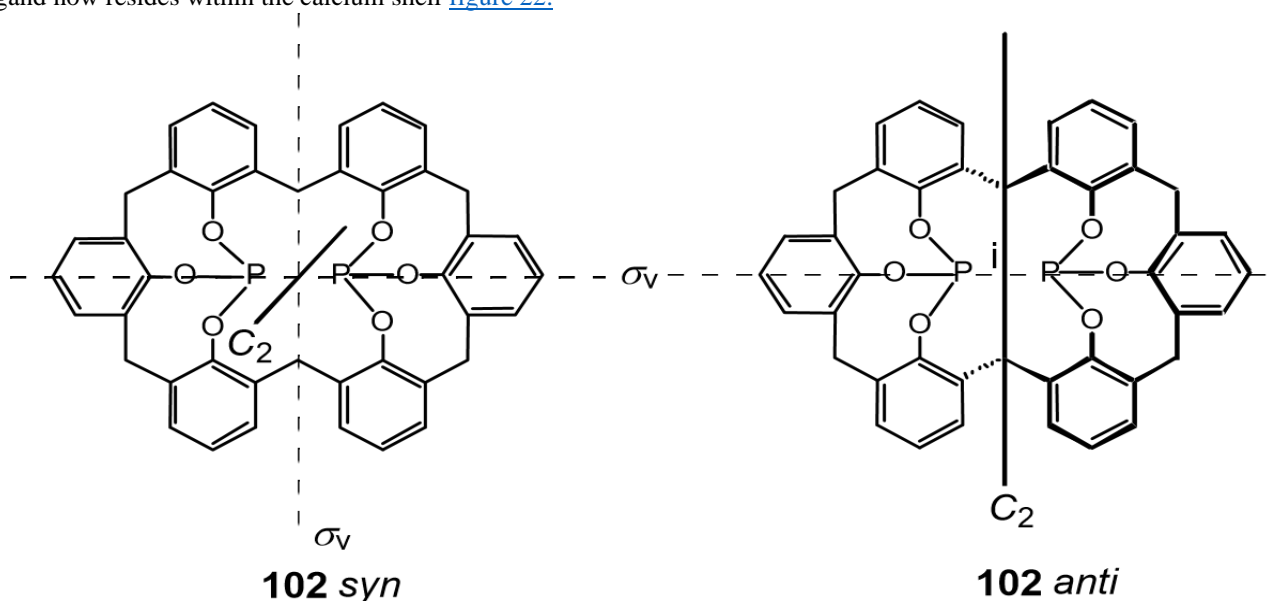
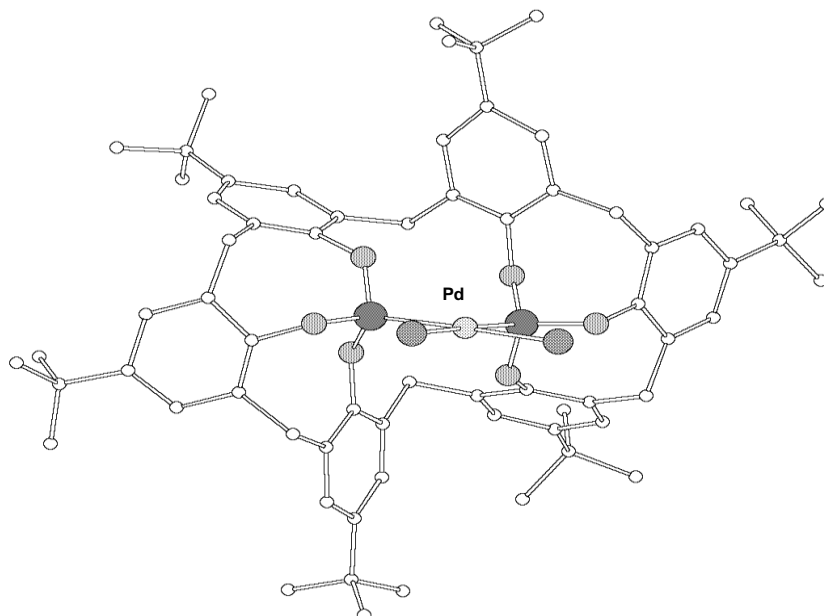


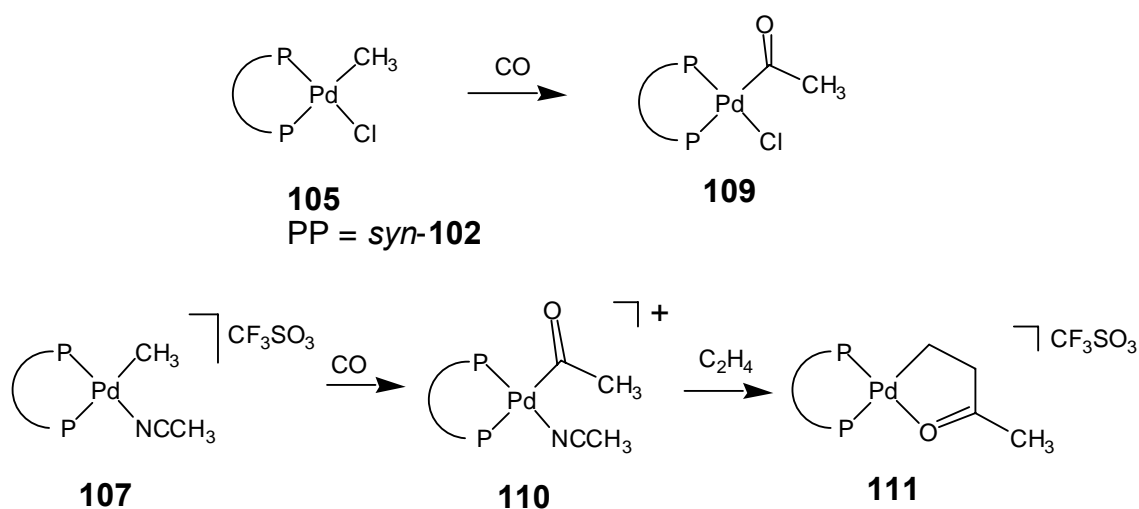
Figure 22

Two studies have revealed the importance of calixarene-derived phosphites in homogeneous catalysis. Chelate complexes $[(syn-102)MCl_2]$ ($M = Pd$, 103; $M = Pt$ = 104), $[(syn-102)M(CH_3)Cl]$ ($M = Pd$, 105; $M = Pt$ = 106), $[(syn-102)M(CH_3)(CH_3CN)]CF_3SO_3$ (107) and $[(syn-102)2Pd(0)]$ (108) all display a cis arrangement of the phosphorus atoms[47], leaving two adjacent sites available for catalytic Pd. The 103 structure ([figure 23](#)) determined by X-ray crystallography indicated that the ligand bite angle in this chiral complex is 94° .




Figure 23. Molecular structure of 103

The cationic complex 110 was observed to react with ethylene to form the five-membered ring species 111. This behavior made complex 110 a potential candidate for catalytic copolymerization of CO and ethylene, despite the fact that such catalysis was not previously hypothesized for phosphites. Notably, complex 110 is the first detailed diphosphide-based complex to demonstrate activity in the copolymerization of ethylene and carbon monoxide. The reaction rates are in the range of 850-5300 mol.mol⁻¹.h⁻¹ (25 °C, 20 bar C₂H₄/CO). Approximately 34,000 polymers obtained had a polydispersity index of 2.3. These results are not uncommon when using active Pd/phosphine complexes. [47]


Scheme 11.

A remarkably high regioselectivity towards n-nonanal was observed in the rhodium-catalyzed hydroformylation of 1-octene using 112 [figure 24](#). [48] A reaction time of 8 hours (1-octene:Rh = 4000, P(H₂-CO) = 20 bar, 100 °C, solvent: 2,2,4-trimethyl-1,3-pentanediol isobutyrate) yielded 63% conversion and aldehyde selectivity of 61% (12% n-octene and 27% octane). The N/iso ratio was 200:1, representing the highest regioselectivity observed to date. Molecular modeling suggests that the P₂-chelated rhodium ion is sandwiched between two sterically demanding 2,6-di-butphenoxy groups, hindering the olefinic approach. The steric hindrance caused by the 1-octyl rhodium complex is much greater than the 2-octyl complex, resulting in a high degree of linear nonanal. Removing the two But substituents on the aryloxy group was found to open the structure and increase catalytic activity, though this was accompanied by a decrease in selectivity. The coordination properties of calixarenes containing two distal branches of CH₂PPh₂ have been studied for a variety of noble metals. [49] Diphosphines of this family are capable of acting as trans-passing ligands, as exemplified in the cationic complexes 113 and 114.

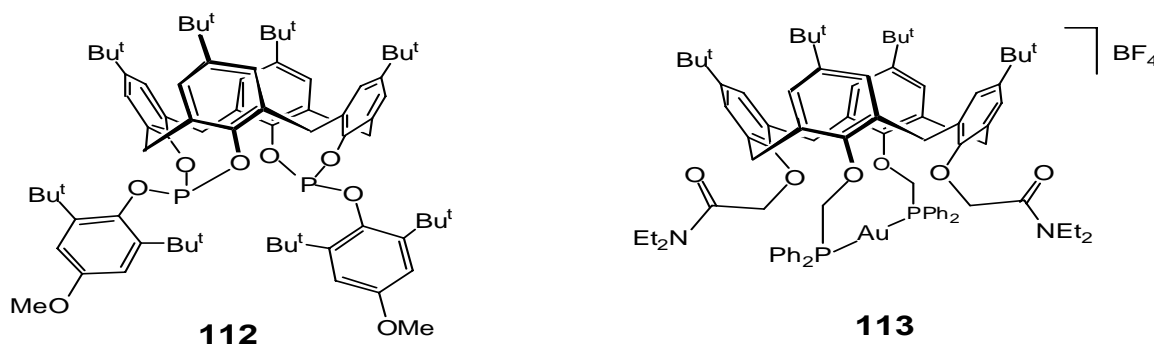


Figure 24

It appears that the central metal 113 is arranged linearly in a PMP fashion, however, the silver atom at 114 is likely to be in a T-shaped P2Oamide coordination. The NMR spectra, which is consistent with the C_{2v} symmetry, implies that the exchange between the coordinated and free amide occurs quickly when in solution [figure 25](#).

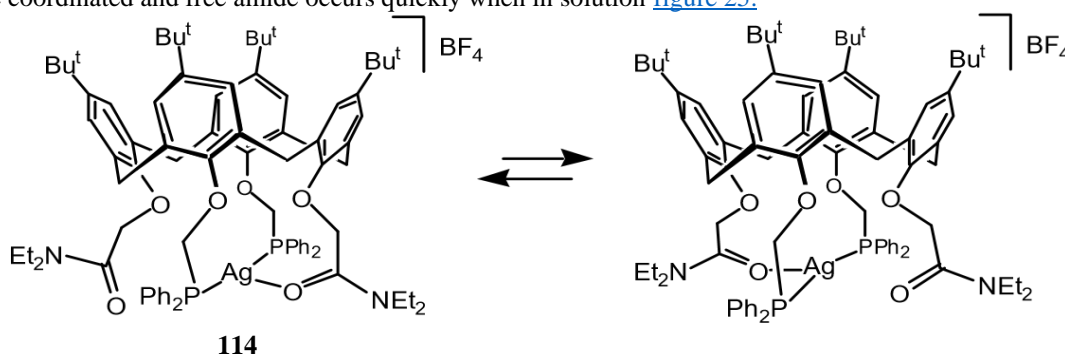


Figure 25

The formation rate of chelates using such diphosphines was found to be significantly impacted by the characteristics of the functional groups attached to the two phenolic oxygen atoms. Compounds 115-118, which have side chains that contain oxygen-donating elements, respond to the hydride complex $[PtHCl(PPh_3)_2]BF_4$, forming a combination of complexes, as depicted in Scheme 12 [figure 26](#).

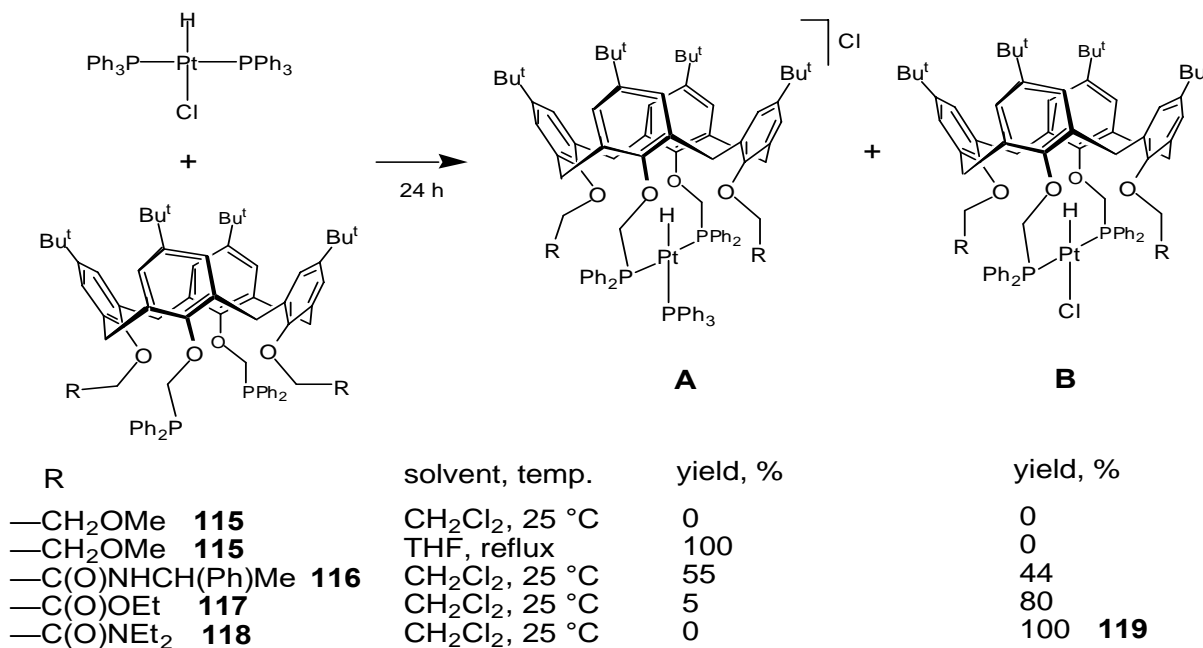
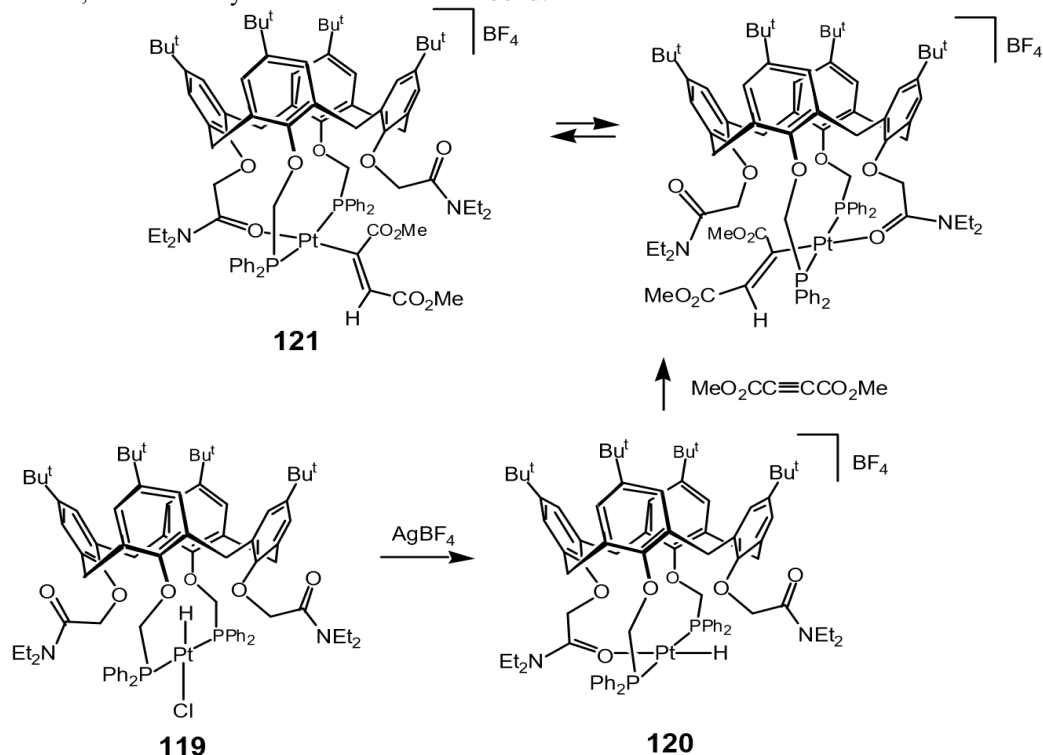


Figure 26

Review of Calixarene-Derivatives in Transition Metal Chemistry.

The reaction between calix-diphosphines and $[PtHCl(PPh_3)_2]$ is facilitated by anchimeric assistance of the functional side groups. Weakly coordinating side groups, such as $-C(O)NEt_2$, typically result in the formation of A-type compounds, albeit slowly, with the remaining PPh_3 ligand, while strong donors form B-type complexes rapidly, replacing both PPh_3 ligands. The formation of A-type complexes is first observed, followed by a gradual transformation to B-type complexes. 115, which has feeble ether donors, does not go through the substitution reaction at room temperature, suggesting that the phosphine groups are not able to contribute to the initiation of the substitution reaction, possibly due to steric hindrance. The B-type complex formation is favored by the auxiliary function having better donating properties. The B-type complex (119) was uniquely observed when using diamide 118. The Pt-H covalent bond in complexes constructed is directed towards the calixarene cavity. As the hydride is sterically shielded, the Pt-H bond is quite secure against reagents such as $MeO_2CC\equiv CCO_2Me$, which usually interact with the Pt-H bond.



Scheme 13.

Under favorable conditions and with the help of a supporting ligand, the direction of the Pt-H vector can be reversed. This reaction of 119 with $AgBF_4$ leads to the formation of complex 120, wherein the Pt-H bond points outward from the plane (Figure 13). [49] In this structure, the metal plane seals off the cavity. In other words, the ligand acts as a hemispherical ligand covering the plane of the metal. This process makes the hydride much more reactive. For instance, the platinum alkenyl addition product 121 is formed with $MeO_2CC\equiv CCO_2Me$. The rapid oscillatory behavior, as depicted in Figure 13, indicates that the reaction proceeds through a transient pentacoordinated platinum species. Substitution of the protonated amide 120 with strong donors facilitates hydride insertion into the aryl ring, as demonstrated by the reaction with 4,4'-bipyridine to yield 122 [figure 27](#).

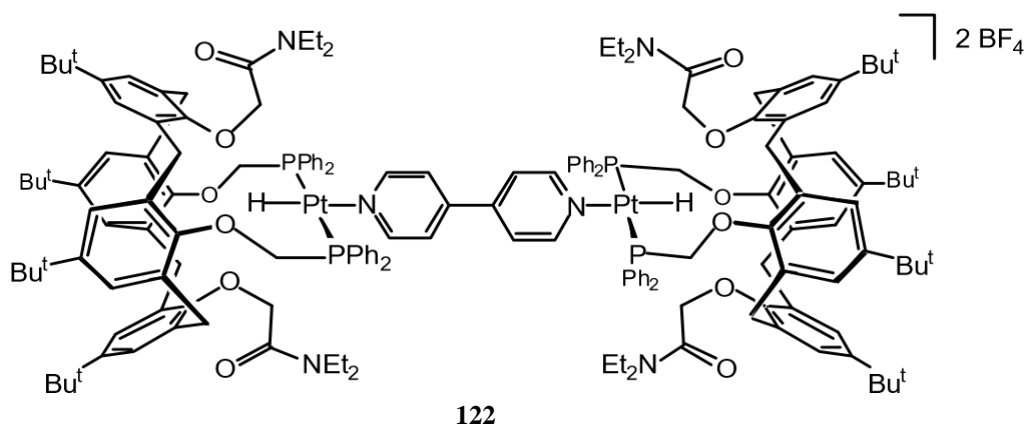


Figure 27

No oscillatory motion was seen in complex 123, indicating a highly stable metallamide bond. [49] Complex 123 was tested as a catalyst for the hydroformylation of styrene (40 bar CO/H_2 , 40 °C, toluene- CH_2Cl_2) and demonstrated remarkable performance.

Review of Calixarene-Derivatives in Transition Metal Chemistry.

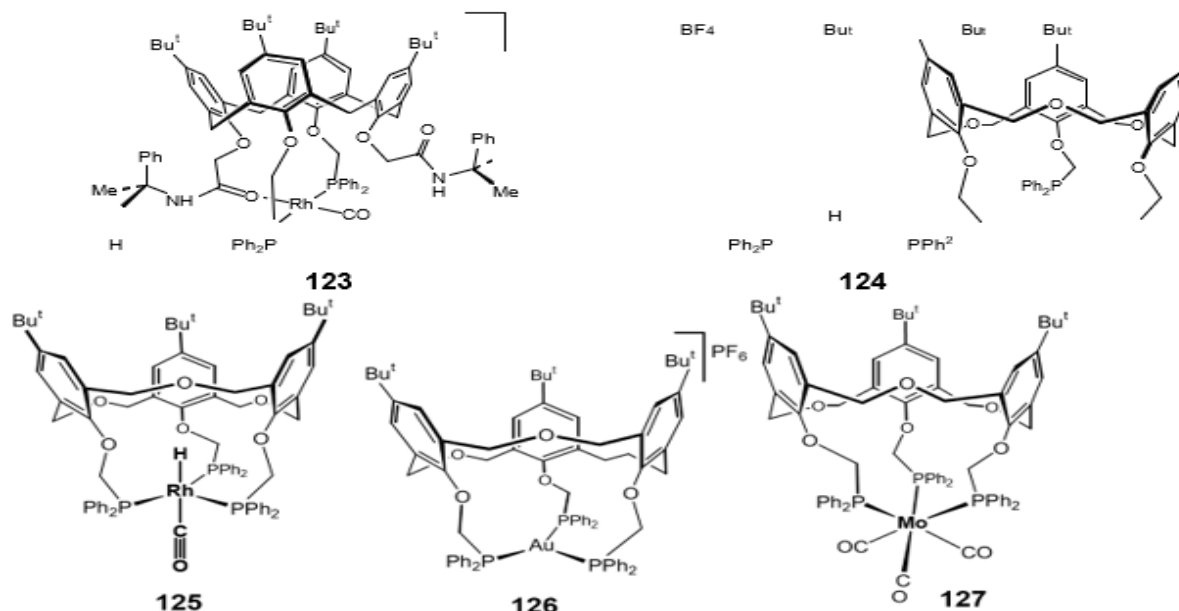


Figure 28

Stereoselectivity around the H-Rh-CO bond was accomplished within the response of C_{3v}-symmetric triphosphine 124 from hexahomotrioxocalix[3]arene [Rh(acac)(CO)₂] beneath 20 bar CO/H₂.^[50] This response causes the arrangement of a trigonal bipyramidal hydrogen carbonyl complex with the Rh-H vector indicating into the depth (125). C_{3v}-symmetric complexes inferred from 124 were moreover gotten for gold (126) and molybdenum (127) figure 28. Union of multinuclear species can be accomplished utilizing tetrapods 128 and 129.^[51] Inclusion of four rises to [AuCl(SC₄H₈)] to 128 gave the tetragold complex 130. The NMR information appear a about C₄-symmetric structure of the complex in arrangement. In any case, a cautious examination of the ¹H NMR range appears that the reverberation of the C(O)NMe bunches appears a complex design. It is likely that the turn of the moderately thick heterocycles around the phosphorus particles is constrained, so that the four phosphorinan parts receive distinctive introductions with regard to the calcium hub. Duration 128 was watched when the last mentioned responded with 2 equiv. [AuCl(SC₄H₈)]. The gold parts of the shaped complex (131) are connected to two distal P particles. Interests, the P solitary sets of the non-complex phosphorus doublets point around within the same heading, so that the two methyl bunches in these heterocycles are not formally identical. Brief intermolecular Au...Au' contacts (3.288(1) Å) result in a free polymeric structure within the strong state.

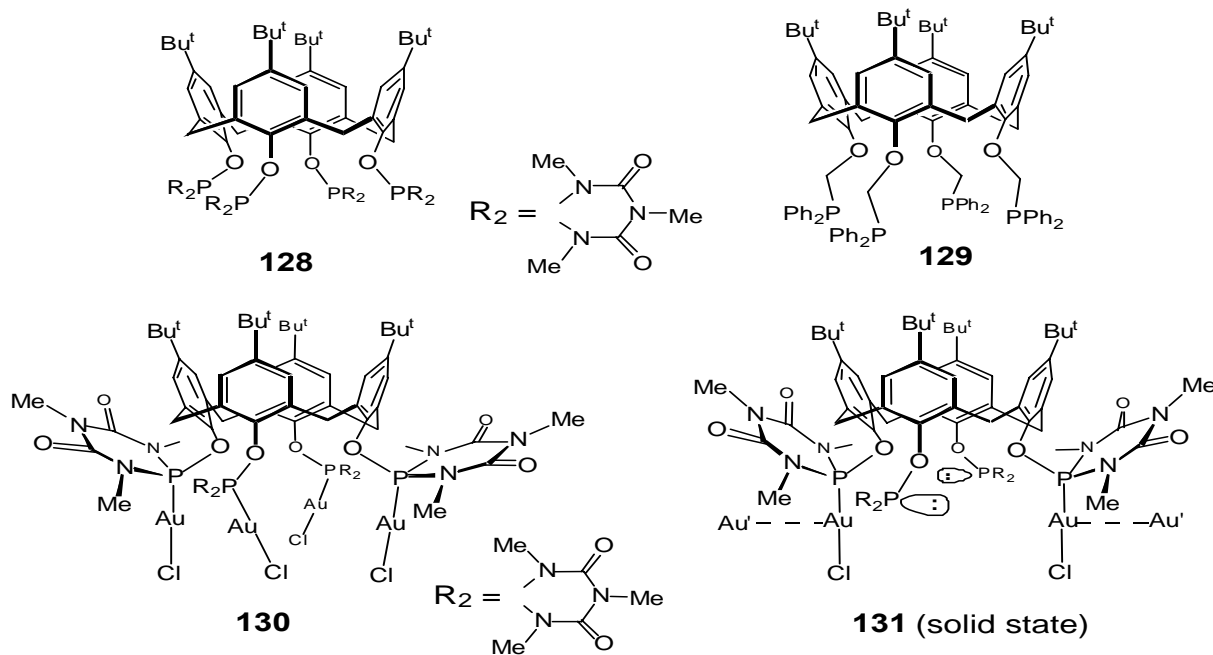


Figure 29

The determination of the structure of 134 in solution revealed a C3-visimetric arrangement of the three Au-Cl units. The reaction of 129 [51] with $[\text{AuCl}(\text{SC}_4\text{H}_8)]$ yields complex 132, which has a C4-visimetric structure in solution and two opposite Au-Cl units oriented in parallel to the linked phenoxy rings in the solid state. Furthermore, the reaction of the tridentate ligand 133 with excess $[\text{AuCl}(\text{SC}_4\text{H}_8)]$ resulted in the trimetallic complex $133 \cdot (\text{AuCl})_3$ (134), whose structure in solution has a C3-visimetric arrangement of the three Au-Cl units [figure 29](#).

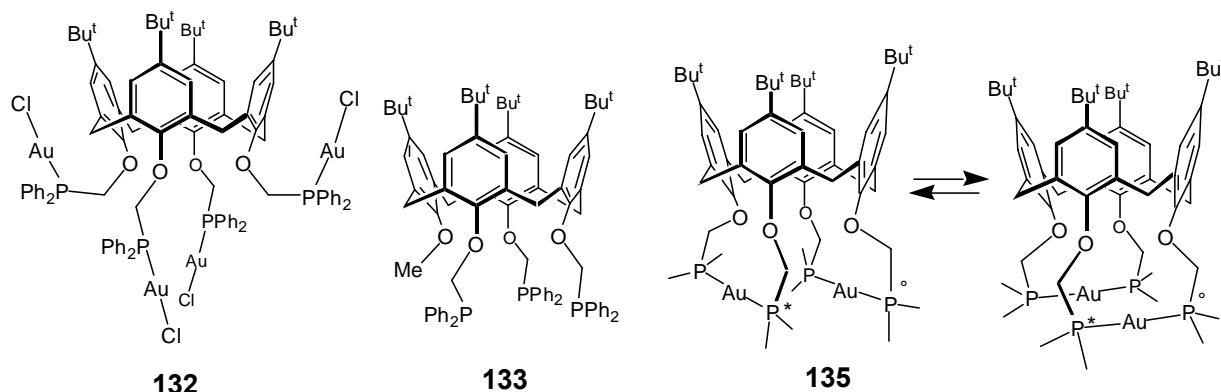
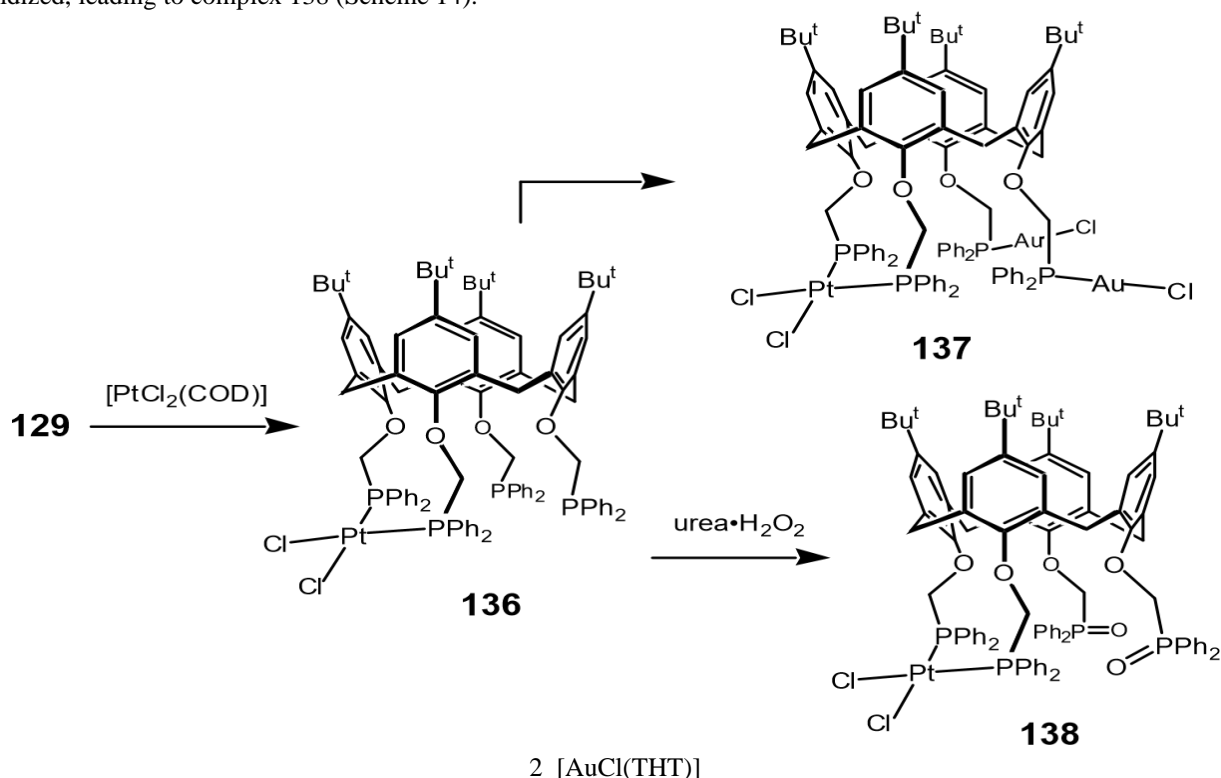


Figure 30

Treatment of 129 with overabundance $[\text{Au}(\text{solvent})_2]\text{BF}_4$ managed cationic digold complex 135 [figure 30](#). [51] This complex appears energetic behavior in arrangement with two gold iotas turning at the same time on the surface of P4 as appeared within the drawing.. Another conceivable application of ligand 129 is the arrangement of heterometallic complexes.44 The response of compound 129 with $[\text{PtCl}_2(\text{COD})]$ gave a chelate complex 136, where the metal is specifically bound to two proximal phosphines. This complex was assist responded with 2 equiv. The formation of PtAu_2 complex 137 can be achieved by using $\text{AuCl}(\text{SC}_4\text{H}_8)$. To prevent polymerization from occurring, P donors can be complexed or oxidized, leading to complex 138 (Scheme 14).



2 $[\text{AuCl}(\text{THT})]$
Scheme 14.

Facial P_3 coordination of 129 and 133 is found in complexes 139-141.^[44] The ruthenium complex 141 binds reversibly two molecules of acetonitrile [figure 31](#).

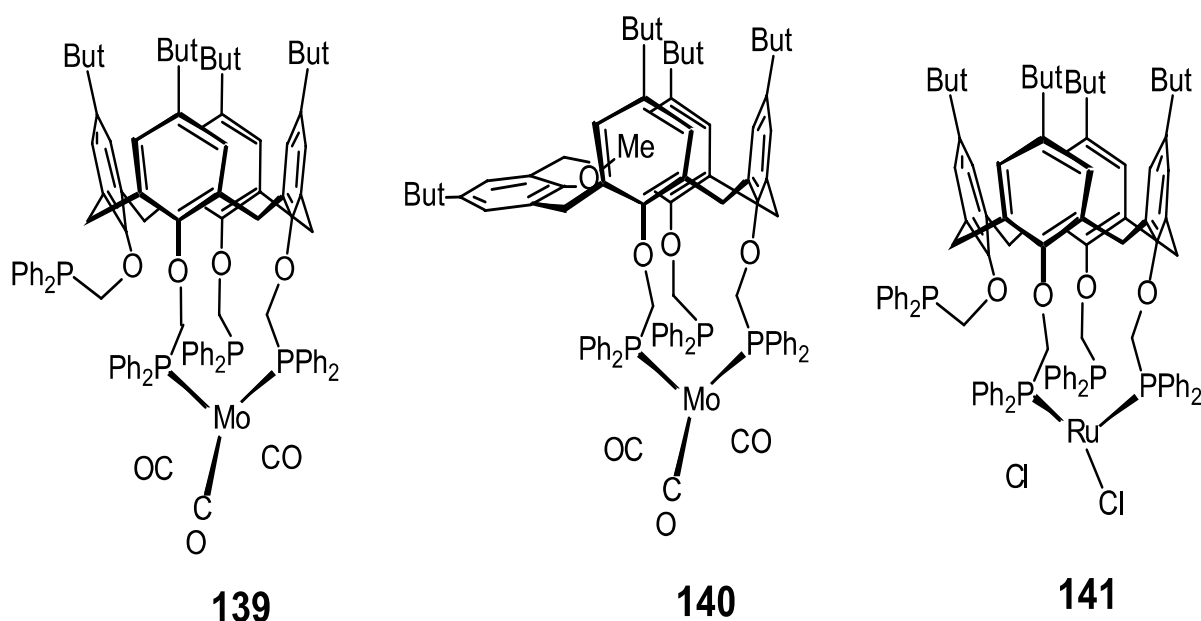
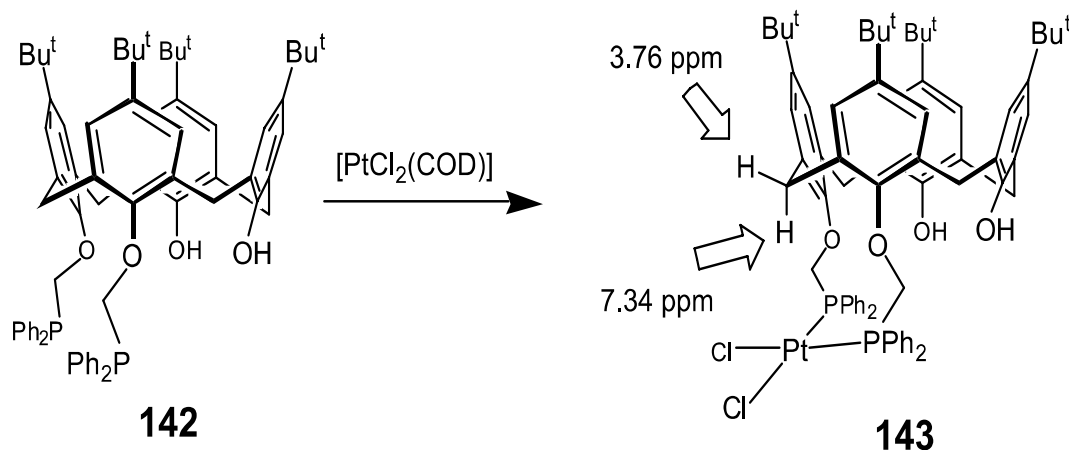


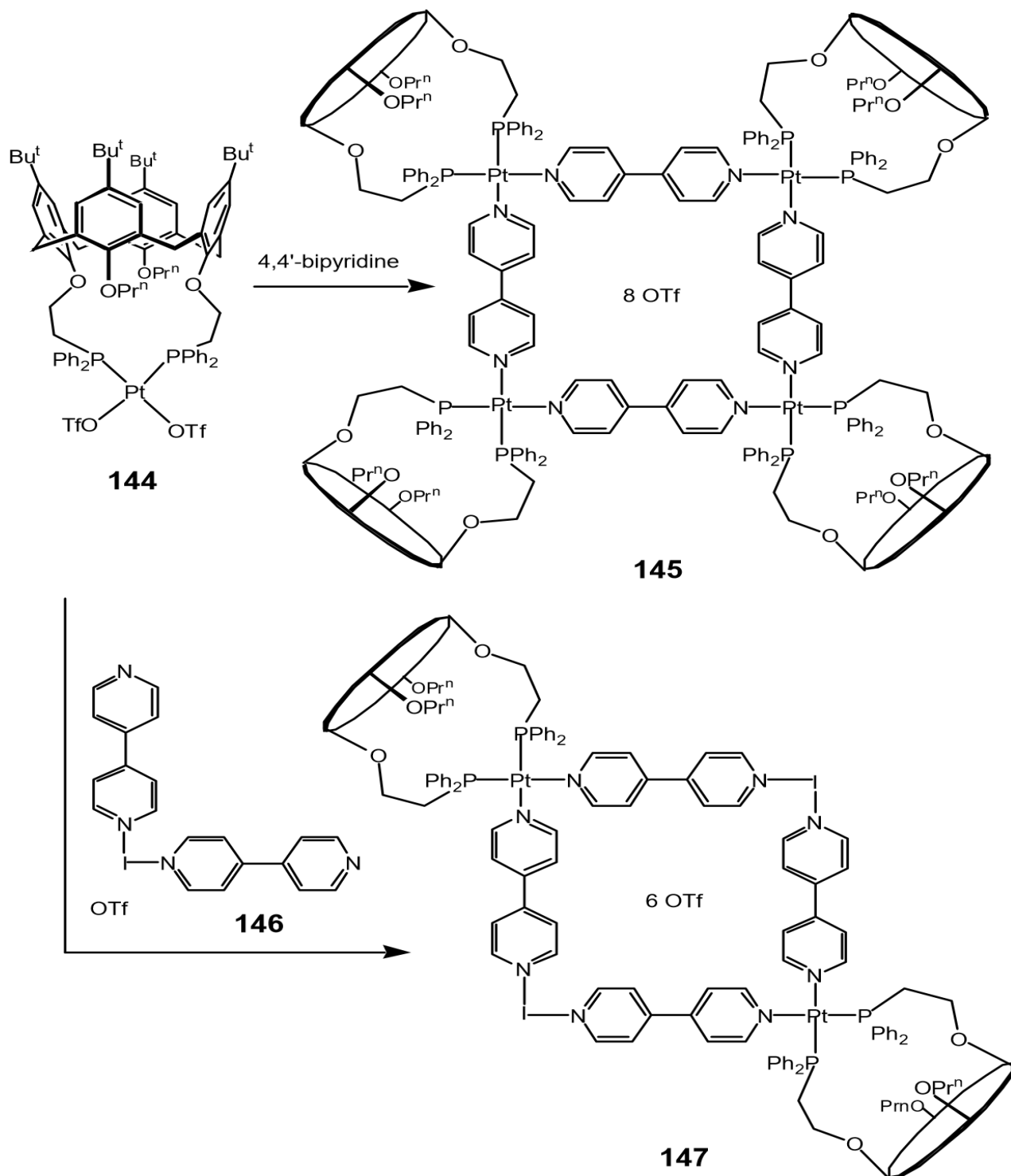
Figure 31

Chelate complex 143 was gotten by response of diphosphine 142 with $[PtCl_2(COD)]$ (Plot 15).[44] Within the strong state, the PPh vectors are coordinated absent from the calixarene hub. A striking include of the NMR range of 143 is the huge partition of the A and B parts of the ArCH₂ bunch between the two phosphines ($\Delta\delta = 3.6$ ppm), with an hub CH flag at 7.34 ppm. This impact may be due to the circular current shaped by the metal macrocycle, which contradicts the outside field. Interaction between the pivotal CH particle and both adjoining oxygen molecules can too be included. Note that within the strong state the pivotal Curve is found precisely apically over the platinum iota, with a H...Pt division of as it were 2.5 Å, so that the unshielding may too be due to interaction with the dz₂ orbital of the metal. A similar geometric relationship was found for complex 137 within the strong state.[52]



Scheme 15.

Complex 143 exhibits an active behavior in arrangement which can be explained as follows: (i) rapid formation of both hydroxyl groups at low temperature, forming hydrogen bonds with each neighboring ether oxygen molecule; ii) reversible rotation of phenolic rings through the lower edge ring, which is initiated by the disruption of hydrogen bonds at higher temperature. Calixarenes have also been used to construct "molecular squares".[53] Reaction of 144 with 4,4'-bipyridine (Scheme 16) yielded 145 and reaction with biheterodiiodonium salt 146 gave another square 147 containing two platinum atoms within the central macrocyclic structure.



Scheme 16.

4.2 Complexes of calixarenes with upper rim P substituents

The use of boron compound 148[54] enabled the trapping of organometallic fragments in the cavity of the cup[4]. In complexes 149-152, the diphosphine used as a trans-containing ligand placed the metal center above the wider entrance. The Pd-Me part of the complex 150 and the Pt-H bond of 151 were located in the calcium cavity. The formation of ruthenium complex 152 included the placement of one M-CO moiety between two parallel aryl rings that were only 5.5 Å apart. This demonstrates a new potential for intracavity catalysis. Ligand 153, which has longer phosphorus arms, generated dinuclear complexes 154-156.[55] The reaction between diphosphide 157 and [Pd(η^3 -Me-allyl)(THF)₂]BF₄ provided a mononuclear chelate complex 158.[55] The activity of compound 156 in the hydroformylation of olefins is comparable to the Rh-PPh₃ systems [figure 32](#).

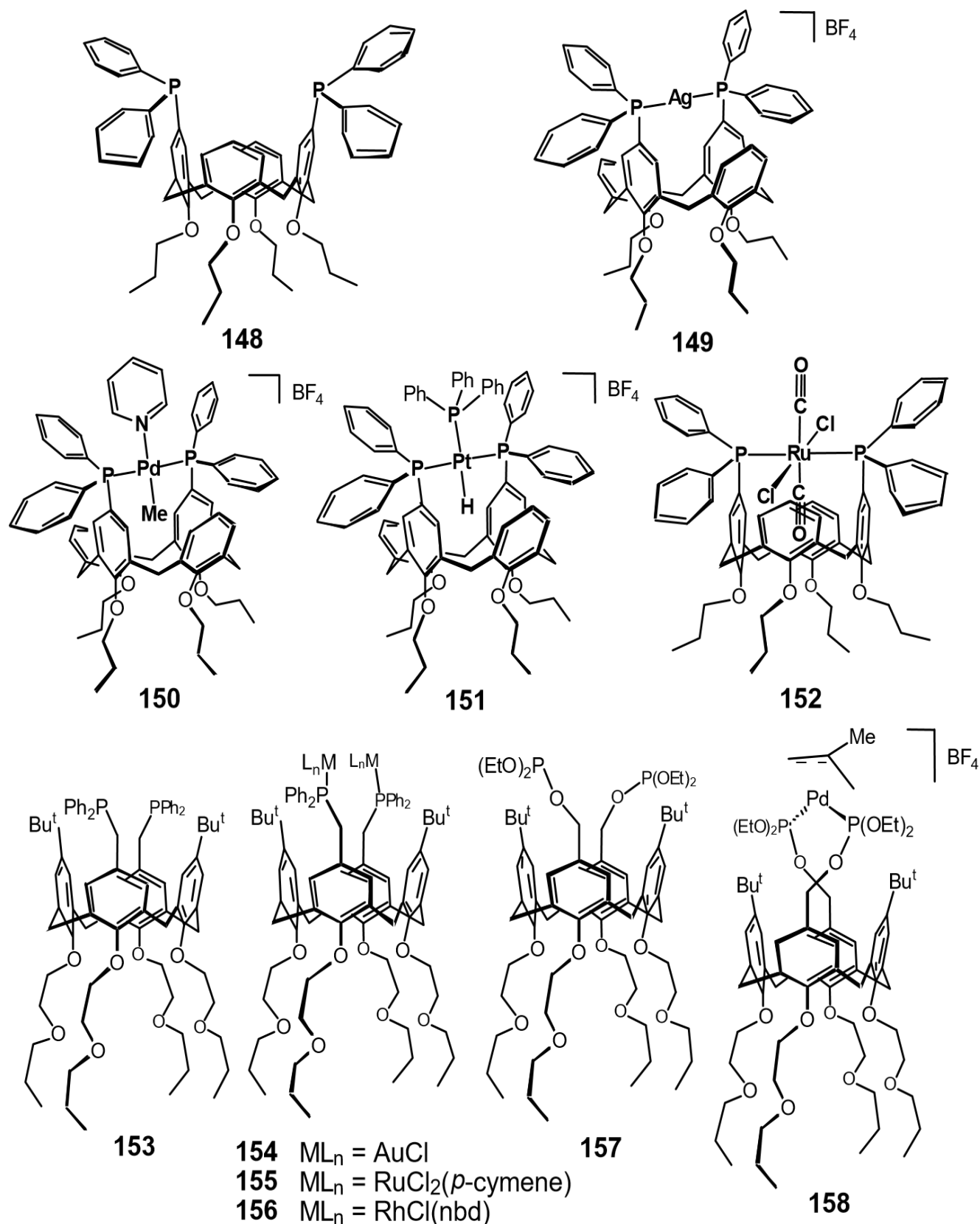


Figure 32

V. METALLOCALIXARENES WITH METAL CENTRES BONDED TO IIDONOR UNITS

Reactions of neutral calixarene precursors with cationic metallarene or metal cyclopentadienyl complexes provided a number of cationic π -metalated calixarenes (159–172) [figure 33](#).[\[56\]](#)

Review of Calixarene-Derivatives in Transition Metal Chemistry.

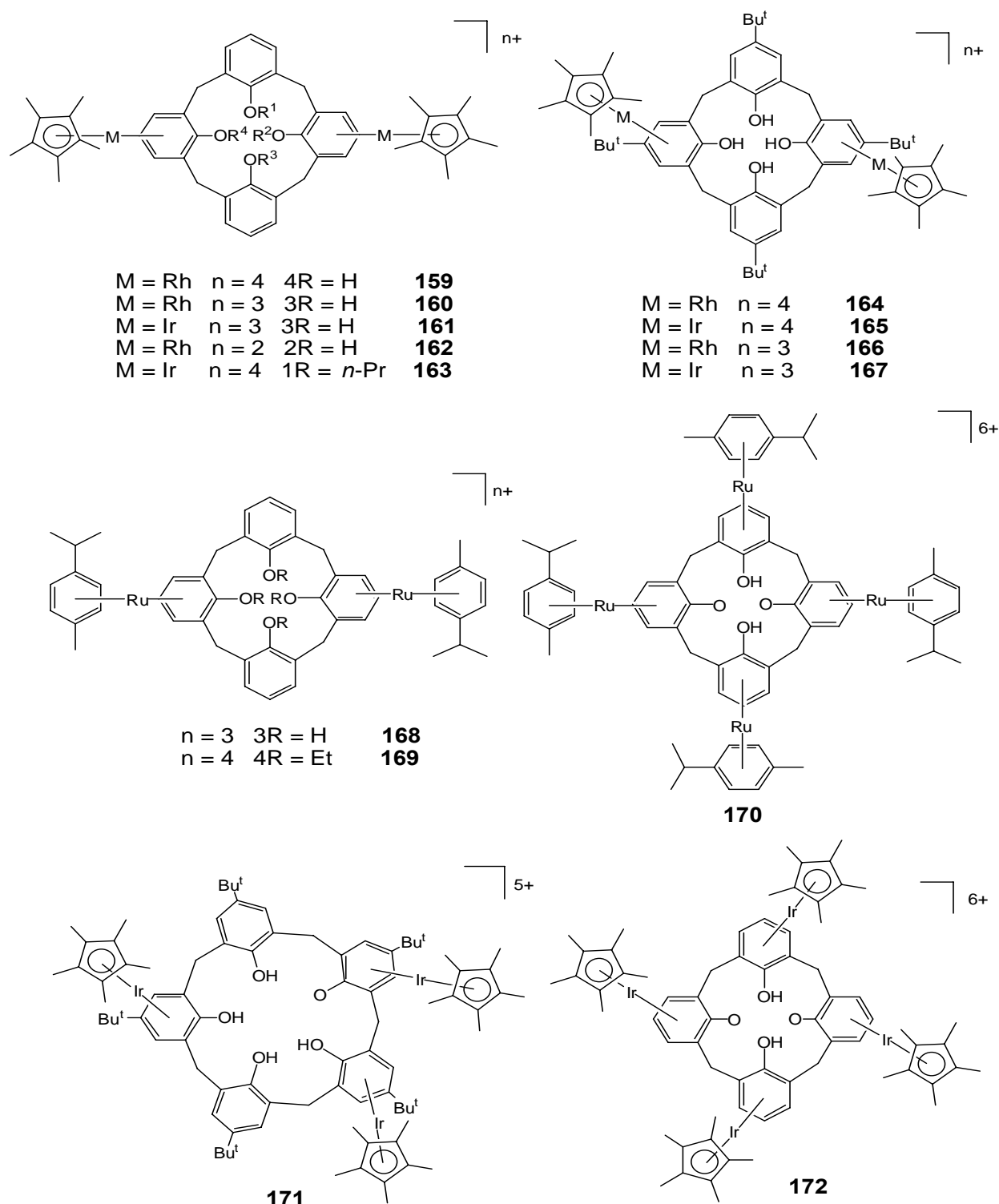


Figure 33

The reaction of pBut-calix[5]arene with refluxing $[\text{Ir}(\eta^5\text{-C}_5\text{Me}_5)(\text{acetone})_3](\text{BF}_4)_2$ in $\text{CF}_3\text{CO}_2\text{H}$ yields the trimetallic iridium cation **171**, which has a transition metal center that makes the lower edge hydroxyl groups more acidic than the parent calixarene. This cation can bind anions such as BF_4^- , SO_4^{2-} , and I^- , and X-ray diffraction studies have determined that anion-host contacts up to 2.85 Å were present in the complex $170 \cdot \text{BF}_4^-$ ($\text{BF}_4^- \dots \text{Ccalix}$). Further investigation through NMR titration experiments in an aqueous environment revealed that the binding constants for nitrate and halide ions were in the range of 100-550 M^{-1} , with the bond of Halides decreasing in the order $\text{Cl}^- > \text{Br}^- > \text{I}^-$. Anion binding was found to be significantly enhanced in a non-aqueous environment [figure 34](#)

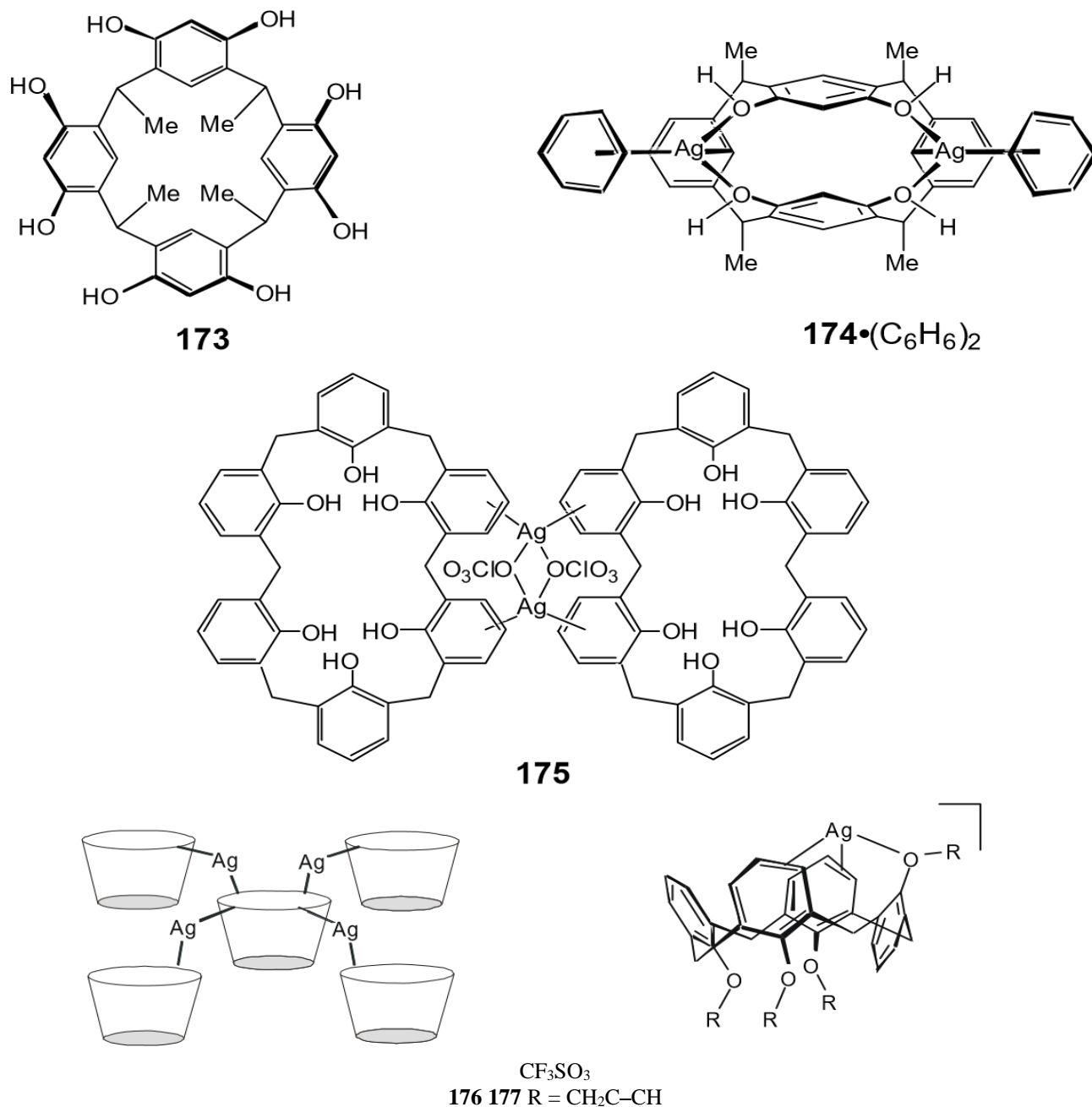
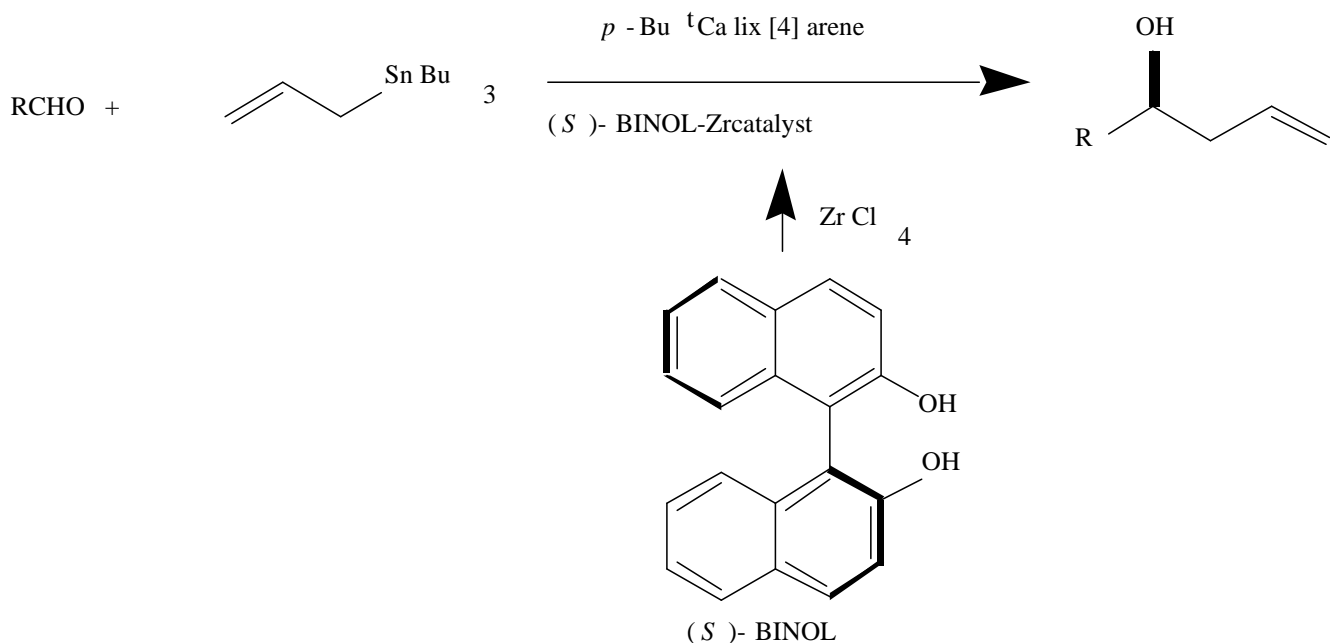


Figure 34

The reaction of AgClO₄ with C-methylcalix[4]resorcinarene 173 yields a dinuclear cation complex 174•(C₆H₆)₂, [57] which is doubly symmetrical; both silver ions are connected to two OH groups, one of which is an aromatic carbon atom from the resorcinarene ring (interacting via π-bonding) and one carbon atom of the benzene molecule. The reaction of calix[6]arene with AgClO₄ leads to the dimeric complex 175. Additionally, the reaction of AgClO₄ with calix[4]arene gives the complex [Ag₂(calixarene)(ClO₄)] 176, which is comprised of a polymeric structure based on cationic π-interactions. In the solid state, each calixarene molecule is π-bonded to four silver atoms, two of which are above the cavity and the other two outside; the silver ions above the calixarene unit are linked to the outside of the adjacent cavity (and vice versa), thus forming a two-dimensional polymer framework. All calixarene units have the same orientation. Partial cone calixarene complex 177, Ag(I) is bound to both **hard** and **soft** donor centers like 174. [58].

VI. SPECIAL USES OF CALIXARENES IN CATALYSIS

The recent use of calixarenes as additives in the zirconium-BINOL-catalyzed enantioselective allylation of aldehydes has been shown to yield higher enantioselectivity values, up to 96% for n-C₇H₁₅CHO, compared to the system without them. [59] The addition of p-But-calix[4]arene to a mixture of BINOL, ZrCl₄(thf)₂, and allyltributyltin strongly activates the catalytic system. However, the species responsible for this improved enantioselectivity has yet to be identified.



Scheme 17.

Modified calix[n]arenes ($n = 4, 5$) can also be used as external donors in late-generation Ziegler-Natta catalysis.[60] The general result is that the addition of calixarenes to Ti/Al catalysts significantly increases the amount of isotactic polypropylene in the bulk polymerization of propylene. These promising results are sure to trigger new research in the ever-evolving field of olefin polymerization.

VII. CONCLUSION

In this study, it was demonstrated that the combination of calixarenes with transition metals can produce novel outcomes. These results are based on two main characteristics of calixarenes: the potential to create intricate coordination complexes through multiple functionalization and the ability to trap organic or organometallic compounds within their cavities or pockets. The intriguing discoveries made in the fields of homogeneous catalysis, anion complexation and supramolecular sensors, as well as the synthesis of large cage compounds, are strong evidence for further research within the rapidly evolving field of metallo-calixarenes.

DECLARATION

Funding/ Grants/ Financial Support	No, I did not receive.
Conflicts of Interest/ Competing Interests	No conflicts of interest to the best of our knowledge.
Ethical Approval and Consent to Participate	No, the article does not require ethical approval and consent to participate with evidence.
Availability of Data and Material/ Data Access Statement	Not relevant.
Authors Contributions	I am only the sole author of the article.

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