Playing with podands based on cone-shaped cavities. How can a cavity influence the properties of an appended metal centre?

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The potential of molecules that combine the properties of a conical cavity with those of a covalently-linked transition-metal centre is highlighted through the assessment of cyclodextrin- and calixarene-derived podands (''cavitand'' ligands) in coordination chemistry and catalysis. Metallocavitands with coordination sites directed towards the interior of the generic cavity provide interesting systems for studying host–guest complexation processes, their enhanced strength of metal-ion binding allowing for regioselective catalysis in a confined environment, and stabilisation of coordination complexes of unusual forms. Where cavitands have *exo*-oriented podand arms, the intrinsic dynamics of the cavity can dramatically modify metal chelation behaviour and the catalytic properties of the complexes. Such functionalised cavities are also useful as metal-ion transporters.

Introduction

Early studies of molecules in which a metal-ion binding centre was combined with an accessible cavity were directed largely towards understanding of metalloprotein functioning.[1–10] Recently, interest in such molecules has focussed on those which bind transition-metal ions and which may provide novel, efficient and selective catalysts of industrial relevance.[11–17] A variety of metallocavitands have been designed in which the metal atom is loosely tethered, at the entrance to a receptor cavity. This favors interactions between properly oriented, coordinated substrates and the inner part of the hollow molecule.[18–28] A good, but certainly not unique, way to optimise metal–cavity synergism with respect to the transformation of a substrate is to cap the cavity entrance with a metal centre possessing vacant coordination sites directed towards the interior of the cavity. If the cavity adopts the shape of a truncated cone, *i.e.* if it possesses two inequivalent entrances, as found for instance in calixarenes or cyclodextrins, then, ideally, the whole complex could function as a funnel able to select substrates according to their size and shape before they undergo a catalytic transformation in the confined space (Fig. 1). Weak forces between the cavity walls and the substrate are expected to control the regioselectivity or the enantioselectivity (in the case of a chiral cavity) of the reaction. Metallocavitands with appended groups engendering water solubility are of particular interest as they constitute potential microreactors that would allow a catalytic reaction to take place in an aqueous medium (in reality, within the hydrophobic space of the interior). In general, cavity-shaped

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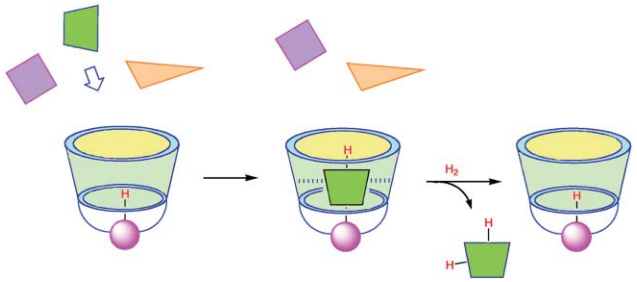
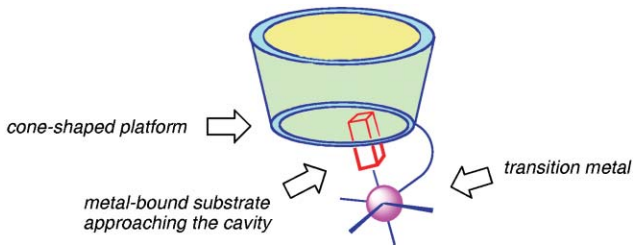


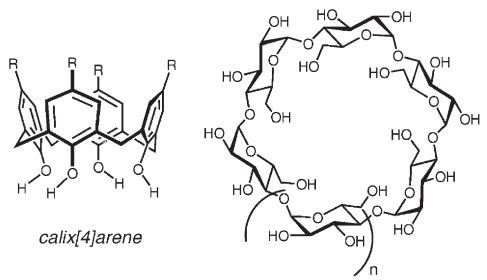
Fig. 1 A metallocavitand functioning as a shape selective receptor.

scaffolds with a large number of external anchoring points display various advantages. They may, for example, serve as a platform for the construction of podands having all their binding arms oriented away from the receptor. This leads to complexes in which the metal centre is located on the surface of the cavity.[22,29,30] The specific geometric attributes of the platform, in particular its flexibility and size, and the properties of the individual substituents anchored onto the platform, all of which may interact with the metal, strongly influence the coordinating properties of such ligands. In addition, the podand arms may also behave as cavity forming units.

The present paper examines the properties of some selected P- and N- donor cavitands based on conical or tubular scaffolds with both *endo*- and *exo*-directed substituents.

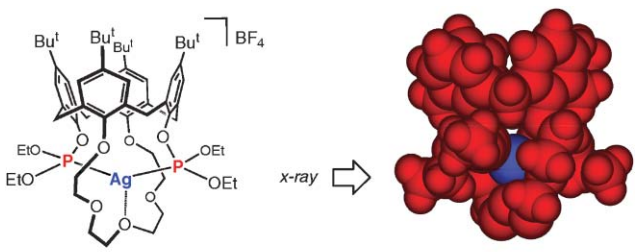


Most conical molecules presented in this article are derived from (α or β)-cyclodextrins and calix[4]arenes. While cyclodextrins are rather rigid molecules, calix[4]arenes only display a conical shape when conformationally stabilized. This is usually achieved by tethering bulky substituents on their narrow rim (*i.e.* the circular line joining the phenolic oxygen atoms), so as to prevent the individual phenol rings from transannular rotation.[31]



Directed metal positioning at the entrance of a cavity. Binding behaviour of cavity-shaped diphosphines

A good strategy for positioning a metal centre across the entrance of a conical cavity is to employ a cavitand functionalised at one entrance by a pendent chelate arm. Provided the coordinating atoms are located close to the cavity, substrates subsequently bound to the attached metal may interact not only with the atoms of the periphery but possibly also enter the cavity. An example of ligand which was designed to meet these criteria is the calixarene-diphosphinite **1**.[31,32] In fact, large P_2-ligands of this type (in the present example the coordinating atoms are separated by 12 bonds) are not necessarily good chelators, especially in view of the known flexibility of the calix[4]arene backbone which may allow the two phosphorus lone pairs to diverge. Thus, reaction of **1** with $[MCl_2(PhCN)_2]$ complexes (M = Pd, Pt) affords the tetrameric complexes **2** and **3**, respectively, in which the diphosphinite behaves as a bridging ligand instead of a chelating one.[31] Chelation by such diphosphinites results, nevertheless, when reactants with two, adjacent labile binding sites are used (Fig. 2). Thus, cationic species bearing poorly coordinating solvent molecules, $[ML_n(solvent)_m]^{m+}$, provide chelate complexes selectively.[31,33–36] Complexes **6** and **7** were obtained quantitatively according to this strategy, and in both of them the metal sits, as expected, below the cavity.[31,34] In these complexes, the metal centres are turned away from the hollow; nevertheless, exo orientation of the binding sides does not exclude confinement of the metal inside a pocket, as seen for example in complexes **8** and **9**, where long side-chains adjacent to the phosphorus arms are tethered to the four phenolic oxygen atoms. In this case, the calixarene simply behaves as a platform, the pocket being generated by the encircling substituents.[34,36]



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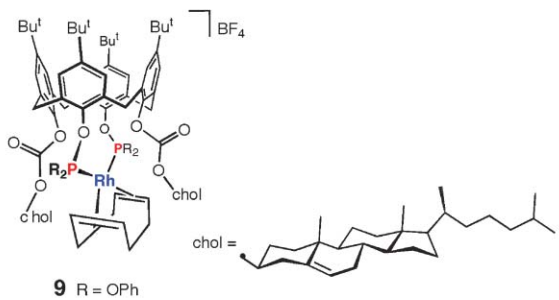


9 R = OPh

In calixarene **10**, the phosphorus arms have been slightly lengthened with respect to the phosphinites or phosphites

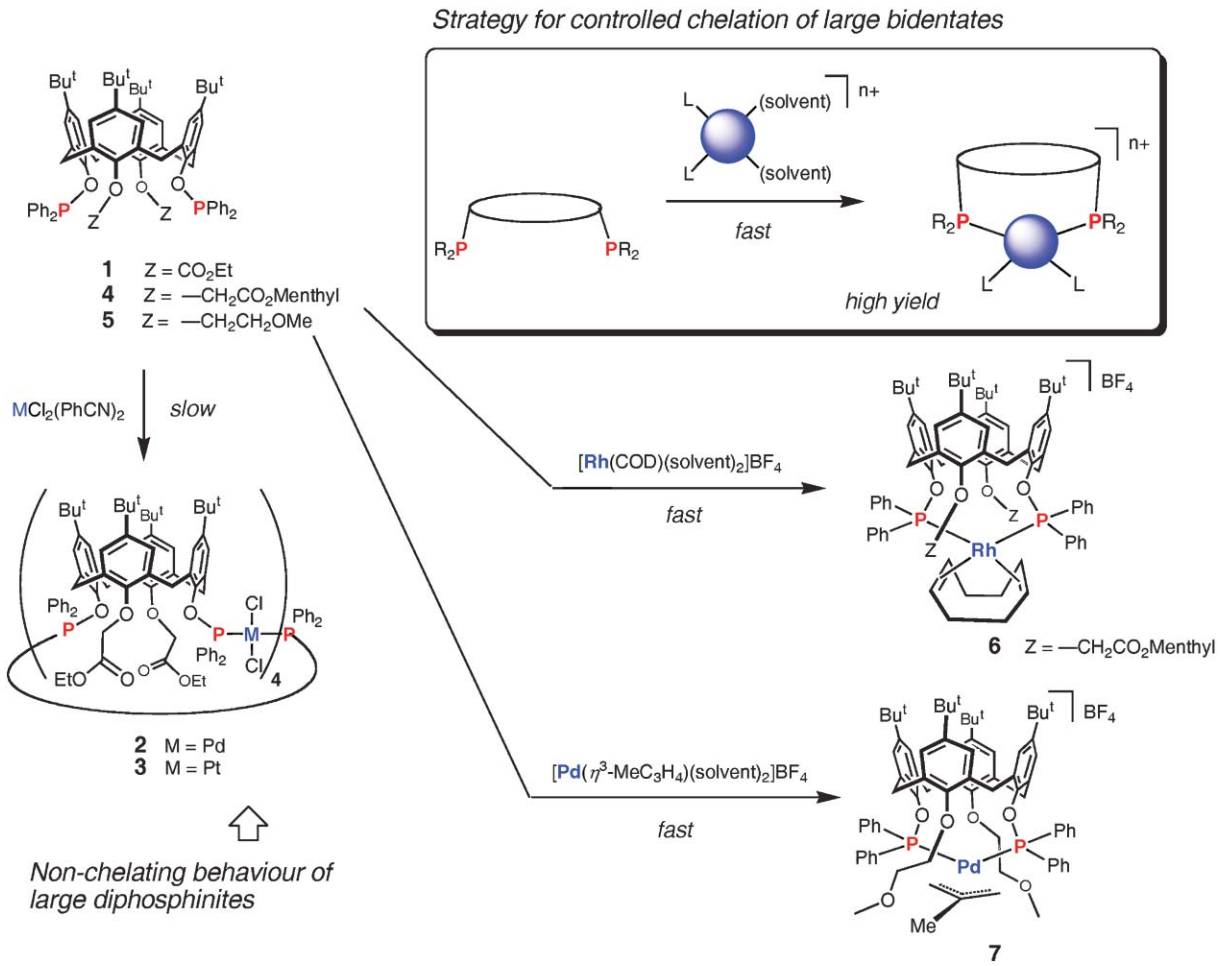


Fig. 2 Controlled *vs.* non-controlled chelating behaviour of large bidentate ligands derived from calixarenes.

shown above. This favors the formation of complexes with trans-arranged phosphorus atoms, and incidentally also that of complexes in which the calixarene may behave as a second coordination sphere. For example, in complex **11**, obtained quantitatively by reacting **10** with $[PtHCl(PPh_3)_2]$, the Pt–H bond points towards the centre of the calixarene, as revealed by an X-ray structure analysis (Fig. 3).[37,38] The particular orientation of this bond probably arises from weak PtH···O interactions (PtH···O[1]: 2.44 Å; PtH···O[3]: 2.73 Å). Unsurprisingly, the sterically well-protected hydride of **11** does not react with activated alkynes to give an insertion product. However, by treatment of **11** with $AgBF_4$, the coordination plane undergoes a rotation of *ca.* 90°. The resulting complex, **12**, contains a less congested hydride which smoothly reacts with dimethylacetylene dicarboxylate to give the alkenyl complex **13**. On the other hand, the semi-protected Pt–H bond of **12** can be reoriented towards the centre of the cavity.[38] This can be achieved by displacement of the coordinated amide with a strong donor, *e.g.* 4,4′-dipyridine, which leads to **14**. Finally, it should be mentioned that the whole complexation process leading to **11** is controlled by the presence of the two $–CH_2CONEt_2$ auxiliary groups. Their replacement by weaker donors, for instance $–CH_2CO_2Et$ or $–CH_2OMe$, decreases or even totally inhibits the complexation process, indicating that the first step in the binding of platinum is attachment to amide-*O* and not directly to either of the phosphine centres.

An example of a conical molecule with a "claw" substituent is the homotrioxacalix[3]arene **15**.[39] The phenol rings of this homotrioxacalixarene are linked through $–CH_2OCH_2–$ spacers, thereby delineating a larger cavity than those defined by the calix[4]arenes described above (distance between the arene centroids *ca.* 6.5 Å). Ligand **15** displays C_{3v}-symmetry and as such is perfectly suited for the stabilisation of complexes with a trigonal bipyramidal stereochemistry. For example, reaction of **15** with $[Rh(acac)(CO)_2]$ under CO/H_2 at 20 bar gave selectively and quantitatively the hydrido carbonyl complex **16**. The fact that this ligand is able to discriminate between the two possible orientations of the H–Rh–CO vector, up- or downwards, probably relies again on weak interactions between the hydride and the oxygen atoms of the cavity. Note that although complex **16** catalyses the hydroformylation of styrene in toluene, the linear/branched aldehyde ratio (12:88) is close to that observed with conventional catalysts, hence excluding a role of the calixarene cavity as a substrate receptor in the whole catalytic process.

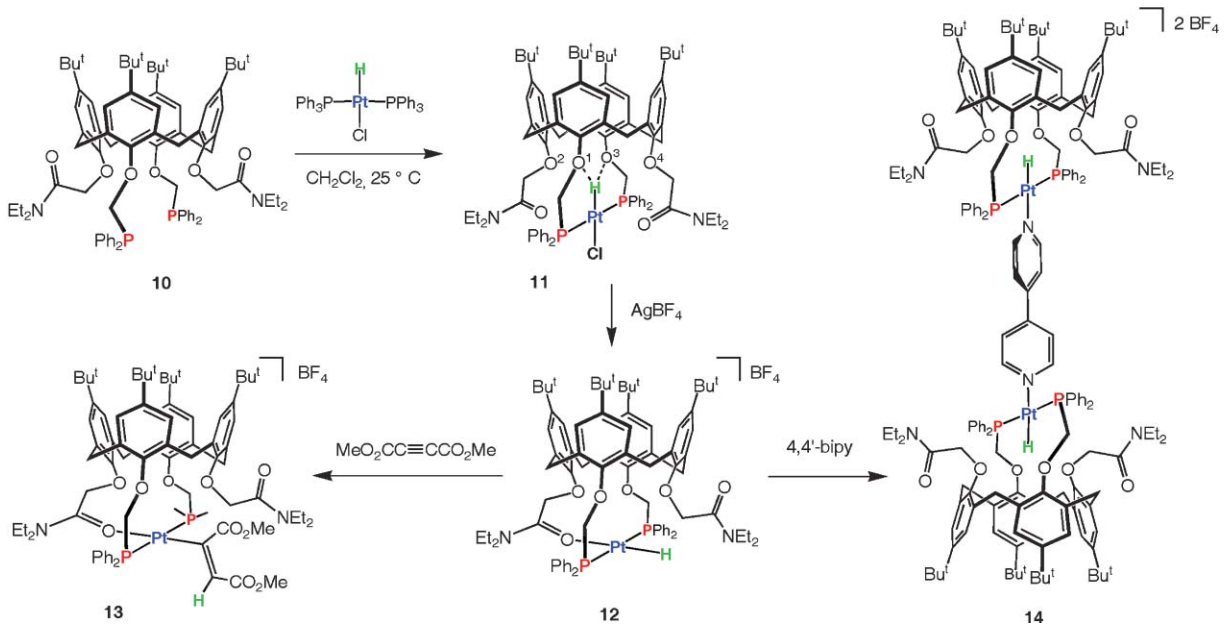
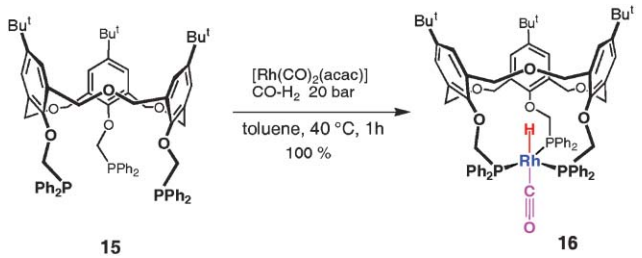


Fig. 3 Encapsulation and release of a Pt–H bond in a molecular pocket.



The introduction of metal-organic fragments inside a calix[4]arene core is possible with the upper-rim diphosphinated calixarenes **17** (Fig. 4). Thus, reaction of **17** with $[RuCl_2(CO)_2]_n$ (obtained by reaction of commercial $RuCl_3$ with CO in refluxing ethoxyethanol) affords the unstable chelate complex **18** which, under illumination, slowly isomerises into the all-trans complex **19**.[20] The introverted carbonyl ligand of this complex, which is sandwiched between two phenol rings, sits deep inside the calixarene, much deeper than guests in the usual calixarene inclusion complexes. The separation between the CO unit and the two ArP rings is relatively short, 2.7 Å, strongly suggesting that weak interactions with the two bordering walls take place.

The strategy discussed above, aimed at positioning metal-organic fragments inside a cavity, is based on the use of cavity-shaped objects in which one opening bears an endo-oriented chelating subunit (or a claw). Most importantly, by immobilizing the metal centre near the entrance of the cavity, it facilitates the formation of metallocavitands directing at least one coordination site towards the interior of the cavity. In fact,

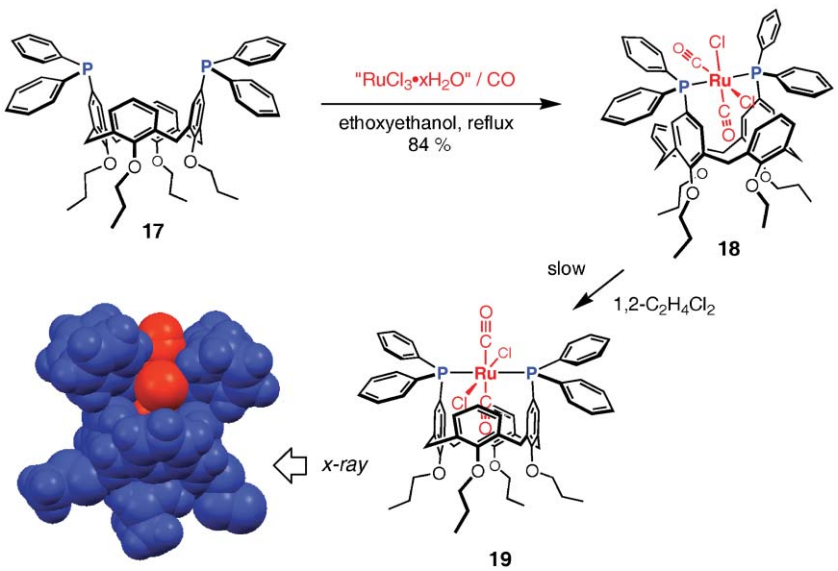


Fig. 4 Directed positioning of a "$RuCl_2(CO)_2$" unit inside a calix[4]arene core.

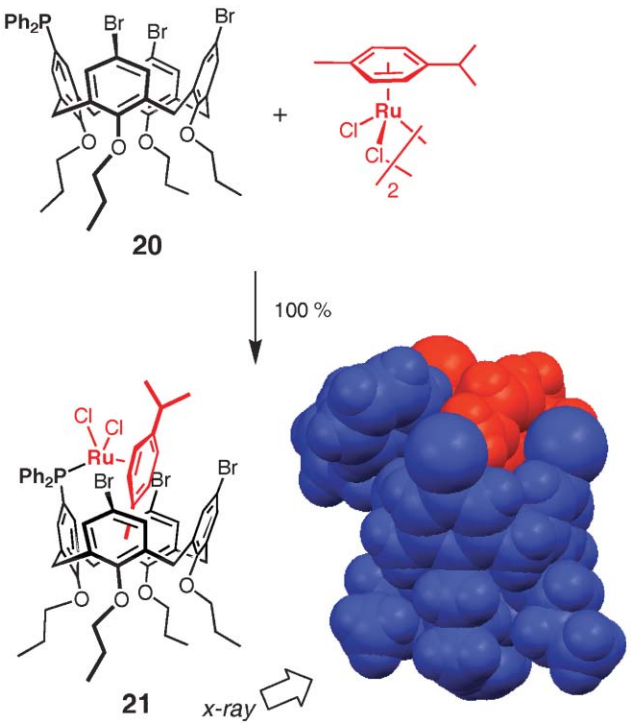


Fig. 5 Entrapment of a "$RuCl_2$(*p*-cymene)" moiety inside an extended calix[4]arene basket.

some particular non-chelating systems may also lead to the same result. For example monophosphine **20** reacts with $[Ru(p\text{-cymene})Cl_2]_2$ to form quantitatively the complex **21** where the bound "$RuCl_2$(arene)" unit sits in the middle of the calixarene basket with the *Me*(Ar) group pointing to the centre of the cavity (Fig. 5).[40] This property holds in the solid state and in solution as well, as inferred from 2D ROESY experiments. Similar reactions carried out with non-brominated versions of **20** result exclusively in complexes where the metal units are oriented away from the cavity.[16] The origin of the directional properties of **20** is not known yet, but probably arises from preorientation of the phosphine lone pair, although anchimeric assistance of an adjacent bromine atom during the complexation process cannot be excluded. On the other hand, the fact that the metal unit is retained in the basket may undoubtedly be assigned to the presence of the two bulky facing Br atoms that hinder rotation about the P–C(calix) axis.

Chemistry at metal sites located inside molecular cavities

As indicated above, when a transition-metal is fixed at the mouth of a conical cavity, the cavity can wrap around the inner ligands so as to behave as a second sphere ligand. To ensure that the catalytic reaction takes place inside the cavity, it is necessary that the cavity can accommodate two substrates located on adjacent coordination sites and also that *intracavity* ligand exchange processes are feasible. Funnel complexes based on cyclodextrin-phosphines were recently shown suitable for such exchanges.[41,42] Thus, the diphosphine silver complex $[Ag\cdot\mathbf{22}]BF_4$ *reversibly* reacts with an excess acetonitrile to result in an equilibrating mixture of complexes **23** and **24** hosting, respectively, one and two acetonitrile ligands

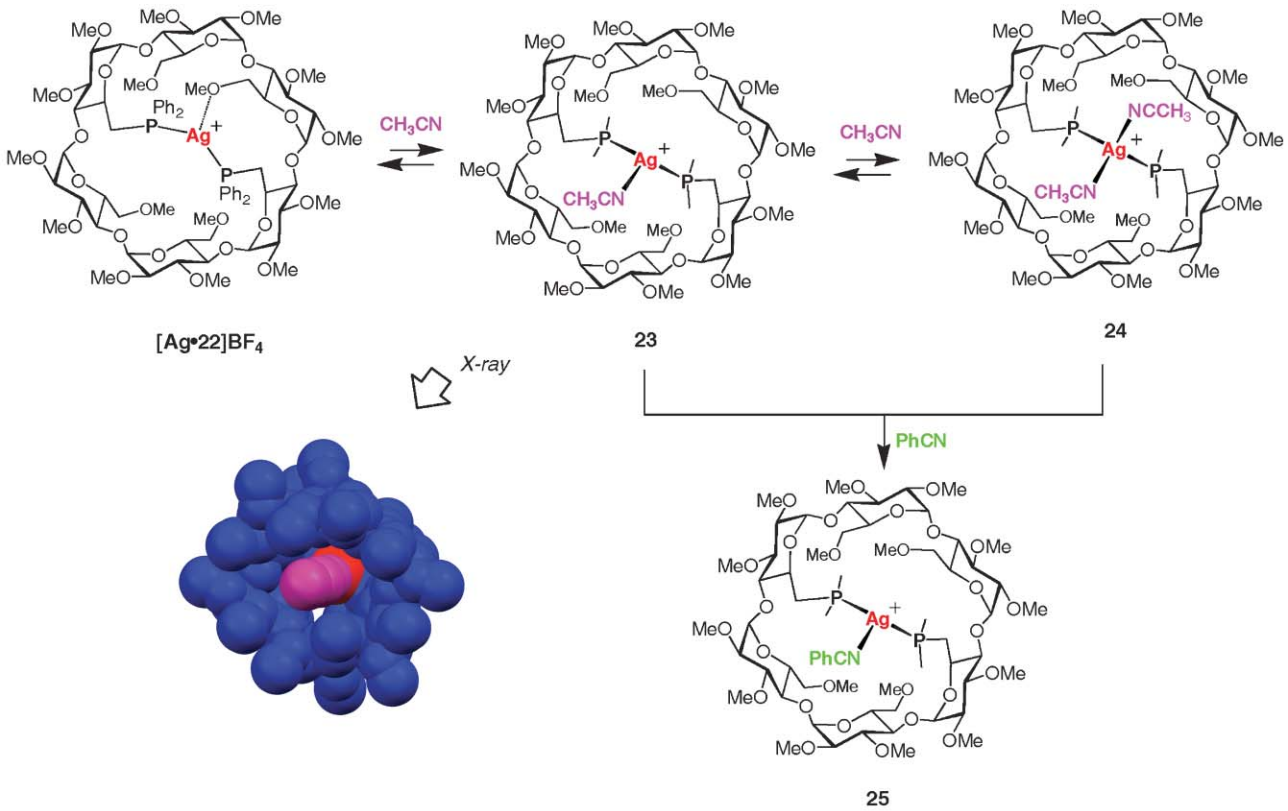


Fig. 6 Ligand exchange processes inside a metallocyclodextrin.

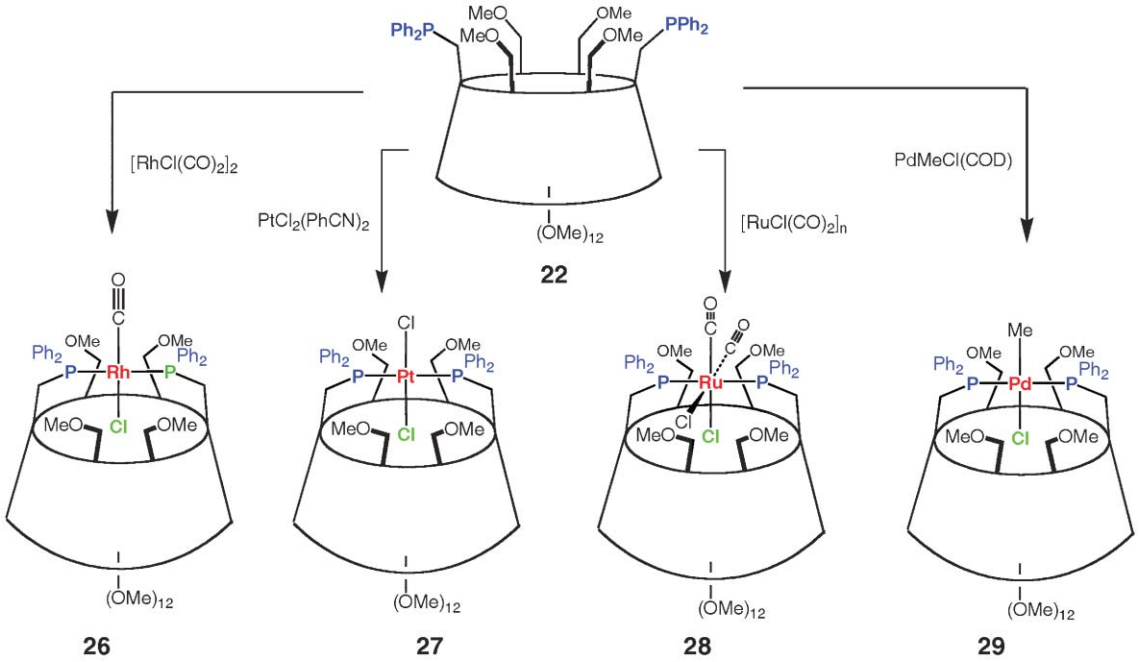


Fig. 7 Reactions of cavitand **22** with various d^8-metal-ion chlorides.

(Fig. 6).[41] It is noteworthy that complex **24** constitutes the only characterized example of a silver cation of the type $[Ag(phosphine)_2(nitrile)_2]^+$, although the existence of such complexes was already postulated 30 years ago by Venanzi and co-workers.[43] The unexpected stability of **24** clearly relies on a *cavity effect*, the cavity walls favoring recombination of the complex as soon as one of the nitriles dissociates. As expected, the acetonitrile ligands of **24** may be exchanged with other nitriles; for example benzonitrile reacts with the **23**/**24** mixture to afford the mononitrile complex **25**.

A remarkable feature of ligand **22** is its propensity to form square planar complexes with d^8-metal-ion chlorides in which the coordinated chloride points to the centre of the cavity, as, *e.g.*, in **26**–**29**.[42,44] In all these complexes the diphosphine exclusively behaves as a trans binder (Fig. 7). Note that chloride entrapment occurs even in the presence of the smaller CO ligand or that of a methyl group which is perfectly compatible with the interior of such a lipophilic cavity. X-Ray structure investigations coupled with 2D NMR experiments (Fig. 8) unambiguously showed that the observed *chlorophilicity* relies on supramolecular interactions between the included chloride atom and some of the inner H-5 atoms of the CD (H-5 atoms are attached to the C-5 atoms of the glucose units, see Fig. 8). In the platinum complex **27**, for example, the encapsulated chloride atom approaches two symmetrically positioned H-5 atoms (Fig. 9) as close as 2.6 Å, while the interacting proton signals have undergone an upfield shift of *ca*. 1 ppm with respect to those of the free ligand.

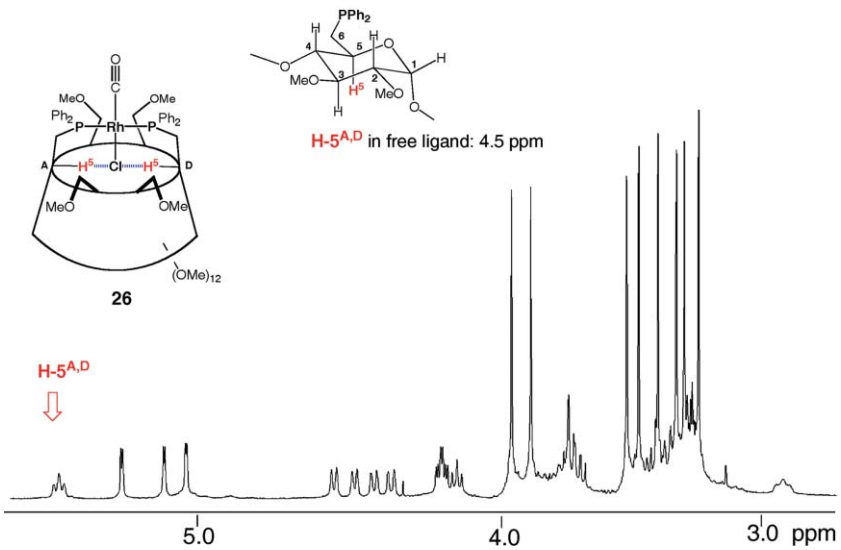


Fig. 8 Supramolecular MCl···HC interactions within the rhodium cyclodextrin complex **26**.

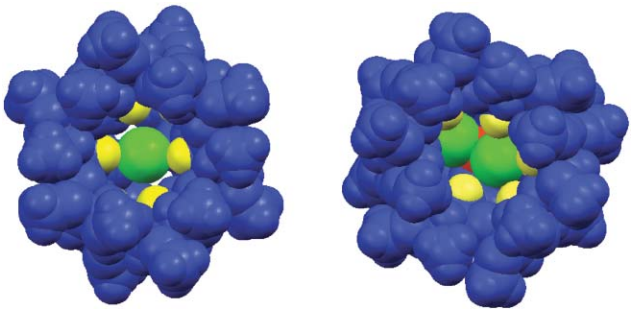
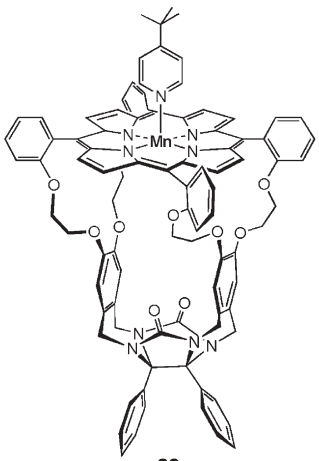


Fig. 9 X-Ray structures of the metallocyclodextrins **27** and **28** seen from the secondary face (space filling representation). The chloride atoms are in green, the H-5 atoms in yellow.

Surprisingly, in the octahedral ruthenium complex **28**, the cavity was also found to be capable (Fig. 9) of hosting two chloride anions, hence demonstrating its strong affinity for metal-bonded halides.[42]

A very challenging idea that arose in recent years is that of achieving metal-catalysed reactions in open, cavity-shaped molecules.[11,17,45] Reactions of this type have to be distinguished from those of supramolecular catalysts in which the substrate alone rather than the whole catalytic centre is temporarily entrapped inside a receptor.[11,17,45–50] Among the pioneering contributions in this area are those of Nolte and Rowan who used the molecular clip **29**.[51] This complex comprises a glycoluril unit capped with a Mn-porphyrin roof. Addition of *p-tert*-butylpyridine activates the Mn centre through exo-coordination and results in a catalyst which epoxidises olefins inside the clip. As shown by comparative experiments with porphyrins having nonshielded faces, the cavity of **29** provides efficient protection from oxidative decomposition. Note that the concept of embedding metal centres inside cavities with the hope of increasing their stability against decomposition reactions has also recently been exploited by the group of Reinaud.[52]



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The only reported olefin polymerisation procatalyst operating in a conical cavity is the iron complex **31** obtained from β-CD **30** (Fig. 10) in which an endo-oriented 1,3-diiminopyridine moiety bridges the primary face of a β-cyclodextrin unit.[45] After activation with MAO, the complex polymerises

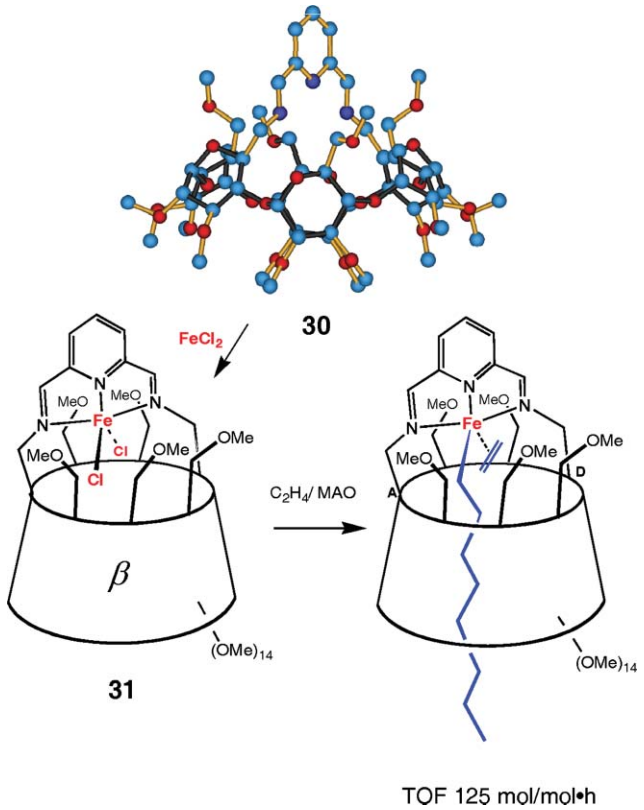
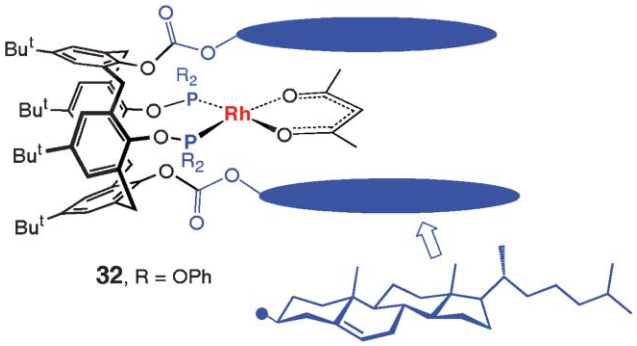


Fig. 10 Ethylene polymerisation through a molecular tube.

ethylene, resulting in the formation of a PE which in terms of melting point and crystallinity is similar to that obtained from the conventional Gibson/Brookhardt catalysts.[53] The catalytic activity of **31** is however weaker than that of the latter systems, possibly because of the steric encumbrance about the iron centre, which is surrounded by five $-CH_2OMe$ groups. Overall this catalyst constitutes the first example of a polymerisation catalyst in which chain growth takes place inside a tubular molecule. Size-optimised, hydrosoluble variants of the latter should lead to new water-soluble polymerisation catalysts.

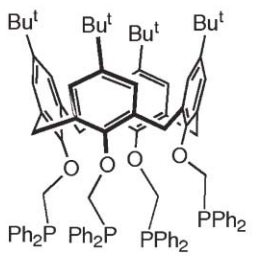
Another expected outcome of intra-cavity catalysis is that of making a catalytic reaction shape-selective. In the rhodium phosphite complex **32** the metal ion is confined in a pocket consisting in two symmetrically located OCO_2–cholesteryl fragments and two $OP(OPh)_2$ subunits.[36] Complex **32**, once activated with H_2/CO (20 bar, $T = 80$ °C) becomes an efficient hydroformylation catalyst of octene leading to a l:b aldehyde ratio of *ca.* 11. When the OCO_2–cholesteryl groups are replaced by the smaller O-*n*-propyl groups, the selectivity drops to *ca.* 2.5, suggesting that a tighter pocket favors the formation of Rh(*n*-alkyl) intermediates over that of Rh(*i*-alkyl) ones. Whether the observed trend is really due to a difference in shape of the metal environment rather than a significant bite angle modification of the ligand cannot be stated with certainty, but recent studies by Börner, Schmutzler and co-workers,[54] Paciello *et al.*[55] and also of our laboratory[56] are consistent with this conclusion. Evaluation of the idea that the cavity effect is predominant requires further investigation, notably with metallocavitands in which the metal sits deeply inside rigid pockets. It is also worth mentioning here that

metallated container molecules were recently shown suitable for highly diastereoselective additions of Br_2 to C=C double bonds.[57] The latter, however, are only stoichiometric.



Cavity-skeleton/metal interplay in metallocavitands with exo oriented metals. Ion movements at the periphery of calixarenes

Many conical molecules such as calixarenes or cyclodextrins provide unique platforms for the multiple attachment of functional groups suitable for exo-coordination.[30,58] The coordination properties of the resulting podands may depend strongly on the properties of the platform itself, notably its flexibility/rigidity and also the separation between the different anchoring points. Tetraphosphine **33**[59] constitutes an interesting example of ligand that may adopt several different binding modes. Examples are found in the structures of complexes **34**–**37**.[60,61]



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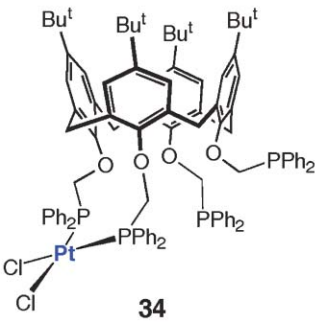

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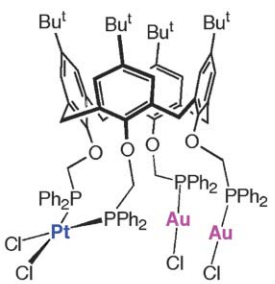
An illustration of the way the calixarene backbone may influence the coordinating properties of **33** was provided by carrying out a UV-visible spectroscopic titration combined with an NMR study of the reaction between **33** and 4 equiv. of [AuCl(tetrahydrothiophene)].[62] This reaction results rapidly in the tetragold complex **37** containing four gold atoms lying at the periphery of the cavity. Detailed analysis of the titration revealed that during the first complexation step a mononuclear species is formed (Fig. 11). This displays dynamic behaviour, NMR studies revealing that all four phosphorus atoms are involved in coordination. In other words, the chloro-gold units jump from one phosphorus atom to the other, and of course, both intermolecular and intramolecular jumps may occur. Calculations favour a tetrahedral geometry of the gold centres. As can be inferred from the β_2 value, the binding of the second gold unit is slightly disfavored over the first one. This observation appears consistent with the fact that all four phosphorus atoms do already participate in metal binding after addition of the first gold moiety. Again, in the then formed intermediate the gold units move between the individual phosphorus atoms. Attempts to crystallise the complex formed after addition of two equivalents of gold, afforded the polymeric complex **38** having the expected stoichiometry and in which the calixarenes are linked together *via* gold centres. The X-ray structure of **38** (Fig. 12) shows that the linking gold atoms have near-trigonal geometry with an axial site being occupied by a chlorine atom. They are coordinated by two phosphine ligands from different calixarenes. The isolated polymer is labile in solution and in fact the solid state structure may be viewed as a snapshot showing the precise moment where the gold jumps from one calixarene to the other. The next step, namely the complexation of the third gold atom, could not be distinguished from the ensuing formation of the tetranuclear complex. Overall tetraphosphine **33** behaves as a ligand bearing four interdependent ligands, its reaction with AuCl units resulting in an intricate complexation process in which each binding step controls the next one, either through positive or negative cooperativity. The ability of the gold units to move along the calixarene backbone while **37** is being formed obviously also reflects the high flexibility of the calixarene backbone.

Rapid metal migration was also observed in the dinuclear complex **39**, formed when tetraphosphine **33** was reacted with the cationic complex $[Au(THT)(THF)]^+$ in excess.[60] As inferred from variable-temperature NMR studies, the complex is dynamic in solution, each gold atom switching from one *P*,*P*′ chelating subunit to an adjacent one (Fig. 13). Thus the two gold atoms rotate simultaneously on the P_4 surface. The same concerted motions were also found in the corresponding disilver complex. Interestingly, the latter showed nonzero *J*(PAg) coupling constants, suggesting that during the fluxional process the metal ions remain permanently linked to at least one phosphorus atom. The origin of the motions



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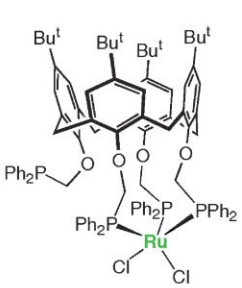

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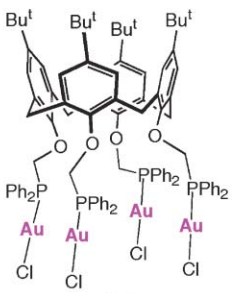

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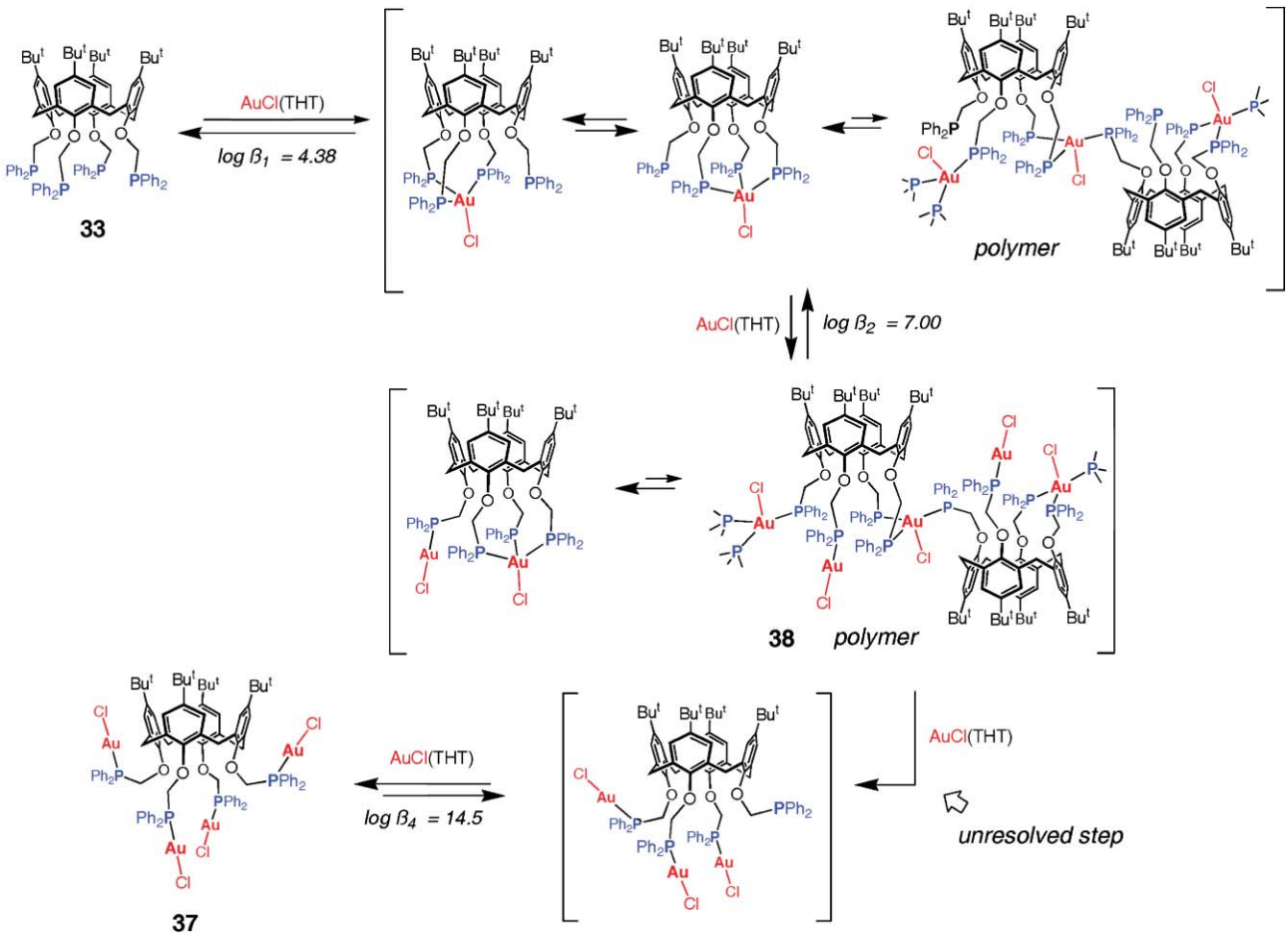


Fig. 11 Cooperativity in the assembly of a tetragold calixarene complex. Intra- and intermolecular migrations of AuCl fragments.

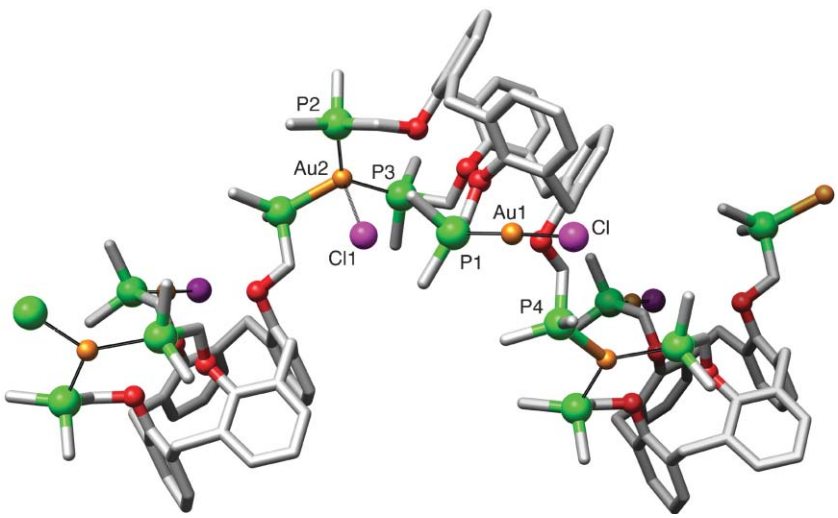


Fig. 12 X-Ray structure of the labile, inorganic polymer **38**. For clarity only the *ipso* C-atoms of the P*Ph* rings are shown.

observed in these complexes is incompletely understood. Exhaustive coordination studies carried out with **33** and related polyphosphines have shown that two adjacent $-CH_2PPh_2$ arms display a marked tendency, when acting as a chelating moiety, to form complexes with *cis*-bonded phosphorus atoms (P–M–P $\sim 90^\circ$ with the metal centres being oriented away from the calixarene axis).[63–65] In fact, the only example where two adjacent phosphine arms approach a *trans* binding situation is that of the [Ni(diphosphine)Br_2] complex **40**, for which the diphosphine bite angle is limited to 158.6° in the solid state. Thus, it appears plausible that the PAuP units of **39** cannot adopt the ideal digonal geometry usually

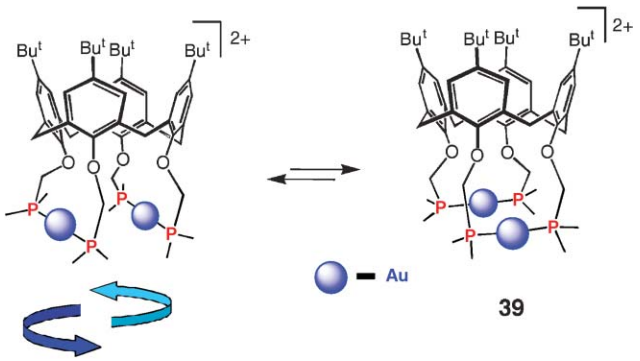
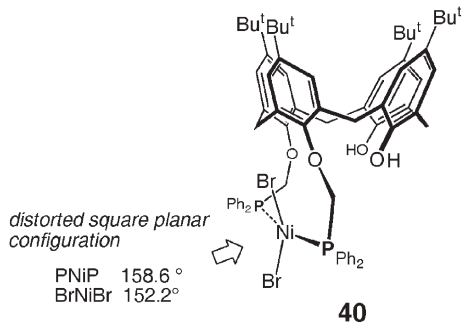


Fig. 13 Mobility of gold ions at the periphery of a calix[4]arene.

observed in gold(I) diphosphine complexes. In other words, the metallomacrocyclic units of **39** are strained, hence leading to facile phosphorus–gold cleavage.



The flexibility of calix[4]arenes is often described in terms of breathing of the calixarene core, involving a fast C_{2v}–C_{2v} equilibrium where distal phenyl rings alternate between near-parallel and inclined arrangements.[66] The ability of the backbone to increase or decrease the separations between the anchoring points is, surprisingly, maintained in complexes such as **41–43** despite the presence on the upper rim of a short Ph_2P–M–PPh_2 capping unit.[67] The solid state structure of these complexes reveals that in all of them the metal plane is roughly perpendicular to the calixarene axis but with the metal displaced to one side of that axis. Similar observations were also made by Tsuji and co-workers[68] As revealed by NMR studies, the complexes undergo a double movement (Fig. 14) in solution: (a) a fanning motion of the metal plane which displaces the metal centre from one side of the calixarene axis to the other; (b) a rotation of each PPh_2 moiety about the corresponding metal–phosphorus bond, so that the two *endo*-oriented rings alternate in blocking the side of the calixarene cavity not covered by the metal. The fanning motion may be viewed as one coupled to the breathing mode of the calixarene unit. Molecular mechanics calculations show the M–P–M angle to significantly increase during this motion, reaching a maximum of *ca.* 124° when the metal crosses the calix axis. Interestingly, as shown by Lejeune and Sémeril, the related nickel complex **44**, once activated with MAO,[67] becomes a remarkably active ethylene dimerisation catalyst when compared with other $[NiX_2(phosphine)_2]$ complexes, notably the industrially used $[NiCl_2(PCy_3)_2]$.[69] Turnover frequencies higher than 10^6 (mol C_2H_4) (mol Ni)$^{-1}$ h^{-1} (!) were observed. Molecular modelling shows that while the angle between the two NiP bonds increases, that between the other two bonds shrinks. In other terms, the two reaction partners of the $[Ni(diphos)(ethyl)(ethene)]^+$ intermediate come closer together, hence favoring the insertion step.

Conclusion and outlook

The examples presented in this study, most of which stem from our laboratory, illustrate the potential of molecules that combine the inherent properties of cavity-shaped moieties with those of covalently-linked transition-metal centres. Clearly, metal centres rigidly fixed at the entrance of a cavity may operate as powerful probes for the study of unusual

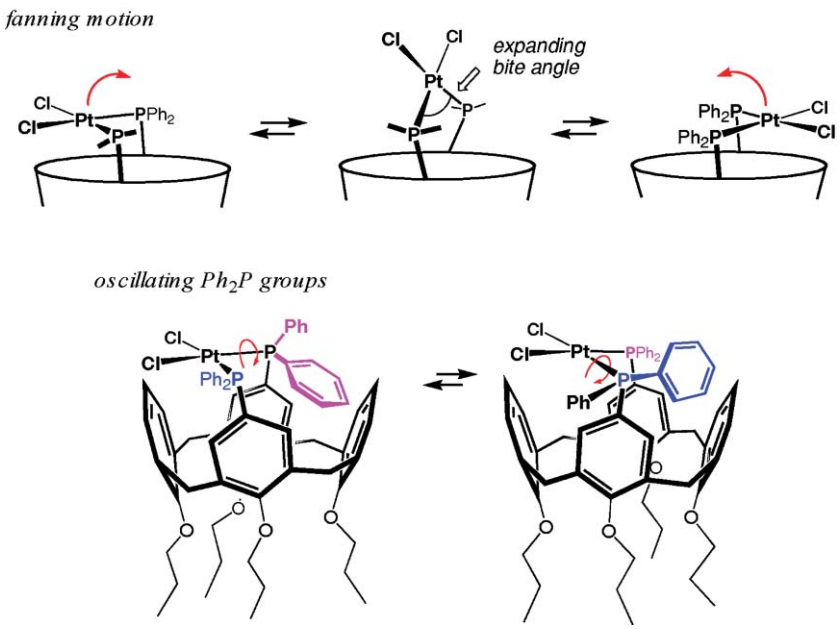
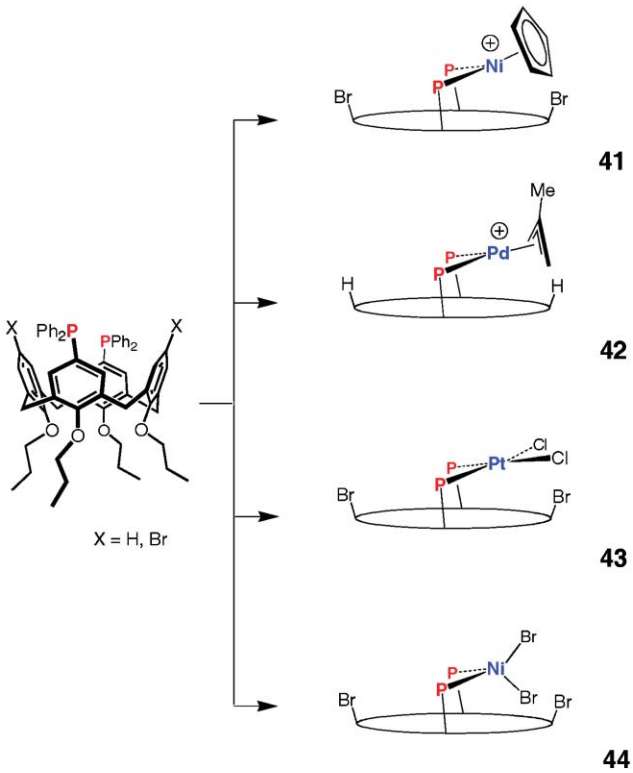


Fig. 14 Double dynamics of complex **43** in solution.



host–guest interactions taking place inside the receptor. Confinement of a metal within a cavity constitutes an novel technique to stabilise reactive metal centres against decomposition and to carry out shape-selective reactions. It further provides a unique way of stabilising unusual coordination compounds. Among the possible future applications of metallocavitands having an endo-oriented metal centre are catalytic reactions occurring inside the cavity. In this respect, two research directions deserve particular attention: (a) the synthesis of water-soluble metallo-cavitands to mediate catalytic reactions in the lipophilic, micro-environment created by the inner part of the cavity, as now the whole catalytic system would be suitable for catalysis in aqueous media; (b) the synthesis of chiral metallocavitands, notably derived from cyclodextrins, in which the proximity of the chiral walls and the catalytic centre should result in high enantioselectivity. Cavity-derived ligands with exo-orienting binding arms also have a high potential. Such platforms, equipped with a large number of ligands that cannot simultaneously bind to the same metal centre, may be useful for simulating ion transport in chaperonin proteins,[70] as the podand arms would be expected to function cooperatively as metal-ion transporters. Last but not least, platforms such as calix[4]arenes, that possess an intrinsic directionally-controlled motion, may strongly influence the complexing and catalytic properties of chelators based on them. In particular, the subset of this group having chelators with variable bite angles will certainly receive increased attention.

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