

# The Development of Platino-Calixarenes

## TRAPPING PLATINUM HYDRIDES IN MOLECULAR CAVITIES

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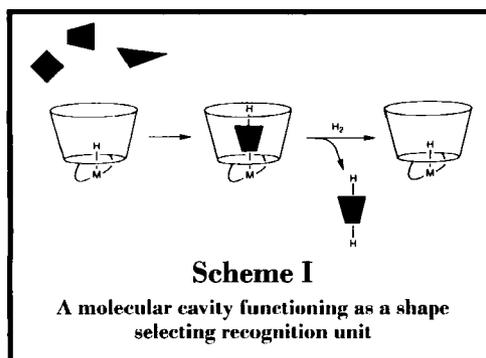
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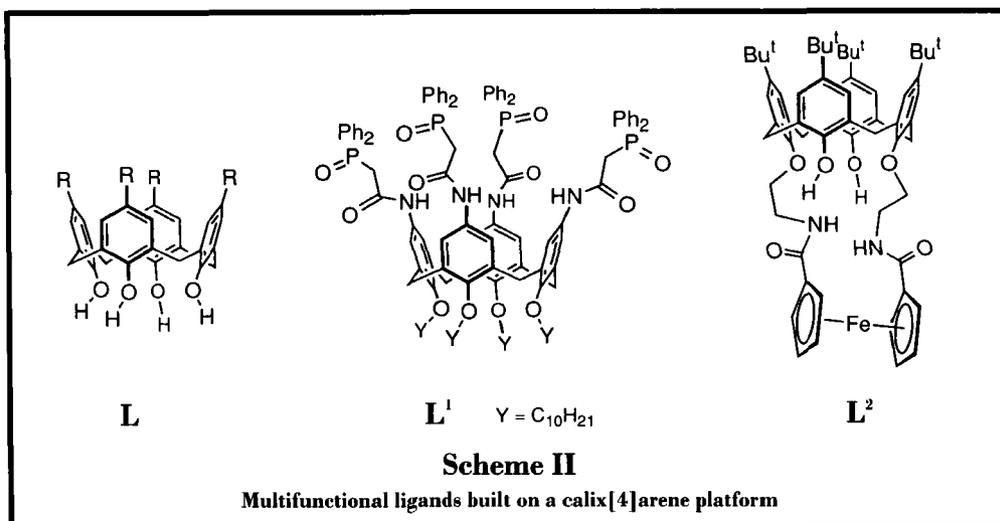
*Although many promising aspects of the chemistry of calix[4]arenes have been highlighted in recent years, relatively little attention has been paid to the coordination chemistry of these macrocyclic molecules. The present paper describes some recent developments made with platinum metal complexes attached to calix phosphine ligands, that is, calixarenes substituted with phosphino groups.*

Hyrido complexes, especially of the platinum group metals, have a pivotal role in homogeneous catalysis (1). They appear as intermediates in many catalytic cycles, including hydroformylation, asymmetric hydrogenation, hydroxycarboxylation, and oligomerisation of olefins. In order to perform highly selective hydrido-mediated catalytic reactions it is essential that ligands are present which allow both fine-tuning of the M-H bond reactivity and proper discrimination of incoming substrates, with the latter being especially important for enantioselectivity. A major limitation of presently available platinum metal hydride catalysts concerns the freely accessible reactive metal centre. With such species, there is no easy way to discriminate between incoming substrates of different shape. A difficult challenge to be overcome during the development of the next generation of hydride catalysts is to locate the platinum metal hydrides inside well-defined

molecular pockets. Such structures are expected to possess valuable properties, in particular with respect to shape-selective reactions, that is, where the cavity functions as a molecular recognition unit by which to channel the substrate to the catalytic site in a preferred orientation, see Scheme I.

Possible synthons for the construction of appropriate molecular cavities are the calix[4]arenes, but there has been little success in combining them with reactive metallo-fragments. Calix[4]arenes (**L**) constitute a class of versatile building blocks that have recently become very useful in the general area of molecular engineering (2). They are cone-shaped macrocyclic compounds comprising four phenolic units linked together in a circular array by methylene bridges connected at the *ortho* positions of the phenolic rings. An essential feature is the presence of phenoxy rings oriented in the same direction, so that, in principle, tethering of functional groups either to the phenolic oxygen atoms or to the *p*-carbon atoms generates well-organised cavities which may provide attractive binding zones for incoming ionic or neutral species. Thus, for instance, the *p*-derivatised calixarene **L'**, see Scheme II, in which the cone shape is retained, displays remarkable complexing properties towards actinides, with a binding affinity being some 200-fold better than that of the monomeric counterparts, namely the *O,O*-chelators, formula  $R_2P(O)CH_2C(O)NRR'$  (3). For other calix[4]arenes showing receptor properties, attachment to the calixarene platform of



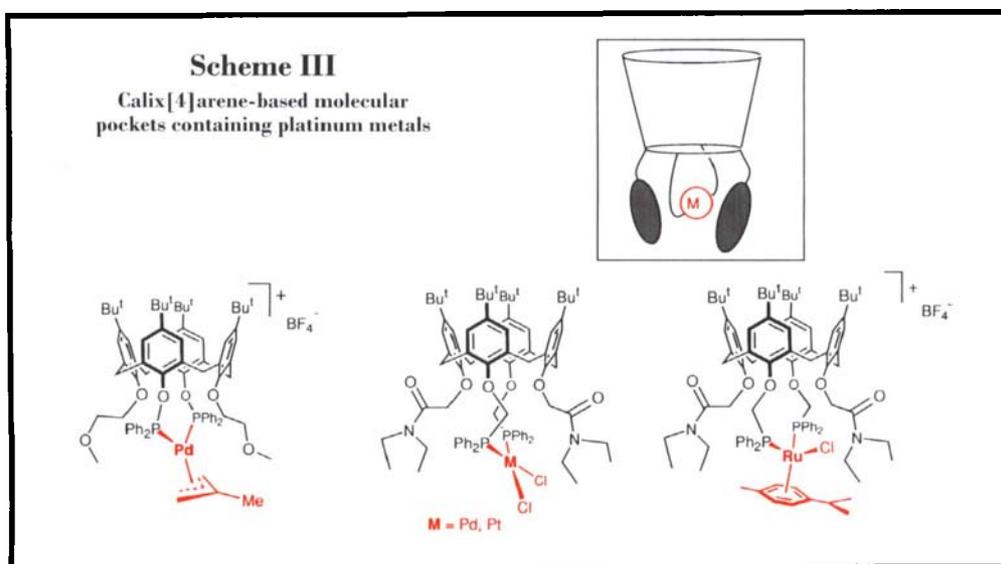


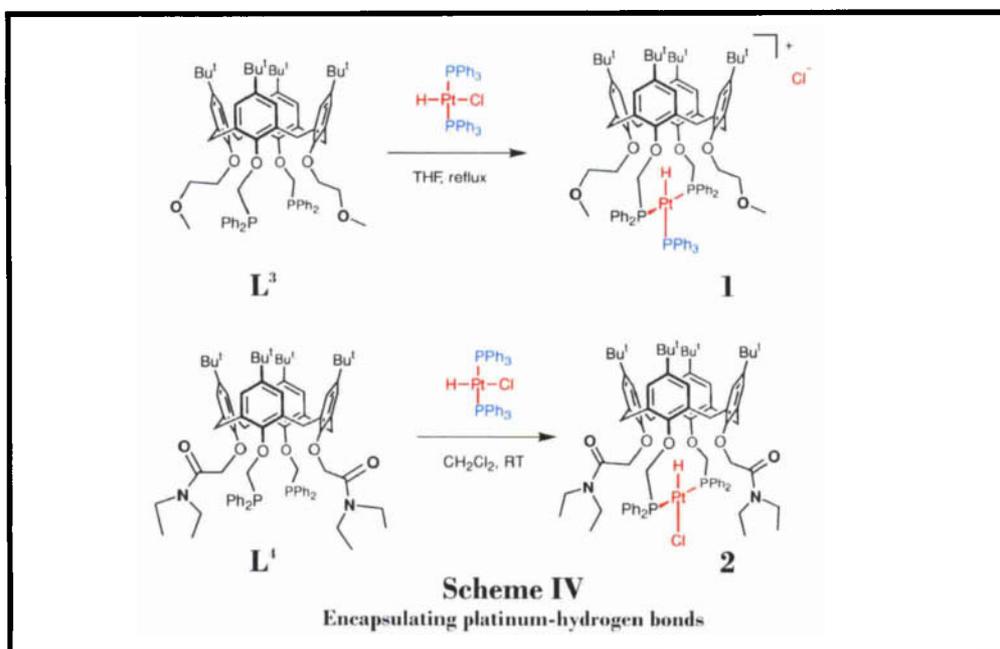
specific additional substituents which contain redox-responsive functionalities – for example a ferrocenyl group as in  $L^2$  – may provide novel potentiometric sensors suitable for the selective detection of various anionic substrates (4).

### Strapping a Metal Centre across the Mouth of a Calix[4]arene

The so-called metallocalixarenes are of particular interest; they form a novel class of complexes having a transition metal centre closely

connected to one mouth of a calixarene. In such compounds several functional groups attached to the calix platform may simultaneously approach the metal atom in a convergent way. They form a protective layer around part of the metallo-fragment that helps in the control of the electronic and redox properties. Examples of compounds in which a metal centre sits at the entrance of a calixarene tunnel are shown in Scheme III. All the complexes in Scheme III were formed from calix[4]arenes bearing two





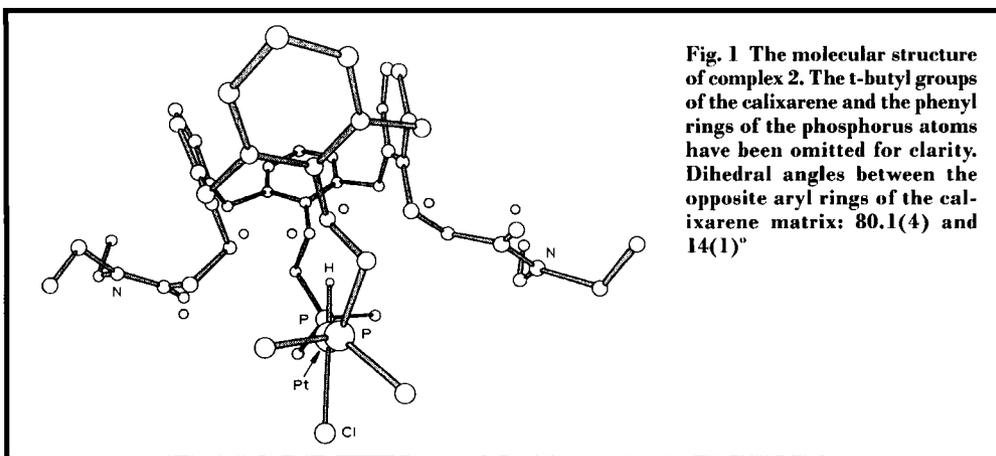
phosphine ligands bound to two distal (or opposite) phenolic units. The auxiliary functions that are attached to the other two phenolic rings ensure the confinement of the metal inside the pocket. The net result is to provide an artificial redox-active enzyme. Phosphino groups were chosen as primary co-ordination sites, because of their ability to form complexes with all transition metals, and their importance to homogeneous catalysis. The auxiliary side-arms are key elements for controlling the solubility, charge, polarity and stereochemistry of the whole complex.

Synthetic methodology for capping a calixarene with a metallo-fragment has been recently developed in our laboratory and is illustrated in Scheme IV (5). The reaction of the mixed ether-phosphine  $L^3$  in refluxing tetrahydrofuran (THF) afforded platinum complex **1**, in 100 per cent yield. The formation of this large metallo-macrocycle (containing two contiguous 16-membered metallo-rings) which occurs quantitatively, regardless of the metal concentration, demonstrates that the macrocycle behaves here as an effective template that allows the diphosphine to function as a chelator.

Replacement of the auxiliary ether groups by other substituents may change the course of the reaction considerably. Thus, if calixarenes with side-chains which possess higher-binding affinities than ethers are used (such as the amide calixarene  $L^4$ ) then both of the triphenylphosphine ligands will be replaced and a neutral hydrido-chloro complex will be formed. The two amide groups of  $L^4$  probably behave as internal solvent molecules, giving rise to the formation of transient penta co-ordinated platinum species which rearrange by successive loss of the triphenylphosphine ligands. A related neighbouring group effect which can promote ligand displacement, sometimes referred to as anchimeric assistance, was also found to operate when the side chains contain ester groups (6).

### Entrapment of Platinum Hydrides within a Cavity

An interesting aspect of the structure of complex **2** is the localisation and orientation of the platinum-hydrogen bond. Two-dimensional rotating frame Overhauser spectroscopy (ROESY) experiments unambiguously demonstrate that the hydride, which resonates at  $-15.04$  ppm



( $J_{\text{H-Pt}} = 1150 \text{ Hz}$ ,  $^3J_{\text{P-H}} = 15 \text{ Hz}$ ), is close to the  $\text{CH}_2$  groups of the four pendant arms and also to the axial H atoms on the bridging methylene groups of the calixarene. In other words, the  $\text{Pt} \rightarrow \text{H}$  vector must point towards the centre of the calixarene cavity. The results of an X-ray structural investigation, see Figure 1, confirms our conclusion drawn from studies of the solution, and shows that the hydride is trapped inside the cavity formed by the substituents. In view of the important crowding that takes place around the platinum-hydrogen bond it is not surprising to find that this bond displays high stability towards potential reagents, such as ethene or  $\text{MeO}_2\text{CC}\equiv\text{CCO}_2\text{Me}$ , which normally insert into the platinum-hydrogen bond, when it is not sterically protected.

Smaller reagents would probably be able to enter the calixarene through the opposite end. If this happens it would result in a reaction taking place inside the cavity, but this goal has not yet been reached. Figure 1 also illustrates the flexibility of the calixarene matrix which adopts a deformed "cone" shape with two phenoxy rings facing each other and the other two lying almost perpendicular. Such a flattened geometry is frequently encountered in calixarenes in the so-called cone conformation (7).

Under forcing conditions, and again with the help of a neighbouring amide group, the direction of the  $\text{Pt-H}$  bond can be modified. Thus, the reaction of complex 2 with silver tetrafluoro-

borate yields the hydrido complex 3, see Figure 2, where the  $\text{Pt-H}$  bond now points to the exterior of the cavity. In this arrangement, the hydride becomes much more reactive and

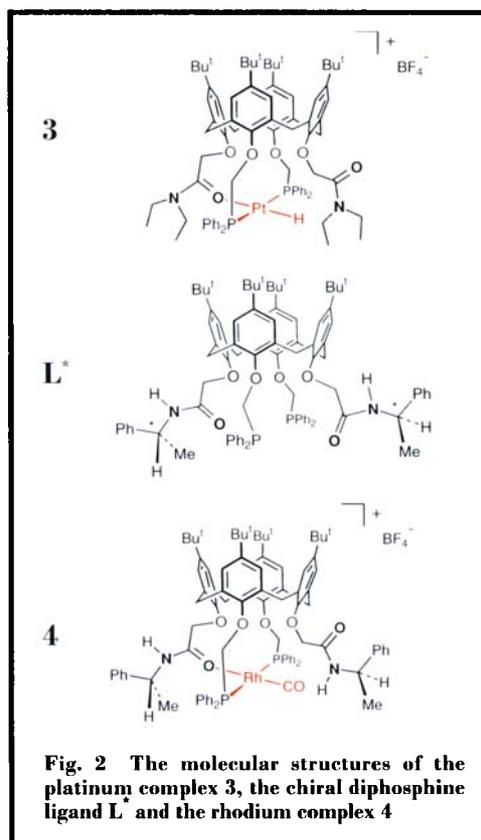


Fig. 2 The molecular structures of the platinum complex 3, the chiral diphosphine ligand  $L^*$  and the rhodium complex 4

participates in insertion reactions with added substrates (*vide infra*). A consequence of the P,P,O-tridentate behaviour of the ligand is that the cavity caps the platinum plane in a way that makes the regions above and below the metal plane asymmetric.

It might be anticipated that structures where a cavity surrounds a co-ordination site would favour activation by the metal of those substrates which possess a shape compatible with the size of the molecular pocket. Furthermore, reactive intermediates formed inside the cavity might be stabilised in such a way as to direct subsequent reactions towards the desired products. We expect to exploit this structural sensitivity of the emerging transition state to optimise catalytic processes such as ethene polymerisation or ethene/CO co-polymerisation.

Structurally-related complexes can also be obtained with rhodium; thus rhodium complex **4** was obtained from the chiral diphosphine **L**<sup>+</sup>, see Figure 2, so as to place the metal in a chiral pocket.

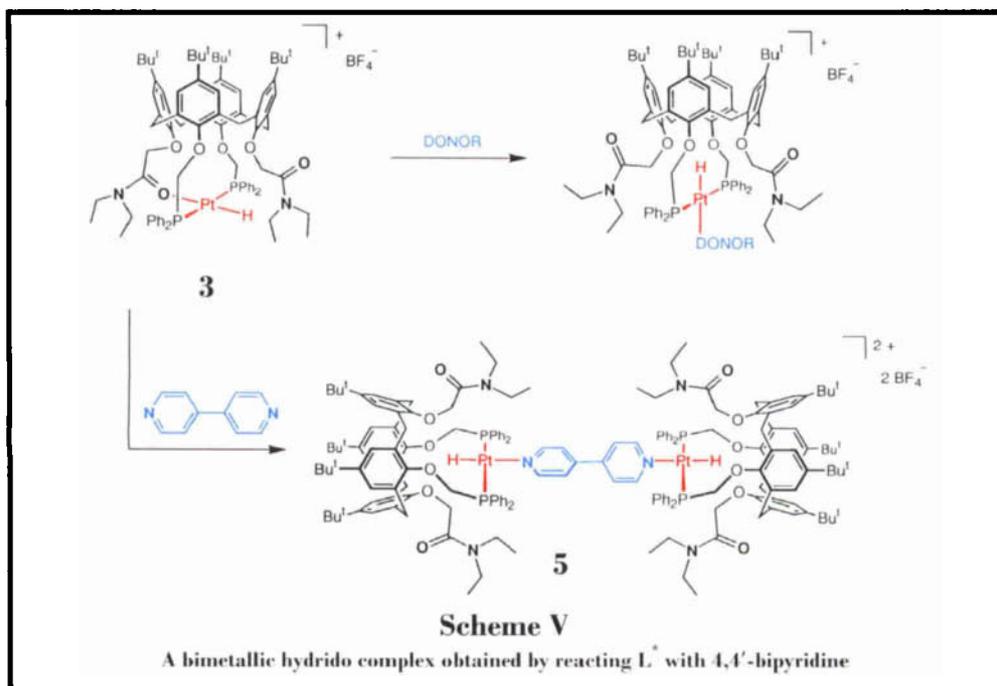
An interesting synthetic methodology for re-inserting the hydride inside the molecular pocket

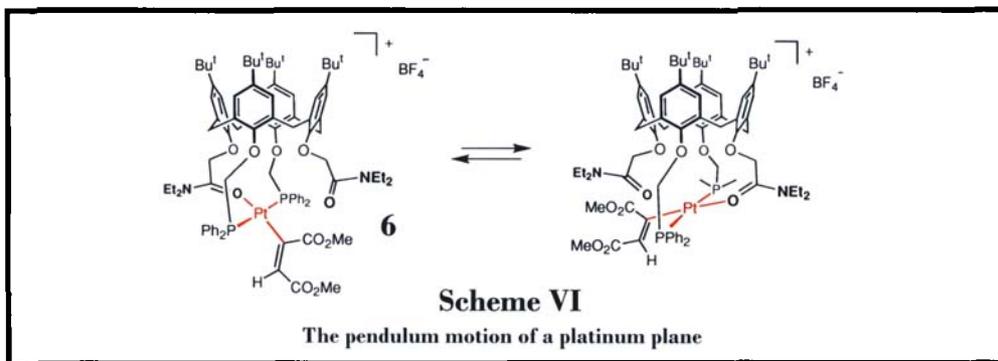
was found when complex **3** was treated with donors that displace the co-ordinated amide group. This strategy not only allows us to vary the electronic properties of the encapsulated hydride, but it also provides access to large assemblies, such as the bimetallic hydrido complex **5**, obtained by reacting **L**<sup>+</sup> with 4,4'-bipyridine, see Scheme V.

In contrast to the encapsulated hydrido complexes which are relatively inert, the "open" hydride **3** reacts readily with electrophilic species resulting in the formation of insertion products. Thus, with dimethylacetylene dicarboxylate (MeO<sub>2</sub>CC≡CCO<sub>2</sub>Me), complex **3** converts into the platinum alkenyl complex **6**.

In this complex the high *trans* influence of the so-formed platinum-carbon bond labilises the co-ordinated amide group and favours substitution at the free co-ordination site by the second amide group. Amide exchange is likely to occur via formation of penta co-ordinated platinum (II) species.

This leads to the pendular motion depicted in Scheme VI. Using a simplified description, this cationic complex can be regarded as containing





a metal centre with a free co-ordination site that remains entrapped inside a cavity and which flips from one amide to the other.

### Future Opportunities

Potential applications of platino-calixarenes are in the field of homogeneous catalysis. The localisation of reactive organometallic fragments inside molecular pockets is primarily expected to favour shape selectivity and promote enantioselectivity, when the pocket is chiral.

A possible extension concerns the development of two-phase catalysts based on cavities substituted with water-solubilising groups located at their periphery. If the interior of the cavity is sufficiently lipophilic, highly efficient phase-transfer catalysis could be achieved. Clearly the dimension of the cavity must be adapted to the size of the substrate. This can be done if one considers that larger calixarenes are now readily accessible. The fact that calixarene matrices offer many opportunities for functionalisation – the aromatic *p*-carbon atoms of the phenol rings may also be functionalised – opens the way for further possible objectives, such as the preparation of immobilised systems suitable for solid state reactions or, provided that the systems contain additional electro- or photo-active functionalities, their use as specific sensors.

### Acknowledgements

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### References

- 1 F. H. Jardine, in "Chemistry of the Platinum Group Metals", ed. F. R. Hartley, Elsevier, New York, 1991, Chapter 13
- 2 C. D. Gutsche, "Monographs in Supramolecular Chemistry", Vol. 1: Calixarenes, ed. J. F. Stoddart, The Royal Society of Chemistry, London, 1989
- 3 F. Arnaud-Neu, V. Böhmer, J.-F. Dozol, C. Grüttner, R. A. Jakobi, D. Kraft, O. Mauprivez, H. Rouquette, M.-J. Schwing-Weill, N. Simon and W. Vogt, *J. Chem. Soc., Perkin Trans. 2*, 1996, 1175
- 4 P. D. Beer, Z. Chen, A. J. Goulden, A. Graydon, S. E. Stokes and T. Wear, *J. Chem. Soc., Chem. Commun.*, 1993, 1834
- 5 C. Wieser, D. Matt, J. Fischer and A. Harriman, *J. Chem. Soc., Dalton Trans.*, 1997, 2391; C. Wieser, C. Dieleman and D. Matt, *Coord. Chem. Rev.*, 1997, **165**, 93; C. Wieser, D. Matt, L. Toupet, H. Bourgeois and J.-P. Kintzinger, *J. Chem. Soc., Dalton Trans.*, 1996, 4041
- 6 E. M. Miller and B. L. Shaw, *J. Chem. Soc., Dalton Trans.*, 1973, 480
- 7 C. Dieleman, D. Matt and P. G. Jones, *J. Organomet. Chem.*, 1997, **545–546**, 461

### Catalytic Reaction Guide

Johnson Matthey has recently updated and re-issued its popular "Catalytic Reaction Guide". In the form of a pocket-sized slide chart, catalyst recommendations, with typical operating conditions are given for 69 key chemical reactions of industrial significance. Over a quarter of the entries are homogeneously catalysed reactions, which acknowledges the increasing importance of this technology.

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