DALTON

Capping calixarenes with metallodiphosphine fragments: towards intracavity reactions†

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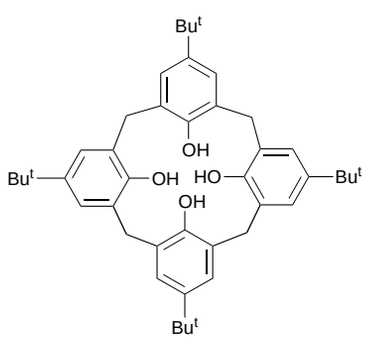
The co-ordinative properties of four disubstituted 5,11,17,23-tetra-*tert*-butyl-25,27-di-RCH_2O-26,28-bis(diphenylphosphinomethoxy)calix[4]arenes [R = $C(O)NEt_2$ L^1, C(O)OEt L^2, (*R*)-C(O)NHCH(Me)Ph L^3 or CH_2OMe L^4] have been investigated. Compound L^1 reacted with $[Au(thf)(SC_4H_8)]BF_4$ (thf = tetrahydrofuran, SC_4H_8 = tetrahydrothiophene) and $AgBF_4$ to yield the chelate complexes $[AuL^1]BF_4$ **1** and $[AgL^1]BF_4$ **2**, respectively. Reaction of L^1 with *trans*-$[PtH(Cl)(PPh_3)_2]$ resulted in quantitative formation of *trans*-$[PtH(Cl)L^1]$ **3** in which the platinum hydrogen bond is partially encapsulated within the calixarene cavity. The structurally related cationic complexes $[PtH(PPh_3)L^i]BF_4$ (L^i = L^1 **4**, L^3 **5** or L^4 **6**), having a PPh_3 ligand *trans* to the hydrido ligand, were obtained in high yield by treating *trans*-$[PtH(thf)(PPh_3)_2]BF_4$ with diphosphine L^i. Abstraction of the chloride ion from **3** with $AgBF_4$ gave $[PtH(L^1)]BF_4$ **7**, a complex in which the calixarene behaves as a tridentate P_2O_{amide} ligand and in which the metal plane caps one end of the calixarene tunnel. Reaction of **7** with PPh_3 resulted in substitution of the co-ordinated amide to form **4**, while reaction with 4,4′-bipyridine gave the binuclear complex $[(L^1)HPt(4,4'\text{-bipy})PtH(L^1)][BF_4]_2$ **8**. Reaction of *trans*-$[PtH(Cl)(PPh_3)_2]$ with L^i resulted in a mixture of complexes of general formula $[PtH(PPh_3)L^i]Cl$ (type **A**) and $[PtH(Cl)L^i]$ (type **B**). The **A**:**B** ratio depends on the co-ordinating ability of the R groups, since these act as internal solvent molecules in promoting PPh_3 substitution. For R groups containing strong donors, *e.g.* as in L^1 and L^2, complexes of type **B** are favoured; with L^4 the reaction leads selectively to $[PtH(PPh_3)L^4]Cl$, no **B**-type complex being formed. In at least one case (L^3) it was shown that complexes of type **A** may be converted into the **B** type. Reaction of **7** with dimethyl acetylenedicarboxylate gave the insertion product *trans*-*P*,*P*′-$[Pt(MeO_2CC{=}CHCO_2Me)L^1]BF_4$ where the two amides compete for co-ordination. Complex **7** reacted instantaneously with tetracyanoethylene (tcne) to yield the platinum(0) complex $[Pt(tcne)L^1]$ for which NMR spectra suggest fast flipping of the co-ordination plane between amides. In contrast to $[Pt(MeO_2CC{=}CHCO_2Me)L^1]BF_4$, strong tridentate P_2O co-ordination abounds in the rhodium carbonyl complexes $[Rh(CO)L^i]BF_4$ (L^i = L^1 or L^3) obtained from $[Rh(CO)_2(thf)_2]BF_4$ and the corresponding diphosphines.

Calix[4]arenes are a class of readily accessible macrocyclic compounds that have become significant in supramolecular chemistry during the last decade.[1–11] They are frequently employed as platforms that permit functional groups to be oriented to provide well organized cavities or clefts. Tethering of pendant arms to such a preorganizing matrix may be achieved at the phenolic oxygen atoms[12–14] and/or at the *para* positions[15–18] of calix[4]arenes. Recent synthetic work concerned with the functionalization of calix[4]arenes has led to the isolation of novel cavity-shaped podands displaying highly selective complexation properties toward certain metal ions,[19,20] and facilitating encapsulation of neutral[21] or anionic[10] substrates. It should be emphasized here that when such selective receptors contain additional redox-responsive functionalities they allow quantitative detection of complexed species, and hence constitute valuable tools for analytical purposes.[22]

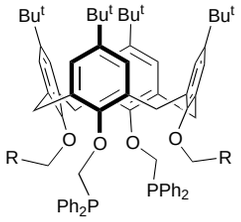
Of particular interest in this area are the calix[4]arene-based transition-metal complexes.[11,23–36] Indeed, it might be anticipated that structures having a metal centre lying close to the mouth of a calix[4]arene pocket would possess interesting catalytic properties with respect to the transformation of suitably shaped substrates. Furthermore, the presence of a high number of converging functional groups located close to a catalytic centre might control the stereochemistry of the reaction and discriminate between several incoming substrates. It is clear that other synergistic effects might be envisaged. We note, however, that studies dealing with the reactivity of organometallic species bound to a calixarene unit remain scarce.[11,37]



p-tert-butylcalix[4]arene

In a preliminary report we have outlined the preparation of an encapsulated hydrido ligand, obtained by entrapment of the 'H–Pt–Cl' fragment by the cone calixarene L^1 (see below), containing the key elements of a diphosphine and two neighbouring amide functions.[38] Structural studies showed that the diphosphine acts as a *trans*-chelator and that the platinum–hydrogen bond lies within the space defined by the four lower-

† *Non-SI units employed*: bar = 101325 Pa.



L^{i}

L^{1} R = C(O)NEt$_2$
L^{2} R = C(O)OEt
L^{3} R = (*R*)-C(O)NHCHMePh
L^{4} R = CH$_2$OMe

rim substituents of the calixarene and is directed toward the centre of the cavity. We now report full synthetic procedures for this work and describe additional hydrides obtained from diphosphines bearing other auxiliary groups.

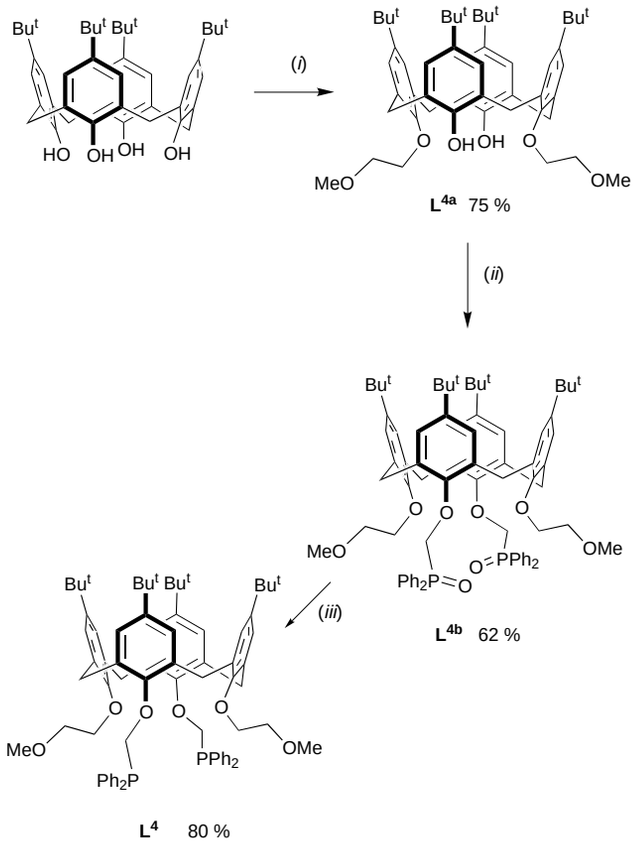
The chemistry reported herein illustrates our basic strategy for the preparation of reactive organometallic fragments located inside or close to a molecular pocket. This approach uses suitably derivatized diphosphinocalixarenes as scaffolds for specific metal fragments. The main advantage of our methodology is that the pendant phosphines are logically sited so as to position the organometallic centre at the mouth of the calixarene cavity. Capped calixarenes of this kind might be expected to utilize the shape selectivity inherent to the pre-formed cavity, the size, polarity and functionality of which can be modulated. An essential feature of our approach is that the reactive component is directed inside the molecular cavity, so as to discriminate in favour of bound substrates. Of the numerous capped calixarenes reported to date, only L^{1} provides a clear example of an encapsulated metal–hydrogen bond. We note that using a different approach, Gardiner *et al.*[39] have recently obtained an aluminium-capped calix[4]arene derivative purported to retain an *endo*-Al–H bond, but a structural determination of this complex remains elusive.

Results and Discussion

In order to strap a transition-metal centre across the mouth of a calix[4]arene it is necessary to attach suitable co-ordinating moieties on distal sites. Owing to their ubiquitous complexing ability,[40] terminal phosphine groups have been selected for the pendant arms, which are kept short to maximize localization of the metal centre. The phosphine groups can be attached at the phenolic oxygen atoms, leaving two further sites where secondary co-ordinating functions can be appended. In order to establish suitable metal complexes assembled at the phosphine ligands, calixarenes L^{1}–L^{4} have been used since these provide the required stereochemical features. These compounds retain a common diphosphine but differ in the nature of the secondary side arms. Synthetic procedures for L^{1}–L^{3} have been described before,[27,28] but compound L^{4} having ether functions is reported here for the first time. This latter compound, each arm of which has two weakly co-ordinating oxygen atoms, is conveniently prepared in a three-step synthesis according to Scheme 1, in 37% yield. Compounds L^{1}–L^{4} allow a gradation of secondary binding sites and, according to NMR spectroscopy,[41] possess the desired cone conformation.

The ability of the diphosphine function to entertain *trans-P,P′* complexation with metal centres was first explored towards Au^{+} and Ag^{+}, since such complexes require no additional ligation.

Compound L^{1} was treated with [Au(thf)(SC$_4$H$_8$)]BF$_4$ (SC$_4$H$_8$ = tetrahydrothiophene) in CH$_2$Cl$_2$ at room temperature (Scheme 2), giving complex **1** in high yield, apparently free of polymeric structures. The FAB mass spectrum of **1** shows an intense peak at 1467, corresponding to the mononuclear



L^{4a} 75 %

L^{4b} 62 %

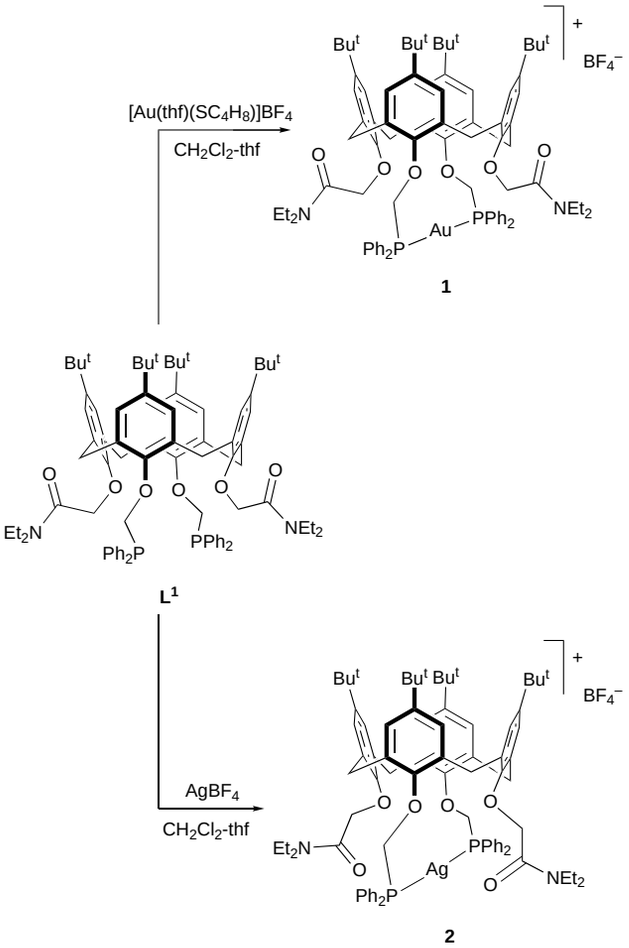
L^{4} 80 %

Scheme 1 Preparation of the mixed ether–phosphine L^{4}. Reagents and conditions: (*i*) K_2CO_3 (1.3 equivalents), $BrCH_2CH_2OMe$ (2.2 equivalents), refluxing MeCN; (*ii*) NaOBu^{t} (2.1 equivalents), *p*-$MeC_6H_4SO_3CH_2P(O)Ph_2$ (2.2 equivalents), refluxing tetrahydrofuran (thf)–dimethylformamide (dmf) (9:1); (*iii*) refluxing $SiPhH_3$

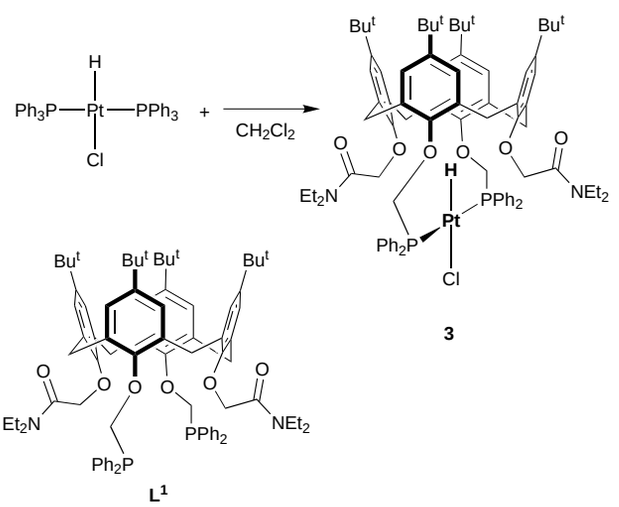
cationic gold species. Its NMR data are consistent with a C_2-symmetrical structure while the chemical shift of the ^{31}P NMR signal is indicative of a linear AuP_2^{+} arrangement.[42] The related silver complex **2** was isolated in high yield by treating L^{1} with $AgBF_4$. As for **1**, NMR data for **2** show equivalence of both phosphine arms and both amide groups. The $J(^{109}Ag–^{31}P)$ value (542 Hz, $CDCl_3$) lies in a range typical for [Ag(L–L)X] complexes (L–L = large diphosphine, X = ClO_4 or NO_3).[43,44] Interestingly, the solution IR spectrum of **2** (thf) shows two strong absorption bands in the carbonyl region (1660, 1629 cm^{-1}), whereas for **1** a single band was found. The situation with **1** is normal and indicates that the secondary side arms are uncomplexed to the metal centre. In contrast the IR data of **2** reflect that the two amide functions lie in different environments as induced by the central silver cation. The most plausible, but unproven, interpretation of this behaviour is that one of the carbonyl groups is weakly bonded to the metal. Presumably, the two amides alternate on a faster time-scale than relevant to NMR spectroscopy. The tight binding constraint imposed by the diphosphine requires that additional complexation with a carbonyl group forms a Y-shaped, rather than a T-shaped, complex. Stable examples of Y-shaped complexes formed from silver(I) appear to be known.[44]

Synthesis of encapsulated and semiencapsulated hydrides

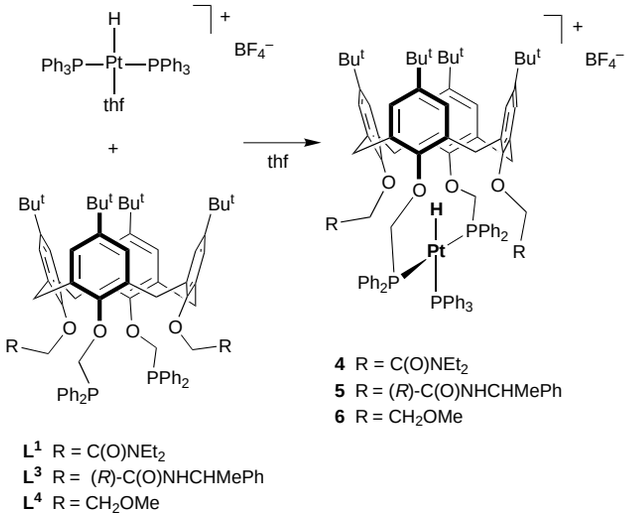
In an effort to increase the co-ordination number of the bound metal, and to employ metals possessing more versatile catalytic properties, attention was turned to the synthesis of platinum complexes. By treating the amidephosphine L^{1} with *trans*-[PtH(Cl)(PPh$_3$)$_2$] in CH$_2$Cl$_2$ ligand exchange occurred, resulting in quantitative formation of the hydrido complex **3** (Scheme 3) which was fully characterized. An important point to emerge from the structural analysis is that vapour-phase osmometry



Scheme 2



Scheme 3



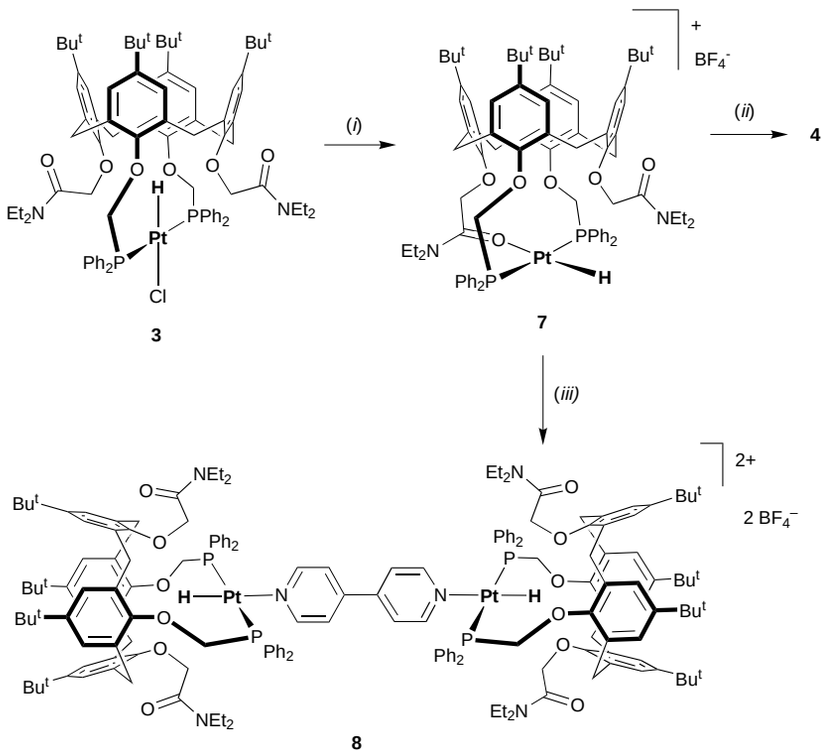
Scheme 4

clearly showed that the complex was monomeric. A two-dimensional ROESY (rotating frame Overhauser enhancement spectroscopy) experiment, performed on a 500 MHz spectrometer, indicated that the hydrido ligand is in close proximity with each OCH_2 group of the pendant arms and also with the axial H atoms of the bridging $C_6H_2CH_2C_6H_2$ units. This suggests that the hydrido ligand is directed into the mouth of the calixarene cavity defined by the four phenolic oxygen atoms. This configuration has been confirmed by single-crystal X-ray crystallography.[38] It is interesting that the formation of **3** requires exchange of the ligated phosphines. It seems likely that such ligand exchange is promoted by the polar amide groups present in L^1, since the analogous reaction did not occur with phosphine L^4. The latter differs from L^1 only by virtue of the co-ordinating ability of the auxiliary side arms.

The presence of the ligated chlorine atom is not mandatory for complex formation since reaction of *trans*-[PtH(thf)$(PPh_3)_2$]-BF_4 with L^1, L^3 and L^4 gave, respectively, complexes **4**–**6** in high yield (Scheme 4). These complexes contain two types of co-ordinated phosphine. According to NMR spectroscopy the resultant complexes are C_2-symmetrical with the co-ordinated diphosphines clearly behaving as *trans-P,P′* chelators [J(Pt–$P_{L'}$) = 2879, 2879 and 2843 Hz, respectively]. The NMR pattern of each hydrido ligand appears as a symmetrical pair of triplets (with platinum satellites) ranging between −4.19 and −4.73 {*cf.* δ −15.04 for **3** and −15.21 for *trans*-[PtH(Cl)$(PPh_3)_2$]}. Interestingly, these hydrido complexes do not transform in solution into the corresponding *cis*-diphosphine isomers, thus contrasting with certain other complexes of the type [PtH(diphosphine)(PPh_3)]$^+$ that contain a *trans*-spanning diphosphine.[45] Extrusion of the Pt–H bond and subsequent isomerization does not take place in our case, presumably because of favourable interaction between the hydrido ligand and one or more oxygen atoms. Such protection against isomerization could be an essential feature of catalytic reactions where a *trans-P,P′* configuration needs to be retained.[46] It should be noted that our synthetic strategy is directed toward the partial encapsulation of the hydride ligand and its subsequent stabilization against extrusion.

Treatment of complex **3** with $AgBF_4$ in CH_2Cl_2 gave the cationic hydrido complex **7**, for which IR (KBr) and NMR spectra unambiguously show one amide group to be free and the other to be co-ordinated (Scheme 5). We consider, therefore, that one pendant carbonyl group fills the vacant co-ordination site. This has the effect of displacing the other carbonyl group away from the metal centre. One important stereological feature of **7** is that the regions immediately above and below the platinum centre are markedly disparate, such environmental asymmetry being rare in platinum chemistry.[45] The P_2O ligand may be regarded as an hemispherical ligand strapping the metal centre across the mouth of the calixarene. There is no indication that the amide groups interconvert and the ^{1}H NMR spectra remain essentially independent of temperature over the range −30 to +80 °C in $C_2D_2Cl_4$.

The co-ordinated amide group was readily replaced by adventitious donors, such as PPh_3 or 4,4′-bipyridine yielding, respectively, the mononuclear complex **4** and the binuclear complex **8** (Scheme 5). This extrusion and subsequent complex-



Scheme 5 Reagents and conditions: (*i*) $AgBF_4$ (1 equivalent), in CH_2Cl_2; (*ii*) PPh_3 (1 equivalent), in CH_2Cl_2; (*iii*) 4,4′-bipyridine (1 equivalent), in $CHCl_3$

ation strategy provides a valuable route to the synthesis of novel calixarene-derived platinum hydrides. In the two examples quoted the hydride ligand is reinserted inside the molecular pocket. In this way the electronic properties of the hydride can be varied over a wide range simply by judicious selection of the external ligand while linear bimetallic complexes can be assembled around different ditopic bridges. It should be possible to change both the length of the spacer and the extent of electronic coupling between the platinum centres whilst maintaining all other structural attributes.

Role of the auxiliary functions for the formation of hydrides of type 3

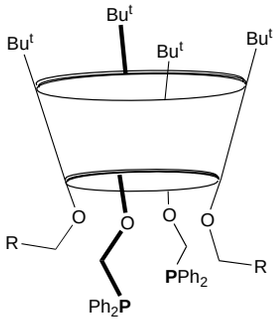
Assemblage of our basic building block **3** is accomplished *via* ligand exchange and it is noteworthy that reaction involves insertion of a sterically congested diphosphine. The driving force for such ligand exchange is far from obvious but several important factors probably contribute towards the initial reaction and stabilization of the emerging bis(phosphine) complex. First, it has proved essential that the basicity of the calixarene-derived residue exceeds that of the incoming [PtH(Cl)(PR'_3)$_2$] complex (*e.g.* exchange does not occur with [PtH(Cl){$P(C_6H_{11})_3$}$_2$]). Thus, the first step is driven by the higher co-ordinative properties of the Ph_2P-calix moiety. Since the co-ordination sites in L^1–L^4 show higher affinity for platinum than does PPh_3 we might expect similar complexation to occur with each of these compounds. However, whereas L^1 gives the platinum complex in high yield, L^4, being similar in size to L^1, does not react with the platinum precursor. This comparison suggests that the auxiliary functions play an active role in formation of the chelate complex. In trying to rationalize the relative reactivity of L^1–L^4 it becomes clear that chelate formation takes place *via* a stepwise process for which stable intermediates could be isolated in some cases (Scheme 6).

The course of reaction was followed by NMR spectroscopy and it was observed that with L^2 and L^3 an additional product (type **A** in Scheme 6) was apparent in the reaction mixture. These products, being reminiscent of the BF_4^- salts **4**–**6**, have a triphenylphosphine residue in place of the chloride ligand. It was clearly demonstrated, at least in the case of L^3, that the chloride became co-ordinated to the platinum centre upon heating. We may surmise, therefore, that a PPh_3 (diphosphine) complex of type **A** is formed as an intermediate. The corresponding intermediate for L^1 was not observed, reaction always proceeding to completion, and was found for L^4 only under forcing conditions (Scheme 6).

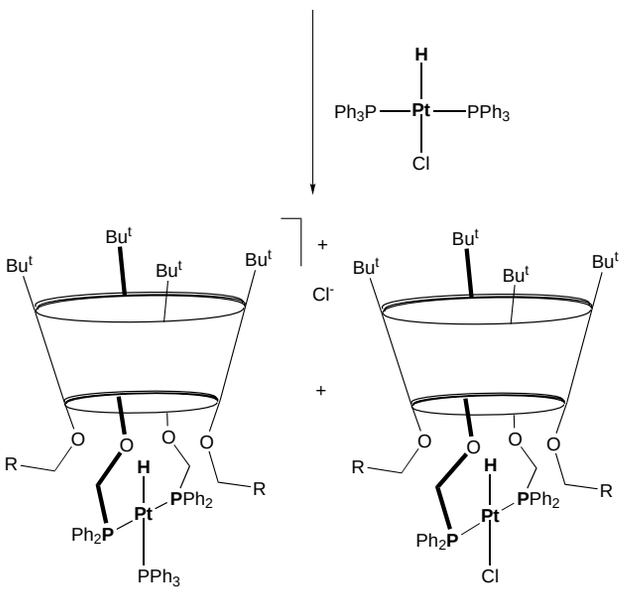
Formation of these intermediate species occurs by way of ejection of the chloride and of one PPh_3 ligand from the incoming organometallic species. The results displayed in Scheme 6 indicate that the nature of the auxiliary side arms has a profound effect upon the rate of conversion of **A** into **B**. Strong donor sites, such as provided by amide and ester functions, promote loss of the bound PPh_3 ligand, thereby facilitating formation of the chloro complex. These ligands can be considered to function as internal solvation sites that induce ligand substitution. The effect is partially lost when the size of the auxiliary side arm is extended, presumably due to steric crowding, and reaction with L^3 is incomplete. This auxiliary effect in which the side arm promotes loss of a tightly bound triphenylphosphine residue is not restricted to the second step in the overall assemblage but must play a part in formation of complexes of type **A**. Indeed, without the co-operative assistance of the auxiliary sites it is not possible to realize the first substitution step in significant yield. Finally, it should be mentioned here that the use of hemilabile phosphines, *i.e.* bearing secondary groups of weak co-ordinating power, has recently proved to be essential for increasing the rate of certain catalytic reactions.[47,48]

Substitution reactions at the metal centre

Compounds such as **3** comprise a calixarene cavity, a diphosphinometal fragment, and an encapsulated metal hydride. Such entities are stable but treatment with silver tetrafluoroborate results in removal of the chloride ligand, providing access to intermediary reagents such as **7**. An important feature inherent to complex **7** is that the hydride is displaced from the cavity and is readily accessible to species in solution. This permits evaluation of the ability of the Pt–H bond to enter into insertion



1 **L**^{1} R = C(O)NEt$_2$[a]
2 **L**^{2} R = C(O)OEt [a]
3 **L**^{3} R = C(O)NHC*H(Ph)Me[a]
4 **L**^{4} R = CH_2OMe[a]
5 **L**^{4} R = CH_2OMe[b]



A

3' (0 %)
9' (5 %)
5' (55 %)
6' (0 %)
6' (100 %)

B

3 (100 %)
9 (80 %)
10 (44 %)
6 (0 %)
6 (0 %)

Scheme 6 Product distribution for the reaction of L^{i} with *trans*-[PtH(Cl)(PPh$_3$)$_2$]. Reaction conditions: [a] CH_2Cl_2, room temperature, 5 d (full conversion of the substrate, except for entry 4, 0%); [b] thf, reflux, 24 h. For the reactions with L^{2} and L^{3} trace amounts of other unidentified hydrido complexes were detected. The numbers in parentheses indicate selectivities

and/or substitution reactions. It is prudent to establish that such reactions can take place outside the cavity where the substrate experiences less severe stereochemical constraints before attempting to design systems where the chemistry takes place within the cavity. Consequently, the reactivity of **7** was investigated towards incoming electrophiles, namely dimethyl acetylenedicarboxylate (dmad) and tetracyanoethylene (tcne).

Compound **3** does not react with dmad, even at elevated temperature, but following activation to **7** reaction proceeded smoothly in CH_2Cl_2 (Scheme 7). This reaction, which was followed by ^{31}P NMR spectroscopy, involves formation of a transient species having two non-equivalent, *cis*-bonded phosphorus atoms [*J*(PPt) = 4541 and 2028 Hz]. By analogy to the findings of Venanzi,[49] we tentatively assign this intermediate to the structure shown in Scheme 7. The FAB^{+} mass spectrum of

Table 1 Selected bond lengths (Å) and angles (°) for complex **12**·3 $CHCl_3$·H_2O

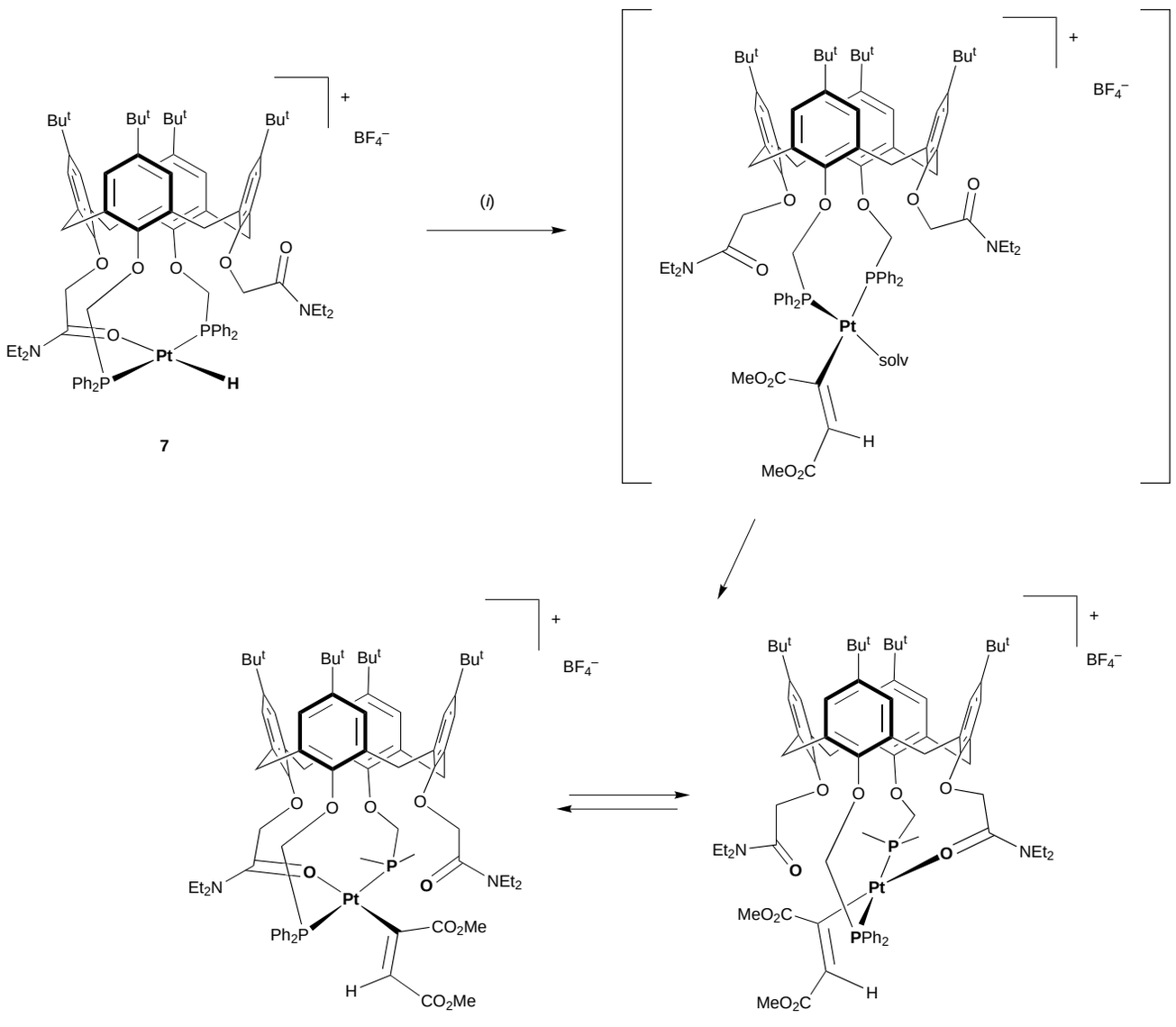
Pt–P(1)	2.277(1)	O(1)–C(1)	1.387(5)
Pt–P(2)	2.300(1)	O(2)–C(30)	1.410(5)
Pt–C(83)	2.109(5)	O(4)–C(43)	1.403(4)
Pt–C(86)	2.105(5)	O(5)–C(67)	1.400(5)
P(1)–C(8)	1.815(5)	C(83)–C(84)	1.428(7)
P(1)–C(14)	1.823(5)	C(86)–C(87)	1.439(8)
P(1)–C(7)	1.845(4)	C(84)–N(3)	1.152(7)
P(2)–C(48)	1.850(4)	C(87)–N(5)	1.122(7)
P(2)–C(49)	1.823(5)	C(83)–C(85)	1.453(7)
P(2)–C(55)	1.820(4)	C(86)–C(88)	1.428(9)
P(1)–Pt–P(2)	101.38(4)	P(1)–C(7)–O(1)	111.0(3)
C(83)–Pt–C(86)	106.1(1)	P(2)–C(48)–O(4)	109.6(2)
Pt–P(1)–C(7)	120.1(4)	Pt–P(2)–C(48)	120.5(4)

the complex obtained after completion of the reaction shows an intense peak at *m/z* 1609.9. This establishes that a molecule dmad has been inserted. Furthermore, the ^{1}H NMR spectrum exhibits two distinct MeO signals each of intensity 3 H and an olefinic CH proton (δ 5.16), consistent with **11**. The ^{31}P NMR spectrum displays a solitary signal at δ 16.4 with corresponding platinum satellites. The *J*(PPt) coupling constant (2926 Hz) is clearly indicative of a *trans* arrangement of the phosphorus atoms.

The NMR spectra show equivalence of each amide and phosphino group over the temperature range −80 to +50 °C. These observations, taken together with the need for a square-planar metal plane, require a fluxional structure for complex **11**, possibly involving fast exchange between co-ordinated and free amide groups (Scheme 7). Note, the solution IR spectrum (as well as the KBr spectrum) shows strong carbonyl bands which may be assigned to free and co-ordinated amide functions in addition to the ester groups (see Experimental section). As such, the platinum centre present in **11** is considered to possess three tightly bound ligands, with the fourth co-ordination site being occupied alternately by one of the amide oxygen donors. This alternation of the auxiliary side arm persists at −80 °C. The bonded alkenyl fragment resembles a pendulum moving between the amido terminals, presumably on a fast time-scale, thereby creating a pseudo-C_2 symmetry about the molecular axis. This fast exchange process may be driven by the high *trans* influence of the alkenyl groups weakening the Pt–O bond. Again, the auxiliary side arms provide key elements in the overall process by stabilizing the insertion product.

The above reaction involves hydride transfer from metal to alkyne, leading to formation of a stable insertion product. In marked contrast, treatment of complex **7** with tcne in $CHCl_3$ results in formation of the corresponding π complex **12** (Scheme 8). This product arises from reductive elimination and is formed in quantitative yield under ambient conditions. Irrefutable proof of the formation of a platinum(0) species accrued from an X-ray diffraction study (Fig. 1, Table 1). The solid-state structure shows that the macrocyclic subunit displays a geometry typical for cone conformers.[50] More importantly, the metal atom is no longer centred under the cavity but is considerably displaced to one side, the metal plane making a dihedral angle of about 40° with the calixarene reference plane. This forces one of the neighbouring auxiliary side arms to lie orthogonal to the cavity. Formation of **12** requires loss of the hydrido ligand, with simultaneous conversion of Pt^{II} into Pt^{0} and co-ordination of the electrophilic species. Such reductive elimination reactions have been observed with related, but non-calixarene-derived, *trans*-diphosphine complexes.[51] Since this transformation proceeds rapidly we may surmise that there are no undue stereological barriers to adoption of the necessary *cis* configuration.

Detailed examination of the NMR spectrum indicates that



Scheme 7 Reagents and conditions: (*i*) $MeO_2CC{\equiv}CCO_2Me$ (1.1 equivalent, 3 d, in $CDCl_3$)

complex **12** has apparent C_2 symmetry in solution. In particular, unlike in the solid state, the auxiliary side arms are equivalent. As outlined above for complex **11**, we envisage that the bis(phosphine) residue must undergo large-scale torsional motion of the type depicted in Scheme 9.

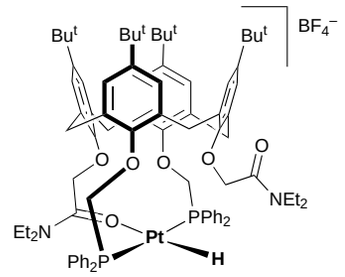
Towards intracavity reactions

Bis(phosphine) compounds such as L^1–L^4 have proved to be suitable ligands for the assembly of capped calixarenes bearing reactive metal centres. These ligands are versatile and should enable formation of metal complexes which might display useful catalytic functions. In fact a major goal of this program is to design capped calixarenes that combine catalytic activity of the metal cap with the size-exclusion capability of the macrocyclic receptor. Such processes are difficult to realize with platinum centres because of their unfavourable steric demands but may be more accommodated with rhodium hydrides.

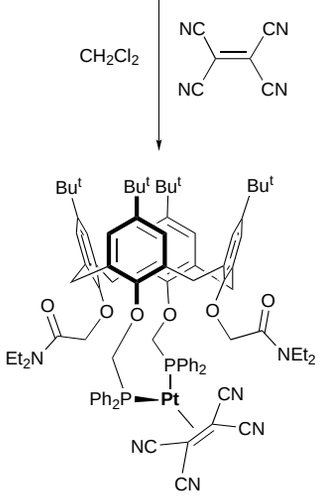
The rhodium(I) complexes **13** and **14** were prepared by treating $[Rh(CO)_2(thf)_2]BF_4$ with L^1 and L^3, respectively (Scheme 10). An interesting feature of this latter compound is that it contains two chiral centres which make the two phosphorus atoms in **14** non-equivalent. This is apparent in the ^{31}P NMR spectrum where the ABX pattern (X = Rh) confirms the *trans* arrangement [*J*(PP) = 331 Hz]. In the absence of a chiral centre (**13**) the phosphorus atoms are equivalent. This is not so for the auxiliary side arms since NMR and IR spectroscopy clearly indicate the presence of both a complexed and a free carbonyl ($C{=}O_{amide}$). In the rhodium complex, therefore, exchange between the amido functions must be slow and the pendulum effect described with **11** is not apparent. The realization that substitution products could not be observed upon treating **13** or **14** with strong donors such as PPh_3 or pyridine confirms our contention that one of the amido groups is tightly bound to the rhodium centre.

The organometallic fragment present in complexes **13** and **14** possesses the key features known to be important for hydroformylation catalysts. Indeed, **13** catalyses the conversion of styrene into the corresponding aldehydes in toluene–CH_2Cl_2 mixtures under 40 bar CO + H_2 (1:1) at 40 °C. Selectivity of linear to branched aldehydes (n:i) lies in the order of 5:95, which is unexceptional for rhodium(I) bis(phosphine) complexes. The frequency of turnover (0.5 per h) was extremely low indicating a steric barrier to reaction. Note, hydrogenation of cyclohexene with **14** (P_{H_2} = 50 bar, 60 °C) in MeOH also led to low catalytic activity (turnover frequency *ca.* 145 per h).

Based on our structural findings with the relevant hydridoplatinum complex **3** we might expect that the rhodium hydrido precursor, which must be the reactive intermediate in hydroformylation, also has a protected rhodium–hydrogen bond. Such a structure is not conducive to ready transfer of the hydride or carbonyl moieties to the incoming olefin. In order



7



12

Scheme 8

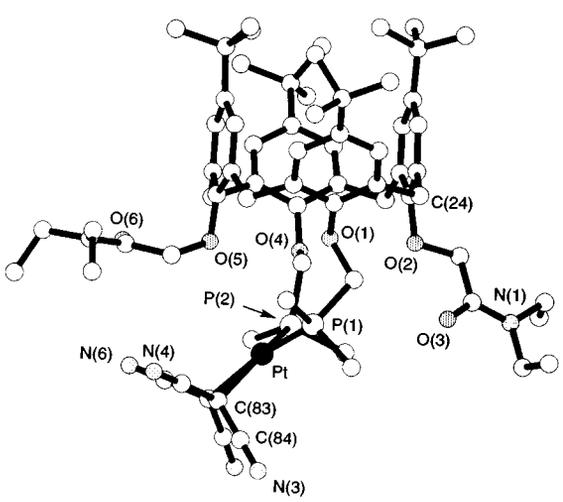
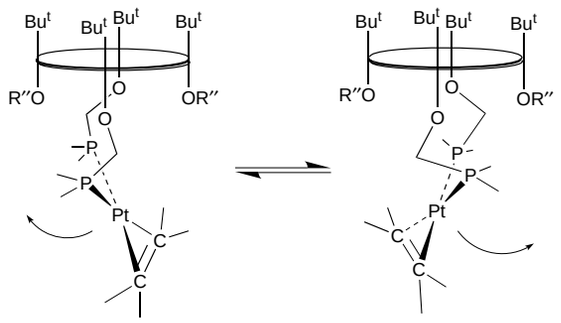
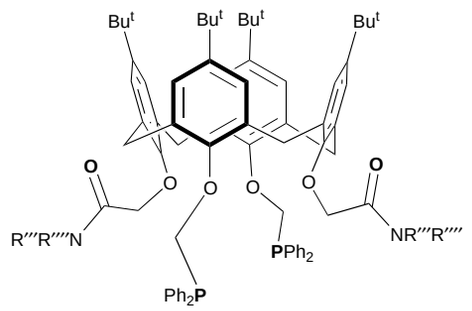


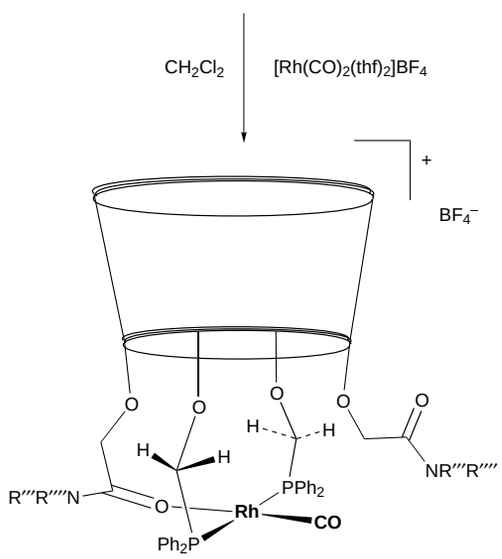
Fig. 1 Crystal structure of a molecule of complex **12** with partial labelling scheme. Only the *ipso*-carbon atoms of the phenyl rings are shown



Scheme 9 Proposed dynamics for complex **12**



L^1 R‴ = R⁗ = Et
L^3 R‴ = H, R⁗ = (*R*)-CHMePh



13
14

Scheme 10

better to accommodate selective homogeneous catalysis, it seems necessary to enlarge the domain bordered by the four functional arms. This could be done by extending the arms but retaining the balance between strong and weak complexation sites.

In summary, we have shown that the hemispherical diphosphines L^1–L^4 derived from 1,3-difunctionalized calix[4]arenes are suitable for the preparation of transition-metal hydrides having the hydrido ligand encapsulated within the cavity generated by the four substituents. We have presented a synthetic methodology that allows modulation of the chemical properties of the entrapped hydrides and for modifying their environment. It was found that the presence of auxiliary binding functions can be helpful for promoting substitution reactions at the metal centre and hence the results presented here open up the way for studying synergistic effects of functional groups surrounding a reactive metal centre located inside a molecular pocket. The particular structures of the hydrido-complexes presented in this work allow us to study reactions inside or outside a molecular cavity.

Experimental

All manipulations involving phosphines were performed in Schlenk-type flasks under argon. Solvents were dried by conventional methods and distilled immediately prior to use; $CDCl_3$ was passed down a 5 cm thick alumina column and stored under argon over molecular sieves (4 Å). Infrared spectra were recorded on a Perkin-Elmer 1600 spectrometer (4000–400 cm^{-1}) and a Bruker FIR spectrometer (500–90 cm^{-1}), routine

^{1}H, ^{31}P-{^{1}H} and ^{13}C-{^{1}H} NMR spectra with an FT Bruker WP-200 SY instrument, 500 MHz spectra on an ARX 500 Bruker instrument. The ^{1}H NMR spectral data were referenced to residual protiated solvents (δ 7.27 for $CDCl_3$), ^{13}C chemical shifts relative to deuteriated solvents (δ 77.0 for $CDCl_3$), and the ^{31}P data relative to external H_3PO_4. Mass spectra of compounds L^{4a}, L^{4b} and L^4 were recorded on a TSQ-70 Finnigan-Mat spectrometer and those of **1**–**7** and **9**–**14** on a ZAB HF VG Analytical spectrometer using *m*-nitrobenzyl alcohol or tetraglyme (2,5,8,11,14-pentaoxapentadecane) as matrix. The molecular weight determinations by vapour-pressure osmometry were performed by Analytische Laboratorien, Lindlar, Germany. Samples of *p-tert*-butylcalix[4]arene,[52] 5,11,17,23-tetra-*tert*-butyl-25,27-bis(diethylcarbamoylmethoxy)-26,28-bis(diphenylphosphinomethoxy)calix[4]arene L^1,[28] 5,11,17,23-tetra-*tert*-butyl-25,27-di(ethoxycarbonylmethoxy)-26,28-bis-(diphenylphosphinomethoxy)calix[4]arene L^2,[27] (*R*,*R*)-(+)-5,11,17,23-tetra-*tert*-butyl-25,27-bis[(1-phenylethyl)carbamoylmethoxy]-26,28-bis(diphenylphosphinomethoxy)calix[4]arene L^3,[28] $Ph_2P(O)CH_2O_3SC_6H_4Me$-*p*,[53] [$AuCl(SC_4H_8)$],[54] [$PtH(Cl)(PPh_3)_2$][55] and [{$RhCl(CO)_2$}$_2$][56] were prepared using literature procedures.

The catalytic runs (hydroformylation of styrene with complex **13**) were performed in a 100 cm^3 glass-lined steel autoclave containing a magnetic stirring bar. In a typical experiment, a solution of **13** (0.025 g, 0.017 mmol) in toluene–CH_2Cl_2 (14:3 v/v, 15 cm^3) was introduced under argon into the autoclave. The autoclave was pressurized (20 bar) with CO–H_2 (1:1) and heated to 40 °C for 2 h. After cooling and depressurization styrene was introduced (1 cm^3, *ca.* 0.906 g, 8.70 mmol). The autoclave was then pressurized again with CO–H_2 (1:1), at 40 bar, and heated to 40 °C. After 144 h the autoclave was cooled and then slowly opened. The liquid phase was analysed by GC. At this stage the conversion was 12%. The linear:branched aldehyde ratio was 5:95.

Preparations

5,11,17,23-Tetra-*tert*-25,27-dihydroxy-26,28-bis(3-oxabutyloxy)calix[4]arene L^{4a}. A suspension of *p-tert*-butylcalix[4]arene (5.000 g, 7.71 mmol) in acetonitrile (200 cm^3) was stirred at room temperature overnight with K_2CO_3 (1.380 g, 10.01 mmol). 2-Bromoethyl methyl ether (2.36 g, 16.94 mmol) was then added and the mixture refluxed for 3 d. During this period three additional portions of $BrCH_2CH_2OMe$ (1.50 mmol for each addition) and K_2CO_3 (1.50 mmol) were added after 24, 36 and 60 h. Reaction was followed by TLC [R_f = 1 (starting compound); 0.49 (monoalkylated compound); 0 (L^{4a}); SiO_2, CH_2Cl_2]. After filtration, the solvent was removed *in vacuo*. The residue was dissolved in CH_2Cl_2 (100 cm^3) and the resultant solution was washed first with saturated NH_4Cl–water (2 × 100 cm^3) and subsequently with water (100 cm^3). The organic layer was dried over $MgSO_4$. After filtration, the purified product was precipitated with EtOH to yield a white solid (4.4 g, 75%), m.p. 222—223 °C. IR (KBr, cm^{-1}): ν(OH) 3360–3314 (br). NMR ($CDCl_3$): ^{1}H, δ 7.40 (s, 2 H, OH), 7.15 and 7.06 (2s, 8 H, *m*-H), 4.39 and 3.32 (AB spin system, 8 H, $C_6H_2CH_2C_6H_2$, ^2J = 12.9 Hz), 4.17 and 3.89 (2m, 8 H, OCH_2CH_2O), 3.56 (s, 6 H, OCH_3), 1.30 [s, 18 H, $C(CH_3)$] and 0.99 [s, 18 H, $C(CH_3)$]; ^{13}C-{^{1}H}, δ 150.28–116.50 (aromatic C), 75.05 (s, OCH_2), 71.23 (s, OCH_2), 59.10 (s, OCH_3), 33.81 and 33.63 [2s, $C(CH_3)$], 31.50 [s, $C(CH_3)$], 31.35 (s, $C_6H_2CH_2C_6H_2$) and 30.91 [s, $C(CH_3)$]. Electron Impact (EI) mass spectrum: *m/z* (%) 764.4 (100), M^+ (Found: C, 78.22; H, 8.85. $C_{50}H_{68}O_6$ requires C, 78.49; H, 8.96%).

5,11,17,23-Tetra-*tert*-butyl-25,27-bis(diphenylphosphinoylmethoxy)-26,28-bis(3-oxabutyloxy)calix[4]arene, cone L^{4b}. A solution of L^{4a} (3.000 g, 3.9 mmol) in thf–dmf (9:1 v/v, 100 cm^3) was refluxed with $NaOBu^t$ (0.791 g, 8.23 mmol) for 1 h. Then $Ph_2P(O)CH_2O_3SC_6H_4Me$-*p* (3.300 g, 8.6 mmol) was added and the solution refluxed for 24 h. After filtration, the solvent was removed under reduced pressure. The residue was taken up in CH_2Cl_2 (100 cm^3) and washed with saturated NH_4Cl–water (2 × 100 cm^3) and then with water (100 cm^3). The organic layer was dried over $MgSO_4$ and concentrated to *ca.* 20 cm^3. Addition of acetone with stirring and cooling gave a white microcrystalline deposit (2.9 g, 62%), m.p. 227–228 °C. IR (KBr, cm^{-1}): ν(P=O) 1208s (tentative). NMR ($CDCl_3$): ^{1}H, δ 7.83–7.74 and 7.47–7.40 (2m br, 20 H, PPh_2), 6.77 and 6.44 (2s, 8 H, *m*-H), 5.01 (s, 4 H, OCH_2PPh_2), 4.42 and 2.92 (AB spin system, 8 H, $C_6H_2CH_2C_6H_2$, ^2J = 12.8), 3.94 and 3.82 (2m, 8 H, OCH_2CH_2O), 3.25 (s, 6 H, OCH_3), 1.12 [s, 18 H, $C(CH_3)$] and 0.93 [s, 18 H, $C(CH_3)$]; ^{13}C-{^{1}H}, δ 153.59–124.55 (aromatic C), 72.48 and 72.00 (2s, OCH_2CH_2O), 72.02 [d, OCH_2PPh_2, J(PC) = 80 Hz], 58.14 (s, OCH_3), 33.63 and 33.45 [2s, $C(CH_3)$], 31.32 [s, $C(CH_3)$], 31.21 (s, $C_6H_2CH_2C_6H_2$) and 31.06 [s, $C(CH_3)$]; ^{31}P-{^{1}H}, δ 24.9 (s, PPh_2). Chemical ionization (CI) mass spectrum: *m/z* (%) 1193.8 (100), M^+ (Found: C, 76.64; H, 7.84. $C_{76}H_{90}O_8P_2$ requires C, 76.48; H, 7.60%).

5,11,17,23-Tetra-*tert*-butyl-25,27-bis(diphenylphosphinomethoxy)-26,28-bis(3-oxabutyloxy)calix[4]arene, cone L^4. A solution of L^{4b} (2.900 g, 2.43 mmol) in phenylsilane (20 cm^3) was refluxed for 72 h. After cooling, unreacted phenylsilane was removed under reduced pressure and recovered for reuse. The residue was taken up in CH_2Cl_2 (*ca.* 5 cm^3) and addition of EtOH with stirring and cooling afforded the product as a white powder (2.3 g, 80%), m.p. 228–230 °C. NMR ($CDCl_3$): ^{1}H, δ 7.53–7.45 and 7.31–7.29 (2m br, 20 H, PPh_2), 6.93 and 6.53 (2s, 8 H, *m*-H), 4.87 [d, 4 H, OCH_2PPh_2, ^2J(PH) = 3.4], 4.35 and 3.05 (AB spin system, 8 H, $C_6H_2CH_2C_6H_2$, ^2J = 12.5 Hz), 4.01–3.90 (m, 8 H, OCH_2CH_2O), 3.33 (s, 6 H, OCH_3), 1.23 [s, 18 H, $C(CH_3)$] and 0.93 [s, 18 H, $C(CH_3)$]; ^{13}C-{^{1}H}, δ 153.89–124.48 (aromatic C), 72.26 (s, OCH_2), 71.74 (s, OCH_2), 58.48 (s, OCH_3), 33.74 and 33.48 [2s, $C(CH_3)$], 31.39 [s, $C(CH_3)$], 31.24 (s, $C_6H_2CH_2C_6H_2$) and 31.02 [s, $C(CH_3)$]; ^{31}P-{^{1}H}, δ −21.9 (s, PPh_2). CI mass spectrum: *m/z* (%) 1161.6 (100), M^+ (Found: C, 78.65; H, 7.86. $C_{76}H_{90}O_6P_2$ requires C, 78.59; H, 7.81%).

{5,11,17,23-Tetra-*tert*-butyl-25,27-bis(diethylcarbamoylmethoxy)-26,28-bis(diphenylphosphinomethoxy)calix[4]arene}-gold(I) tetrafluoroborate 1. A solution of $AgBF_4$ (0.024 g, 0.122 mmol) in thf (1 cm^3) was added to a solution of [$AuCl(SC_4H_8)$] (0.039 g, 0.122 mmol) in CH_2Cl_2 (3 cm^3). Stirring was stopped after 5 min and the solution was decanted in order to remove AgCl. The supernatant was filtered over Celite and added to a solution of L^1 (0.155 g, 0.122 mmol) in CH_2Cl_2 (30 cm^3). After 2 h the solution was concentrated to *ca.* 1 cm^3 and addition of pentane afforded the product as an analytically pure white powder (0.160 g, 84%), m.p. 238–240 °C (decomp.). IR (KBr, cm^{-1}): ν(C=O) 1654s and ν(B–F) 1058s (br). NMR ($CDCl_3$): ^{1}H, δ 7.91–7.82 and 7.59–7.43 (20 H, PPh_2), 7.05 (s, 4 H, *m*-H), 6.37 (s, 4 H, *m*-H), 5.70 (s, 4 H, OCH_2PPh_2), 3.94 (s, 4 H, OCH_2CONEt_2), 3.91 and 2.83 (AB spin system, 8 H, $C_6H_2CH_2C_6H_2$, ^2J = 12.8), 3.47 (q, 4 H, NCH_2CH_3, ^3J = 6.7), 3.05 (q, 4 H, NCH_2CH_3, ^3J = 6.7), 1.34 (s, 18 H, Bu^t), 1.22 (t, 12 H, NCH_2CH_3, ^3J = 6.7), 1.08 (t, 12 H, NCH_2CH_3, ^3J = 6.7) and 0.78 (s, 18 H, Bu^t); ^{13}C-{^{1}H}, δ 166.88 (s, C=O), 155.42–125.06 (aromatic C), 72.36 (s, OCH_2CONEt_2), 72.01 [t, OCH_2PPh_2, $|J(PC) + {}^3J(P'C)| = 41$ Hz], 40.46 and 40.05 (2s, NCH_2CH_3), 34.06 and 33.55 [2s, $C(CH_3)_3$], 31.56 and 30.94 [2s, $C(CH_3)_3$], 30.24 (s, $C_6H_2CH_2C_6H_2$), 14.07 and 13.08 (2s, NCH_2CH_3); ^{31}P-{^{1}H}, δ 36.9 (s, PPh_2). FAB mass spectrum: *m/z* (%) 1467.6 (100), [$M - BF_4$]$^+$ (expected isotopic profile) (Found: C, 61.98; H, 6.16. $C_{82}H_{100}AuBF_4N_2O_6P_2 \cdot 0.5\ CH_2Cl_2$ requires C, 62.01; H, 6.37%).

{5,11,17,23-Tetra-*tert*-butyl-25,27-bis(diethylcarbamoylmethoxy)-26,28-bis(diphenylphosphinomethoxy)calix[4]arene}-silver(I) tetrafluoroborate 2. To a solution of L^1 (0.150 g, 0.118

mmol) in CH_2Cl_2 (20 cm^3) was added a solution of $AgBF_4$ (0.025 g, 0.129 mmol) in thf (1 cm^3). After stirring for 5 min the suspension was filtered over Celite. The pale pink solution was concentrated to *ca.* 1 cm^3 and addition of pentane afforded the product as an analytically pure precipitate (pale pink) (0.126 g, 74%), m.p. >280 °C (slow decomp.). IR (cm^{-1}): (Nujol) ν(C=O) 1654s, 1620s and ν(B–F) 1058s (br); (thf) 1660s and 1629s. NMR ($CDCl_3$): ^{1}H, δ 7.71–7.32 (20 H, PPh_2), 6.99 (s, 4 H, *m*-H), 6.32 (s, 4 H, *m*-H), 5.69 (s br, 4 H, OCH_2PPh_2), 4.09 (s, 4 H, OCH_2CONEt_2), 3.86 and 2.80 (AB spin system, 8 H, $C_6H_2CH_2C_6H_2$, ^2J = 12.8), 3.48 (q, 4 H, NCH_2CH_3, ^3J = 7.0), 3.12 (q, 4 H, NCH_2CH_3, ^3J = 7.0), 1.34 (s, 18 H, Bu^t), 1.21 (t, 12 H, NCH_2CH_3, ^3J = 7.0), 1.13 (t, 12 H, NCH_2CH_3, ^3J = 7.0) and 0.76 (s, 18 H, Bu^t); ^{13}C-{^{1}H}, δ 167.11 (s, C=O), 155.42–125.14 (aromatic C), 72.62 (m, OCH_2PPh_2, signal of low intensity), 72.18 (s, OCH_2CONEt_2), 40.54 and 40.28 (2s, NCH_2CH_3), 33.92 and 33.45 [2s, $C(CH_3)_3$], 31.46 and 30.77 [2s, $C(CH_3)_3$], 30.25 (s, $C_6H_2CH_2C_6H_2$), 13.90 and 12.87 (2s, NCH_2CH_3); ^{31}P-{^{1}H}, δ −0.93 [2d, PPh_2, $J(P^{109}Ag)$ = 542, $J(P^{107}Ag)$ = 469 Hz]. FAB mass spectrum: *m/z* (%) 1379.6 (100), $[M - BF_4]^+$ (expected isotopic profile) (Found: C, 67.36; H, 6.68; N, 1.73. $C_{82}H_{100}AgBF_4N_2O_6P_2$ requires C, 67.17; H, 6.87; N, 1.91%).

***trans*-*P*,*P*′-Chlorohydrido{5,11,17,23-tetra-*tert*-butyl-25,27-bis(diethylcarbamoylmethoxy)-26,28-bis(diphenylphosphinomethoxy)calix[4]arene}platinum(II) 3.** To a solution of L^1 (0.178 g, 0.24 mmol) in CH_2Cl_2 (15 cm^3) was added dropwise a solution of *trans*-[PtH(Cl)(PPh_3)$_2$] (0.300 g, 0.24 mmol) in CH_2Cl_2 (15 cm^3). After stirring for 5 d the solution was concentrated to *ca.* 5 cm^3 and pentane was added to yield complex **3** as an analytically pure white powder. It was dried *in vacuo* (0.325 g, 90%), m.p. 254–255 °C. IR (KBr, cm^{-1}): ν(C=O) 1658s. ^{1}H NMR ($CDCl_3$): δ 7.93–7.91 and 7.42 (m br, 20 H, PPh_2), 7.12 (s, 4 H, *m*-H), 6.53 (s, 4 H, *m*-H), 5.35 [s with platinum satellites, 4 H, OCH_2PPh_2, J(HPt) = 33], 4.63 and 3.04 (AB spin system, 8 H, $C_6H_2CH_2C_6H_2$, ^2J = 13.0), 4.12 (s, 4 H, OCH_2CONEt_2), 3.21 (q, 4 H, NCH_2CH_3, ^3J = 7.1), 2.77 (q, 4 H, NCH_2CH_3, ^3J = 7.1), 1.35 (s, 18 H, Bu^t), 1.01 (t, 6 H, NCH_2CH_3, ^3J = 7.0), 0.99 (t, 6 H, NCH_2CH_3, ^3J = 7.1), 0.81 (s, 18 H, Bu^t) and −15.04 [t with platinum satellites, 1 H, PtH, ^2J(HP) = 15, J(HPt) = 1150 Hz]. ^{1}H NMR (C_6D_6): δ −14.22 [t with platinum satellites, PtH, ^2J(HP) = 15, J(PtH) = 1150 Hz]. ^{13}C-{^{1}H} NMR ($CDCl_3$): δ 168.00 (s, C=O), 154.71–124.73 (aromatic C), 71.27 (s, OCH_2CONEt_2) 70.24 [t, OCH_2PPh_2, $|J(PC) + {}^3J(P'C)|$ = 51 Hz], 40.33 and 39.64 (2s, NCH_2CH_3), 33.96 and 33.51 [2s, $C(CH_3)_3$], 31.93 (s, $C_6H_2CH_2C_6H_2$), 31.67 and 31.07 [2s, $C(CH_3)_3$], 14.18 and 12.99 (2s, NCH_2CH_3). ^{31}P-{^{1}H} NMR ($CDCl_3$): δ 22.7 [s with platinum satellites, PPh_2, J(PPt) = 3122 Hz]. FAB mass spectrum: *m/z* (%) 1467 (100), $[M - Cl]^+$. *M*(Osmometry, CH_2Cl_2): 1490 (Found: C, 62.79; H, 6.74; N, 1.60. $C_{82}H_{101}ClN_2O_6P_2Pt{\cdot}CH_2Cl_2$ requires C, 62.77; H, 6.54; N, 1.76%).

***trans*-*P*,*P*′-Hydrido{5,11,17,23-tetra-*tert*-butyl-25,27,bis-(diethylcarbamoylmethoxy)-26,28-bis(diphenylphosphinomethoxy)calix[4]arene}(triphenylphosphine)platinum(II) tetrafluoroborate 4.** A solution of $AgBF_4$ (0.023 g, 0.12 mmol) in thf (1 cm^3) was added to a stirred solution of [PtH(Cl)(PPh_3)$_2$] (0.089 g, 0.12 mmol) in CH_2Cl_2 (3 cm^3). Stirring was stopped after 5 min and the solution was decanted in order to remove AgCl. The supernatant and combined dichloromethane washings of the AgCl precipitate were filtered through Celite into a solution of L^1 (0.150 g, 0.12 mmol) in CH_2Cl_2 (25 cm^3). After stirring for 12 h, the solution was concentrated to *ca.* 2 cm^3 before addition of pentane afforded the product as a pale yellow precipitate (0.160 g, 80%), m.p. 188–190 °C. IR (KBr, cm^{-1}): ν(C=O) 1653, ν(B–F) 1057. NMR ($CDCl_3$): ^{1}H, δ 7.49–7.08 (35 H, PPh_3 and PPh_2), 6.93 (s, 4 H, *m*-H), 6.27 (s, 4 H, *m*-H), 5.85 [s with platinum satellites, 4 H, OCH_2PPh_2, ^3J(HPt) = 52], 4.05 (s, 4 H, OCH_2CONEt_2), 3.88 and 2.68 (AB spin system, 8 H, $C_6H_2CH_2C_6H_2$, ^2J = 13.0), 3.66 (q, 4 H, NCH_2CH_3, ^3J = 7.0), 3.02 (q, 4 H, NCH_2CH_3, ^3J = 7.0), 1.40 (t, 6 H, NCH_2CH_3, ^3J = 7.0), 1.28 (s, 18 H, Bu^t), 1.05 (t, 6 H, NCH_2CH_3, ^3J = 7.0), 0.74 (s, 18 H, Bu^t) and −4.31 [dt with platinum satellites, 1 H, PtH, $^2J(HP_{cis})$ = 16, $^2J(HP_{trans})$ = 168, J(HPt) = 774]; ^{13}C-{^{1}H}, δ 167.44 (s, C=O), 155.39–124.44 (aromatic C), 73.21 [t, OCH_2PPh_2, $|J(PC) + {}^3J(P'C)|$ = 52], 72.18 (s, OCH_2CONEt_2), 40.83 and 40.25 (2s, NCH_2CH_3), 33.78 and 33.45 [2s, $C(CH_3)_3$], 31.43 and 30.87 [2s, $C(CH_3)_3$], 30.07 (s, $C_6H_2CH_2C_6H_2$), 14.08 and 13.16 (2s, NCH_2CH_3); ^{31}P-{^{1}H}, δ 22.35 [t with platinum satellites, PPh_3, $^2J(PP')$ = 20, J(PPt) = 2020] and 14.38 (d with platinum satellites, PPh_2, $^2J(PP')$ = 20, J(PPt) = 2879 Hz]. FAB mass spectrum: *m/z* (%) 1467.6 (100), $[M - PPh_3 - BF_4]^+$ (Found: C, 64.79; H, 6.38; N, 1.46. $C_{100}H_{116}BF_4N_2O_6P_3Pt{\cdot}0.5CH_2Cl_2$ requires C, 64.90; H, 6.35; N, 1.50%).

***trans*-*P*,*P*′-(*R*,*R*)-Hydrido{5,11,17,23-tetra-*tert*-butyl-25,27-bis[(1-phenylethyl)carbamoylmethoxy]-26,28-bis(diphenylphosphinomethoxy)calix[4]arene}(triphenylphosphine)platinum(II) tetrafluoroborate 5.** A solution of $AgBF_4$ (0.021 g, 0.110 mmol) in thf (1 cm^3) was added to a stirred solution of [PtH(Cl)(PPh_3)$_2$] (0.083 g, 0.110 mmol) in CH_2Cl_2 (3 cm^3). Stirring was stopped after 5 min and the solution was decanted in order to remove AgCl. The supernatant and dichloromethane washings of the AgCl precipitate were filtered through Celite into a solution of L^3 (0.150 g, 0.110 mmol) in CH_2Cl_2 (30 cm^3). After strirring for 24 h the solution was concentrated to *ca.* 2 cm^3 and addition of pentane afforded a white precipitate (0.150 g, 75%), m.p. 179–182 °C. IR (KBr, cm^{-1}): ν(C=O) 1676s and ν(B–F) 1054 (br). NMR ($CDCl_3$): ^{1}H, δ 7.37–6.86 (m, 49 H, aromatic H), 6.50 (d, 2 H, NH, ^3J = 6.9), 6.26 (s br, 4 H, *m*-H), 5.70 and 5.56 [AB spin system with platinum satellites, 4 H, OCH_AH_B-PPh_2, J(AB) = 9.8, J(HPt) ≈ 46], 5.26 (dq, AMX_3 spin system, 2 H, NHC*H*MePh, $^3J_{AM} \approx {}^3J_{AX}$ = 6.9), 4.34 and 4.22 (AB spin system, 4 H, OCH_AH_BCONHR, J = 13.8), 3.81 and 2.78 (AB spin system, 4 H, $C_6H_2CH_2C_6H_2$, J = 13.1), 3.63 and 2.55 (AB spin system, 4 H, $C_6H_2CH_2C_6H_2$, J = 13.1), 1.53 (d, 6 H, $NHCHCH_3Ph$, ^3J = 5.9), 1.28 (s, 18 H, Bu^t), 0.75 (s, 18 H, Bu^t) and 4.73 [dt with platinum satellites, 1 H, PtH, $^2J(HP_{cis})$ = 18, $^2J(HP_{trans})$ = 169, J(HPt) = 762]; ^{13}C-{^{1}H}, δ 168.77 (s, C=O), 155.24–124.78 (aromatic C), 74.17 [dt, OCH_2PPh_2, $|J(PC) + {}^3J(P_{trans}C)| \approx 60$, $^2J(P_{cis}C)$ = 5], 73.73 (s, OCH_2CONHR), 48.76 (s, NH*C*HMePh), 33.84 [s, $C(CH_3)_3$], 33.48 [s, $C(CH_3)_3$], 31.52 [s, $C(CH_3)_3$], 30.96 [s, $C(CH_3)_3$], 30.05 (s, $C_6H_2CH_2C_6H_2$) and 22.09 (s, $NHCHCH_3Ph$); ^{31}P-{^{1}H}, δ 22.7 [t with platinum satellites, PPh_3, $^2J(PP')$ = 20, J(PPt) ~ 2006] and 15.9 (d with platinum satellites, PPh_2, $^2J(PP')$ = 20, J(PPt) = 2879 Hz). FAB mass spectrum: *m/z* (%) 1824.7 (2), $[M - BF_4]^+$ (expected isotopic profile); 1563.6 (100), $[M - PPh_3 - BF_4]^+$ (Found: C, 67.61; H, 6.12; N, 1.31. $C_{108}H_{116}BF_4N_2O_6P_3Pt$ requires C, 67.81; H, 6.11; N, 1.46%).

***trans*-*P*,*P*-Hydrido{5,11,17,23-tetra-*tert*-butyl-25,27-bis-(diphenylphosphinomethoxy)-26,28-bis(3-oxabutyloxy)calix[4]-arene}(triphenylphosphine)platinum(II) tetrafluoroborate 6.** A solution of $AgBF_4$ (0.025 g, 0.13 mmol) in thf (1 cm^3) was added to a stirred solution of [PtH(Cl)(PPh_3)$_2$] (0.098 g, 0.013 mmol) in CH_2Cl_2 (3 cm^3). Stirring was stopped after 5 min and the solution was decanted in order to remove AgCl. The supernatant and dichloromethane washings of the AgCl precipitate were filtered through Celite into a solution of L^4 (0.150 g, 0.13 mmol) in CH_2Cl_2 (25 cm^3). After stirring for 12 h the solution was concentrated to *ca.* 2 cm^3. Addition of pentane afforded the product as a pale pink powder (0.163 g, 74%), m.p. 209 °C (slow decomp.). NMR ($CDCl_3$): ^{1}H, δ 7.38–7.15 (35 H, PPh), 6.96 and 6.35 (2s, 8 H, *m*-H), 5.60 [s with platinum satellites, 4 H, OCH_2PPh_2, ^3J(HPt) = 51], 3.94 and 2.73 (AB spin system, 8 H, $C_6H_2CH_2C_6H_2$, ^2J = 12.8 Hz), 3.77 and 3.47 (2m, 8 H, OCH_2CH_2O), 3.45 (s, 6 H, OCH_3), 1.30 [s, 18 H, $C(CH_3)$], 0.76 [s, 18 H, $C(CH_3)$] and −4.19 [dt, with platinum satellites, 1 H, PtH,

$^3J(HP_{cis}) = 14$, $^3J(HP_{trans}) = 167$, $^2J(HPt) = 772$]; ^{13}C-{^1H}, δ 155.26–124.36 (aromatic C), 74.15 and 70.25 (s, O*C*H_2-*C*H_2O), 73.02 [t, O*C*H_2PPh_2, $|J(PC) + {}^3J(P'C)| = 55$], 58.50 (s, O$CH_3$), 33.84 and 33.47 [2s, *C*(CH_3)], 31.52 and 31.01 [2s, C(*C*H_3)] and 30.05 (s, $C_6H_2CH_2C_6H_2$); ^{31}P-{^1H}, δ 22.0 [t with platinum satellites, PPh_3, $^2J(PP') = 20$ Hz, $J(PPt) = 2009$] and 15.6 [d with platinum satellites, PPh_2, $^2J(PP') = 20$, $J(PPt) = 2843$ Hz]. FAB mass spectrum: *m/z* (%) 1619.7 (20), $[M - BF_4]^+$ (expected isotopic profile): 1357.6 (100), $[M - BF_4 - PPh_3]^+$ (Found: C, 66.24; H, 6.39. $C_{94}H_{106}BF_4O_6P_3Pt$ requires C, 66.15; H, 6.25%).

***trans*-*P*,*P*-Hydrido{5,11,17,23-tetra-*tert*-butyl-25-(diethylcarbamoylmethoxy)-27-(diethylcarbamoylmethoxy-κ*O*)-26,28-bis(diphenylphosphinomethoxy)calix[4]arene}platinum(II) tetrafluoroborate 7.** To a solution of complex **3** (0.217 g, 0.14 mmol) in CH_2Cl_2 (20 cm^3) was added a solution of $AgBF_4$ (0.282 g, 0.14 mmol) in thf (1 cm^3). After stirring for 30 min the suspension was filtered through Celite. The filtrate was concentrated to *ca.* 5 cm^3. Addition of pentane afforded a pale yellow precipitate (0.150 g, 70%), m.p. 218–219 °C. IR (KBr, cm^{-1}): ν(C=O) 1655s, 1606s, ν(B–F) 1060s. NMR ($CDCl_3$): ^1H, δ 7.84–7.40 (20 H, PPh_2), 7.18 and 7.05 (AB spin system, 4 H, *m*-H, $^4J = 3$), 6.54 and 6.33 (2s, 4 H, *m*-H), 6.23 and 5.01 [ABXX′ spin system with X, X′ = P, 4 H, O*C*H_2PPh_2, $^2J(AB) = 12$, $|J(AX) + J(AX')| = 10$, $J(BX)$ not determined], 4.32 and 3.59 (2s, 4 H, O*C*H_2CONEt_2), 4.32 and 3.31 (AB spin system, 4 H, $C_6H_2CH_2C_6H_2$, $^2J = 13$), 3.77 (q, 2 H, NCH_2CH_3, $^3J = 7$), 3.55 and 2.42 (AB system, 4 H, $C_6H_2CH_2C_6H_2$, $^2J = 13$), 3.39 (q, 2 H, NCH_2CH_3, $^3J = 7$), 3.11 (q, 2 H, NCH_2CH_3, $^3J = 7$), 3.09 (q, 2 H, NCH_2CH_3, $^3J = 7$), 1.41 (t, NCH_2CH_3, $^3J = 7$), 1.36 (s, 18 H, Bu^t), 1.15, 1.08 and 0.94 (3t, NCH_2CH_3, $^3J = 7$ Hz), 0.84 (s, 9 H, Bu^t), 0.75 (s, 9 H, Bu^t) and −22.95 [with platinum satellites, 1 H, PtH, $J(HPt) = 1306$, $^2J(HP) = 15$]; ^{13}C-{^1H}, δ 170.27 and 166.07 (2s, C=O), 155.49–125.21 (aromatic C), 75.67 [t, OCH_2PPh_2, $|J(PC) + J(P'C)| = 48$ Hz], 72.73 and 70.34 (2s, OCH_2CONEt_2), 40.87, 40.57 and 40.13 (NCH_2CH_3), 34.21, 33.73 and 33.59 [3s, *C*(CH_3)$_3$], 31.72, 31.09 and 30.98 [3s, C(*C*H_3)$_3$], 31.53 and 29.97 (2s, $C_6H_2CH_2C_2H_2$), 14.33, 13.41, 13.19 and 13.05 (4s, NCH_2CH_3); ^{31}P-{^1H}, δ 24.8 [s with platinum satellites, PPh_2, $J(PPt) = 3166$ Hz). FAB mass spectrum: *m/z* (%) 1467 (100), $[M - BF_4]^+$ (Found: C, 61.39; H, 6.35; N, 1.73. $C_{82}H_{101}BF_4N_2O_6P_2Pt \cdot 0.75\ CH_2Cl_2$ requires C, 61.42; H, 6.38; N, 1.73%).

μ-4,4′-Bipyridine-bis(*trans*-*P*,*P*′-hydrido{5,11,17,23-tetra-*tert*-butyl-25,27-bis(diethylcarbamoylmethoxy)-26,28-bis(diphenylphosphinomethoxy)calix[4]arene}platinum(II) bis(tetrafluoroborate) 8. To a solution of complex **7** (0.160 g, 0.103 mmol) in $CHCl_3$ (20 cm^3) was added a solution of 4,4′-bipyridine (0.008 g, 0.051 mmol) in $CHCl_3$ (1 cm^3). After stirring for 15 h the solution was concentrated to *ca.* 1 cm^3. Addition of pentane afforded the product as an analytically pure white powder (0.160 g, 92%), m.p. 250–255 °C (decomp.). IR (KBr, cm^{-1}): ν(C=O) 1654s, ν(B–F) 1057 s (br). NMR ($CDCl_3$): ^1H, δ 8.47 and 7.30 (AB spin system, 8 H, CH of bipyridine, $^3J = 6$ Hz),7.57–7.39 (40 H, PPh_2), 7.04 (s, 8 H, *m*-H), 6.42 (s, 8 H, *m*-H), 5.82 [s with platinum satellites, 8 H, O*C*H_2PPh_2, $J(HPt) = 50$], 4.32 and 2.89 (AB spin system, 16 H, $C_6H_2CH_2$-C_6H_2, $^2J = 12.8$), 4.11 (s, 8 H, O*C*H_2CONEt), 3.55 (q, 8 H, NCH_2CH_3, $^3J = 7.0$), 3.08 (q, 8 H, NCH_2CH_3, $^3J = 6.9$), 1.36 (t, 12 H, NCH_2CH_3, $^3J = 7.0$), 1.32 (s, 36 H, Bu^t), 1.09 (t, 12 H, NCH_2CH_3, $^3J = 7.0$), 0.79 (s, 36 H, Bu^t) and −15.92 [t with platinum satellites, 2 H, PtH, $J(HP) = 15$, $J(HPt) = 998$]; ^{13}C-{^1H}, δ 167.56 (s, C=O), 155.12–123.07 (aromatic C), 71.80 (s, OCH_2CONEt_2), 70.04 [t, OCH_2PPh_2, $|J(PC) + {}^3J(P'C)| \approx 55$ Hz], 40.60 and 40.45 (2s, NCH_2CH_3), 33.91 and 33.54 [2s, *C*(CH_3)$_3$], 31.60 and 31.05 [2s, C(*C*H_3)$_3$], 14.14 and 13.14 (2s, NCH_2CH_3), $C_6H_2CH_2C_6H_2$ not found; ^{31}P-{^1H}, δ 22.3 [s with platinum satellites, PPh_2, $J(PPt) = 3072$ Hz] (Found: C, 60.07; H, 6.25; N, 2.32. $C_{174}H_{210}B_2F_8N_6O_{12}P_4Pt_2 \cdot CHCl_3$ requires C, 60.21; H, 6.09; N, 2.4%).

***trans*-*P*,*P*′-Chlorohydrido{5,11,17,23-tetra-*tert*-butyl-25,27-di(ethoxycarbonylmethoxy)-26,28-bis(diphenylphosphinomethoxy)calix[4]arene}platinum(II) 9.** To a solution of L^2 (0.200 g, 0.164 mmol) in CH_2Cl_2 (15 cm^3) was added dropwise a solution of *trans*-[PtH(Cl)(PPh_3)$_2$] (0.124 g, 0.164 mmol) in CH_2Cl_2 (15 cm^3). After stirring for 3 d the solvent was removed *in vacuo*. The residue was adsorbed onto silica gel. Subsequent elution with CH_2Cl_2 yielded small amounts of two unidentified compounds. Further elution with CH_2Cl_2–MeOH (95:5 v/v) ($R_f = 0.9$; SiO_2, CH_2Cl_2–MeOH 95:5) gave **9** (0.170 g, 71%), m.p. 170–173 °C (slow decomp.). IR (KBr, cm^{-1}): ν(C=O) 1755s and 1727s. NMR ($CDCl_3$): ^1H, δ 7.99 (m br) and 7.47 (m br, 20 H, PPh_2), 7.12 (s, 4 H, *m*-H), 6.54 (s, 4 H, *m*-H), 5.24 [s with platinum satellites, 4 H, O*C*H_2PPh_2, $J(HPt) = 51$], 4.44 and 2.99 (AB spin system, 8 H, $C_6H_2CH_2C_6H_2$, $^2J = 12.8$), 4.02 (q, 4 H, $CO_2CH_2CH_3$, $^3J = 6.9$), 3.87 (s, 4 H, O*C*$H_2CO_2CH_2CH_3$), 1.35 (s, 18 H, Bu^t), 1.14 (t, 6 H, $CO_2CH_2CH_3$, $^3J = 6.9$), 0.81 (s, 18 H, Bu^t) and −15.00 [t with platinum satellites, 1 H, PtH, $^2J(HP) = 14.8$, $J(HP) = 1154$]; ^{31}P-{^1H}, δ 23.8 [s with platinum satellites, PPh_2, $J(PPt) = 3148$ Hz]. FAB mass spectrum: *m/z* (%) 1412.6 (100), $[M - Cl]^+$ (expected isotopic profile) (Found: C, 64.52; H, 6.51. $C_{78}H_{91}ClO_8P_2Pt$ requires C, 64.65; H, 6.33%).

Reaction of *trans*-[PtH(Cl)(PPh_3)$_2$] with L^3. This reaction was followed by ^{31}P NMR spectroscopy (CH_2Cl_2, external $CDCl_3$). After 12 h only [PtH(PPh_3)L^3]Cl **5′** (*ca.* 20%) and the starting complex were detected. Full conversion of the starting complex was observed after 36 h. At this stage, the reaction mixture contains **5′** (80%) and **10** (20%). The reaction mixture was then heated and slow conversion of **5′** into **10** was observed. After 5 d the **5′**:**10** ratio was 55:44 (1% of an unidentified hydride was also detected). Complex **10** was not isolated and its structure was assigned on the basis of its ^{31}P and its ^1H NMR spectra ($CDCl_3$). ^{31}P-{^1H}, δ 20.5 [s with platinum satellites, PPh_2, $J(PPt) = 3153$]; ^1H, δ −15.16 [t with platinum satellites, 1 H, PtH, $^2J(HP) = 15.15$, $J(HP) = 1150$ Hz].

***trans*-*P*,*P*′-[1,2-Di(methoxycarbonyl)ethenyl]{5,11,17,23-tetra-*tert*-butyl-25,27-bis(diethylcarbamoylmethoxy)-26,28-bis(diphenylphosphinomethoxy)calix[4]arene}platinum(II) tetrafluoroborate 11.** To a solution of complex **7** (0.200 g, 0.129 mmol) in $CDCl_3$ (10 cm^3) was added $MeO_2CC{\equiv}CCO_2Me$ (0.020 g, 0.140 mmol). The reaction was monitored by ^{31}P NMR spectroscopy. After 3 d the solution was concentrated to *ca.* 1 cm^3 and pentane was added to yield the product as an analytically pure white powder (0.180 g, 82%), m.p. 212–215 °C (decomp.). IR (cm^{-1}): (KBr) $\nu(C{=}O_{ester})$ 1718s, $\nu(C{=}O_{amide})$ 1654s, 1632s, 1590s, ν(B–F) 1054s; (thf) $\nu(C{=}O_{ester})$ 1720s, $\nu(C{=}O_{amide})$ 1654s, 1633s, 1590s. The presence of four strong ν(C=O) absorption bands in the IR spectrum, instead of three, suggests that several isomers resulting from dynamics within the chelate backbone are interconverting (atropisomers). NMR ($CDCl_3$): ^1H, δ 7.88–7.49 (m br, 18 H, PPh_2), 7.18 (s, 4 H, *m*-H), 6.95 (s, 2 H, PPh_2), 6.46 (s, 4 H, *m*-H), 5.59 (br s, 4 H, O*C*H_2PPh_2), 5.16 [s, 1 H, C*H*(CO_2Me)], 4.46 and 3.19 (AB spin system, 8 H, $C_6H_2CH_2C_6H_2$, $^2J = 13.0$), 4.20 (s, 4 H, O*C*H_2-$CONEt_2$), 3.50 (q, 4 H, NCH_2CH_3, $^3J = 7.3$), 3.42 (s, 3 H, CO_2CH_3), 3.03 (s, 3 H, CO_2CH_3), 2.93 (q, 4 H, NCH_2CH_3, $^3J = 6.4$), 1.36 (s, 18 H, Bu^t), 1.24 (t, 6 H, NCH_2CH_3, $^3J = 7.0$), 1.01 (t, 6 H, NCH_2CH_3, $^3J = 7.0$) and 0.82 (s, 18 H, Bu^t); ^{13}C-{^1H} (500 MHz), δ 173.22 (s, *C*O_2CH_3), 168.09 [s, C(O)N], 163.71 (s, *C*O_2CH_3), 154.03–122.74 (aromatic C and C=C), 72.23 (s, OCH_2CONEt_2), 70.64 [t, OCH_2PPh_2, $|J(PC) + {}^3J(P'C)| = 42$], 50.59 and 50.53 (2s, CO_2CH_3), 40.58 (s, NCH_2CH_3), 34.19 and 33.82 [2s, *C*(CH_3)$_3$], 32.96 and 32.80 (s, $C_6H_2CH_2C_6H_2$), 31.60 and 31.06 [2s, C(*C*H_3)$_3$], 13.87 and 13.08 (2s, NCH_2CH_3); ^{31}P-{^1H}, δ 16.4 [s with platinum satellites,

PPh_2, J(PPt) = 2926 Hz]. FAB mass spectrum of **11** after recrystallisation from CH_2Cl_2–pentane: *m/z* (%) 1609.9 (100) $[M - BF_4]^+$ (expected isotopic profile) (Found: C, 62.07; H, 6.11; N, 1.61. $C_{88}H_{107}BF_4N_2O_{10}P_2Pt$ requires C, 62.27; H, 6.36; N, 1.65%).

***trans*-*P*,*P*′-{5,11,17,23-Tetra-*tert*-butyl-25,27-di(ethylcarbamoylmethoxy)-26,28-bis(diphenylphosphinomethoxy)calix[4]arene}(tetracyanoethene)platinum(0) 12.** To a solution of complex **3** (0.100 g, 0.066 mmol) in $CHCl_3$ (10 cm^3) was added $(NC)_2C{=}C(CN)_2$ (0.009 g, 0.066 mmol). After stirring for 10 h the solution was concentrated to *ca.* 1 cm^3. Addition of pentane afforded **12** as an analytically pure pale yellow powder (0.105 g, 94%), m.p. 252 °C (decomp.). IR (KBr, cm^{-1}): ν(C=O) 1667s, ν(C≡N) 2224m. NMR ($CDCl_3$): ^{1}H, δ 7.94–7.90 and 7.51–7.50 (20 H, PPh_2), 6.99 (s, 4 H, *m*-H), 6.52 (s, 4 H, *m*-H), 6.09 [s with platinum satellites, 4 H, OCH_2PPh_2, J(HPt) = 24], 4.45 and 3.05 (AB spin system, 8 H, $C_6H_2CH_2C_6H_2$, ^2J = 13.4), 4.12 (s, 4 H, OCH_2CONEt_2), 3.37 (q, 4 H, NCH_2CH_3, ^3J = 7.0), 3.03 (q, 4 H, NCH_2CH_3, ^3J = 7.0), 1.30 (s, 18 H, Bu^t), 1.16 (t, 6 H, NCH_2CH_3, ^3J = 7.0), 1.12 (t, 6 H, NCH_2CH_3, ^3J = 7.0) and 0.78 (s, 18 H, Bu^t); ^{13}C-{^{1}H}, δ 166.52 (s, C=O), 152.26–124.81 (aromatic C), 112.83 [m, CN and/or $C(CN)_2$], 72.10 [d, OCH_2PPh_2, J(PC) = 38], 71.71 (s, OCH_2CONEt_2), 40.54 and 39.99 (s, NCH_2CH_3), 33.74 and 33.56 [2s, $C(CH_3)_3$], 31.39 and 30.88 [2s, $C(CH_3)_3$], 30.47 (2s, $C_6H_2CH_2C_6H_2$), 14.08 and 12.83 (2s, NCH_2CH_3); ^{31}P-{^{1}H}, δ 11.9 [s, with platinum satellites, PPh_2, J(PPt) = 3621 Hz] (Found: C, 64.12; H, 5.66; N, 5.28. $C_{88}H_{100}N_6O_6P_2Pt$·0.75 CH_2Cl_2 requires C, 64.25; H, 6.15; N, 5.05%).

***trans*-*P*,*P*′-Carbonyl{5,11,17,23-tetra-*tert*-butyl-25-(diethylcarbamoylmethoxy)-27-(diethylcarbamoyl-κ*O*-methoxy)-26,28-bis(diphenylphosphinomethoxy)calix[4]arene}rhodium(I) tetrafluoroborate 13.** A solution of $AgBF_4$ (0.023 g, 0.118 mmol) in thf (1 cm^3) was added to a stirred solution of $[\{Rh(CO)_2Cl\}_2]$ (0.023 g, 0.059 mmol) in CH_2Cl_2 (5 cm^3). Stirring was stopped after 5 min. The suspension containing AgCl was carefully filtered through Celite and the filtrate added to a solution of L^1 (0.150 g, 0.118 mmol) in CH_2Cl_2 (20 cm^3). After standing for 0.5 h the solution was concentrated to *ca.* 5 cm^3. Addition of pentane afforded a yellow precipitate (0.150 g, 83%), m.p. 199 °C (slow decomp.). IR (KBr, cm^{-1}): ν(C≡O) 1989s, ν(C=O) 1657m and 1611s, ν(B–F) 1055. NMR ($CDCl_3$): ^{1}H, δ 7.94–7.31 (20 H, PPh_2), 7.25 and 7.17 (AB spin system, 4 H, *m*-H, ^4J = 2), 6.53 and 6.49 (2s, 4 H, *m*-H), 5.98 and 5.11 [ABXX′ spin system with X,X′ = P, 4 H, OCH_2PPh_2, ^2J(AB) = 12.8, $|J(AX) + J(AX')|$ = 12.8, J(BX) not determined], 4.89 and 3.37 (AB spin system, 4 H, $C_6H_2CH_2C_6H_2$, ^2J = 12.8), 4.37 (s, 2 H, OCH_2CONEt_2), 3.81 and 2.67 (AB system, 4 H, $C_6H_2CH_2C_6H_2$, ^2J = 11.8), 3.60 (q, 2 H, NCH_2CH_3, ^3J = 7), 3.26 (s, 2 H, OCH_2CONEt_2), 3.11 (q, 2 H, NCH_2CH_3, ^3J = 7), 2.90 (m, 4 H, two NCH_2CH_3, ^3J = 7), 1.39 (s, 18 H, Bu^t), 1.36 and 1.34 (2t, 6 H, two NCH_2CH_3, ^3J = 7), 0.82 (s, 9 H, Bu^t), 0.81 (s, 9 H, Bu^t), 0.74 and 0.70 (2t, 6 H, two NCH_2CH_3, ^3J = 7); ^{13}C-{^{1}H}, δ 170.28 and 167.37 (2s, C=O), 155.39–125.12 (aromatic C), 72.99 (t, OCH_2PPh_2, $|J(PC) + {}^3J(P'C)|$ = 43), 72.38 and 69.63 (2s, OCH_2CONEt_2), 40.74, 40.09, 39.95 and 39.66 (4s, NCH_2CH_3), 34.14 and 33.59 [2s, $C(CH_3)_3$], 31.64, 31.06 and 30.84 [3s, $C(CH_3)_3$], 30.47 (s, $C_6H_2CH_2C_6H_2$), 13.82, 12.86, 12.64 and 12.54 (4s, NCH_2CH_3); ^{31}P-{^{1}H}, δ 18.1 [d, PPh_2, J(PRh) = 127 Hz]. FAB mass spectrum: *m/z* (%) 1401.2 (20), $[M - BF_4]^+$ (expected isotopic profile); 1373.2 (100), $[M - BF_4 - CO]^+$ (Found: C, 66.20; H, 6.60; N, 1.87. $C_{83}H_{100}BF_4N_2O_7P_2Rh$·0.25 CH_2Cl_2 requires C, 66.19; H, 6.71; N, 1.85%).

***trans*-*P*,*P*′-(*R*,*R*)-Carbonyl{5,11,17,23-tetra-*tert*-butyl-25-[(1-phenylethyl)carbamoylmethoxy]-27-[(1-phenylethyl)-carbamoyl-κ*O*-methoxy]-26,28-bis(diphenylphosphinomethoxy)-calix[4]arene}rhodium(I) tetrafluoroborate 14.** A solution of $AgBF_4$ (0.021 g, 0.054 mmol) in thf (1 cm^3) was added to a stirred solution of $[\{Rh(CO)_2Cl\}_2]$ (0.021 g, 0.110 mmol) in CH_2Cl_2 (3 cm^3). Stirring was stopped after 5 min and the solution was decanted in order to remove AgCl. The supernatant and dichloromethane washings of the AgCl precipitate were filtered through Celite into a solution of L^3 (0.150 g, 0.110 mmol) in CH_2Cl_2 (30 cm^3). After stirring for 1 h the solution was concentrated to *ca.* 2 cm^3 and addition of a diethyl ether–pentane mixture afforded a white precipitate (0.110 g, 63%), m.p. 211–213 °C. IR (KBr, cm^{-1}): ν(C≡O) 1988s, ν(C=O) 1680m, 1634s and ν(B–F) 1054s (br). NMR (CD_2Cl_2): ^{1}H, δ 8.05–7.15 (m, 31 H, aromatic H + NH), 7.03 and 7.00 [AB spin system, 2 H, *m*-H, J(AB) = 3], 6.66–6.45 (three overlapping AB spin systems, 6 H, *m*-H), 5.94 (d, 1 H, NH, ^3J = 7.6), 5.68 and 5.32 [ABXY system, X = P, Y = Rh, 2 H, PCH_2, J(AB) = 12, J(PA) = 8, J(RhA) = 0, J(PB) = 9, J(RhB) = 2 Hz), 5.46 and 5.31 [ABXY system, X = P, Y = Rh, 2 H, PCH_2, J(AB) = 12, J(PA) = 12, J(RhA) = 0, J(PB) = 12, J(RhB) = 3], 4.90 [dq, AMX_3 spin system, 1 H, $NHCH$MePh, $^3J(AM) \approx {}^3J(AX)$ = 7.1], 4.75 [dq, AMX_3 spin system, 1 H, $NHCH$MePh, $^3J(AM) \approx {}^3J(AX)$ = 7.1], 4.54 and 3.29 (AB spin system, 2 H, $C_6H_2CH_2C_6H_2$, J = 12.9), 4.39 and 3.23 (AB spin system, 2 H, $C_6H_2CH_2C_6H_2$, J = 13.1), 4.15 and 4.03 (AB spin system, 2 H, OCH_AH_BCONHR, J = 14.2), 3.96 and 2.92 (AB spin system, 4 H, $C_6H_2CH_2C_6H_2$, J = 12.5), 3.55 and 2.52 (AB spin system, 4 H, $C_6H_2CH_2C_6H_2$, J = 12.5), 3.45 and 3.17 (AB spin system, 2 H, OCH_AH_BCONHR, J = 16.2), 1.41 and 1.37 (2s, 18 H, 2 Bu^t), 1.10 (d, 3 H, $NHCHCH_3$Ph, ^3J = 6.8 Hz), 0.84 and 0.80 (2s, 18 H, 2 Bu^t); the second Me(amide) group overlaps the Bu^t signals at 1.4. ^{13}C-{^{1}H} NMR (CD_2Cl_2): δ 172.70 (s, C=O), 168.11 (s, C=O), 155.72–125.44 (aromatic C), 75.75 (s, OCH_2CONHR), 73.35 [centre of a pseudo-q, OCH_2PPh_2, $|J(PC) + {}^3J(P_{trans}C)| \approx 46$ Hz), 69.87 (s, OCH_2CONHR), 50.69 (s, $NHCHMePh$), 48.89 (s, $NHCHMePh$), 34.52 [s, $C(CH_3)_3$], 34.00 [s, $C(CH_3)_3$], 32.13 (s, $C_6H_2CH_2C_6H_2$), 31.84 [2 $C(CH_3)_3$], 31.47 (s, $C_6H_2CH_2C_6H_2$), 31.32 and 31.17 [2s, $C(CH_3)_3$], 30.95 (s, $C_6H_2CH_2C_6H_2$), 30.85 (s, $C_6H_2CH_2C_6H_2$), 22.54 (s, $NHCHCH_3Ph$) and 21.69 (s, $NHCHCH_3Ph$). ^{31}P-{^{1}H} NMR ($CDCl_3$): δ 20.70 and 14.26 [ABX spin system with X = Rh, J(AB) = 331, J(RhA) = 132, J(RhB) = 132 Hz]. FAB mass spectrum: *m/z* (%) 1498 (18), $[M - BF_4]^+$ (expected isotopic profile), 1470 (100), $[M - CO - BF_4]^+$ (Found: C, 68.16; H, 6.01; N, 1.56. $C_{91}H_{100}BF_4N_2O_7P_2Rh$·0.5 CH_2Cl_2 requires C, 68.21; H, 6.30; N, 1.74%).

Crystallography

Suitable yellow crystals of complex **12**·3$CHCl_3$·H_2O were obtained by slow diffusion of hexane into a solution of **12** in $CHCl_3$ at room temperature. Complex **12** crystallizes in the monoclinic system, space group $P2_1/c$, with Z = 4. The unit-cell parameters were determined, refined (using 25 high-angle reflections) and data were collected on a Nonius MACH3 diffractometer at 293 K using graphite-monochromated Mo-Kα radiation, λ = 0.710 73 Å. The data collection [ω–2θ scan type, $2\theta_{max} = 52°$, $\pm h + k + l$, intensity controls without appreciable decay (0.2%)] gave 20 483 reflections from which 12 592 were unique with $I > 3\sigma(I)$. Crystallographic data are summarized in Table 2.

After Lorentz-polarization and absorption (transmission factors derived from the ψ scans of four reflections) corrections, the structure was solved by direct methods. After refinement of the heavy atoms, a Fourier-difference map revealed maxima of residual electron density close to the positions expected for hydrogen atoms; they were introduced into structure-factor calculations by their computed coordinates (C–H 0.95 Å) and isotropic thermal parameters such as $B(H) = 1.3\ B_{eq}(C)$ Å but not refined. Solvent hydrogen atoms were omitted. One of the chlorine atoms of a solvent molecule [Cl(6)] is disordered over two sites with an occupancy ratio of 1:1. Full-matrix least-squares refinements on F, $\sigma^2(F^2) = \sigma^2$ (counts) + $(pI)^2$. A final

Table 2 Crystallographic data for complex **12**·3$CHCl_3$·H_2O

Formula	$C_{88}H_{100}N_6O_6P_2Pt$·3$CHCl_3$·H_2O
M	1971.0
a/Å	16.900(5)
b/Å	16.445(4)
c/Å	34.436(10)
β/°	98.12(2)
U/Å^3	9474.7(7)
D_c/g cm^{-3}	1.382
μ/cm^{-1}	18.372
θ Range/°	2–26
R^a	0.051
R'^b	0.074

^{a} $R = \Sigma(||F_o| - |F_c||)/\Sigma|F_o|$. ^{b} $R' = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{\frac{1}{2}}$; $w^{-1} = \sigma^2(F_o)$.

difference map revealed no significant maxima; the highest peak was at 0.8 Å from the platinum site. Atomic scattering factors were taken from ref. 57. All calculations were performed on a DEC Alpha 3100 computer using the MOLEN[58] package. Fig. 1 was drawn using the MolView program.[59]

Atomic coordinates, thermal parameters, and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1997, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 186/556.

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References

1 C. D. Gutsche, *Monographs in Supramolecular Chemistry, Vol. I: Calixarenes*, ed. J. F. Stoddart, The Royal Society of Chemistry, Cambridge, 1989.
2 J.-C. G. Bünzli and J. M. Harrowfield, in *Calixarenes, a versatile class of macrocyclic compounds*, eds. J. Vicens and V. Böhmer, Kluwer Academic Publishers, Dordrecht, 1990, p. 211.
3 V. Böhmer and M. A. McKervey, *Chem. Unserer Zeit*, 1991, **25**, 195.
4 J. K. Moran and D. M. Roundhill, *Inorg. Chem.*, 1992, **31**, 4213.
5 S. Shinkai, *Tetrahedron*, 1993, **49**, 8933.
6 E. van Dienst, W. I. I. Bakker, J. F. J. Engbersen, W. Verboom and D. N. Reinhoudt, *Pure Appl. Chem.*, 1993, **65**, 387.
7 O. Aleksiuk, F. Grynszpan and S. Biali, *J. Incl. Phenom.*, 1994, **19**, 237.
8 V. Böhmer, *Angew. Chem., Int. Ed. Engl.*, 1995, **34**, 713.
9 I. Shevchenko, H. Zhang and M. Lattman, *Inorg. Chem.*, 1995, **34**, 5405.
10 P. D. Beer, *Chem. Commun.*, 1996, 689.
11 C. Wieser, C. B. Dieleman and D. Matt, *Coord. Chem. Rev.*, 1997, in the press.
12 E. M. Collins, M. A. McKervey and S. J. Harris, *J. Chem. Soc., Perkin Trans. 1*, 1989, 372.
13 S. Pappalardo, L. Giunta, M. Foti, G. Ferguson, J. F. Gallagher and B. Kaitner, *J. Org. Chem.*, 1992, **57**, 2611.
14 C. Dieleman, C. Loeber, D. Matt, A. De Cian and J. Fischer, *J. Chem. Soc., Dalton Trans.*, 1995, 3097.
15 V. Böhmer, F. Marschollek and L. Zetta, *J. Org. Chem.*, 1987, **52**, 3200.
16 J.-D. van Loon, A. Arduini, W. Verboom, R. Ungaro, G. J. van Hummel, S. Harkema and D. N. Reinhoudt, *Tetrahedron Lett.*, 1989, **30**, 2681.
17 J.-D. van Loon, A. Arduini, L. Coppi, W. Verboom, A. Pochini, R. Ungaro, S. Harkema and D. N. Reinhoudt, *J. Org. Chem.*, 1990, **55**, 5639.
18 A. Arduini, S. Fanni, G. Manfredi, A. Pochini, R. Ungaro, A. R. Sicuri and F. Ugozzoli, *J. Org. Chem.*, 1995, **60**, 1448.
19 R. Ungaro, A. Casnati, F. Ugozzoli, A. Pochini, J.-F. Dozol, C. Hill and H. Rouquette, *Angew. Chem., Int. Ed. Engl.*, 1994, **33**, 1506.
20 A. Varnek and G. Wipff, *J. Comput. Chem.*, 1996, **13**, 1520.
21 O. Struck, J. P. M. Duynhoven, W. Verboom, S. Harkema and D. N. Reinhoudt, *Chem. Commun.*, 1996, 1517.
22 P. D. Beer, D. Hesek, J. E. Kingston, D. K. Smith, S. E. Stokes and M. G. B. Drew, *Organometallics*, 1995, **14**, 3288.
23 M. H. Chisholm, K. Folting, J. C. Huffman and R. J. Tatz, *J. Am. Chem. Soc.*, 1984, **106**, 1153.
24 M. M. Olmstead, G. Sigel, H. Hope, X. Xu and P. P. Power, *J. Am. Chem. Soc.*, 1985, **107**, 8087.
25 C. D. Gutsche and K. C. Nam, *J. Am. Chem. Soc.*, 1988, **110**, 6153.
26 F. Corazza, C. Floriani, A. Chiesi-Villa and C. Rizzoli, *Inorg. Chem.*, 1991, **30**, 4465.
27 C. Loeber, D. Matt, A. De Cian and J. Fischer, *J. Organomet. Chem.*, 1994, **475**, 297.
28 C. Loeber, C. Wieser, D. Matt, A. De Cian, J. Fischer and L. Toupet, *Bull. Soc. Chim. Fr.*, 1994, **132**, 166.
29 W. Xu, R. J. Puddephatt, L. Manojlovic-Muir, K. W. Muir and C. S. Frampton, *J. Incl. Phenom.*, 1994, **19**, 277.
30 H. Iki, T. Kikuchi, H. Tsuzuki and S. Shinkai, *J. Incl. Phenom.*, 1994, **19**, 227.
31 T. M. Swager and B. Xu, *J. Incl. Phenom.*, 1994, **19**, 389.
32 J. A. Acho and S. J. Lippard, *Inorg. Chim. Acta*, 1995, **229**, 5.
33 I. Neda, H.-J. Plinta, R. Sonnenburg, A. Fischer, P. G. Jones and R. Schmutzler, *Chem. Ber.*, 1995, **128**, 267.
34 D. M. Roundhill, *Prog. Inorg. Chem.*, 1995, **43**, 533.
35 E. Solari, W. Lesueur, A. Klose, K. Schenk, C. Floriani, A. Chiesi-Villa and C. Rizzoli, *Chem. Commun.*, 1996, 807.
36 B. R. Cameron and S. J. Loeb, *Chem. Commun.*, 1996, 2003.
37 L. Giannini, E. Solari, A. Zanotti-Gerosa, C. Floriani, A. Chiesi-Villa and C. Rizzoli, *Angew. Chem., Int. Ed. Engl.*, 1996, **35**, 85.
38 C. Wieser, D. Matt, L. Toupet, H. Bourgeois and J.-P. Kintzinger, *J. Chem. Soc., Dalton Trans.*, 1996, 4041.
39 M. G. Gardiner, G. A. Koutsantonis, S. M. Lawrence, P. J. Nichols and C. L. Raston, *Chem. Commun.*, 1996, 2035.
40 *The Chemistry of Organophosphorus Compounds*, ed. F. R. Hartley, Wiley, Chichester, 1990, vol. 1.
41 C. Jaime, J. de Mendoza, P. Prados, P. M. Nieto and C. Sánchez, *J. Org. Chem.*, 1991, **56**, 3372.
42 D. K. Johnson, P. S. Pregosin and L. M. Venanzi, *Helv. Chim. Acta*, 1976, **59**, 2691.
43 L. M. Venanzi, *Pure Appl. Chem.*, 1980, **52**, 1117.
44 M. Camalli, F. Caruso, S. Chaloupka, P. N. Kapoor, P. S. Pregosin and L. M. Venanzi, *Helv. Chim. Acta*, 1984, **67**, 1603.
45 G. Bracher, D. M. Grove, L. M. Venanzi, F. Bachechi, P. Mura and L. Zambonelli, *Helv. Chim. Acta*, 1980, **63**, 2519.
46 M. Kranenburg, Y. E. M. van der Burgt, P. C. J. Kamer, P. W. N. M. van Leeuwen, K. Goubitz and J. Franjee, *Organometallics*, 1995, **14**, 3081.
47 A. Bader and E. Lindner, *Coord. Chem. Rev.*, 1991, **108**, 27.
48 C. Abu-Gnim and I. Amer, *J. Chem. Soc., Chem. Commun.*, 1994, 115.
49 L. M. Venanzi, in *20th Int. Conf. Coord. Chem.*, 1979, ed. D. Banerjea, Pergamon, Oxford, 1980, pp. 99–105.
50 J.-B. Regnouf de Vains, R. Lamartine, B. Fenet, C. Bavoux, A. Thozet and M. Perrin, *Helv. Chim. Acta*, 1995, **78**, 1607.
51 R. B. Osborne and J. A. Ibers, *J. Organomet. Chem.*, 1982, **232**, 371.
52 C. D. Gutsche and M. Iqbal, *Org. Synth.*, 1989, **68**, 234.
53 W. Z. Wegener, *Z. Chem.*, 1971, **11**, 262.
54 R. Uson, A. Laguna and M. Laguna, *Inorg. Synth.*, 1989, **26**, 85.
55 J. C. Bailar, jun. and H. Itatani, *Inorg. Chem.*, 1965, **4**, 1618.
56 J. A. McCleverty and G. Wilkinson, *Inorg. Synth.*, 1990, **28**, 84.
57 *International Tables for X-Ray Crystallography*, D. Riedel, Boston, MA, 1983, p. A183.
58 C. K. Fair, MOLEN, An Interactive Intelligent System for Crystal Structure Analysis, Enraf-Nonius, Delft, 1990.
59 MolView, J.-M. Cense, Ecole Nationale Supérieure de Chimie de Paris, 1990.

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