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Calix[4]arene-derived diphosphines, diphosphinites and diphosphites as chelating ligands for transition metal ions. Encapsulation of silver(I) in a calix-crown diphosphite

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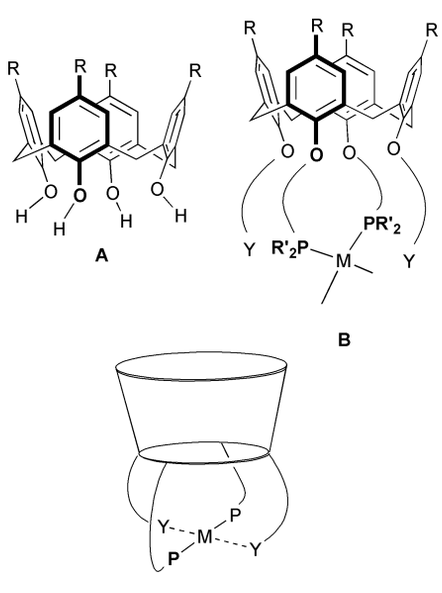
A series of lower rim-functionalised calix[4]arenes bearing 1,3-positioned phosphorus(III) ligands **L**^{1}–**L**^{9} have been synthesized and their coordinative properties examined. **L**^{1} and **L**^{2} {5,11,17,23-tetra-*tert*-butyl-25,27-bis[2-(diphenylphosphino)ethoxy]- and -25,27-bis(diphenylphosphinomethoxy)-26,28-bis(3-oxabutyloxy)calix[4]arene} react with $[Rh(nbd)(THF)_2]BF_4$ (nbd = 1,5-norbornadiene; THF = tetrahydrofuran) to afford in high yield the complexes $[Rh(nbd)\mathbf{L}^1]BF_4$ and $[Rh(nbd)\mathbf{L}^2]BF_4$, respectively, where the calixarene behaves as a *P*,*P*′ chelator. Both complexes catalyse hydroformylation of styrene at comparable rates, the linear : branched aldehyde ratio being 5 : 95. The presence of the ether side groups did not exert a noticeable effect on the selectivity nor the catalytic activity. Reaction of **L**^{1}–**L**^{8} with $[Pd(\eta^3\text{-}C_3H_4Me)(THF)_2]BF_4$ gave the corresponding cationic chelate complexes $[Pd(\eta^3\text{-}C_3H_4Me)\mathbf{L}^i]BF_4$ that are active in the catalytic alkylation of 1,3-diphenylprop-2-enyl acetate with dimethyl malonate. Owing to the presence of a non-planar Pd–allyl fragment, the achiral calixarene subunits of some of these complexes are no longer C_{2v}-symmetrical, as evidenced by the ^{1}H and ^{13}C NMR spectra that show non-equivalent side groups. Selective chelation *via* the two phosphorus atoms was also observed in the complexes $[RuCl(p\text{-}MeC_6H_4Pr^i)\mathbf{L}^i]BF_4$ (**L**^{i} = **L**^{3} or **L**^{4}) obtained by reaction of the amide phosphines **L**^{i} with $[RuCl(p\text{-}MeC_6H_4Pr^i)(THF)_2]BF_4$ [**L**^{3} = 5,11,17,23-tetra-*tert*-butyl-25,27-bis(diethylcarbamoylmethoxy)-26,28-bis(diphenylphosphinomethoxy)- and **L**^{4} = 5,11,17,23-tetra-*tert*-butyl-25,27-bis(diphenylphosphinomethoxy)-26,28-bis{(1-(*R*)-phenylethyl)carbamoylmethoxy}-calix[4]arene]. Reaction of **L**^{3} or **L**^{4} with neutral $[RuCl_2(p\text{-}MeC_6H_4Pr^i)]_2$ afforded the bimetallic complexes $[\{RuCl(p\text{-}MeC_6H_4Pr^i)\}_2\text{-}\mathbf{L}^i]$ where the calixarene acts as a *P*,*P*′ bridging ligand. Reaction of $AgBF_4$ with calix-crown **L**^{9} {25,27-bis(diethoxyphosphinoxy)-26,28-(3,6,9-trioxaundecane-1,11-dioxy)calix[4]arene} resulted in quantitative formation of the complex $[Ag\mathbf{L}^9]BF_4$ in which the silver(I) ion lies inside the cavity constituted by the crown ether fragment and the two phosphorus arms. As revealed by a single crystal X-ray diffraction study, the Ag^+ ion has a trigonal P_2O coordination environment with a P–Ag–P angle of 134.74(4)°.

Calix[4]arenes (**A**) continue to attract considerable attention in synthetic chemistry, notably as platforms for the build-up of sophisticated molecular cages and claw-like ligands.[1,2] Such architectures have been exploited in recent years for producing a number of compounds of practical interest, in particular ion-selective receptors,[3–7] molecular sensors,[8–12] homogeneous catalysts[13–15] and highly ordered materials.[16,17]

In the last decade several research groups have reported on the phosphorus functionalisation[18] of calixarenes and initiated the co-ordination chemistry of some phosphorus(III) derivatives.[19–26] Our group was mainly involved in the design and study of conical calix[4]arenes bearing two phosphine ligands tethered at distal phenol units.[21,27–29] We found that, towards transition metals, these diphosphines usually behave as chelators resulting in the formation of complexes (**B**) where the metal centre is located at the entrance of the calixarene cavity. Functional groups can be introduced on the adjacent phenol units in order to control the degree of encapsulation of the chelated metal atom. In such complexes the side groups are expected to exert a critical steric control on a reaction taking place at the metal centre and, for example, favour shape-selective reactions or induce enantioselectivity. When the diphosphine acts as a *trans* spanning ligand the whole ligand behaves as a so-called *hemispherical* diphosphine[30] (**C**) in which the cavity blocks a half-space about the chelated metal centre.



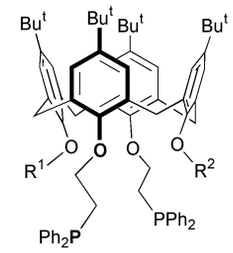
In the present study we report synthetic methodology leading to transition metal chelate complexes starting from calix[4]-arenes that are distally substituted by phosphorus arms of various lengths. The calixarenes also contain auxiliary functions, including chiral groups, that may display coordinating behaviour. Particular attention is paid to possible steric or

binding interactions between the auxiliary groups and the metal centre, in particular in some palladium–allyl complexes. We also describe the crystal structure of a silver(I) complex containing a diphosphite ligand built on a 1,3-calix[4]arene crown-5 matrix (crown-5[2] represents a bridging $O(CH_2CH_2O)_5$ unit).

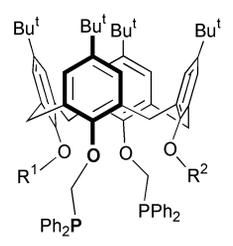
Results and discussion

Synthesis of calix-phosphines

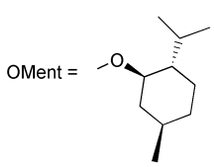
The *P*,*P*-chelators used for the present study, **L**[1]–**L**[9], differ from each other in the length of the two pendant phosphine ligands tethered to the calix platform as well as in the nature of the adjacent groups. The phosphorus atoms are either directly connected to the phenolic oxygen atoms (phosphinites **L**[7] and **L**[8] and phosphite **L**[9]) or separated from these by CH_2CH_2 (phosphine **L**[1]) or CH_2 spacers (phosphines **L**[2–6]). The neighbouring auxiliary functions bear oxygen atoms of various donor strengths, namely ethers, esters and amides, some of them (**L**[4–6], **L**[8]) being linked to chiral groups.

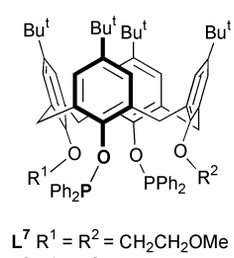


L[1] $R^1 = R^2 = CH_2CH_2OMe$

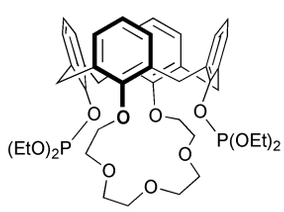


L[2] $R^1 = R^2 = CH_2CH_2OMe$
L[3] $R^1 = R^2 = CH_2C(O)NEt_2$
L[4] $R^1 = R^2$ = (*R*)-$CH_2C(O)NHCHMePh$
L[5] $R^1 = CH_2CH_2OMe$, R^2 = (*R*)-$CH_2C(O)NHCHMePh$
L[6] $R^1 = R^2 = CH_2C(O)OMent$





L[7] $R^1 = R^2 = CH_2CH_2OMe$
L[8] $R^1 = R^2 = CH_2C(O)OMent$



L[9]

The calixarene with the longest dangling phosphorus ligands is **L**[1]. This compound, presented here for the first time, was prepared in 40% overall yield starting from *p*-*tert*-butylcalix[4]arene (**1**) according to Scheme 1. The introduction of the phosphino groups was achieved by treating the PPh_2^- anion with the ditosylated intermediate **L**[1d] (see Experimental section). A similar strategy for tethering $CH_2CH_2PPh_2$ groups has been employed by the Reinhoudt group for a related calixarene.[31] Phosphine **L**[1] possesses the expected cone conformation, as deduced from the ^1H and ^{13}C NMR spectra.[32,33] The phosphorus atoms appear as a single peak (at δ −23.4) in the ^{31}P NMR spectrum. It should be emphasised here that attempts to generate **L**[1] by treating $TsOCH_2CH_2P(O)Ph_2$ (Ts = *p*-Me-$C_6H_4SO_2$) with the corresponding doubly deprotonated calixarene were unsuccessful. In this case TsOH elimination occurs which is followed by polymerisation of the resulting alkene.

The general strategy used for the preparation of the diphosphines **L**[2]–**L**[6], bearing the shorter CH_2PPh_2 arms, has been reported in a previous work,[23] and is exemplified by the new chiral diphosphine **L**[5] (Scheme 2). The synthesis of **L**[5] starts with the introduction of a methoxyethyl group followed by attachment of a chiral (*R*)-$CH_2C(O)NHCH(Me)Ph$ substituent on the distal phenolic position (see Experimental section). The two CH_2PPh_2 groups were then introduced in a single step as phosphine oxides, employing $TsOCH_2P(O)Ph_2$. High yield reduction of the phosphine oxide moieties was achieved in a refluxing $PhSiH_3$–toluene mixture. As expected, owing to the presence of an asymmetric carbon atom in **L**[5], the four $ArCH_2Ar$ bridges appear as four distinct AB patterns in the ^1H NMR spectrum. The chemical shifts of the corresponding ^{13}C carbon atoms are consistent with a cone conformation.

Preparation of diphosphinite **L**[7] was achieved by treating the dihydroxy precursor **L**[1a] with *n*-BuLi followed by addition of Ph_2PCl in THF. Compound **L**[8] has been described previously.[27]

Diphosphite **L**[9] was readily prepared using *n*-BuLi–THF and $PCl(OEt)_2$ (see Experimental section). The phosphite signal was found at δ 140.0 in the ^{31}P NMR spectrum. All important spectroscopic data for **L**[1]–**L**[9] are reported in the Experimental section.

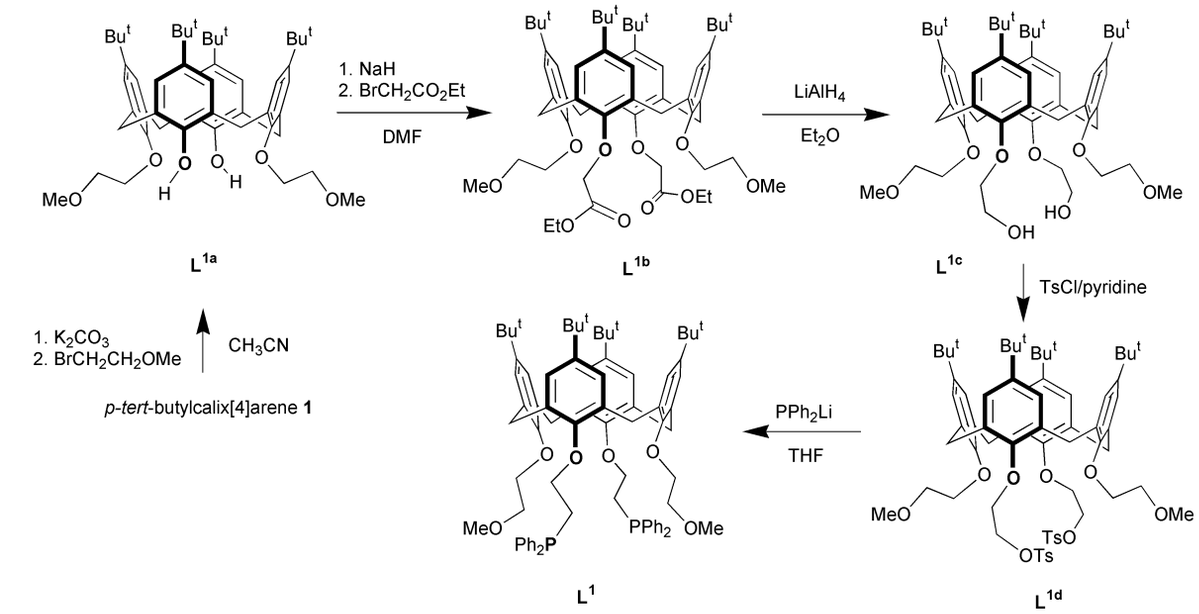
Preparation of rhodium(I), palladium(II), ruthenium(II), and silver(I) chelate complexes

All ligands employed in this study comprise two phosphorus atoms that are separated by relatively long spacers comprising 11–15 atoms. Such diphosphines may therefore, *a priori*, either lead to mononuclear chelate complexes or form polynuclear complexes where the ligand behaves as a bridging ligand. Examples of the latter type have recently been found in our group.[27] We have now found that a convenient method that favours chelating behaviour over oligomer formation consists in treating such diphosphines with precursors containing weak donors, typically cationic species stabilised by solvent molecules, so as to facilitate fast binding of both phosphorus(III) centres at the same metal. Most complexes outlined below were obtained according to this strategy. It is noteworthy that this methodology does not require that the reaction be carried out under high dilution conditions.

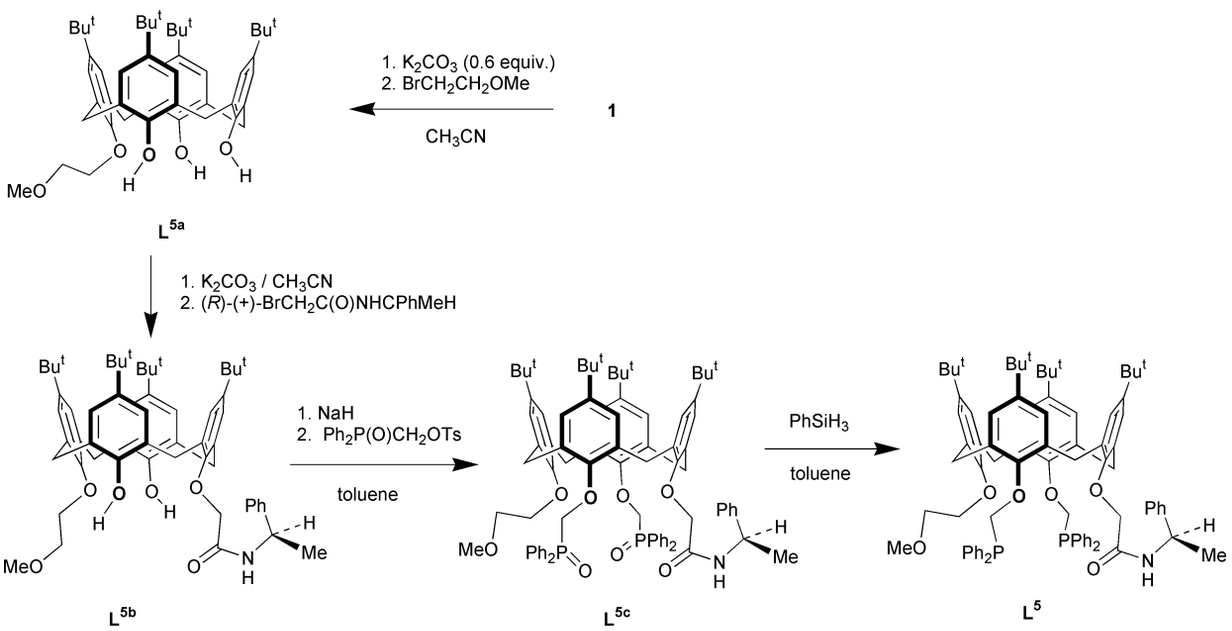
Treatment of $[RhCl(nbd)]_2$ (nbd = norbornadiene) in CH_2Cl_2 with $AgBF_4$ followed by reaction of the resulting cationic species with **L**[1] afforded complex **2** in high yield. There was no indication for oligomer formation. The FAB MS spectrum of **2** shows an intense peak at *m*/*z* = 1383 (with the expected isotopic profile) corresponding to the $[Rh\mathbf{L}^1]^+$ ion. The NMR spectra are in keeping with a C_{2v}-symmetrical structure. The expected *cis* stereochemistry about Rh was confirmed by the ^{31}P NMR spectrum (doublet at δ 16.3 with $J(RhP) = 153$ Hz) which is consistent with those reported for other *cis*-[Rh(nbd)(diphosphine)]$^+$ complexes.[34] Complex **3** was obtained in high yield using conditions similar to those employed for **2**, but starting from **L**[2].

The rhodium complexes **2** and **3** display comparable catalytic activity in styrene hydroformylation (turnover frequency, TOF = *ca.* 7 h^{-1}). Thus, operating at a temperature of 40 °C and under a $CO–H_2$ (1 : 1) pressure of 40 bar, 2-phenylpropanal and 3-phenylpropanal were formed in a 95 : 5 ratio (see Experimental section). This high regioselectivity in favour of the branched aldehyde is not unusual for rhodium phosphine complexes.[35] The activity being similar to that of other cationic $[Rh(diphosphine)(S)_2]^+$ (s = solvent) complexes, it must be concluded that the pendant ether groups do not behave as transient ligands during the catalytic process. It should be remembered here that hemilabile[36] ether phosphines[37] as well as mixed phosphine oxide–phosphines[38,39] have recently been shown to enhance the reactivity of rhodium catalysed methanol carbonylation when compared with related, PPh_3-based systems.

The cationic palladium complexes **4**–**11** were readily formed by treating $[Pd(\eta^3\text{-}C_3H_4Me)(THF)_2]BF_4$ (obtained by reaction of $AgBF_4$ with $[Pd(\eta^3\text{-}C_3H_4Me)Cl]_2$ in THF) with the corre-

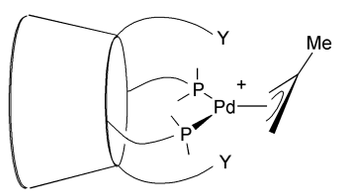


Scheme 1 Stepwise build-up of diphosphine $\mathbf{L^1}$.



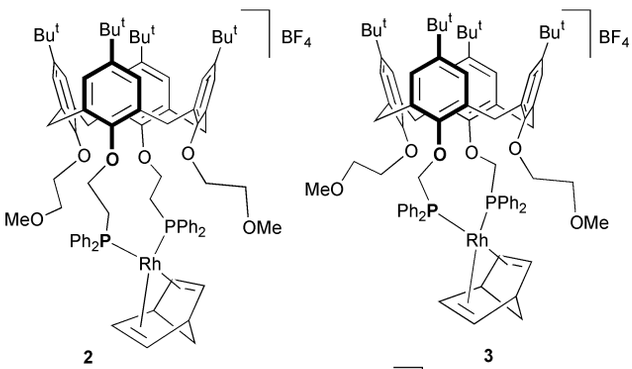
Scheme 2 Synthesis of the chiral diphosphine $\mathbf{L^5}$.

sponding phosphorus(III) ligands. All complexes were characterised by ^{1}H, ^{13}C and ^{31}P NMR and elemental analysis. The formation of *chelate* complexes was unambiguously inferred from FAB mass spectra which all show the corresponding $[Pd\mathbf{L}(C_3H_4Me)]^+$ peak. In almost all ^{1}H NMR spectra the H_{anti} and H_{syn} protons of the allylic part could be identified, and in each case were found to give distinct signals, indicating that, where present, allyl rotation is slow on the NMR timescale. As in other Pd^{II}–diphosphine complexes bearing a slowly rotating allyl ligand, the two half spaces defined by the metal plane are non-equivalent. This asymmetry becomes evident in some ^{1}H NMR spectra showing that the calixarene units no longer retain the C_{2v} symmetry of the ligand. For example, the ^{1}H NMR spectrum of complex **6** displays two distinct amide groups (Y in the drawing), two AB patterns for the ArCH_2Ar groups and three Bu^t signals (intensity 1 : 1 : 2). It is interesting that (to the best of our knowledge) such spatial anisotropy has not previously been detected in other $[PdCl(C_3H_4Me)(L)]$ complexes where **L** is an achiral phosphine. The same asymmetry was also evident in complexes **4**, **5** and **10** where the metal centres are located in pockets constituted by two non-



equivalent CH_2CH_2OMe groups. We anticipated that for **10**, where the allyl/methoxy proximity is the highest, the two OMe groups would be significantly differentiated. This is indeed the case. Thus, the methoxy signal separation is 0.18 ppm for complex **10** *vs.* 0.00 and 0.02 ppm, respectively, for **4** and **5**. Clearly in **10** one side group comes close to the C_3H_4Me fragment.

The complexes **7**–**9** contain chiral carbon atoms and hence the corresponding ^{31}P NMR spectra each display an AB pattern. The *J*(PP) coupling constant of *ca.* 40 Hz confirms the *cis* arrangement of the two phosphorus atoms. The ^{31}P NMR spectrum of **11** which is also chiral shows only an A_2 spectrum, probably accidentally, but as expected the two menthyl



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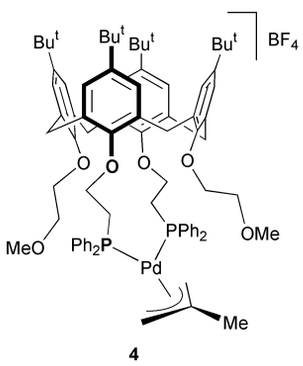

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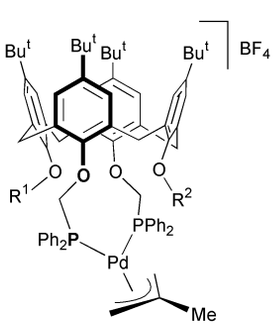
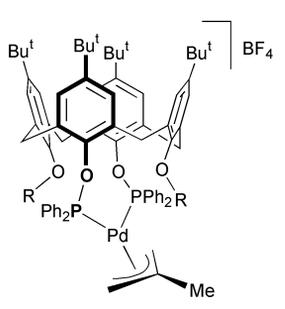


5 $R^1 = R^2 = CH_2CH_2OCH_3$
6 $R^1 = R^2 = CH_2C(O)NEt_2$
7 $R^1 = R^2 = CH_2C(O)NHCHMePh$
8 $R^1 = CH_2CH_2OCH_3$, $R^2 = CH_2C(O)NHCHMePh$
9 $R^1 = R^2 = CH_2C(O)OMent$



10 $R = CH_2CH_2OMe$
11 $R = CH_2C(O)OMent$

fragments are non-equivalent in the ^{1}H NMR spectrum. Interestingly, the ^{31}P NMR spectrum of complex **8** displays two AB patterns (intensity 1 : 3) owing to the formation of two isomers characterised by different orientations of the C_3H_4Me groups (Fig. 1). The ^{1}H NMR spectrum confirms this observation.

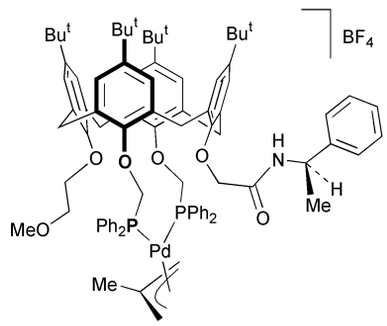
Complexes **4, 7**–**9** and **10** and **11** were assessed in allylic alkylation catalysis. Dimethyl malonate was treated with 1,3-diphenylprop-2-enyl acetate in the presence of NaH as base. Using the reaction conditions outlined in Table 1, full conversion of the substrate was observed after *ca.* 4 h. There are no striking differences between these catalysts in terms of activity. The turnover numbers were close to those observed for good, conventional allylation catalysts.[40] These findings show that the palladium centre remains accessible to the substrate despite its location inside a pocket. In terms of enantioselectivity, the complexes tested did not fulfil our expectations. The low enantiomeric excess (e.e.) of these reactions will be presented elsewhere, together with results obtained for other chiral calixphosphines.[41]

A further example where the side groups of **L**^{3} are differentiated upon complexation is shown in Scheme 3(a). Thus, reaction of **L**^{3} with the cationic complex [RuCl(*p*-$MeC_6H_4Pr^i$)(THF)]BF_4 afforded **12** that was characterized by elemental

Table 1 Palladium catalysed alkylation of 1,3-diphenylprop-2-enyl acetate[a]

Complex	Ligand	Reaction time/h	Turnover[b]
4	**L**^{1}	5	20
7	**L**^{4}	3	33
8	**L**^{5}	5	20
9	**L**^{6}	3	33
10	**L**^{7}	4	25
11	**L**^{8}	4	25

[a] Reaction conditions: 1.2 mmol allyl acetate, 0.012 mmol catalyst, 2.4 mmol dimethyl malonate, 2.4 mmol NaH; Pd : allyl acetate : malonate ratio = 1 : 100 : 200; T = 67 °C; solvent THF. [b] In mol per mol per h.



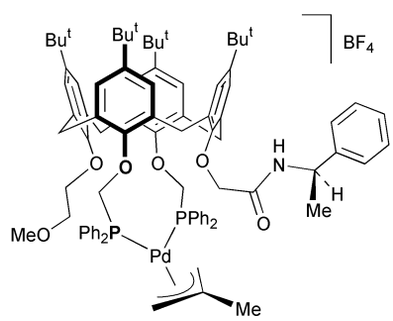
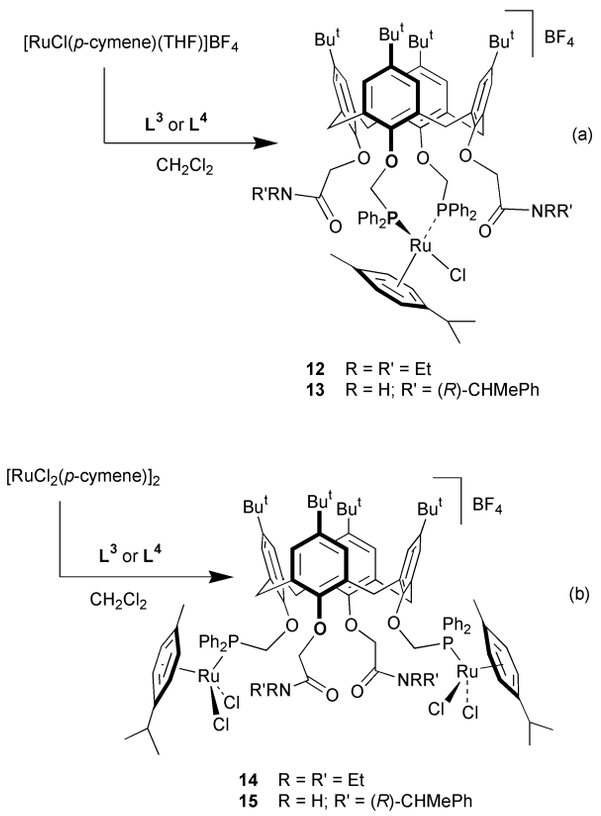


Fig. 1 Possible orientations of the allyl ligand in complex **8**.

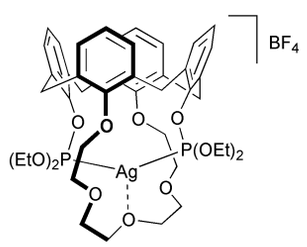
analysis, mass and multinuclear NMR spectroscopy. The only symmetry element of this molecule is a plane that contains the Ru–Cl bond and which bisects the P–Rh–P angle. Hence the two amide groups are no longer equivalent, as confirmed by ^{1}H and ^{13}C NMR. The chiral complex **13** was obtained in a similar way starting from **L**^{4}. The presence in the ^{1}H NMR spectrum of four AB systems for the ArCH_2Ar groups as well as that of four *tert*-butyl signals is consistent with a C_1-symmetrical molecule. As expected, the ^{31}P NMR spectrum displays an AB spectrum(^2J(pp) = 49 Hz). It is noteworthy that the reactions of **L**^{3} and **L**^{4} with [$RuCl_2$(*p*-$MeC_6H_4Pr^i$)]$_2$ in dichloromethane gave quantitatively the dimetallic complexes **14** and **15**, respectively, Scheme 3(b), in which the amide side groups remain *unbonded*. The reaction of [RuClL(*p*-$MeC_6H_4Pr^i$)] complexes with other hybrid *P*,*O* phosphines results in loss of the arene fragment and formation of *P*,*O*-chelate complexes.[42]

Molecular models and previous studies carried out in our laboratory showed that calixarenes bearing two phosphino groups directly appended to distal phenolic oxygen atoms may form *cis* complexes,[27] but are unsuitable for formation of chelate complexes having a pure *trans* stereochemistry. Nevertheless, considering their size and backbone flexibility it may be anticipated that complexes with P–M–P angles larger than 120° can be obtained from such ligands. In order to assess their potential bite angle, we investigated the complexing behaviour of the calix-crown diphosphite **L**^{9} towards Ag^+. **L**^{9} may simply be regarded as a variation of ligand **L**^{7} where the phosphorus atoms bear small substituents (OEt) and the two side groups are replaced by a single polyether chain that straps two opposing



Scheme 3 Formation of cationic (a) and neutral (b) ruthenium complexes from calix diphosphines containing amide side groups.

phenol units. Silver(I) was chosen for its ability readily to form $[MP_2]^+$ and $[MP_2(S)]^+$ complexes (P = phosphine; S = 2e donor ligand), the latter providing access to a wide range of P–M–P angles, usually lying between 120 and 180°. Reaction of **L**[9] with $AgBF_4$ in THF afforded quantitatively complex **16**.



16

The mass spectrum shows an intense peak at $m/z = 931.2$ with the isotopic profile exactly as expected for $[Ag\mathbf{L}^9]^+$. The NMR spectra indicate C_{2v} symmetry for the molecule. Complexation of silver was inferred from the ^{31}P NMR spectrum that displays two doublets centred at δ 105.9 ($J(P–Ag^{107}) = 778$, $J(P–Ag^{109}) = 900$ Hz). A single crystal X-ray diffraction study confirmed the chelating behaviour of the diphosphite (Fig. 2). Important structural parameters are given in Table 2. The molecule possesses a symmetry axis in the solid state. The silver atom adopts a trigonal P_2O stereochemistry, involving the central O(6) atom of the crown-5 unit. The Ag–P bond lengths are 2.378(1) Å, while the Ag–O(6) bond length is 2.360(5) Å. The P(1)–Ag–P(2) angle of 134.74(4)° is not unusual for a trigonal $AgOP_2$ arrangement (P = monophosphine), but such large bite angles have rarely been observed in diphosphine–silver complexes.[43] The fact that such an angle can be obtained with **L**[9] illustrates the flexibility of the calix[4]arene scaffold. Notably, another calixarene diphosphite with a large natural bite angle has recently been described by van Leeuwen and co-workers, but in this case the ligand derives from calix[6]arene.[44]

Table 2 Selected bond distances (Å) and angles (°) for complex **16**

Ag–P	2.3785(8)	P–O(1)	1.612(2)
Ag–O(6)	2.360(5)	P–O(2)	1.593(2)
Ag–O(5)	2.591(2)	P–O(3)	1.592(2)
P–Ag–P	134.74(4)	P–Ag–O(5)	139.4(5)
P–Ag–O(6)	121.8(1)/103.4(1)[a]	O(1)–P–O(2)	102.5(1)
O(1)–P–O(3)	102.5(1)	O(2)–P–O(3)	107.5(1)

[a] The O(6) atom is disordered over two C_2-symmetrical positions.

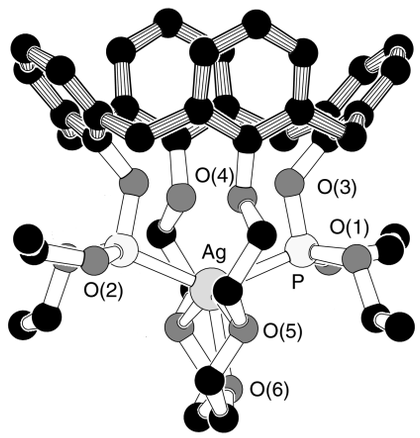


Fig. 2 Molecular structure of the silver(I) complex **16**. The BF_4^- anion is not shown.

In conclusion, we have shown that 1,3-disubstituted calix-[4]arenes bearing PR_2, CH_2PPh_2, or $CH_2CH_2PPh_2$ substituents readily form chelate complexes when exposed to starting complexes that contain weak donor ligands. In the complexes thus formed the presence of two side functions lying close to the metal centre constitutes a useful tool for probing the local symmetry about the metal. Interaction with the side group was found in one instance, namely the calix-crown complex **16**, where the *P*,*P*-chelated silver ion interacts with the central oxygen atom of the crown-5 bridge. The structural attributes of diphosphite **L**[9], as revealed by an X-ray diffraction study, show that 1,3-calix diphosphites give access to chelating ligands having a large bite angle. Futher studies will be aimed at exploiting this latter feature.

Experimental

General procedures can be taken from ref. 33. Samples of *p*-*tert*-butylcalix[4]arene **1**,[45] 5,11,17,23-tetra-*tert*-butyl-25,27-dihydroxy-26,28-bis(3-oxabutyloxy)calix[4]arene **L**[1a],[23] 5,11,17,23-tetra-*tert*-butyl-25,27-bis(diphenylphosphinomethoxy)-26,28-bis(3-oxabutyloxy)calix[4]arene **L**[2],[23] 5,11,17,23-tetra-*tert*-butyl-25,27-bis(diethylcarbamoylmethoxy)-26,28-bis(diphenylphosphinomethoxy)calix[4]arene **L**[3],[34] 5,11,17,23-tetra-*tert*-butyl-25,27-bis(diphenylphosphinomethoxy)-26,28-bis{(1-(*R*)-phenylethyl)carbamoylmethoxy}calix[4]arene] **L**[4],[34] (+)-(*R*)-2-bromo-*N*-(1-phenylethyl)acetamide,[34] 5,11,17,23-tetra-*tert*-butyl-25,27-dihydroxy-26,28-bis{(1*R*,2*S*,5*R*)-menthyloxycarbonylmethoxy}calix[4]arene **L**[6a],[27] 5,11,17,23-tetra-*tert*-butyl-25,27-bis(diphenylphosphinooxy)-26,28-bis{(1*R*,2*S*,5*R*)-menthyloxycarbonylmethoxy}calix[4]arene **L**[8],[27] 25,27-dihydroxy-26,28-(3,6,9-trioxaundecane-1,11-dioxy)calix[4]arene,[46] $Ph_2P(O)CH_2OTs$,[47] $[RhCl(nbd)]_2$[48] $[Pd(\eta^3\text{-}C_3H_4Me)Cl]_2$,[49] and $[RuCl_2(p\text{-}MeC_6H_4Pr^i)]_2$[50] were prepared by using literature procedures.

Preparations

5,11,17,23-Tetra-*tert*-butyl-25,27-dihydroxy-26,28-bis(3-oxabutyloxy)calix[4]arene L[1a]. 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. Over this period during which the formation of intermediate **L**^{5a} could be detected (see below) three portions of $BrCH_2CH_2OMe$ (1.50 mmol for each) and K_2CO_3 (1.50 mmol) were added after 24, 36 and 60 h. The reaction was followed by TLC (R_f of starting compound = 1; R_f (**L**^{5a}) = 0.5; R_f (**L**^{1a}) = 0; 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 washed first with saturated NH_4Cl–water (2 × 100 cm^3), then 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%), mp 222–223 °C. IR: (KBr) *ν*(OH) 3360–3314br; (toluene) *ν*(OH) 3394s and 3295s cm^{-1}. ^{1}H NMR ($CDCl_3$): *δ* 7.40 (s, 2H, OH), 7.15 and 7.06 (2s, 8H, *m*-H), 4.39 and 3.32 (AB spin system, 8H, ArCH_2Ar, ^2J = 12.9 Hz), 4.17 and 3.89 (2m, 8H, OCH_2CH_2O), 3.56 (s, 6H, OCH_3), 1.30 (s, 18H, C(CH_3)) and 0.99 (s, 18H, C(CH_3)). ^{13}C-{^{1}H} NMR ($CDCl_3$): *δ* 150.28–116.50 (arom. 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(*C*H_3)), 31.35 (s, Ar*C*H_2Ar) and 30.91 (s, C(*C*H_3)). MS(EI): *m*/*z* (%) 764.4(100) [M^+]. Found: C, 78.22; H, 8.85. Calc. for $C_{50}H_{68}O_6$: C, 78.49; H, 8.96%.

5,11,17,23-Tetra-*tert*-butyl-25,27-bis(ethoxycarbonylmethoxy)-26,28-bis(3-oxabutyloxy)calix[4]arene L^{1b}. A suspension of **L**^{1a} (5.000 g, 6.50 mmol) in DMF (200 cm^3) was stirred at room temperature for 2 h with NaH (0.784 g, 32.70 mmol; freed from mineral oil by washings with THF and pentane). Ethyl bromoacetate (5.458 g, 32.7 mmol) was then added and the mixture stirred overnight at 60 °C. The solvent was removed under reduced pressure, and the residue taken up with CH_2Cl_2 (200 cm^3). After washing with saturated NH_4Cl–water (3 × 200 cm^3), then with brine (200 cm^3), the organic layer was dried over $MgSO_4$. After filtration, the solvent was removed *in vacuo* and the product precipitated with MeOH to yield **L**^{1b} as a white solid. Yield: 5.200 g, 85%. mp 132–133 °C. IR(KBr, cm^{-1}): *ν*(C=O) 1760s and 1725s. ^{1}H NMR ($CDCl_3$): *δ* 6.87 and 6.72 (2s, 8H, *m*-H), 4.83 (s, 4H, OC$H_2$$CO_2$Et), 4.71 and 3.18 (AB spin system, 8H, ArCH_2Ar, ^2J = 12.8), 4.25 (q, 4H, OC$H_2$$CH_3$, ^3J = 7), 4.11 and 3.87 (2t, 8H, OCH_2CH_2O, ^3J = 5.1), 3.45 (s, 6H, OCH_3), 1.31 (t, 6H, OCH_2CH_3, ^3J = 7 Hz), 1.14 (s, 18H, C(CH_3)) and 1.04 (s, 18H, C(CH_3)). ^{13}C-{^{1}H} NMR ($CDCl_3$): *δ* 170.70 (C=O), 153.10–124.84 (arom. C), 73.17 (s, OCH_2), 71.91 (s, OCH_2), 70.89 (s br, O*C*H_2CO), 60.19 (s, O*C*$H_2$$CH_3$), 58.54 (s, OCH_3), 33.77 and 33.66 (2s, *C*(CH_3)), 31.34 and 31.27 (2s, C(*C*H_3)), 30.94 (s, Ar*C*H_2Ar) and 14.1 (s, OCH_2CH_3). MS(EI): *m*/*z* (%) 936.4(100) [M^+]. Found: C, 74.15; H, 8.87. Calc. for $C_{58}H_{80}O_{10}$: C, 74.33; H, 8.60%.

5,11,17,23-Tetra-*tert*-butyl-25,27-bis(2-hydroxyethoxy)-26,28-bis(3-oxabutyloxy)calix[4]arene L^{1c}. To a solution of **L**^{1b} (3.000 g, 3.2 mmol) in diethyl ether (150 cm^3) was added $LiAlH_4$ (0.970 g, 25.5 mmol) in small portions at −10 °C and the mixture stirred overnight at room temperature. HCl (2 M) was added carefully until a precipitate had formed and the diethyl ether layer was separated. The precipitate was treated with another portion of diethyl ether (150 cm^3) and the two fractions were dried over $MgSO_4$. After filtration, the solvent was removed under reduced pressure. The residue was taken up with CH_2Cl_2 and addition of MeOH gave a white product. Yield: 2.300 g, 84%. mp 238–239 °C. IR (KBr, cm^{-1}): *ν*(OH) 3447br. ^{1}H NMR ($CDCl_3$): *δ* 7.16 and 6.52 (2s, 8H, *m*-H), 4.92 (t, 2H, CH_2O*H*, exchanges with D_2O, ^2J = 4), 4.45 and 3.18 (AB spin system, 8H, ArCH_2Ar, ^2J = 12.8), 4.18–4.16 and 4.15–4.14 (2m, 8H, OCH_2CH_2OH), 3.95 and 3.75 (2t, 8H, OCH_2C$H_2$$OCH_3$, ^3J = 4.0 Hz), 3.42 (s, 6H, OCH_3), 1.36 (s, 18H, C(CH_3)) and 0.83 (s, 18H, C(CH_3)). ^{13}C-{^{1}H} NMR ($CDCl_3$): *δ* 153.84–124.76 (arom. C), 76.77 (s, OCH_2), 74.78 (s, OCH_2), 71.00 (s, OCH_2), 61.66 (s, OCH_2), 58.54 (s, OCH_3), 34.03 and 33.55 (2s, *C*(CH_3)), 31.64 and 30.97 (2s, C(*C*H_3)) and 30.46 (s, Ar*C*H_2Ar). MS(CI): *m*/*z* (%) 852.5 (100) [M^+]. Found: C, 76.22; H, 8.95. Calc. for $C_{54}H_{76}O_8$: C, 76.02; H, 8.98%.

5,11,17,23-Tetra-*tert*-butyl-25,27-bis[2-{[(4-methylphenyl)-sulfonyl]oxy}ethoxy]-26,28-bis(3-oxabutyloxy)calix[4]arene L^{1d}. To a solution of **L**^{1c} (2.500 g, 2.90 mmol) in pyridine (10 cm^3) was added *p*-toluenesulfonyl chloride (1.106 g, 5.80 mmol) at 0 °C. The mixture was stored at 0 °C for 4 days. The mixture was then poured into an ice-cold 2 M HCl solution (100 cm^3) and the precipitate formed filtered off. The product was taken up with CH_2Cl_2 and washed with HCl (2 × 100 cm^3), then with brine (2 × 100 cm^3). After drying over $MgSO_4$ the solution was concentrated under reduced pressure and addition of hexane gave a white, microcrystalline product. Yield: 3.102 g, 92%. mp 78–79 °C. ^{1}H NMR ($CDCl_3$): *δ* 7.80 and 7.34 (AB spin system, 8H, $OC_6H_4CH_3$, *J*(AB) = 8.2), 7.04 and 6.47 (2s, 8H, *m*-H), 4.66 (t, 4H, OCH_2, ^2J = 6.1), 4.31 and 3.07 (AB spin system, 8H, ArCH_2Ar, ^2J = 12.8), 4.27 (t, 4H, OCH_2, ^3J = 5.2), 3.86 and 3.63 (2t, 8H, OCH_2C$H_2$$OCH_3$, ^3J = 4.0 Hz), 3.37 (s, 6H, OCH_3), 2.47 (s, 6H, $C_6H_4CH_3$), 1.31 (s, 18H, C(CH_3)) and 0.83 (s, 18H, C(CH_3)). ^{13}C-{^{1}H} NMR ($CDCl_3$): *δ* 153.50–124.54 (arom. C), 73.90, 71.40, 70.63 and 69.38 (4s, OCH_2), 58.50 (s, OCH_3), 33.95 and 33.47 (2s, *C*(CH_3)), 31.56 and 31.01 (2s, C(*C*H_3)), 30.79 (s, Ar*C*H_2Ar) and 21.60 (s, $C_6H_4CH_3$). FAB mass spectrum: *m*/*z* (%) 1160.4(5) [M^+]. Found: C, 70.26; H, 7.45. Calc. for $C_{68}H_{88}O_{12}$: C, 70.31; H, 7.64%.

5,11,17,23-Tetra-*tert*-butyl-25,27-bis[2-(diphenylphosphino)-ethoxy]-26,28-bis(3-oxabutyloxy)calix[4]arene L^{1}. To a solution of Ph_2PH (0.337 g, 1.8 mmol) in THF (10 cm^3) was added *n*-BuLi (1.2 cm^3, 1.8 mmol, 1.5 M solution in hexane). The Ph_2PLi solution was then added to a solution of **L**^{1d} (1.000 g, 0.86 mmol) in dry THF (100 cm^3). The mixture was refluxed for 6 h. After cooling to room temperature the solvent was removed *in vacuo*. The residue was taken up with CH_2Cl_2 and addition of EtOH gave a white pure product. Yield: 0.720 g, 70%. mp 172–173 °C. ^{1}H NMR ($CDCl_3$): *δ* 7.49–7.42 and 7.35–7.33 (2 broad m, 20H, PPh_2), 6.91 and 6.64 (2s, 8H, *m*-H), 4.36 and 3.07 (AB spin system, 8H, ArCH_2Ar, ^2J = 12.8), 4.13 (t, 4H, OCH_2, ^3J = 6.1), 4.05–3.87 (two overlapping t, 8H, OCH_2), 3.28 (s, 6H, OCH_3), 2.80 (t, 4H, PCH_2, ^3J = 8.2 Hz), 1.18 (s, 18H, C(CH_3)) and 0.97 (s, 18H, C(CH_3)). ^{13}C-{^{1}H} NMR ($CDCl_3$): *δ* 153.50–124.65 (arom. C), 72.50, 71.88, 71.58 and 71.33 (4 peaks, OCH_2), 58.65 (s, OCH_3), 33.84 and 33.62 (2s, *C*(CH_3)), 31.45 and 31.19 (2s, C(*C*H_3)), 30.90 (s, Ar*C*H_2Ar), 28.46 (d, PCH_2, *J*(PC) = 13 Hz). ^{31}P-{^{1}H} NMR ($CDCl_3$) *δ* −23.4 (s, PPh_2). Found: C, 78.59; H, 7.95. Calc. for $C_{78}H_{94}O_6P_2$: C, 78.76; H, 7.97%.

5,11,17,23-Tetra-*tert*-butyl-25,26,27-trihydroxy-28-(3-oxabutyloxy)calix[4]arene L^{5a}. A suspension of *p*-*tert*-butylcalix[4]arene (10.000 g, 15.41 mmol) in acetonitrile (200 cm^3) was stirred at room temperature for 2 h with K_2CO_3 (1.280 g, 9.24 mmol). 2-Bromoethyl methyl ether (2.140 g, 15.41 mmol) was then added and the mixture refluxed for 5 days. During this period several portions of $BrCH_2CH_2OCH_3$ (1.0 mmol for each addition) and K_2CO_3 (0.5 mmol) were added after 1, 2, 3, and 4 d reaction time. The reaction was followed by TLC [R_f = 1 (starting compound); 0.49 (**L**^{5a}); 0 (**L**^{1a}); SiO_2, CH_2Cl_2] and stopped when all the starting compound had been consumed. The solvent was removed under reduced pressure, and the residue taken up with CH_2Cl_2 (200 cm^3). After washing with saturated NH_4Cl–water (3 × 200 cm^3), then with brine (200 cm^3), the organic layer was dried over $MgSO_4$. After filtration, the solvent was removed *in vacuo* and the product purified by column chromatography (SiO_2, CH_2Cl_2) to yield **L**^{5a} as a white solid (7.500 g, 69%); mp 260–261 °C. IR (toluene, cm^{-1}): *ν*(OH) 3430 and 3290. ^{1}H NMR ($CDCl_3$): *δ* 10.31 (s, 1H, OH), 9.42 (s,

2H, OH), 7.19–7.00 (8H, *m*-H), 4.47 and 3.44 (AB spin system, 4H, ArCH_2Ar, ^2J = 13.1), 4.34 (m, 2H, OCH_2), 4.30 and 3.41 (AB spin system, 4H, ArCH_2Ar, ^2J = 13.1 Hz), 4.00 (m, 2H, OCH_2), 3.59 (s, 3H, OCH_3), 1.24 (s, 9H, C(CH_3)) and 1.21 (s, 27H, C(CH_3)). ^{13}C-{^{1}H} NMR ($CDCl_3$): δ 148.03–125.65 (arom. C), 74.93 (s, OCH_2), 71.30 (s, OCH_2), 59.13 (s, OCH_3), 34.22, 33.96 and 33.04 (3s, *C*(CH_3)), 32.05 and 31.51 (2s, Ar-*C*H_2Ar), 31.50 (br signal, C(*C*H_3)) and 31.27 (s, C(*C*H_3)). Found: C, 79.53; H, 9.07. Calc. for $C_{47}H_{62}O_5$: C, 79.85; H, 8.84%.

(*R*)-5,11,17,23-Tetra-*tert*-butyl-25,27-dihydroxy-26-(3-oxabutyloxy)-28-[(1-phenylethyl)carbamoylmethoxy]calix[4]arene L^{5b}. A suspension of L^{5a} (6.500 g, 9.2 mmol) in acetonitrile (150 cm^3) was stirred at room temperature for 2 h with K_2CO_3 (0.762 g, 5.5 mmol). (*R*)-(+)-2-Bromo-*N*-(1-phenylethyl)acetamide (2.200 g, 9.2 mmol) was then added and the mixture refluxed for 2 d. The solvent was removed under reduced pressure, and the residue taken up with CH_2Cl_2 (200 cm^3). After washing with saturated NH_4Cl–water (3 × 200 cm^3), then with brine (200 cm^3), the organic layer was dried over $MgSO_4$. After filtration, the solvent was removed *in vacuo* and the product purified by column chromatography (R_f = 0.3, SiO_2, CH_2Cl_2–MeOH 95 : 5 v/v). Yield: 6.500 g, 88%. mp 118–120 °C. IR (KBr, cm^{-1}): ν(C=O) 1684s and 1653s; (toluene) ν(OH) 3422s and 3298, ν(C=O) 1697s and 1669s. ^{1}H NMR ($CDCl_3$): δ 9.11 (d, 1H, NH, ^3J = 7.7), 7.53–6.79 (m, 13H, arom. H), 5.32 (dq, AMX_3 spin system, 1H, NHC*H*MePh, ^3J(AM) ≈ ^3J(AX) = 7.0), 4.52 (s, 2H, $OCH_2C(O)$), 4.41, 4.34, 4.24, 4.15 (4d, 4H, axial ArC*H*Ar), 4.11 (m, 2H, OCH_2), 3.54 (m, 2H, OCH_2), 3.37 (d, 3H, equat. ArC*H*Ar, ^2J(HH) = 13), 3.32 (d, 1H, equat. ArC*H*Ar, ^2J(HH) = 13), 3.25 (s, 3H, OCH_3), 1.70 (d, 1H, NHC*H*MePh, ^3J = 7.0 Hz), 1.34 (s, 18H, C(CH_3)), 0.96 and 0.94 (2s, 18H, C(CH_3)), OH signals not identified. ^{13}C-{^{1}H} NMR ($CDCl_3$): δ 167.93 (C=O), 150.28–125.22 (arom. C), 75.55 (s, OCH_2), 74.29 (s, OCH_2), 70.86 (s, O*C*H_2CO), 58.87 (s, OCH_3), 48.87 (s, CONH-*C*HCH$_3$Ph), 33.96 (*C*(CH_3)), 31.78 and 31.01 (2s, C(*C*H_3)), 31.40 and 31.25 (2s, Ar*C*H_2Ar) and 22.85 (s, CONHCH-*C*H$_3$Ph). Found: C, 78.71; H, 8.42; N, 1.59. Calc. for $C_{57}H_{73}NO_6$: C, 78.86; H, 8.48; N, 1.61%.

(*R*)-5,11,17,23-Tetra-*tert*-butyl-25,27-bis[(diphenylphosphinoyl)methoxy]-26-(3-oxabutyloxy)-28-[(1-phenylethyl)carbamoylmethoxy]calix[4]arene L^{5c}. A solution of L^{5b} (6.000 g, 6.9 mmol) in toluene (150 cm^3) was heated at 40 °C for 1 h in the presence of NaH (0.415 g, 17.30 mmol). $Ph_2P(O)CH_2OTs$ (5.601 g, 14.50 mmol) was then added and the mixture stirred for 3 d at 80 °C. The solvent was removed under reduced pressure, and the residue taken up with CH_2Cl_2 (200 cm^3). After washing with saturated NH_4Cl–water (3 × 200 cm^3), then with brine (200 cm^3), the organic layer was dried over $MgSO_4$. After filtration, the solvent was removed *in vacuo* and addition of MeOH afforded the product as a white solid. Yield: 8.5 g, 90%. mp 162–164 °C. IR (KBr, cm^{-1}): ν(C=O) 1684s. ^{1}H NMR ($CDCl_3$): δ 9.38 (d, 1H, NH, ^3J = 8.2), 7.87–7.21 (25H, arom. H), 6.78 (s, 2H, *m*-H), 6.67 and 6.66 (AB spin system, 2H, *m*-H, ^4J(AB) = 1), 6.52 and 6.41 (AB spin system, 2H, *m*-H, ^4J(AB) = 2), 6.47 (s, 2H, *m*-H), 5.19 (dq, AMX_3 spin system, 4H, NHC*H*MePh, ^3J(AM) ≈ ^3J(AX) = 7.0), 5.07 (s, 2H, PCH_2), 4.98 (s, 2H, PCH_2), 4.83 and 4.61 (AB spin system, 2H, $OCH_2C(O)$, ^2J(AB) = 13.7), 4.66 and 3.04 (AB spin system, 2H, ArCH_2, ^2J(AB) = 13.1), 4.55 and 2.79 (AB spin system, 2H, ArCH_2, ^2J(AB) = 13.1), 4.45 and 2.98 (AB spin system, 2H, ArCH_2, ^2J(AB) = 12.8), 4.43 and 2.98 (AB spin system, 2H, ArCH_2, ^2J(AB) = 12.8), 3.73 (m, 2H, OCH_2), 3.40 (m, 2H, OCH_2), 2.96 (s, 3H, OCH_3), 1.56 (d, 1H, NHCH*Me*Ph, ^2J = 7.0 Hz), 1.13 (s, 9H, C(CH_3)$_3$), 1.08 (s, 9H, C(CH_3)$_3$) and 0.95 (s, 18H, C(CH_3)). ^{13}C-{^{1}H} NMR ($CDCl_3$): δ 168.91 (C=O), 153.65–124.99 (arom. C), 72.96 (s, OCH_2), 72.47 (s, OCH_2), 71.92 (s, OCH_2), 71.53 (s, OCH_2), 71.26 (s, O*C*H_2CO), 57.91 (s, OCH_3), 48.37 (NH*C*H), 33.75, 33.67 and 33.60 (3s, *C*(CH_3)), 32.17 and 31.91 (s, Ar*C*H_2Ar), 31.40 and 31.20 (2s, C(*C*H_3)) and 21.72 (NHCH*C*H_3Ph). ^{31}P NMR ($CDCl_3$): δ 26.8 and 24.4 (2s, PPh_2). Found: C, 76.95; H, 7.18; N, 1.04. Calc. for $C_{83}H_{95}NO_8P_2$: C, 76.89; H, 7.39; N, 1.08%.

(*R*)-5,11,17,23-Tetra-*tert*-butyl-25,27-bis[diphenylphosphinomethoxy]-26-(3-oxabutyloxy)-28-[(1-phenylethyl)carbamoylmethoxy]calix[4]arene L^5. A suspension of L^{5c} (3.5 g, 2.9 mmol) in toluene (150 cm^3) was stirred for 10 days at 80 °C in the presence of $PhSiH_3$ (2 cm^3, 30 mmol). The solvent was removed under reduced pressure, and the residue taken up with CH_2Cl_2 (10 cm^3). Addition of EtOH afforded the product as a white solid. Yield: 2.5 g, 69%. mp 90–95 °C. IR (KBr, cm^{-1}): ν(C=O) 1663s. ^{1}H NMR ($CDCl_3$): δ 7.83–7.17 (arom. H + NH), 6.69–6.49 (8H, *m*-H), 5.23 (dq, AMX_3 spin system, 1H, NHC*H*MePh, ^3J(AM) ≈ ^3J(AX) = 7.5), 5.15 (s, 2H, PCH_2), 5.08 (s, 2H, PCH_2), 5.09, 4.45, 4.41, 4.40 (4d, 4H, axial ArC*H*Ar), 4.63 and 4.51 (AB spin system, $OCH_2C(O)$, ^2J(AB) = 15), 3.93 (m, 2H, OCH_2, ^3J(HH) = 5.5), 3.70 (m, 2H, OCH_2, ^3J(HH) = 5.5 Hz), 3.14 (s, 3H, OCH_3), 3.06, 3.02, 2.97 and 2.92 (4d, 4H, equat. ArC*H*Ar, av. $J(H_{ax}H_{eq})$ = 12.8), 1.48 (d, 1H, NHC*H*MePh, ^2J = 7.5 Hz), 1.09, 1.07, 1.05 and 1.00 (4s, 36H, C(CH_3)). ^{13}C-{^{1}H} NMR ($CDCl_3$): δ 168.98 (C=O), 152.98–124.17 (arom. C), 75.40 (d, PCH_2, J(PC) = 8 Hz), 73.85 (s, OCH_2), 72.41 (s, OCH_2), 71.30 (s, O*C*H_2CO), 57.79 (s, OCH_3), 47.69 (NHCH), 33.11 and 33.01 (2s, *C*(CH_3)), 31.63 and 31.34 (2s, Ar*C*H_2Ar), 30.75 and 30.65 (2s, C(*C*H_3)) and 20.52 (s, NHCH*C*H_3Ph). ^{31}P NMR ($CDCl_3$): δ −21.4 (s, PPh_2). Found: C, 75.03; H, 6.59; N, 0.86. Calc. for $C_{83}H_{95}NO_6P_2$·CH_2Cl_2: C, 74.76; H, 7.24; N, 1.04%.

5,11,17,23-Tetra-*tert*-butyl-25,27-bis(diphenylphosphinoylmethoxy)-26,28-bis{(1*R*,2*S*,5*R*)-menthyloxycarbonylmethoxy}-calix[4]arene L^{6b}. A solution of L^{6a} (7.842 g, 7.53 mmol) in dry THF–DMF (9 : 1, v/v) (250 cm^3) was refluxed with Bu^{t}ONa (1.664 g, 17.30 mmol) for 1 h. Then $Ph_2P(O)CH_2OTs$ (6.400 g, 16.56 mmol) was added and the mixture refluxed for 3 d. After cooling and filtration, the solvents were removed under reduced pressure. The residue was taken up in CH_2Cl_2 (200 cm^3) and washed with a saturated NH_4Cl–water solution (150 cm^3) and then with water (100 cm^3). The organic layer was dried over $MgSO_4$, filtered and concentrated to *ca.* 15 cm^3. Addition of acetone with stirring and cooling gave a white precipitate (R_f = 0.44 CH_2Cl_2–MeOH 94 : 6, v/v). Yield: 6.120 g, 55%. mp 264–270 °C. IR (KBr, cm^{-1}): ν(C=O) 1749s, ν(P=O) 1205s. ^{1}H NMR ($CDCl_3$): δ 7.88–7.65 and 7.46–7.24 (m, 20H, $P(O)Ph_2$), 6.59–6.50 (m, 8H, *m*-H), 5.55 (m, 4H, $OCH_2P(O)Ph_2$), 4.79–4.45 (m, 10H, OCH of Ment, O*C*H_2CO$_2$Ment and ArCH_2Ar), 3.01–2.87 (m, 4H, ArCH_2Ar), 1.96–0.63 (36H, Ment), 1.07 (s, 18H, Bu^t) and 0.95 (s, 18H, Bu^t). ^{13}C-{^{1}H} NMR ($CDCl_3$): δ 170.16 (s, C=O), 152.83–124.62 (arom. C), 74.17 (s, OCH of OMent), 71.19 (s, O*C*H_2CO$_2$Ment), 70.68 (d, O*C*H_2P(O)Ph$_2$, J(PC) = 74.8 Hz), 46.70, 27.96 and 25.91 (3s, CH of Ment), 40.70, 34.17 and 23.29 (3s, CH_2 of Ment), 33.68 and 33.57 (2s, *C*(CH_3)$_3$), 32.33 and 31.94 (2s, ArCH_2Ar), 31.35 and 31.16 (2s, C(*C*H_3)$_3$), 22.00, 20.70 and 16.16 (3s, CH_3 of Ment). ^{31}P-{^{1}H} NMR ($CDCl_3$): δ 24.89 (s, P(O)Ph$_2$). Found: C, 76.80; H, 8.42. Calc. for $C_{94}H_{118}O_{10}P_2$: C, 76.81; H, 8.09%.

5,11,17,23-Tetra-*tert*-butyl-25,27-bis(diphenylphosphinomethoxy)-26,28-bis{(1*R*,2*S*,5*R*)-menthyloxycarbonylmethoxy}-calix[4]arene L^6. A mixture of the bis(phosphine oxide) L^{6b} (4.500 g, 3.06 mmol) and phenylsilane (6.665 g, *ca.* 7.6 cm^3, 61.6 mmol) in toluene (40 cm^3) was refluxed for 2 days. After cooling, the solution was filtered and the solvent removed *in vacuo*. The residue was dissolved in CH_2Cl_2 (*ca.* 5 cm^3). Addition of EtOH (40 cm^3) with stirring and cooling afforded the product as a white precipitate. Yield: 3.95 g, 90%. mp 164–169 °C. IR (KBr, cm^{-1}): ν(C=O) 1753s. ^{1}H NMR ($CDCl_3$): δ 7.52–7.40 and 7.36–7.28 (m, 20H, PPh_2), 6.88 and 6.85 (AB spin system, 4H,

m-H, $^4J = 2.4$), 6.53 and 6.50 (AB spin system, 4H, *m*-H, $^4J = 2.4$), 5.15 and 4.94 (ABX spin system, 4H, $OCH_AH_BPPh_2$, $J(AX) \approx J(BX) = 3.1$ Hz), 4.84–4.44 (m, 10H, OCH of Ment, OCH_2CO_2Ment and $ArCH_2Ar$), 3.10–2.98 (m, 4H, $ArCH_2Ar$), 2.06–0.66 (36H, Ment), 1.17 (s, 18H, Bu^t) and 0.94 (s, 18H, Bu^t). ^{13}C-{^1H} NMR ($CDCl_3$): δ 170.02 (s, C=O), 153.51–124.653 (arom. C), 76.79 (d, OCH_2PPh_2, $J(PC) = 6.5$ Hz), 74.14 (s, OCH of CO_2Ment), 70.75 (s, OCH_2CO_2Ment), 46.93, 28.10 and 25.89 (3s, CH of CO_2Ment), 40.97, 34.32 and 23.26 (3s, CH_2 of Ment), 33.83 and 33.68 (2s, $C(CH_3)_3$), 32.32 (br s, $ArCH_2Ar$), 31.49 and 31.26 (2s, $C(CH_3)_3$), 22.10, 20.98 and 16.21 (3s, CH_3 of Ment). ^{31}P-{^1H} NMR ($CDCl_3$): δ −21.40 (s, PPh_2). Found: C, 78.36; H, 8.46. Calc. for $C_{94}H_{118}O_8P_2$: C, 78.52; H, 8.27%.

5,11,17,23-Tetra-*tert*-butyl-25,27-bis(diphenylphosphinooxy)-26,28-bis(3-oxabutyloxy)calix[4]arene L[7]. A solution of *n*-BuLi (1.51 M in hexane, 3.5 cm^3, 5.2 mmol) was slowly added to a stirred solution of **L**[1a] (2.000 g, 2.614 mmol) in THF (100 cm^3) at −78 °C. After stirring for 30 min, a precooled solution (*ca.* −40 °C) of Ph_2PCl (1.147 g, 5.228 mmol) in THF (30 cm^3) was added dropwise. The mixture was maintained at −78 °C for 1 h, then warmed to room temperature. The solvent was removed *in vacuo* and the residue taken up with toluene (50 cm^3); the resulting suspension was filtered through Celite to remove LiCl. The filtrate and the toluene washings were combined before concentration to *ca.* 10 cm^3. Addition of pentane afforded a white product which was recrystallised from dichloromethane–pentane. Yield: 2.200 g, 75%. mp 220–225 °C. ^1H NMR ($CDCl_3$): δ 7.71–7.66 and 7.45–7.42 (2 sets of signals, 20H, PPh_2), 7.00 (s, 4H, *m*-H), 6.32 (s, 4H, *m*-H), 4.15 (t, 4H, OCH_2, $^3J = 5$), 4.14 and 2.78 (AB spin system, 8H, $ArCH_2Ar$, $^2J(AB) = 13.0$), 3.67 (t, 4H, OCH_2, $^3J = 5$ Hz), 3.11 (s, 6H, OCH_3), 1.31 (s, 18H, $C(CH_3)$) and 0.81 (s, 18H, $C(CH_3)$). ^{13}C-{^1H} NMR ($CDCl_3$): δ 153.50–124.67 (arom. C), 71.56 and 70.94 (s, OCH_2), 58.61 (s, OCH_3), 34.06 and 33.63 (2s, $C(CH_3)$), 31.75 and 31.16 (2s, $C(CH_3)$), $ArCH_2$ signals are probably overlapping with $C(CH_3)$ signals. ^{31}P-{^1H} NMR ($CDCl_3$): δ 122.6 (s, PPh_2). Found: C, 77.40; H, 7.56. Calc. for $C_{74}H_{86}O_6P_2 \cdot 0.25CH_2Cl_2$: C, 77.24; H, 7.55%.

25,27-Bis(diethoxyphosphinooxy)-26,28-(3,6,9-trioxaundecane-1,11-dioxy)calix[4]arene L[9]. A solution of *n*-BuLi (1.60 M in hexane, 1.1 cm^3, 1.76 mmol) was slowly added to a solution of 25,27-dihydroxy-26,28-(3,6,9-trioxaundecane-1,11-dioxy)-calix[4]arene (0.500 g, 0.86 mmol) in THF (100 cm^3) at −78 °C. After 0.5 h neat $(EtO)_2PCl$ (0.26 cm^3, 1.80 mmol) was added dropwise within 1 h to the orange solution maintained at −78 °C. After stirring for 0.5 h at room temperature the solvent was evaporated to dryness and the residue dissolved in pentane. After storage at −20 °C for 1 h the suspension formed was filtered through a glass frit. The solution was evaporated to dryness yielding **L**[9] as a colourless powder. Yield: 0.551 g, 78%. mp 220–221 °C. ^1H NMR ($CDCl_3$): δ 7.16 and 6.98 (AB_2 spin system, $^3J = 8$, t(2H) + d(4H), *m*- and *p*-H of calix), 6.23 and 6.06 (AB_2 spin system, $^3J = 8$, t(2H) + d(4H), *m*- and *p*-H of calix), 4.47 and 3.21 (AB quartet, $^2J = 14$, 4H each, $ArCH_2Ar$), 4.30–4.00 (m, 16H, CH_2 of crown-5 + $POCH_2CH_3$), 3.77 (s, 8H, $ArOCH_2CH_2OCH_2CH_2$) and 1.31 (t, 12H, $POCH_2CH_3$). ^{13}C-{^1H} NMR ($CDCl_3$): δ 154.68 (quat. aryl C-O), 147.10 (d, $^2J(PC) = 6$ Hz, quat. aryl C-O), 135.13 and 133.16 (2s, quat. aryl C), 129.88, 128.28, 124.97 and 124.06 (4s, aryl CH), 74.10, 72.36 and 71.43 (3s, CH_2 of crown-5), 61.42 (s, $POCH_2CH_3$), 31.89 (s, $ArCH_2$) and 16.43 (s, $POCH_2CH_3$). ^{31}P-{^1H} NMR ($CDCl_3$): δ 140.0 (s). Found: C, 64.33; H, 6.62. Calc. for $C_{44}H_{56}O_{11}P_2$: C, 64.22; H, 6.86%.

(Norbornadiene){*cis*-*P*,*P*′-[5,11,17,23-tetra-*tert*-butyl-25,27-bis(2-diphenylphosphinoethoxy)-26,28-bis(3-oxabutyloxy)calix-[4]arene]}rhodium(I) tetrafluoroborate 2. A solution of $AgBF_4$ (0.025 g, 0.126 mmol) in THF (1 cm^3) was added to a solution of $[RhCl(nbd)]_2$ (0.029 g, 0.064 mmol) in CH_2Cl_2 (3 cm^3). Stirring was stopped after 5 min and the solution decanted to eliminate AgCl. The supernatant was filtered through Celite and added to a solution of **L**[1] (0.150 g, 0.126 mmol) in CH_2Cl_2 (30 cm^3). After stirring for 12 h the solution was concentrated to *ca.* 5 cm^3. Addition of pentane afforded an orange precipitate. Yield: 0.136 g, 74%. mp 196–198 °C (slow decomp.). ^1H NMR ($CDCl_3$): δ 7.67–7.52 (20H, PPh_2), 7.10 and 6.40 (2s, 8H, *m*-H), 4.41 (s br, 4H, HC=CH of nbd), 4.26 and 3.12 (AB spin system, 8H, $ArCH_2Ar$, $^2J = 12.8$ Hz), 4.00 (m, 8H, OCH_2), 3.96 (s br, 2H, CH of nbd), 3.75 (m, 4H, OCH_2), 3.56 (m, 4H, OCH_2), 3.48 (s, 6H, OCH_3), 1.54 (s br, 2H, CH_2 of nbd), 1.32 (s, 18H, $C(CH_3)$) and 0.79 (s, 18H, $C(CH_3)$). ^{13}C-{^1H} NMR ($CDCl_3$): δ 153.00–124.81 (arom. C), 72.98, 71.39 and 68.10 (3 peaks, OCH_2), 58.12 (s, OCH_3), 34.09 and 33.72 (2s, $C(CH_3)$), 31.64 and 31.22 (2s, $C(CH_3)$), 31.08 (s, $ArCH_2Ar$) and 29.5 (PCH_2, tentative assignment). ^{31}P-{^1H} NMR ($CDCl_3$) δ 16.33 (d, PPh_2, $J(PRh) = 153$ Hz). FAB mass spectrum: *m*/*z* (%): 1383.6 (56) [$(M - BF_4)^+$, expected isotopic profile]. Found: C, 64.30; H, 6.67. Calc. for $C_{85}H_{102}BF_4O_6P_2Rh \cdot 0.75CH_2Cl_2$: C, 64.32; H, 6.56%.

(Norbornadiene){*cis*-*P*,*P*′-[5,11,17,23-tetra-*tert*-butyl-25,27-bis(diphenylphosphinomethoxy)-26,28-bis(3-oxabutyloxy)calix-[4]arene]}rhodium(I) tetrafluoroborate 3. A solution of $AgBF_4$ (0.033 g, 0.172 mmol) in THF (1 cm^3) was added to a solution of $[Rh(Cl)(nbd)]_2$ (0.039 g, 0.086 mmol) in CH_2Cl_2 (3 cm^3). Stirring was stopped after 5 min and the solution decanted to eliminate AgCl. The supernatant was filtered through Celite and added to a solution of **L**[2] (0.150 g, 0.129 mmol) in CH_2Cl_2 (30 cm^3). After 12 h the solution was concentrated to *ca.* 5 cm^3 and addition of pentane afforded a white precipitate. Yield: 0.195 g, 79%. mp 198–199 °C (decomp.). ^1H NMR ($CDCl_3$): δ 8.01–7.60 (20H, PPh_2), 6.96 and 6.48 (2s, 4H, *m*-H), 5.60 (s br, 4H, OCH_2P), 4.18 (s br, 4H, HC=CH of nbd), 4.07 and 2.88 (AB spin system, 4H, $ArCH_2CH_2$, $^2J = 13.4$ Hz), 3.94 (s br, 2H, CH of nbd), 3.42 (s br, 4H, OCH_2), 3.40 (s, 6H, OCH_3), 3.22 (s br, 4H, OCH_2), 1.55 (s, 2H, CH_2 of nbd), 1.28 (s, 18H, $C(CH_3)$) and 0.79 (s, 18H, $C(CH_3)$). ^{13}C-{^1H} NMR ($CDCl_3$): δ 154.12–124.72 (arom. C), 82.05 (s, HC=CH of nbd), 73.75 (s, OCH_2), 71.73 (OCH_2P, tent. assign.), 69.60 (s, OCH_2), 69.50 (CH_2 of nbd), 58.76 (s, OCH_3), 52.29 (s, CH of nbd), 33.84 and 33.62 (2s, $C(CH_3)$), 31.49 and 30.97 (2s, $C(CH_3)$) and 29.54 (s, $ArCH_2$). ^{31}P-{^1H} NMR ($CDCl_3$): δ 23.7 (d, PPh_2, $J(PRh) = 152$ Hz). FAB mass spectrum: *m*/*z* (%) 1355.7 (30) [$(M - BF_4)^+$, expected isotopic profile]. Found: C, 66.28; H, 6.68. Calc. for $C_{83}H_{98}BF_4O_6P_2Rh \cdot CH_2Cl_2$: C, 66.02; H, 6.60%.

(η^3-2-Methylallyl)-{*P*,*P*′-[5,11,17,23-tetra-*tert*-butyl-25,27-bis(2-diphenylphosphinoethoxy)-26,28-bis(3-oxabutyloxy)-calix[4]arene]}palladium(II) tetrafluoroborate 4. A solution of $AgBF_4$ (0.025 g, 0.128 mmol) in THF (1 cm^3) was added to a solution of $[Pd(\eta^3\text{-}C_3H_4Me)Cl]_2$ (0.029 g, 0.063 mmol) in CH_2Cl_2 (3 cm^3). Stirring was stopped after 5 min and the solution decanted to eliminate AgCl. The supernatant was filtered through Celite and added to a solution of **L**[1] (0.150 g, 0.126 mmol) in CH_2Cl_2 (30 cm^3). After 12 h the solution was concentrated to *ca.* 5 cm^3 and addition of pentane afforded a white precipitate. Yield: 0.123 g, 70%. mp 182–184 °C (slow decomp.). ^1H NMR ($CDCl_3$): δ 7.63–7.51 (20H, PPh_2), 7.11 and 6.41 (2s, 8H, *m*-H), 4.26 and 3.12 (AB spin system, 8H, $ArCH_2Ar$, $^2J = 12.7$ Hz), 4.17 (m, 4H), 3.80 (m, 2H), 3.77 (m, 2H), 3.75 (m, 4H), 3.46 (m, 4H), 3.39 (s, 6H, OCH_3), 3.23 (m, 2H), 1.75 (s, 3H, $CH_3C_3H_4$), 1.32 (s, 18H, $C(CH_3)$) and 0.79 (s, 18H, $C(CH_3)$). ^{13}C-{^1H} NMR ($CDCl_3$): δ 154.16–124.58 (arom. C and C_{quat} of allyl), 73.42 (d, PCH_2CH_2, $^2J(PC) = 7$), 70.70, 70.41 and 69.34 (3s, OCH_2 and CH_2 of allyl), 58.54 (s, OCH_3), 34.06 and 33.47 (2s, $C(CH_3)$), 31.56 and 30.94 (2s, $C(CH_3)$), 30.83 (s, $ArCH_2$), 29.39 (m, PCH_2, $J(PC) = 22$ Hz) and 23.15

($CH_3C_3H_4$). ^{31}P-{^{1}H} NMR ($CDCl_3$): δ 12.3 (s, PPh_2). FAB mass spectrum: *m*/*z* (%) 1349.6 (100) [$(M - BF_4)^+$, expected isotopic profile]. Found: C, 67.69; H, 7.14. Calc. for $C_{82}H_{101}BF_4O_6P_2Pd$: C, 67.71; H, 7.01%.

(η^3-2-Methylallyl)-{*P*,*P*′-[5,11,17,23-tetra-*tert*-butyl-25,27-bis(diphenylphosphinomethoxy)-26,28-bis(3-oxabutyloxy)calix[4]arene]}palladium(II) tetrafluoroborate 5. A solution of $AgBF_4$ (0.025 g, 0.128 mmol) in THF (1 cm^3) was added to a solution of [Pd(η^3-C_3H_4Me)Cl]$_2$ (0.029 g, 0.073 mmol) in CH_2Cl_2 (3 cm^3). Stirring was stopped after 5 min and the solution decanted to eliminate AgCl. The supernatant was filtered through Celite and added to a solution of **L**^{2} (0.150 g, 0.129 mmol) in CH_2Cl_2 (30 cm^3). After 12 h the solution was concentrated to *ca.* 5 cm^3 and addition of pentane afforded a white precipitate. Yield: 0.130 g, 72%. mp 200–205 °C (decomp.). ^{1}H NMR ($CDCl_3$): δ 7.82–7.52 (20H, PPh_2), 6.97 and 6.96 (AB spin system, 4H, *m*-H, *J*(AB) = 3), 6.48 and 6.45 (2s, 4H, *m*-H), 5.85 and 5.74 (AB spin system, 4H, OCH_2P, *J*(AB) = 12.9), 4.13 and 2.94 (AB spin system, 4H, ArCH_2Ar, ^2J = 12.9), 4.07 and 2.90 (AB spin system, 4H, ArCH_2Ar, ^2J = 13.5 Hz), 3.81 (s br, 2H, CH of allyl), 3.61 and 3.49 (2 broad signals, 2 × 2H, CH_3OCH_2), 3.29 and 3.27 (2s, 6H, OCH_3), 3.26 (m, 2H, CH of allyl), 3.15 (m, 4H, CH_3OCH_2-CH_2), 1.56 (s, 3H, $CH_3C_3H_4$), 1.29 (s, 18H, $C(CH_3)$), 0.79 (s, 9H, $C(CH_3)$) and 0.78 (s, 9H, $C(CH_3)$). ^{13}C-{^{1}H} NMR ($CDCl_3$): δ 152.51–124.69 (arom. C and C_{quat} of allyl), 73.75 (s, $CH_2CH_2OCH_3$), 72.54 (t, OCH_2P, tent. assignment, |*J*(PC) + ^3J(P′C)| = 30 Hz), 69.93 and 69.56 (2s, $CH_3OCH_2CH_2$), 58.65 and 58.57 (2s, OCH_3), 33.89 and 33.62 (2s, $C(CH_3)$), 31.49 and 30.97 (2s, $C(CH_3)$), 29.87 and 29.73 (2s, ArCH_2), 22.82 ($CH_3C_3H_4$), CH_2 of allyl not identified. ^{31}P-{^{1}H} NMR ($CDCl_3$): δ 18.3 (s, PPh_2). FAB mass spectrum: *m*/*z* (%) 1321.6 (100) [$(M - BF_4)^+$, expected isotopic profile]. Found: C, 68.03; H, 6.89. Calc. for $C_{80}H_{97}BF_4O_6P_2Pd$: C, 68.16; H, 6.94%.

(η^3-2-Methylallyl){*P*,*P*′-[5,11,17,23-tetra-*tert*-butyl-25,27-bis(diethylcarbamoylmethoxy)-26,28-bis(diphenylphosphinomethoxy)calix[4]arene]}palladium(II) tetrafluoroborate 6. A solution of $AgBF_4$ (0.023 g, 0.118 mmol) in THF (1 cm^3) was added to a solution of [Pd(η^3-C_3H_4Me)Cl]$_2$ (0.023 g, 0.059 mmol) in CH_2Cl_2 (3 cm^3). Stirring was stopped after 5 min and the solution decanted to eliminate AgCl. The supernatant was filtered through Celite and added to a solution of **L**^{3} (0.150 g, 0.118 mmol) in CH_2Cl_2 (30 cm^3). After 12 h the solution was concentrated to *ca.* 5 cm^3 and addition of pentane afforded a dark brown precipitate. Yield: 0.120 g, 67%. mp 181–183 °C (slow decomp.). IR (KBr, cm^{-1}): *ν*(C=O) 1653, *ν*(B-F) 1060. ^{1}H NMR ($CDCl_3$): δ 7.85–7.76 and 7.57–7.30 (m, 20H, PPh_2), 7.02 and 6.80 (AB spin system, 4H, *m*-H, *J*(AB) = 2), 6.59 (ABXX′ spin system with X,X′ = P, 4H, OCH_2PPh_2, ^2J(AB) = 9, |*J*(AX) + *J*(AX′)| = 4, *J*(BX) = not determined), 6.46 (s, 2H, *m*-H), 6.20 (s, 2H, *m*-H), 4.38 and 3.18 (AB spin system, 4H, ArCH_2Ar, ^2J = 13.4), 4.07 and 4.02 (2s, 4H, OCH_2CONEt_2), 3.70 (s br, 2H, CH_{syn} of allyl), 3.63 and 2.49 (AB spin system, 2H, ArCH_2Ar, ^2J = 13.1), 3.52–3.42 (3q, 6H, NCH_2CH_3), 3.15 (s br, 2H, CH_{anti} of allyl), 3.03 (q, 2H, NCH_2CH_3, ^3J = 7.0), 1.30 (s, 18H, Bu^t), 1.23–1.17 (3t, 9H, NCH_2CH_3), 1.15 (t, 3H, NCH_2CH_3, ^3J = 7.0 Hz), 0.91 (s, 3H, $CH_3C_3H_4$), 0.83 (s, 9H, Bu^t) and 0.70 (s, 9H, Bu^t). ^{13}C-{^{1}H} NMR ($CDCl_3$): δ 166.77 and 166.55 (2s, C=O), 153.95–107.79 (arom. C and Cquat-allyl), 73.24 (t, OCH_2PPh_2, |*J*(PC) + ^3J(P′C)| = 30 Hz), 72.62 and 72.47 (2s, OCH_2CONEt_2), 40.94, 40.46 and 39.95 (3s, NCH_2CH_3), 33.84, 33.66 and 33.47 (3s, $C(CH_3)_3$), 31.50 and 30.94 (2s, $C(CH_3)_3$), 31.30 and 29.21 (s, ArCH_2Ar), 21.68 (s, $CH_3C_3H_4$), 14.29, 14.07 and 13.08 (3s, NCH_2CH_3), CH_2 of allyl not detected. ^{31}P-{^{1}H} NMR ($CDCl_3$): δ 14.7 (s, PPh_2). FAB mass spectrum: *m*/*z* (%) 1431.4 (100) [$(M - BF_4)^+$, expected isotopic profile] and 1377.3 (35) [$(M - BF_4 - C_3H_4Me)^+$, expected isotopic profile]. Found: C, 67.95; H, 6.96; N, 1.73. Calc. for $C_{86}H_{107}BF_4N_2O_6P_2Pd$: C, 67.96; H, 7.1; N, 1.84%.

(*R*,*R*)-(η^3-2-Methylallyl)-{*P*,*P*′-[5,11,17,23-tetra-*tert*-butyl-25,27-bis(diphenylphosphinomethoxy)-26,28-bis[(1-phenylethyl)-carbamoylmethoxy]calix[4]arene]}palladium(II) tetrafluoroborate 7. A solution of $AgBF_4$ (0.029 g, 0.146 mmol) in THF (1 cm^3) was added to a solution of [Pd(η^3-C_3H_4Me)Cl]$_2$ (0.029 g, 0.073 mmol) in CH_2Cl_2 (3 cm^3). Stirring was stopped after 5 min and the solution decanted to eliminate AgCl. The supernatant was filtered through Celite and added to a solution of **L**^{4} (0.200 g, 0.110 mmol) in CH_2Cl_2 (30 cm^3). After 12 h the solution was concentrated to *ca.* 5 cm^3 and addition of pentane afforded a dark brown precipitate. Yield: 0.193 g, 93%. mp 185–187 °C (slow decomp.). IR (KBr, cm^{-1}): *ν*(N–H) 3340, *ν*(C=O) 1683, *ν*(B-F) 1057. ^{1}H NMR ($CDCl_3$): δ 7.64–7.21 (m, 30H, PPh_2), 6.91 (d, 1H, NH, ^3J = 7), 6.89–6.23 (8H, *m*-H), 6.38 (d, 1H, NH, ^3J = 7 Hz), 6.05 and 5.80 (ABX spin system with X = P, 4H, $OCH_AH_BPPh_2$, *J*(AB) = 13, *J*(AX) = 13, *J*(BX) = 20), 5.03 and 5.02 (2 quint, AMX_3 spin system, 2H, NHC*H*MePh, ^3J(AM) ≈ ^3J(AX) = 7), 4.32 (AB spin system, 4H, OCH_2CONHR, ^2J(AB) = 15), 4.05–3.68 and 3.05–2.59 (two complex m, 12H, 4 overlapping $ArCH_AH_BAr$ signals and CH_2 of allyl), 1.47 and 1.40 (2d, 6H, NHCH-CH_3Ph, ^3J = 7.0 Hz), 1.34 (s, 3H, C_3H_4Me), 1.28 (s, 18H, $C(CH_3)$), 0.78 (s, 9H, $C(CH_3)$) and 0.72 (s, 9H, $C(CH_3)$). ^{13}C-{^{1}H} NMR ($CDCl_3$): δ 168.10 (s, C=O), 167.99 (s, C=O), 153.84–124.80 (arom. C and Cquat allyl), 73.83 and 73.53 (2s, OCH_2CONHR), 73.06 (t, OCH_2P, |*J*(PC) + ^3J(P′C)| = 37 Hz), 49.39 and 49.06 (2s, NH*C*HMePh), 33.85, 33.53 and 33.51 (3s, $C(CH_3)$), 31.49 and 30.90 (2s, $C(CH_3)$), 30.28 and 29.95 (2s, ArCH_2Ar), 22.38 (s), 22.23 (s) ($CH_3C_3H_4$). ^{31}P-{^{1}H} NMR ($CDCl_3$): δ 16.7 and 16.1 (AB spin system, PPh_2, ^2J(AB) = 43 Hz). FAB mass spectrum: *m*/*z* (%) 1527.1 (100) [$(M - BF_4)^+$, expected isotopic profile] and 1473.1 (20) [$(M - BF_4 - C_3H_4Me)^+$, expected isotopic profile]. Found: C, 69.61; H, 6.81; N, 1.68. Calc. for $C_{94}H_{107}BF_4N_2O_6P_2Pd$: C, 69.86; H, 6.67; N, 1.73%.

(*R*)-(η^3-2-Methylallyl)-{*P*,*P*′-[5,11,17,23-tetra-*tert*-butyl-25,27-bis[diphenylphosphinomethoxy]-26-(3-oxabutyloxy)-28-[(1-phenylethyl)carbamoylmethoxy]calix[4]arene]}palladium(II) tetrafluoroborate 8. A solution of $AgBF_4$ (0.023 g, 0.118 mmol) in THF (1 cm^3) was added to a solution of [Pd(η^3-C_4H_7)Cl]$_2$ (0.023 g, 0.059 mmol) in CH_2Cl_2 (3 cm^3). Stirring was stopped after 5 min and the solution decanted to eliminate AgCl. The supernatant was filtered through Celite and added to a solution of **L**^{5} (0.150 g, 0.119 mmol) in CH_2Cl_2 (30 cm^3). After 12 h the solution was concentrated to *ca.* 5 cm^3 and addition of pentane afforded a white precipitate. Yield: 0.130 g, 72%. mp >280 °C. IR (KBr, cm^{-1}): 1676s. The NMR spectra show that two isomers are present. Below are given only the ^{1}H NMR data of the major compound. ^{1}H NMR ($CDCl_3$): δ 7.83–7.17 (arom. H + NH), 7.02 (s, 2H, *m*-H), 6.80 and 6.75 (AB spin system, 2H, *m*-H, *J*(AB) ≈ 3), 6.60 and 6.55 (AB spin system, 2H, *m*-H, *J*(AB) ≈ 2.5), 6.27 and 6.18 (AB spin system, 2H, *m*-H, *J*(AB) ≈ 3), 6.11 and 5.50 (two m, 4H, PCH_2), 4.95 (dq, AMX_3 spin system, 1H, NHC*H*MePh, ^3J(AM) ≈ ^3J(AX) = 7), 4.45 (AB spin system, 2H, $OCH_2C(O)$, tent. assign.), 3.80 (2d, 2H, axial ArC*H*Ar), 3.60 (2d, 2H, axial ArC*H*Ar), 3.65–3.10 (several m, not assigned), 3.20 (s, 3H, OCH_3), 2.75 (d, 2H, equat. ArC*H*Ar, $J(H_{ax}H_{eq})$ = 13), 2.55 (d, 2H, equat. ArC*H*Ar, $J(H_{ax}H_{eq})$ = 13), 1.55 (d, 1H, NHCH*Me*Ph, ^2J = 7 Hz), 1.30 (s, 18H, $C(CH_3)_3$), 0.80 (s, 9H, $C(CH_3)_3$) and 0.70 (s, 9H, $C(CH_3)_3$). Signals of allyl CH_2 and OCH_2CH_2O could not be assigned due to overlapping. ^{31}P NMR ($CDCl_3$): δ 17.03 and 15.24 (AB spin system, PPh_2 (isomer 1), *J*(AB) = 38), 17.94 and 16.53 (AB spin system, PPh_2 (isomer 2), *J*(AB) = 39 Hz). FAB mass spectrum: *m*/*z* (%) 1424.1 (100) [$(M - BF_4)^+$, expected isotopic profile] and 1370.0 (30) [$(M - BF_4 - C_3H_4Me)^+$]. Found: C, 67.29; H,

6.36; N, 0.87. Calc. for $C_{87}H_{102}BF_4NO_6P_2Pd\cdot0.5CH_2Cl_2$: C, 67.57; H, 6.67; N, 0.90%.

(η³-2-Methylallyl){*P*,*P*′-[5,11,17,23-tetra-*tert*-butyl-25,27-bis(diphenylphosphinomethoxy)-26,28-bis{(1*R*,2*S*,5*R*)-menthyloxycarbonylmethoxy}calix[4]arene]}palladium(II) tetrafluoroborate 9. A solution of $AgBF_4$ (0.029 g, 0.146 mmol) in THF (1 cm^3) was added to a solution of $[Pd(\eta^3\text{-}C_3H_4Me)Cl]_2$ (0.029 g, 0.073 mmol) in CH_2Cl_2 (3 cm^3). Stirring was stopped after 5 min and the solution decanted to eliminate AgCl. The supernatant was filtered through Celite and added to a solution of **L**[6] (0.210 g, 0.146 mmol) in CH_2Cl_2 (30 cm^3). After 12 h the solution was concentrated to *ca.* 5 cm^3 and addition of pentane afforded a yellow crystalline powder. Yield: 0.150 g, 60%. mp >280 °C. IR (KBr, cm^{-1}): *ν*(C=O) 1747, *ν*(B–F) 1057. ^{1}H NMR ($CDCl_3$): *δ* 7.75–7.67 and 7.61–7.35 (20H, PPh_2), 7.00 and 6.87 (AB spin system, 4H, *m*-H, *J*(AB) ≈ 2), 6.45 (s, 2H, *m*-H), 6.29 (s, 2H, *m*-H), 6.14 and 5.59 (m, A parts of two overlapping AB spin systems, 2H, PCH_2), 5.59 (m, B parts of two overlapping AB spin systems, PCH_2), 4.74 and 4.68 (2 dt, 2H, OCH of Ment, $^3J \approx 10$, $^3J \approx 4$ Hz), 4.35–3.27 (several unresolved signals), 3.08 (d, 2H, ArC*H*Ar), 2.72 (d, 1H, ArC*H*Ar), 2.65 (d, 1H, ArC*H*Ar), 2.05–1.95 and 1.95–0.71 (several multiplets br, 36 H of Ment), 1.50 (s, 3H, $CH_3C_3H_4Me$), 1.29 (s, 18H, Bu^t), 0.77 (s, 9H, Bu^t) and 0.72 (s, 9H, Bu^t). ^{31}P-{^{1}H} NMR ($CDCl_3$): *δ* 16.5 and 15.9 (AB spin system, PPh_2, *J*(PP′) = 38 Hz). FAB mass spectrum: *m*/*z* (%) 1597.4 (100) [$(M - BF_4)^+$, expected isotopic profile]. Found: C, 69.63; H, 7.30. Calc. for $C_{98}H_{125}BF_4O_8P_2Pd$: C, 69.81; H, 7.47%.

(η³-2-Methylallyl){*P*,*P*′-[5,11,17,23-tetra-*tert*-butyl-25,27-bis(diphenylphosphinooxy)-26,28-bis(3-oxabutyloxy)calix[4]arene]}palladium(II) tetrafluoroborate 10. A solution of $AgBF_4$ (0.026 g, 0.134 mmol) in THF (1 cm^3) was added to a solution of $[Pd(\eta^3\text{-}C_3H_4Me)Cl]_2$ (0.026 g, 0.066 mmol) in CH_2Cl_2 (3 cm^3). Stirring was stopped after 5 min and the solution was decanted to eliminate AgCl. The supernatant was filtered through Celite and added to a solution of **L**[7] (0.150 g, 0.132 mmol) in CH_2Cl_2 (30 cm^3). After 12 h the solution was concentrated to *ca.* 5 cm^3 and addition of pentane afforded a white precipitate. Yield: 0.90 g, 50%. mp 185–187 °C (decomp.). ^{1}H NMR ($CDCl_3$): *δ* 8.28–8.01 and 7.67–7.62 (20H, PPh_2), 7.00 (s broad, 4H, *m*-H), 6.17 and 6.07 (2s, 2 × 2H, *m*-H), 3.91 and 3.79 (2 m, 4H, OCH_2), 3.72 and 2.61 (AB spin system, 4H, $ArCH_2Ar$, ^2J = 13.4), 3.41 and 2.45 (AB spin system, 4H, $ArCH_2Ar$, ^2J = 13.3 Hz), 3.38 (s br, 2H, H_{syn} of allyl), 3.11 (s, 3H, OCH_3), 3.00 (m, 4H, OCH_2), 2.93 (s, 3H, OCH_3), 1.60 (s, 3H, $CH_3C_3H_4Me$), 1.36 (s, 18H, $C(CH_3)$), 0.76 (s, 9H, $C(CH_3)$) and 0.68 (s, 9H, $C(CH_3)$). ^{13}C-{^{1}H} NMR ($CDCl_3$): *δ* 150.77–123.71 (arom. C and C_{quat} of allyl), 72.36 (s, $CH_2CH_2OCH_3$), 69.89 and 69.21 (2s, CH_3OCH_2), 58.61 and 58.09 (2s, OCH_3), 34.22 and 33.66 (2s, $C(CH_3)$), 32.09 (s, $ArCH_2Ar$), 31.63, 31.12 and 31.00 (3s, $C(CH_3)$), 22.36 ($CH_3C_3H_4Me$), CH_2 of allyl not found. ^{31}P-{^{1}H} NMR ($CDCl_3$): *δ* 128.2 (s, PPh_2). FAB mass spectrum: *m*/*z* (%) 1293.5 (100) [$(M - BF_4)^+$, expected isotopic profile] and 1238.4 (15) [$M - BF_4 - C_3H_4Me)^+$, expected isotopic profile]. Found: C, 67.62; H, 6.97. Calc. for $C_{78}H_{93}BF_4O_6P_2Pd$: C, 67.8; H, 6.78%.

(η³-2-Methylallyl)-{*P*,*P*′-[5,11,17,23-tetra-*tert*-butyl-25,27-bis(diphenylphosphinooxy)-26,28-bis{(1*R*,2*S*,5*R*)-menthyloxycarbonylmethoxy}calix[4]arene]}palladium(II) tetrafluoroborate 11. A solution of $AgBF_4$ (0.029 g, 0.146 mmol) in THF (1 cm^3) was added to a solution of $[Pd(\eta^3\text{-}C_3H_4Me)Cl]_2$ (0.029 g, 0.073 mmol) in CH_2Cl_2 (3 cm^3). Stirring was stopped after 5 min and the solution decanted to eliminate AgCl. The supernatant was filtered through Celite and added to a solution of **L**[8] (0.210 g, 0.149 mmol) in CH_2Cl_2 (30 cm^3). After 12 h the solution was concentrated to *ca.* 5 cm^3 and addition of pentane afforded a yellow crystalline powder. Yield: 0.150 g, 60%. mp 190–195 °C (slow decomp.). IR (KBr, cm^{-1}): *ν*(C=O) 1758 and 1727, *ν*(B–F) 1062. ^{1}H NMR ($CDCl_3$): *δ* 8.21–8.07, 7.63–7.50 and 7.41–7.20 (20H, PPh_2), 7.03 and 6.97 (AB spin system, 4H, *m*-H, *J*(AB) = 3), 6.17 (s, 2H, *m*-H), 6.08 (s, 2H, *m*-H), 4.60 and 4.53 (2 dt, 2H, OCH of Ment, ^3J = 10.7, 4), 4.20 (s, 2H, OCH_2-C(O)Ment), 4.03 and 2.94 (AB spin system, 2H, OCH_2C-(O)Ment, *J*(AB) = 16.8), 3.82 and 2.76 (AB spin system, 4H, $ArCH_2Ar$, ^2J = 13.2), 3.76 and 2.53 (ABX spin system with X = P, 2H, $ArCH_2Ar$, ^2J = 13.2, ^5J(PH) = 4 Hz), 3.52, 3.50 and 3.42 (2H, 3 signals of H_{syn} of allyl), 3.48 (pseudo t, 2H, CH_{anti} of allyl), 1.65–0.62 (several multiplets br, 36 H of Ment), 1.55 (s, 3H, $CH_3C_3H_4Me$), 1.35 (s, 18H, Bu^t), 0.73 (s, 9H, Bu^t) and 0.66 (s, 9H, Bu^t). ^{13}C-{^{1}H} NMR ($CDCl_3$): *δ* 168.49 and 168.36 (2s, C=O), 151.34–124.01 (arom. C), 75.05 and 74.68 (2s, OCH of Ment), 71.39 and 71.37 (2s, OCH_2CO_2Ment), 46.78, 46.62, 26.14 (3s, CH of Ment), 40.89, 40.62, 34.13 and 23.50 (4s, CH_2 of Ment), 34.19 (s, $C(CH_3)_3$), 32.50 and 32.13 (2s, $ArCH_2Ar$), 31.60, 31.11 and 30.95 (3s, $C(CH_3)_3$), 22.22, 22.06, 20.74 and 16.35 (4s, $CH_3C_3H_4Me$ and CH_3 of Ment). ^{31}P-{^{1}H} NMR ($CDCl_3$): *δ* 128.7 (s, PPh_2). FAB mass spectrum: *m*/*z* (%) 1569.6 (100) [$(M - BF_4)^+$, expected isotopic profile] and 1514.6 (11) [$(M - BF_4 - C_3H_4Me)^+$, expected isotopic profile]. Calc. for $C_{96}H_{121}BF_4O_8P_2Pd$: C, 67.80; H, 6.78. Found: C, 67.62; H, 6.97%.

Chloro(η⁶-*p*-cymene)[{*P*,*P*′-[5,11,17,23-tetra-*tert*-butyl-25,27-bis-(diethylcarbamoylmethoxy)-26,28-bis(diphenylphosphinomethoxy)calix[4]arene]}ruthenium(II) tetrafluoroborate 12. A solution of $AgBF_4$ (0.023 g, 0.118 mmol) in THF (1 cm^3) was added to a stirred solution of $[RuCl_2(p\text{-}MeC_6H_4Pr^i)]_2$ (0.036 g, 0.059 mmol) in CH_2Cl_2 (5 cm^3). Stirring was stopped after 5 min and the solution decanted in order to remove AgCl. The supernatant and CH_2Cl_2 washings of the AgCl precipitate were filtered through Celite into a solution of **L**[3] (0.150 g, 0.118 mmol) in CH_2Cl_2 (30 cm^3). After stirring for 3 h the solution was concentrated to *ca.* 2 cm^3. The yellow product was obtained by slow recrystallisation from a CH_2Cl_2–Et_2O–hexane mixture. Yield: 0.050 g, 52%. mp 218–220 °C. IR (KBr, cm^{-1}): *ν*(C=O) 1650s, *ν*(B–F) 1055s br. ^{1}H NMR ($CDCl_3$): *δ* 7.88–7.69 and 7.48–7.33 (m, 20H, PPh_2), 6.93 and 6.90 (2 s br, 4H, *m*-H), 6.43 and 5.25 (ABXX′ spin system with X = X′ = P, 4H, OCH_2PPh_2, ^2J(AB) = 13.4, *J*(AX) and *J*(BX) not determined), 6.27 and 6.23 (2s, 4H, *m*-H), 5.75 and 4.85 (AA′BB′ spin system, 8H, C_6H_4 of *p*-cymene, ^3J = 6.1), 4.43 and 3.05 (AB spin system, 8H, $ArCH_2Ar$, ^2J = 14.3), 4.30 and 3.92 (2s, 4H, OCH_2CONEt_2), 3.77 and 2.62 (AB spin system, 8H, $ArCH_2Ar$, ^2J = 13.1), 3.41 (q, 4H, $N(CH_2CH_3)_2$, ^3J = 7.0), 3.15 (m, 4H, two $N(CH_2CH_3)_2$), 2.57 (q, 4H, $N(CH_2CH_3)_2$, ^3J = 7.0), 2.42 (m, 2H, $CH(CH_3)_2$ of *p*-cymene), 1.29 (s, 18H, Bu^t), 1.25 (s, 6H, $ArCH_3$ of *p*-cymene), 1.21 (m, 12H, two NCH_2CH_3), 0.98 (t, 6H, NCH_2CH_3, ^3J = 6.7 Hz), 0.94 (d, 12H, $CH(CH_3)_2$ of *p*-cymene), 0.75 (s, 9H, Bu^t) and 0.73 (s, 9H, Bu^t). ^{13}C-{^{1}H} NMR ($CDCl_3$): *δ* 168.14 and 166.49 (2s, C=O), 152.30–123.54 (arom. C of PPh_2 and calixarene), 0.98 (s, C_{quat} of *p*-cymene), 72.77 and 70.09 (2s, OCH_2CONEt_2), 71.01 (m, OCH_2PPh_2, tentative assignment), 41.26, 41.06 and 40.28 (3s, NCH_2CH_3), 33.52 and 32.24 (2s, $C(CH_3)_3$), 31.35, 30.95 and 30.76 (3s, $C(CH_3)_3$), 31.69 (s, $ArCH_2Ar$), 20.73 (s, $(CH_3)_2CH$ of *p*-cymene), 14.81, 14.52, 14.15, 12.94 and 12.50 (5s, $N(CH_2CH_3)$ and $ArCH_3$ of *p*-cymene), C_{quat}, $(CH_3)_2CH$ and CH arom. of *p*-cymene not determined. ^{31}P-{^{1}H} NMR ($CDCl_3$): *δ* 26.4 (s, PPh_2). FAB mass spectrum: *m*/*z* (%) 1541.6 (23) [$(M - BF_4)^+$] and 1407.6 (100) [$(M - BF_4 - p\text{-cymene})^+$]. Found: C, 68.05; H, 6.87; N, 1.69. Calc. for $C_{92}H_{114}BClF_4N_2O_6P_2Ru$: C, 67.83; H, 7.05; N, 1.72%.

Chloro(η⁶-*p*-cymene){*P*,*P*′-[(*R*,*R*)-5,11,17,23-tetra-*tert*-butyl-25,27-bis(diphenylphosphinomethoxy)-26,28-bis{(1-phenylethyl)-carbamoylmethoxy}calix[4]arene]}ruthenium(II) tetrafluoroborate 13. A solution of $AgBF_4$ (0.021 g, 0.110 mmol) in THF (1 cm^3) was added to a stirred solution of $[RuCl_2(p\text{-}MeC_6$-

$H_4Pr^i)]_2$ (0.034 g, 0.055 mmol) in CH_2Cl_2 (5 cm^3). Stirring was stopped after 5 min and the solution 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, 0.110 mmol) in CH_2Cl_2 (30 cm^3). After stirring for 3 h, the solution was concentrated to *ca.* 2 cm^3 and the product precipitated with Et_2O. Recrystallisation from CH_2Cl_2–Et_2O–hexane afforded **13** as an analytically pure yellow powder. Yield: 0.175 g, 90%. mp 206–209 °C. IR (KBr, cm^{-1}): *ν*(C=O) 1685 and 1653. ^{1}H NMR ($CDCl_3$): *δ* 7.77–7.66 and 7.53–7.17 (m, 32H, arom. H and NH), 6.92 and 6.75 (AB spin system, 2H, *m*-H, $^4J = 2.2$), 6.87 (s, 2H, *m*-H), 6.56 (d, 2H, NH, $^3J = 8$), 6.30 and 6.27 (AB spin system, 2H, *m*-H, $^4J = 1.8$), 6.21 and 6.11 (AB spin system, 2H, *m*-H, $^4J = 2.2$), 5.84 and 4.62 (ABX spin system with X = P, 2H, PCH_2 tent. assign., *J*(AB) = 1, *J*(AX) = 17, *J*(BX) = 0), 5.79 and 5.75 (ABX spin system, 2H, ArH of *p*-cymene (tent. assign.), *J*(AB) = 2), 5.62 (s br, 2H, PCH_2), 5.10 (dq, 1H, C*H*Me), 4.96 and 4.78 (AB spin system, 2H, Ar H of *p*-cymene, ^3J(AB) = 3), 4.43 and 4.16 (AB spin system, 2H, OCH_2CONH, *J*(AB) = 15), 3.79 and 3.64 (A parts of 4 overlapping AB spin systems, 4H, $ArCH_2Ar$), 3.58 (s, 2H, $OCH_2C(O)$), 2.97 (d, B parts of AB spin systems, 1H, $ArCH_2Ar$, *J*(AB) = 15), 2.72–2.62 (B part of 3 overlapping AB spin systems, 3H, $ArCH_2Ar$), 2.55 (hept, 2H, $CH(CH_3)_2$ of *p*-cymene), 1.58 (d, 3H, $NCHCH_3$, $^3J = 7$), 1.37 (d, 3H, $NCHCH_3$, $^3J = 7$), 1.29 (s, 9H, Bu[t]), 1.28 (s, 9H, Bu[t]), 1.17 (s, 3H, $ArCH_3$ of *p*-cymene), 1.05 (d, 6H, $CH(CH_3)_2$ of *p*-cymene, $^3J = 7$), 1.01 (d, 6H, $CH(CH_3)_2$ of *p*-cymene, $^3J = 7$ Hz), 0.80 (s, 9H, Bu[t]) and 0.71 (s, 9H, Bu[t]). ^{31}P-{^{1}H} NMR ($CDCl_3$): *δ* 26.9 and 25.37 (AB spin system, PPh_2, *J*(AB) = 49 Hz). FAB mass spectrum: *m*/*z* (%) 1981 (13) [M^+], 1637.7 (4) [$(M - BF_4)^+$] and 1503.6 (3) [$(M - BF_4 - p\text{-}MeC_6H_4Pr^i)^+$]. Found: C, 64.82; H, 6.92; N, 1.30. Calc. for $C_{51}H_{64}Cl_2NO_3PRu$: C, 65.03; H, 6.85; N, 1.49%.

μ-*P*,*P*′-[5,11,17,23-Tetra-*tert*-butyl-25,27-bis(diethylcarbamoylmethoxy)-26,28-bis(diphenylphosphinomethoxy)calix[4]arene]-bis[dichloro(*p*-cymene)ruthenium(II)] 14. To a solution of $[RuCl_2(p\text{-}MeC_6H_4Pr^i)]_2$ (0.175 g, 0.280 mmol) in CH_2Cl_2 (30 cm^3) was added at 0 °C a solution of **L**[3] (0.360 g, 0.280 mmol) in CH_2Cl_2 (20 cm^3). After stirring for 1 h the solution was concentrated to *ca.* 5 cm^3. Diethyl ether was added to yield complex **14** as an analytically pure orange powder (0.300 g, 60%). mp 224–226 °C. IR (KBr, cm^{-1}): *ν*(C=O) 1646s. ^{1}H NMR ($CDCl_3$): *δ* 8.13–8.05 and 7.40–7.27 (m, 20H, PPh_2), 6.82 (s, 4H, *m*-H), 6.07 (s, 4H, *m*-H), 5.72 (broad signal, 4H, OCH_2PPh_2), 5.21 and 5.15 (AA′BB′ spin system, 8H, C_6H_4 of *p*-cymene, $^3J = 5.5$), 4.46 (s, 4H, OCH_2CONEt_2), 4.11 and 2.52 (AB spin system, 8H, $ArCH_2Ar$, $^2J = 13.1$), 3.28 (q, 4H, $N(CH_2CH_3)_2$, $^3J = 7.0$), 2.68 (q, 4H, $N(CH_2CH_3)_2$, $^3J = 7.0$), 2.60 (m, 2H, $CH(CH_3)_2$ of *p*-cymene), 1.90 (s, 6H, $ArCH_3$ of *p*-cymene), 1.25 (s, 18H, Bu[t]), 1.01 (d, 12H, $CH(CH_3)_2$ of *p*-cymene), 1.00 (t, 6H, NCH_2CH_3, $^3J = 7.0$), 0.73 (s, 18H, Bu[t]) and 0.67 (t, 6H, NCH_2CH_3, $^3J = 7.0$ Hz). ^{13}C-{^{1}H} NMR ($CDCl_3$): *δ* 168.43 (s, C=O), 155.09–124.44 (arom. C of PPh_2 and calixarene), 108.82 and 93.75 (2s, arom. C_{quat} of *p*-cymene), 90.99 and 84.82 (2s, arom. CH of *p*-cymene), 72.29 (d, OCH_2PPh_2, *J*(PC) = 22 Hz), 69.75 (s, OCH_2CONEt_2), 41.23 and 39.95 (2s, NCH_2CH_3), 33.92 and 33.41 (2s, $C(CH_3)_3$), 31.67 and 30.39 (2s, $C(CH_3)_3$), 31.49 (d, $ArCH_2Ar$), 21.83 (s, $(CH_3)_2CH$ of *p*-cymene), 17.38 (s, $ArCH_3$ of *p*-cymene), 14.26 and 13.08 (2s, $N(CH_2CH_3)_2$). ^{31}P-{^{1}H} NMR ($CDCl_3$): *δ* 27.2 (s, PPh_2). FAB mass spectrum: *m*/*z* (%) 1678 (3) [$(M - 2Cl - p\text{-}MeC_6H_4Pr^i)^+$] and 1578 [$(M - 2Cl - Ru - p\text{-}MeC_6H_4Pr^i)^+$]. Found: C, 64.82; H, 6.92; N, 1.39. Calc. for $C_{51}H_{64}Cl_2NO_3PRu$: C, 65.03; H, 6.85; N, 1.49%.

μ-*P*,*P*′-[(*R*,*R*)-5,11,17,23-Tetra-*tert*-butyl-25,27-bis(diphenylphosphinomethoxy)-26,28-bis{(1-phenylethyl)carbamoylmethoxy}calix[4]arene]-bis[dichloro(*p*-cymene)ruthenium(II)] 15. To a solution of $[RuCl_2(p\text{-}MeC_6H_4Pr^i)]_2$ (0.090 g, 0.146 mmol) in CH_2Cl_2 (30 cm^3) was added at 0 °C a solution of **L**[4] (0.200 g, 0.146 mmol) in CH_2Cl_2 (20 cm^3). After stirring for 24 h the solution was evaporated to dryness and the residue taken up with $CHCl_3$. Addition of diethyl ether yielded complex **15** as an orange powder. Yield: 0.150 g, 55%. mp 187–190 °C. IR (KBr, cm^{-1}): *ν*(NH) 3425 and 3330, *ν*(C=O) 1684s, 1669s and 1656s. ^{1}H NMR ($CDCl_3$): *δ* 8.05–7.83 and 7.80–7.12 (30H, arom. H), 6.89 and 6.83 (AB spin system, 4H, *m*-H, $^4J \approx 2$), 6.09 (d, 2H, NH, $^3J = 8$), 6.01 and 5.99 (AB spin system, 4H, *m*-H, $^4J < 1$), 5.46 (s br, 4H, OCH_2PPh_2), 5.15 and 5.10 (AB spin system, 4H, arom. of *p*-cymene, $^3J = 7$), 5.04 (dq, 2H, NHC*H*MePh), 4.47 and 4.36 (AB spin system, 4H, OCH_2CO, *J*(AB) = 16 Hz), 4.25 and 2.72 (AB spin system, 4H, $ArCH_2Ar$, $^2J = 15.0$), 4.14 and 2.61 (AB spin system, 4H, $ArCH_2Ar$, $^2J = 13.7$), 2.60 (m, 2H, $CH(CH_3)_2$ of *p*-cymene), 1.85 (s, 6H, $ArCH_3$ of *p*-cymene), 1.28 (d, 6H, $NHCHCH_3$, $^3J = 7.0$), 1.26 (s, 18H, Bu[t]), 0.98 (d, 6H, $CH(CH_3)_2$ of *p*-cymene, $^3J = 7.0$), 0.90 (d, 3H, $CH(CH_3)_2$ of *p*-cymene, $^3J = 7.0$ Hz) and 0.69 (s, 18H, Bu[t]). ^{13}C-{^{1}H} NMR ($CDCl_3$): *δ* 169.19 (s, C=O), 154.58–124.41 (arom. C of PPh_2 and calix), 108.68 and 93.93 (2s, C_{quat} of *p*-cymene), 91.61, 90.07, 85.50 and 84.87 (4s, arom. CH of *p*-cymene), 72.11 (s, OCH_2CO), 71.70 (d, OCH_2PPh_2, *J*(PC) = 21 Hz), 48.76 (s, $NHCH(CH_3)Ph$), 33.97 and 33.40 (2s, $C(CH_3)_3$), 32.02 and 30.28 (s, $ArCH_2Ar$), 31.64 and 31.02 (2s, $C(CH_3)_3$), 22.60 (s, CH_3), 22.00 and 21.43 (3s, CH_3) and 17.43 (s, $ArCH_3$ of *p*-cymene). ^{31}P-{^{1}H} NMR ($CDCl_3$): *δ* 23.4 (s, PPh_2). FAB mass spectrum: *m*/*z* (%) 1981.5 (13) [M^+] and 1943.6 (50) [$(M - Cl)^+$]. Found: C, 65.15; H, 6.08; N, 1.27. Calc. for $C_{102}H_{128}Cl_4N_2O_6P_2Ru_2 \cdot CHCl_3$: C, 65.07; H, 6.35; N, 1.37%.

[25,27-Bis(diethoxyphosphinooxy)-26,28-(3,6,9-trioxaundecane-1,11-dioxy)calix[4]arene]silver(I) tetrafluoroborate 16. To a stirred solution of **L**[9] (0.200 g, 0.24 mmol) in THF (10 cm^3) was added a solution of $AgBF_4$ (0.047 g, 0.25 mmol) in THF (10 cm^3). After 0.5 h, concentration to *ca.* 5 cm^3 resulted in formation of a white precipitate which was filtered off. Yield: 0.224 g, 92%. mp 220 °C (decomp.). ^{1}H NMR ($CDCl_3$): *δ* 7.15 and 6.96 (AB_2 spin system, t(2H) + d(4H), $^3J = 8$, *m*- and *p*-H of calix), 6.70 and 6.53 (AB_2 spin system, t(2H) + d(4H), $^3J = 8$, *m*- and *p*-H of calix), 4.77 and 3.28 (AB quartet, $^2J = 14$ Hz, 4H each, $ArCH_2$), 4.30–3.80 (m, 24H, CH_2 of crown-5 + $POCH_2CH_3$) and 1.38 (t, 12H, $POCH_2CH_3$). ^{13}C-{^{1}H} NMR ($CDCl_3$): *δ* 154.69 and 147.66 (2s, quat. aryl C-O), 135.14 and 133.16 (2s, quat. aryl C), 129.88, 128.29, 124.98 and 124.06 (4s, aryl C-O), 74.11, 72.38, 71.52 and 71.40 (4s, CH_2 of crown-5), 61.43 (s, $POCH_2CH_3$), 31.91 (s, $ArCH_2$) and 16.42 (s, $POCH_2CH_3$). ^{31}P-{^{1}H} NMR ($CDCl_3$): *δ* 105.9 (2d, *J*(P–Ag^{107}) = 778, *J*(P–Ag^{109}) = 900 Hz). FAB mass spectrum: *m*/*z* (%) 931.2 (100) [M^+]. Found: C, 52.11; H, 5.62. Calc. for $C_{44}H_{56}AgBF_4O_{11}P_2$: C, 51.94; H, 5.55%.

Hydroformylation reactions with complexes 2 and 3

The catalytic runs were performed in a 100 cm^3 glass-lined steel autoclave containing a magnetic stirring bar. In a typical experiment, a solution of the complex (0.017 mmol) in benzene–CH_2Cl_2 (14 : 3, v/v, 15 cm^3) was introduced under argon into the autoclave. The autoclave was pressurised (20 bar) with CO–H_2 (1 : 1) and heated at 40 °C for 2 h. After cooling and depressurisation, styrene was introduced (870 equivalents for **2** and 600 for **3**). The reaction was then carried out under 40 bar CO–H_2 at 40 °C. The observed conversions were 80% for **2** (after 100 h reaction time) and 95% for **3** (after 80 h). In both experiments, 2-phenylpropanal and 3-phenylpropanal were formed in a 95 : 5 ratio.

Palladium catalysed allylic alkylation

A suspension of sodium malonate (2.4 mmol) was prepared at 25 °C from dimethyl malonate (0.29 mmol) in THF (5 cm^3) and NaH (0.100 g, 60% in mineral oil). A solution of 1,3-diphenyl-

2-propenyl acetate (0.300 g, 1.2 mmol) in THF (1 cm^3) and a solution of the catalyst were then added to the malonate solution. The mixture was stirred under reflux until completion of the reaction. The reaction was monitored by TLC ($R_f = 0.5$ (starting compound), 0.2 (alkylation product); SiO_2; hexane–ethyl acetate 5 : 1, v/v).

X-Ray crystallography

Crystals of complex **16** suitable for diffraction study were obtained by slow diffusion of tetrahydrofuran into a dichloromethane solution of the compound.

Crystal data. $C_{44}H_{56}AgBF_4O_{11}P_2$, $M = 1017.55$, orthorhombic, space group *Pccn*, colourless crystals, $a = 11.9325(2)$, $b = 17.6619(2)$, $c = 21.2455(3)$ Å, $U = 21.2455(3)$ $Å^3$, $Z = 4$, $\mu = 0.588$ mm^{-1}. Data were collected on a Nonius KappaCCD diffractometer (graphite-monochromated Mo-Kα radiation, 0.71073 Å) at −100 °C. 39738 Reflections collected, 4299 with $I > 3\sigma(I)$. The structure was solved by direct methods and refined anisotropically on F^2 using the OpenMoleN package.[51] Hydrogen atoms were included using a riding model or rigid methyl groups. Final results: $R(F) = 0.049$, $wR(F) = 0.062$, 312 parameters.

CCDC reference number 151653.

See http://www.rsc.org/suppdata/dt/b0/b009005k/ for crystallographic data in CIF or other electronic format.

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