DALTON

Transition–metal complexation by calix[4]arene-derived phosphinites

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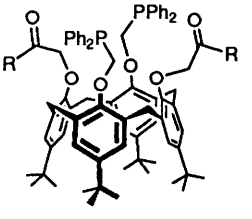
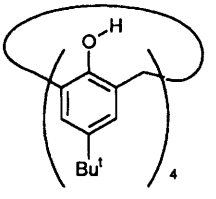
A series of 26,28-di(alkoxy)-5,11,17,23-tetra-*tert*-butyl-25,27-bis(diphenylphosphinooxy)calix[4]arenes [alkoxy = OH L^{10}, OMe L^{11}, OEt L^{12}, OPr^n L^{13}, OCH_2CO_2Me L^{14}, OCH_2CO_2Et L^{15} or (−)-$OCH_2CO_2C_{10}H_{19}$ L^{16} ($C_{10}H_{19}$ = menthyl = 2-isopropyl-5-methylcyclohexyl)] and 28-(alkoxy)-5,11,17,23-tetra-*tert*-butyl-25,27-bis(diphenylphosphinooxy)-26-ethoxycalix[4]arenes [alkoxy = OCH_2CO_2Et L^{17} or (−)-$OCH_2CO_2C_{10}H_{19}$ L^{18}] have been prepared selectively as cone conformers by treating the corresponding 25,27-dihydroxycalix[4]arene precursor with $LiNPr^i_2$ or LiBu at temperatures below −50 °C, followed by reaction with PPh_2Cl. All compounds exist in solution in a stable cone conformation, except L^{11} for which a fast exchange between the cone conformer and a partial-cone isomer occurs. Phosphination of 5,11,17,23-tetra-*tert*-butyl-25,27-di(ethoxycarbonylmethoxy)-26,28-dihydroxycalix[4]arene L^6 using NEt_3 instead of $LiNPr^i_2$ gave 5,11,17,23-tetra-*tert*-butyl-25-diphenylphosphinooxy-26,28-di(ethoxycarbonylmethoxy)-27-hydroxycalix[4]arene L^{19}. When the reaction leading to L^{10} was performed in refluxing tetrahydrofuran (thf), the 1,2-alternate conformer L^{21} was formed in addition to L^{10}. As shown by a variable-temperature NMR study, L^{21} undergoes fast homomerization in solution. Reaction of $[MCl_2(PhCN)_2]$ (M = Pt or Pd) with 2 equivalents of monophosphinite L^{19} gave selectively the corresponding *trans*-$[MCl_2L^{19}_2]$ complexes (M = Pt or Pd). For the diphosphinites, it was found that their complexation properties depend on both the calixarene substituents and the nature of the starting complex. Thus, reaction of the C_2 symmetrical diphosphinites L^{12}, L^{15} and L^{16} with $[PtCl_2(PhCN)_2]$ gave cyclooligomeric complexes of formula $[\{trans\text{-}PtCl_2(diphosphinite)\}_4]$ in which the diphosphinites behave as bridging ligands between two metal centres. Reaction of L^{15} with $[PdCl_2(PhCN)_2]$ gave $[(trans\text{-}PdCl_2L^{15})_4]$. When the unsymmetrically substituted diphosphinite L^{17} was treated with $[PtCl_2(PhCN)_2]$, the dimer $[(trans\text{-}PtCl_2L^{17})_2]$ was formed. Diphosphinite L^{18} and $[PdCl_2(PhCN)_2]$ gave $[(trans\text{-}PdCl_2L^{18})_2]$. Chelating behaviour was found for the chiral diphosphinite L^{16} in $[Rh(cod)L^{16}]BF_4$ (cod = cycloocta-1,5-diene) obtained by reaction of $[\{RhCl(cod)\}_2]$ with 2 equivalents of $AgBF_4$ and 2 equivalents of L^{16} in thf.

Interest in synthetic receptors containing pendant phosphine groups arises from anticipation that such ligands will facilitate both molecular recognition and reactions with certain transition-metal ions. Although the chemistry of macrocyclic compounds incorporating phosphorus donor atoms has been thoroughly investigated by several research groups,[1] phosphines closely appended to a cavity-shaped molecule appear to be novel materials.[2] Such ligands are expected to favour shape-selectivity during catalytic reactions and, if the cavity contains several distinct binding sites, facilitate the transformation of a substrate *via* synergistic effects. Thus, in these systems the function of the host is mainly selectively to bind and properly orient a substrate with respect to the catalytic centre. It is also important to realize that such ligands are capable of modifying specific physical properties of a P-bound transition-metal centre, by the presence of a non-transition-metal trapped in the cavity (*e.g.* a lanthanide or alkali metal) and maintained closely to the transition metal so as to allow interaction. An elegant illustration of this concept has been described by Balch *et al.*[3] who reported on several heterobimetallic Pt–M systems (M = Pb or Tl) based on exo-P^{III} macrocycles.

In the course of our studies concerning the preparation of polyfunctional phosphine ligands, it was found that lower rim diphosphinomethylation of *p-tert*-butylcalix[4]arenes provides diphosphine ligands of type L^A suitable for partial encapsulation of transition-metal centres.[4] In order to bring the transition-metal cation closer to the centre of the calix[4]arene cavity, phosphinito analogues of L^A appear to possess interesting possibilities. Indeed, molecular models have been used to show



L^A



L^1

that the presence of two phosphino groups (PR_2), directly connected to phenolic oxygen atoms in a distal arrangement, will increase the degree of encapsulation of a P-bound metal centre, provided the ligand displays chelating behaviour. It is noteworthy that calixarenes, or resorcinarenes, containing several P^{III} atoms directly attached to the phenolic oxygen atoms have been reported recently,[5] some of them being used for the complexation of transition-metal ions.[5–7] Considering the few reported studies on such multi-phosphorus ligands, it is not yet possible to identify the properties that localise the bound metal atom inside or outside the substituent cavity, and in particular whether the ligand will behave as a chelator or a bridging ligand. In this paper we report the synthesis and co-ordinative properties of a series of functionalized mono- and di-*p-tert*-butylcalix[4]arene phosphinites derived from *p-tert*-butylcalix[4]arene (L^1). A preliminary account of these results has appeared.[8] In the following, calix[4]arenes bearing substituents located at two opposite phenolic moieties

will conventionally be termed '1,3-difunctionalized calix[4]-arenes'.

Results and Discussion

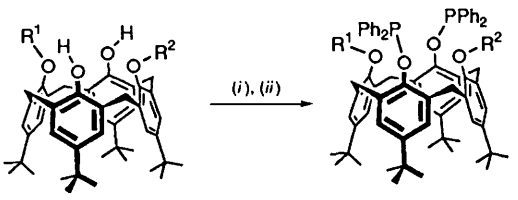
Synthesis of mono- and di-phosphinites

All ligands presented herein were obtained from calix[4]arene precursors pre-existing in a cone conformation. The diphosphinites L^{10}–L^{18} were obtained by treating, respectively, the corresponding 1,3-dihydroxycalix[4]arene precursor with 2 equivalents of a strong base ($LiBu^n$ for L^1–L^4, $LiNPr^i_2$ for L^5–L^9) in tetrahydrofuran (thf), followed by reaction with 2 equivalents of chlorodiphenylphosphine (Scheme 1). These reactions were performed at −78 °C, except for the syntheses of L^{10} and L^{13} which were performed, respectively, at 0 and −50 °C in order to avoid precipitation of the corresponding lithium salt. Owing to the tendency of ester-functionalized calixarenes to form complexes with Li^+,[9] separation of LiCl formed during the reactions leading to L^{14}–L^{18} presented some difficulty for the work-up of these compounds. Elimination of LiCl was best achieved by precipitation with toluene–pentane (1:1) at 5 °C. The assignment of a cone conformation for calixarenes L^{10}–L^{18} was made on the basis of ^{13}C NMR spectra; indeed, for each of these compounds the chemical shift of the methylene carbon atoms bridging two proximal aryl groups lie in the critical range δ 29–33, typical for methylene groups bridging aryl rings in a *syn* arrangement.[10] The ^{31}P NMR spectra display a single phosphinite signal (see Table 1), establishing equivalence of the phosphorus atoms. Due to hindered rotation around the OCH_2–CH_2 bonds in L^{13}, the room-temperature ^1H NMR spectrum of this compound appears as an AA'MM'X_3 spin system (Fig. 1). Since the corresponding signal in precursor L^4 has a classical $A_2M_2X_3$ pattern, it is likely that this effect originates from strong steric interactions between propoxy and PPh_2 groups in L^{13}.

All compounds need to be handled carefully since hydrolysis of the phosphinites occurs readily with subsequent formation of $Ph_2P(O)H$ [$\delta_{^{31}P}$ signals at δ 19 and 25 due to the $Ph_2POH \rightleftharpoons Ph_2P(O)H$ equilibrium]. Synthesis of the diphosphinites described above also required the use of a strong base since weak bases, such as NEt_3, resulted in monofunctionalization. Thus, when diester L^6 was treated with 2.5 equivalents of NEt_3, monophosphinite L^{19} was formed selectively (Scheme 2). The ^1H and ^{13}C NMR spectra of L^{19} are in keeping with a cone conformation for the calixarene matrix (see Table 1). The phenolic proton of L^{19} is characterised by a singlet at δ 7.43 in the ^1H NMR spectrum (*vs.* δ 10.34 in L^1) and a ν(OH) absorption band at 3445 cm^{-1} (*vs.* 3145 cm^{-1} for L^1). In contrast to the diphosphinites described above, a coupling constant between the phosphorus atoms and the adjacent CH_2 protons of the methylene spacers in the calixarene is observed for L^{19} [J(PH) = 2 Hz]. Note, this non-zero value involves only axial hydrogen atoms, there being no splitting of the signals of the equatorial hydrogens. This coupling possibly originates from a through-space interaction. The presence of two distinct ν(C=O) absorption bands (1762 and 1734 cm^{-1}) in the IR (KBr) spectrum of L^{19} is consistent with hydrogen bonding between the OH group and one of the two ester groups.

Characteristic infrared data are given in Table 1 for the esters L^{14}–L^{18}. It is worth mentioning that, whereas the IR (KBr) spectra of the diesters L^{14}, L^{15} and L^{17} display the expected single ν(C=O) absorption band, those of the menthyl esters L^{16} and L^{18} show two distinct ν(C=O) bands. There seems no obvious explanation for this effect, although we note that crowding of the menthyl groups prevents adoption of a C_2 symmetrical structure in the solid state, possibly leading to ester groups in different spatial environments.

It should be emphasised that the reaction conditions given above lead selectively to calixarenes in the cone conformation.



L^1	$R^1 = R^2 = H$	L^{10}
L^2	$R^1 = R^2 = Me$	L^{11}
L^3	$R^1 = R^2 = Et$	L^{12}
L^4	$R^1 = R^2 = Pr^n$	L^{13}
L^5	$R^1 = R^2 = CH_2CO_2Me$	L^{14}
L^6	$R^1 = R^2 = CH_2CO_2Et$	L^{15}
L^7	$R^1 = R^2 = CH_2CO_2C_{10}H_{19}$	L^{16}
L^8	$R^1 = CH_2CO_2Et$; $R^2 = Et$	L^{17}
L^9	$R^1 = CH_2CO_2C_{10}H_{19}$; $R^2 = Et$	L^{18}

Scheme 1 (*i*) LiBu or $LiNPr^i_2$ (2 equivalents), thf; (*ii*) PPh_2Cl (2 equivalents); $C_{10}H_{19}$ = (−)-menthyl = 2-isopropyl-5-methylcyclohexyl

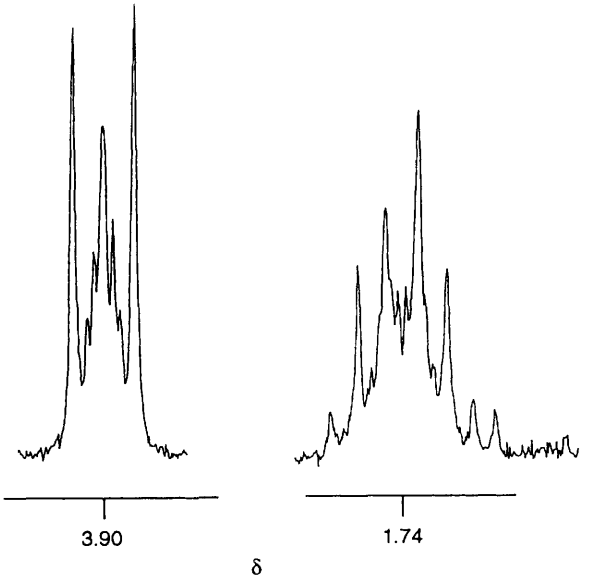
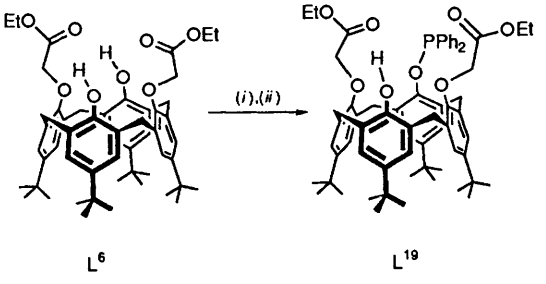


Fig. 1 Part of the ^1H NMR ($CDCl_3$) spectrum of L^{13} showing the signals of the OCH_2CH_2 hydrogen atoms

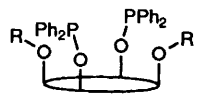
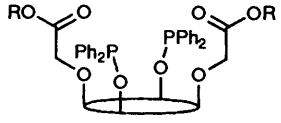
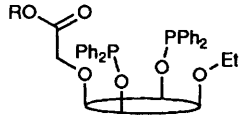
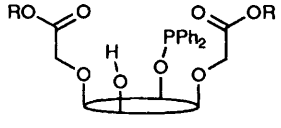


L^6 L^{19}

Scheme 2 (*i*) NEt_3 (2.5 equivalents), thf, 0 °C; (*ii*) PPh_2Cl (2 equivalents), reflux, 12 h

However, it was noted that L^{10} had a tendency to form a partial-cone conformer if the reported procedure was not done rigorously. This latter isomer could not be isolated as a pure compound. Since NMR spectroscopy was used to establish that pure cone-L^{10} does not undergo isomerisation in solution, it follows that isomerisation occurs during work-up, possibly due to complexation of lithium ions. This complexation, which involves bonding to the phenolic oxygen atoms, leads to cleavage of the hydrogen bonds responsible for maintaining L^{10} in a cone conformation. A further non-cone isomer was detected when L^2 was treated with LiBu–PPh_2Cl at 0 °C and

Table 1 Important spectroscopic data of phosphinites L^{10}–L^{20}

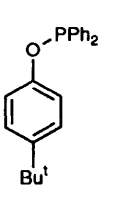
Compound[a]	R	Yield (%)	δ(¹H)[b] *m*-H	δ(¹H)[b] Calix CH_aH_b	δ(¹H)[b] Δδ	δ(¹H)[b] Bu^t	δ(¹³C)[c] Calix CH_2	δ(³¹P)[d] $OPPh_2$	IR[e]/cm^{-1}
L^{10}	H	65	6.96 6.60	3.96/3.01	0.95	1.27 0.84	32.06	124.6	3472
L^{11} 	Me	81	6.98 6.45	3.88/2.90	0.98	1.29 0.89	32.79	120.3	
L^{12}	Et	61	7.00 6.34	4.14/2.79	1.35	1.30 0.81	32.08	121.9	
L^{13}	Pr	64	7.00 6.33	4.15/2.79	1.36	1.30 0.81	32.12	122.8	
L^{14} 	Me	54	6.99 6.37	4.39/2.85	1.54	1.29 0.83	32.27	123.0	1759
L^{15}	Et	65	6.97 6.36	4.39/2.84	1.55	1.28 0.81	32.52	123.3	1762
L^{16}	(−)-menthyl	65	6.95 6.41/6.37	4.38/2.88 4.28/2.79	1.50 1.49	1.27 0.81	32.29	123.9	1758 1722
L^{17} 	Et	50	7.00 6.97 6.35/6.33	4.45/2.87 4.10/2.77	1.58 1.33	1.30* 1.28* 0.81*	32.76 31.80	123.2	1761
L^{18}	(−)-menthyl	78	7.00 6.95 6.35/6.33	4.42/2.85 4.41/2.85	1.57 1.56	1.30* 1.28* 0.81* 0.80*	32.70 32.65 32.08 32.03	123.8 123.7	1759 1717
L^{19} 	Et	71	6.95 6.91 6.72/6.67	4.54/3.21 4.16/2.94	1.33 1.22	1.23* 1.18* 0.93	31.40 31.28	122.9	3445 1762 1734
$Ph_2POC_6H_4Bu^t$-*p* L^{20}		98	7.38 (2 H)	—		1.38*	—	110.8	—

[a] The ellipsoids represent a *p-tert*-butylcalix[4]arene matrix. [b] Chemical shift in $CDCl_3$; values separated by a bar correspond to an AB system of intensity 8 H (except for L^{16}–L^{19}, 4 H). Other δ values: *m*-H, singlets of intensity 4 H (except for L^{17}–L^{20}, 2 H); Bu^t, singlets of intensity 18 H (except for the starred values, 9 H). [c] In $CDCl_3$; these signals are singlets except for L^{12}–L^{15} (doublets $^4J_{PC} \approx 4$ Hz). [d] In thf–C_6D_6 except for L^{10} and L^{12} ($CDCl_3$). [e] In KBr; values near 1700 correspond to ν(C=O), near 3400 cm^{-1} to ν(OH).

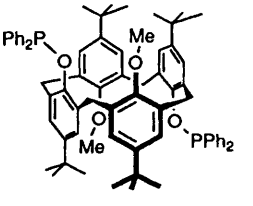
the resulting mixture heated under reflux for 2 h. Fractional precipitation of the reaction mixture with pentane yielded L^{21} (60%) as a first precipitate, followed by L^{11} (25%). The ¹H NMR spectrum of the former compound, measured at −30 °C, is characterized by a singlet for the six methoxy groups, two 1 : 1 singlets for the Bu^t groups and two distinct CH_AH_B spin systems of the calixarene methylene spacers (calix CH_2). The ^{31}P-{^1H} NMR spectrum of L^{21} shows a single signal at δ 113.6. These data are consistent with a 1,2-alternate conformation, a conclusion also confirmed by a preliminary X-ray diffraction study (see Experimental section).

Dynamic processes for compounds L^{11} and L^{21}

Because room-temperature signals of the ¹H NMR ($CDCl_3$) spectrum of L^{11} are relatively broad, a variable-temperature study was undertaken for this compound (Fig. 2). On lowering the temperature, the signals gradually broaden and coalesce at *ca.* 260 K. At still lower temperatures, the signals sharpen and two distinct sets of signals appear. One of these shows patterns typical for a cone conformer [spectrum at 210 K: δ 6.99 (s) and 6.29 (s) (8 H, aryl H), 3.88, 2.77 (calix CH_2, AB spin system), 3.75 (6 H, OMe)] whereas the other is characterized by three *m*-H singlets at, respectively, δ 6.93, 6.78 and 6.39 having relative intensity 1 : 2 : 1, and two distinct MeO signals at δ 3.24 and 2.93 (1 : 1). These latter data are consistent with a partial cone conformation (Scheme 3). The cone : partial cone ratio is considered 2.7 at 210 K. A similar fast exchange between cone and partial cone conformers has been reported recently for an analogue of L^{11} (ref. 11) (containing Et groups instead of PPh_2). In this latter case, however, the equilibrium lies on the side of the partial-cone isomer (cone : partial-cone ratio = 1 : 4 at −30 °C in $CDCl_3$). The preference of L^{11} for a cone *vs.* a partial-cone conformation (the partial cone is usually regarded as the most stable conformer) arises from high steric repulsions



L^{20}



L^{21}

between the phosphino groups and the flipped aryl ring generated in the partial-cone isomer. The calculated energy barrier for the exchange process is 51.8 kJ mol^{-1} at 233 K. This value is close to that recently reported for the cone to partial-cone exchange of the tetramethoxy derivative of L^1 (65.2 kJ mol^{-1} at 270 K).[12] Note for this latter compound, unlike L^{11}, all four possible conformations are detected at equilibrium.

Compound L^{21} also displays dynamic behaviour in solution as shown by a variable-temperature NMR study ($CDCl_3$, 200 MHz, Fig. 3). Thus, signals of the two calix CH_AH_B systems broaden on raising the temperature, coalesce respectively at 307 ± 1 and 335 ± 5 K and finally converge to a single averaged AB spin system. These observations, which are reversible, demonstrate that a rapid interconversion occurs between two opposite 1,2-alternate conformers. In view of recent studies on interconverting methoxy-substituted conformers,[13] it is likely that this homomerization (Scheme 4) proceeds *via* stepwise flipping of the two methoxy-substituted aryl rings. Flipping of the phosphino groups can be ruled out on steric grounds.

Co-ordination chemistry of calixarene phosphinites

A few phosphinito calix[4]arenes have recently been used as transition-metal ligands. The reported studies mainly focus on

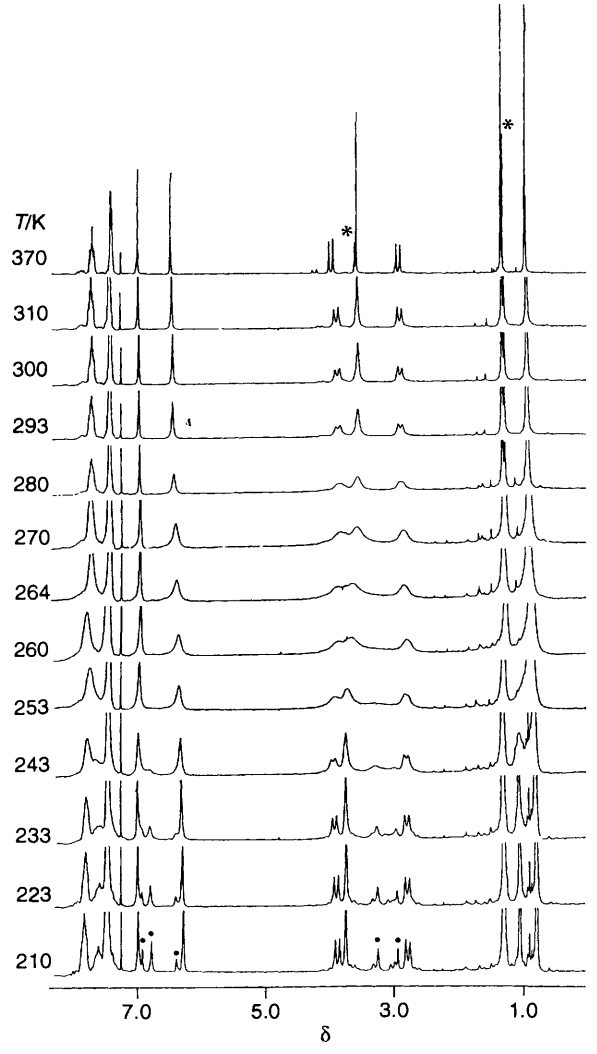
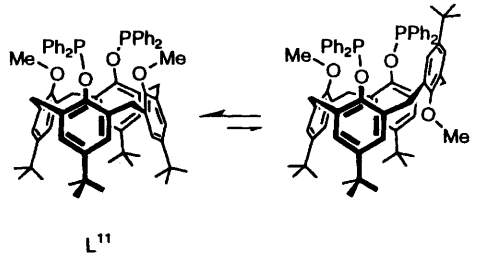


Fig. 2 Variable-temperature ^{1}H NMR spectrum of L^{11} ($CDCl_3$). The signals marked with a dot correspond to the partial-cone conformer. The starred signals are due to an unidentified impurity which appears after prolonged heating



L^{11}

Scheme 3 Dynamic behaviour of **11**

tetrasubstituted calixarene phosphinites (complexes obtained from ligands L^B,[5a,7c] L^{C} [6a] and L^{D}[7a]); only one work describes the formation of a metal complex from a diphosphinite, namely a copper complex containing L^{13}.[7b] The potential of these phosphinites to act as chelators *via* two distally located phosphorus atoms, leading to a fish-net structure, has been proposed but hard proof exists only for the copper complex $[(Cu_3Cl_4L^C)_2]$ prepared by Floriani *et al.*[5a] The present study was undertaken in order to get some insight into the parameters which govern the complexation mode of 1,3-diphosphinooxycalix[4]arenes toward palladium(II), platinum(II) and rhodium(I). Three distinct types of binding were, *a priori*, expected for these diphosphinites, *cis*- or *trans*-chelating and the (η^1-*P*, η^1-*P*) bridging mode. The co-ordinative properties of monophosphinite L^{19} were first investigated.

Reaction of 2 equivalents of monophosphinite L^{19} with

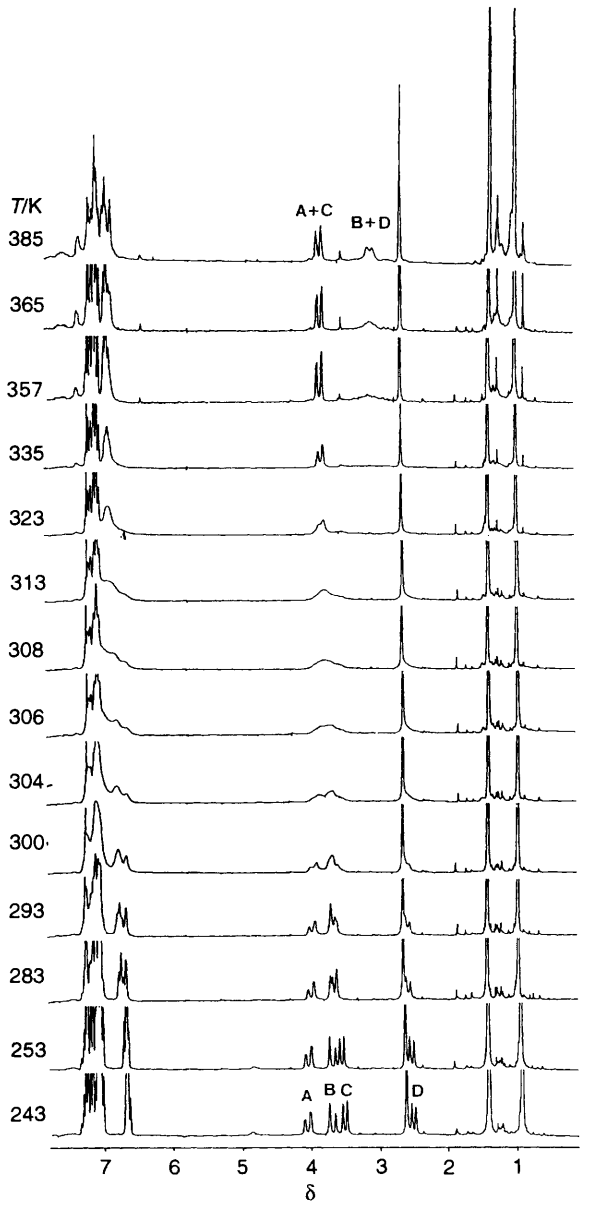
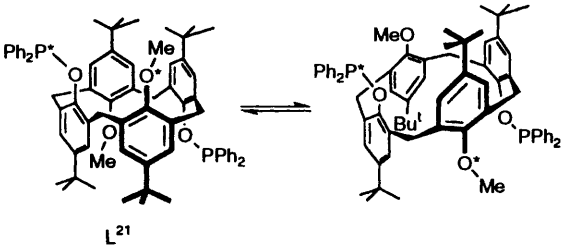


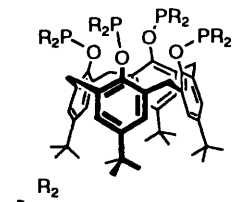
Fig. 3 Variable-temperature spectrum of L^{21} ($CDCl_3$). The letters A and B represent calix CH_2 (*anti*) hydrogen atoms; C and D are for calix CH_2 (*syn*) hydrogen atoms



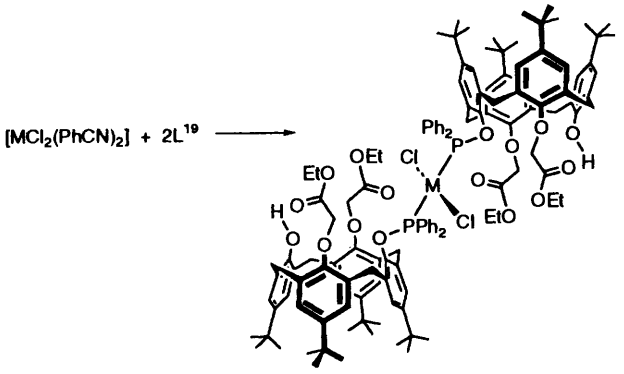
L^{21}

Scheme 4 Dynamic behaviour of **21**

$[PtCl_2(PhCN)_2]$ in tetrahydrofuran (thf) afforded *trans*-$[PtCl_2L^{19}{}_2]$ **1** in 78% yield (Scheme 5). The *trans* arrangement of the chloride ligands was deduced from the presence of a single ν(Pt–Cl) absorption band in the far IR region (349 cm^{-1}). Selective formation of a *trans* complex may be due to the sterically demanding calixarene substituent. This argument is supported by the fact that, under similar experimental conditions, the less bulky phosphinite $Ph_2POC_6H_4Bu^t$-*p* L^{20} leads to the *cis*-dichloro complex *cis*-$[PtCl_2L^{20}{}_2]$ **3** [two ν(Pt–Cl) bands: 324 and 298 cm^{-1}]. It is noteworthy that, as might be expected for platinum–phosphine complexes,[14] the

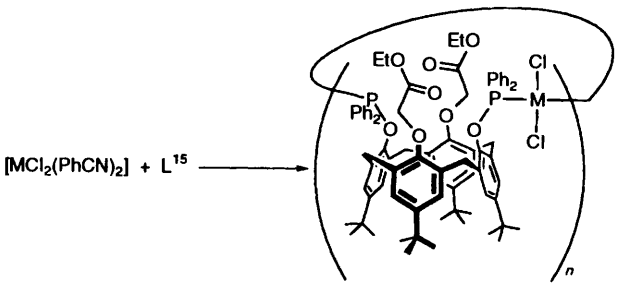


L^B $R_2 = Ph_2$
L^C $N(Bu^t)CH_2CH_2O$
L^D $N(Me)C(O)N(Me)C(O)N(Me)$



M
1 Pt
2 Pd

Scheme 5



M
4 Pt
5 Pd

Scheme 6

J(P–Pt) coupling constant for the *trans* complex **1** (3041 Hz) is smaller than that observed for the *cis*-complex **3** (4172 Hz). In the ^{1}H NMR spectrum, one of the Bu^t groups of **1** appears to be somewhat shielded (δ 0.55) relative to the Bu^t groups in free diphosphinites (see Table 1), suggesting that this group protrudes into the calixarene cavity and hence becomes shielded by two neighbouring aryl rings. Molecular models show that this effect is likely to arise from steric interactions between the Bu^t groups connected to a phosphinite moiety and the PPh_2 group in a *trans* position.

The related palladium complex **2** was prepared from $[PdCl_2(PhCN)_2]$. The *trans* stereochemistry of this complex was inferred from the far-IR spectrum [ν(Pd–Cl) 361 cm^{-1}] and preliminary X-ray diffraction results (see Experimental section). Note, for both complexes **1** and **2** the IR (KBr) spectrum displays two absorption bands in the ester region (see Table 1). As for L^{19}, this observation suggests hydrogen bonding of one of the ester groups with the neighbouring hydroxy group.

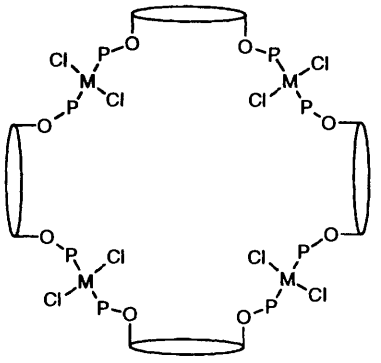
Reaction of 2 equivalents of the mixed diphosphinite-diester L^{15} with $[PtCl_2(PhCN)_2]$ in thf (Scheme 6) afforded, after precipitation with pentane, a white powder which, on the basis of microanalytical data, could be formulated as $[(PtCl_2L^{15})_n]$ **4** (see Experimental section). The tetrameric nature of this compound was deduced from molecular weight determination experiments (vapour-phase osmometry in CH_2Cl_2 {M(found) = 5445 *vs.* 1455.47 for monomeric $[PtCl_2L^{15}]$}). The presence of a single ν(Pt–Cl) absorption band in the far-IR spectrum (346 cm^{-1}) indicates a *trans* arrangement of the chloride ligands around each metal atom. In the ^{31}P NMR spectrum, the phosphorus atoms appear as a broad ($\Delta\nu_{\frac{1}{2}}$ = 20 Hz) signal at δ 101.8 with a J(P–Pt) (3032 Hz) coupling constant in keeping with the proposed *trans* stereochemistry. The osmometric data, which do not strictly prove the formation of a *single* cyclic oligomer in the reaction in Scheme 6, demonstrate the tendency of L^{15} to behave as a bridging ligand. The formation of a single cyclic tetramer is, however, likely in view of results found with other diphosphinites (see below). The room-temperature ^{1}H NMR spectrum displays broad signals, indicating fluxional behaviour. The capacity of diphosphinite L^{15} to generate oligomers is reminiscent of the structure of $[(Cu_3Cl_4L^C)_2]$ (see above), a complex in which L^C acts as a bridging ligand *via* two distal P^{III} donors.

For the related palladium complex $[(PdCl_2L^{15})_n]$ **5** obtained from $[PdCl_2(PhCN)_2]$, osmometric measurements also indicate the formation of a tetramer {M(found) = 5400 *vs.* 1367 for monomeric $[PdCl_2L^{15}]$}. As shown by the far-IR spectrum [ν(Pd–Cl) 363 cm^{-1}], the chloride ligands are in a *trans* arrangement. For both $[(trans\text{-}PtCl_2L^{15})_4]$ **4** and $[(trans\text{-}PdCl_2L^{15})_4]$ **5**, the IR (KBr) spectrum shows two distinct $\nu(C{=}O)_{ester}$ bands. Since hydrogen bonding can be ruled out for these complexes with an A-type structure, it is likely that the presence of two ester bands is due to solid-state effects.

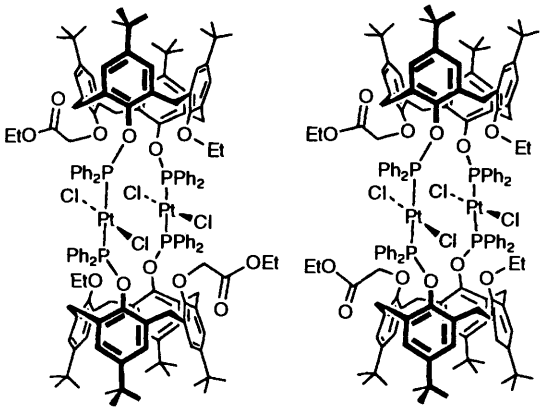
The formation of analogous tetranuclear assemblies was also achieved by treating $[PtCl_2(PhCN)_2]$ with other symmetrically substituted diphosphinites, namely L^{12} and L^{16}. For the resultant complexes, $[(trans\text{-}PtCl_2L^{12})_4]$ **6** and $[(trans\text{-}PtCl_2L^{16})_4]$ **7**, the *trans* stereochemistry around the metal atoms was deduced from the far-IR and ^{31}P NMR spectra (see Experimental section).

The propensity of 1,3-diphosphinooxycalix[4]arenes to behave as bridging ligands capable of forming oligomeric complexes was also verified with the unsymmetrically substituted diphosphinites L^{17} and L^{18}. Thus, when L^{17} was treated with $[PtCl_2(PhCN)_2]$ in thf, a pale yellow compound, analysed as $[(PtCl_2L^{17})_n]$ was formed. In this case, however, the molecular-weight determination (vapour phase osmometry, CH_2Cl_2) indicates the formation of a dimer {M(found) = 2920 *vs.* 1397 for monomeric $[PtCl_2L^{17}]$}. The *trans* arrangement of the chloride ligands was inferred from the far-IR spectrum [ν(Pt–Cl) 346 cm^{-1}] and from the J(P–Pt) coupling constant (3026 Hz). As for the oligomers described above, the room-temperature ^{1}H NMR spectrum of $[(trans\text{-}PtCl_2L^{17})_2]$ **8** is broad, presumably due to fluxional behaviour of the metallomacrocycle. The spectroscopic data did not allow distinction between the two possible positional isomers drawn for **8** in Scheme 7.

The reaction of L^{18} with $[PdCl_2(PhCN)_2]$ gave $[(trans\text{-}PdCl_2L^{18})_2]$ **9** (see Experimental section) and hence confirms the tendency of unsymmetrically substituted diphosphinites to form smaller oligomers with Pt^{II} and Pd^{II} than the symmetrically substituted calixarenes L^{12}, L^{15} and L^{16}. It is noteworthy that for the reactions described in this section, high dilution techniques did not lead to formation of monomeric species. The fact that dimers are formed with L^{17} and L^{18} and tetramers with L^{12}, L^{15} and L^{16} likely originates from subtle differences in the calixarene shapes in the two types of ligand. It is well known that in calix[4]arenes the orientation of each individual aryl ring influences that of the others. In the non-symmetric compound L^{17}, the two aryl rings bearing, respectively, ester and Et groups are possibly oriented unsymmetrically with respect to the calixarene axis, forcing the



A

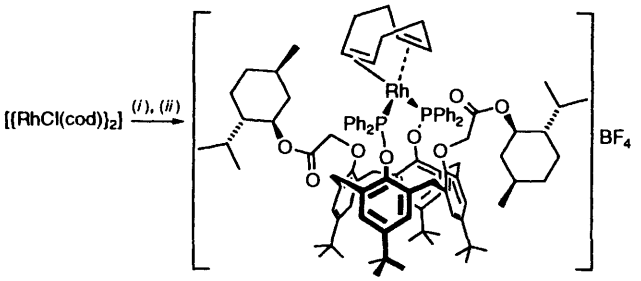


Scheme 7 Two possible isomeric forms of [(*trans*-$PtCl_2L^{17}$)$_2$] **8**

phosphorus atoms to come closer together than in the symmetrical structures and, therefore, allowing the build-up of a smaller metallomacrocycle.

In contrast to the results found with $[MCl_2(PhCN)_2]$ complexes (M = Pt or Pd), chelating behaviour was observed when the chiral diphosphinite L^{16} was treated with $[Rh(cod)(thf)_2]^+$ (cod = cycloocta-1,5-diene). This reaction resulted in the formation of complex **10** (Scheme 8), the monomeric nature of which was inferred from molecular weight determinations [osmometry, CH_2Cl_2, found (Calc.) *M*, 1760 (1708)]. As shown by the presence of a doublet at δ 131.3 (J_{PRh} = 175 Hz) in the ^{31}P NMR spectrum, both phosphorus atoms are involved in co-ordination to the rhodium atom. The fact that L^{16} displays chelating behaviour towards rhodium(I) implies a correct overlap of the phosphorus lone pairs and d orbitals of the metal plane. One important parameter which may control this fit is the phosphorus–phosphorus separation in the ligand. The presence of bulky ester substituents in L^{16}, and their possible repulsive interaction with the Rh(cod) fragment, is expected to orient the aryl(ester) groups in a parallel fashion. This, in turn, might result in flipping of the other two aryl rings so as to bring the P atoms closer together, and hence favour *cis* chelation.

In summary, this study describes the high-yield synthesis of a variety of calix[4]arene-derived mono- and di-phosphinites. Complexation studies establish that, with the *bulky* monophosphinite ligand L^{19}, *trans*-$[MCl_2L^{19}{}_2]$ complexes (M = Pd or Pt) are selectively formed. In contrast to results found for some tetraphosphinites,[7a] the cone diphosphinites used for this study show a marked tendency to behave as bridging ligands toward palladium or platinum, thus forming with these metals di- or tetra-metallic assemblies built around metal centres having a *trans* stereochemistry. The degree of oligomerization of these complexes appears to be controlled by the shape of the calixarene matrix, itself being determined by the nature of any other substituents. With the Rh(cod) fragment, formation of a



10

Scheme 8 (*i*) $AgBF_4$ (2 equivalents)–thf; (*ii*) L^{16} (2 equivalents)

cis-chelate complex has been achieved in one case, leading to the formation of a semiencapsulated transition-metal ion, and thus illustrating the co-ordination versatility of calixarene-diphosphinites. Further studies will be aimed at exploiting the hemispherical environment that such diphosphinites may generate around a transition metal, in particular for new chiral hydrogenation catalysts.

Experimental

Reagents and physical measurements

All manipulations involving phosphinites were performed in Schlenk-type flasks under argon. Solvents were dried by conventional methods and distilled immediately prior to use. Triethylamine was dried over KOH and distilled under argon. Deuteriochloroform was passed through a 5 cm thick alumina column and stored under argon over molecular sieves (0.4 nm). IR spectra were recorded on an IFS 25 Bruker spectrometer (4000–400 cm^{-1}) and a Bruker FIR spectrometer (500–90 cm^{-1}). The ^1H, ^{31}P-{^1H} and ^{13}C-{^1H} NMR spectra were recorded by using a FT Bruker WP-200 SY instrument. The ^1H NMR data were referenced to residual protiated solvents (δ 7.25 for $CDCl_3$), ^{13}C chemicals shifts are reported relative to deuteriated solvents (δ 77.0 for $CDCl_3$) and the ^{31}P NMR data are given relative to external H_3PO_4. The mass spectra of compounds L^8, L^9 and L^{21} were recorded on a TSQ-70 Finnigan-Mat spectrometer and those of compounds L^7, L^{10}–L^{20} and **1**–**3** on a ZAB HF VG Analytical using *m*-nitrobenzyl alcohol or tetraglyme (2,5,8,11,14-pentaoxapentadecane) as a matrix. The molecular weight determination by vapour pressure osmometry were performed by Analytische Laboratorien Malissa & Reuter, D-51647 Gummersbach, Germany. The compounds *p-tert*-butylcalix[4]arene (L^1),[15] 5,11,17,23-tetra-*tert*-butyl-25,27-dihydroxy-26,28-dimethoxycalix[4]-arene (L^2),[16] 5,11,17,23-tetra-*tert*-butyl-25,27-diethoxy-26,28-dihydroxycalix[4]arene (L^3),[17] 5,11,17,23-tetra-*tert*-butyl-25,27-dihydroxy-26,28-dipropoxycalix[4]arene (L^4),[18] 5,11,17,23-tetra-*tert*-butyl-25,27-diethoxycarbonylmethoxy-26,28-dihydroxycalix[4]arene (L^6),[19] 5,11,17,23-tetra-*tert*-butyl-25-ethoxy-26,27,28-trihydroxycalix[4]arene,[20] $[PdCl_2(PhCN)_2]$,[21] $[PtCl_2(PhCN)_2]$[21] and $[\{RhCl(cod)\}_2]$[22] were prepared by using literature procedures. The $LiBu^n$ solutions were titrated according to ref. 23.

Preparation of dihydroxyprecursors L^5 and L^7–L^9

5,11,17,23-Tetra-*tert*-butyl-25,27-dihydroxy-26,28-di(methoxycarbonylmethoxy)calix[4]arene L^5. A suspension of *p-tert*-butylcalix[4]arene (30.00 g, 46.2 mmol) and K_2CO_3 (7.03 g, 51.0 mmol) in acetone (1200 cm^3) was stirred overnight at room temperature. Methyl bromoacetate (15.35 g, *ca.* 100 mmol, *ca.* 9.5 cm^3) was then added and the mixture was refluxed for 10 h. After cooling and filtration, the solvent was evaporated to dryness. The residue was partitioned between

water (300 cm^3) and CH_2Cl_2 (500 cm^3). The aqueous phase was neutralized with a 1 mol dm^{-3} HCl solution. The organic layer was separated and the aqueous phase extracted with CH_2Cl_2 (2 × 100 cm^3). The combined organic extracts were dried with $MgSO_4$. Recrystallization from CH_2Cl_2–hexane yielded L^5 as a pure white solid [R_f = 0.36 (acetone–hexane, 3:7 v/v)]. Yield 29.50 g, 80%, m.p. 189–194 °C (Found: C, 75.65; H, 7.95. $C_{50}H_{64}O_8$ requires C, 75.75; H, 8.15%; M_r = 793.06); $\tilde{\nu}_{max}/cm^{-1}$ (KBr), 3442m (OH) and 1760s (CO). NMR ($CDCl_3$): ^1H δ 7.05 (s, 2 H, OH), 7.03 (s, 4 H, *m*-H), 6.83 (s, 4 H, *m*-H), 4.75 (s, 4 H, OCH_2CO_2Me), 4.46 and 3.33 (AB spin system, 8 H, calix CH_2, J = 13.2 Hz), 3.85 (s, 6 H, OCH_3), 1.27 (s, 18 H, Bu^t) and 0.99 (s, 18 H, Bu^t); ^{13}C-{^1H} δ 169.61 (s, C=O), 150.64, 150.21, 147.11, 141.52, 132.53 and 128.03 (6s, aromatic C_{quat}), 125.75 and 125.06 (2 × s, aromatic CH), 72.17 (s, OCH_2CO_2Me), 51.99 (s, OCH_3), 33.91 and 33.80 [2 × s, $C(CH_3)_3$], 31.82 (s, calix CH_2), 31.64 and 31.03 [2 × s, $C(CH_3)_3$].

(−)-5,11,17,23-Tetra-*tert*-butyl-25,27-dihydroxy-26,28-bis-[(1*R*,2*S*,5*R*)menthyloxycarbonylmethoxy]calix[4]arene L[7]. A suspension of *p*-*tert*-butylcalix[4]arene L^1 (13.000 g, 20.03 mmol) and K_2CO_3 (3.045 g, 22.032 mmol) in acetone (500 cm^3) was stirred under argon overnight at room temperature. (−)-(1*R*,2*S*,5*R*)-Menthyl bromoacetate (12.200 g, 56.17 mmol) was then added and the mixture was stirred under reflux for 30 h. After filtration, the solvent was evaporated to dryness and the residue dissolved in CH_2Cl_2 (300 cm^3). The organic layer was washed successively with a saturated NH_4Cl solution (250 cm^3), with water (250 cm^3) and then dried with $MgSO_4$. After filtration and concentration, the product was purified by flash chromatography over silica gel 60 (230–400 mesh) with hexane–CH_2Cl_2 (7:3, v/v) as eluent [R_f = 0.51 (hexane–CH_2Cl_2, 1:4 v/v)] (14.6 g, 70%), m.p. 92–96 °C, α −44° (589 nm, 20 °C, c = 2 g per 100 cm^3, toluene) (Found: C, 78.45; H, 9.50. $C_{68}H_{96}O_8$ requires C, 78.40; H, 9.30%; M_r = 1041.52); $\tilde{\nu}_{max}/cm^{-1}$ (KBr) 3472s (OH), 1757s and 1738s (C=O). NMR ($CDCl_3$): ^1H, δ 7.05 (s, 4 H, *m*-H), 6.94 (s, 2 H, OH), 6.78 (s, 4 H, *m*-H), 4.84 (dt, 2 H, OCH of menthyl, ^3J = 4.4, ^3J = 10.8), 4.72 (br s, 4 H, OCH_2), 4.51 and 3.33 (AB spin system, 4 H, calix CH_2, J = 13.2), 4.48 and 3.33 (AB spin system, 4 H, calix CH_2, J = 13.2 Hz), 2.14–0.76 (36 H, menthyl), 1.30 (s, 18 H, Bu^t) and 0.95 (s, 18 H, Bu^t); ^{13}C-{^1H}, δ 168.83 (s, C=O), 150.95, 150.46, 146.81, 141.23, 132.30, 132.19, 127.90 and 127.83 (8s, aromatic C_{quat}), 125.64 and 125.00 (2 × s, aromatic CH), 75.35 (s, OCH of $CO_2C_{10}H_{19}$), 72.48 (s, OCH_2), 46.82, 31.41 and 26.10 (3s, CH of $CO_2C_{10}H_{19}$), 40.75, 34.12 and 23.32 (3s, CH_2 of menthyl), 33.83 and 33.77 [2 × s, $C(CH_3)_3$], 31.81 (s, calix CH_2), 31.69 and 30.99 [2 × s, $C(CH_3)_3$], 21.99, 20.78 and 16.28 (3 × s, CH_3 of menthyl). Chemical ionization (CI) mass spectrum: m/z 1040 (31%) (M^+).

5,11,17,23-Tetra-*tert*-butyl-25-ethoxy-27-ethoxycarbonylmethoxy-26,28-dihydroxycalix[4]arene L[8]. A solution of 5,11,17,23-tetra-*tert*-butyl-25-ethoxy-26,27,28-trihydroxycalix[4]arene (8.124 g, 12.00 mmol) in acetonitrile (360 cm^3) was treated with K_2CO_3 (0.945 g, 6.84 mmol). After stirring for 0.5 h, ethyl bromoacetate (2.338 g, 14.00 mmol, *ca.* 1.6 cm^3) was added and the mixture was refluxed for 15 h. After filtration, the solvent was removed *in vacuo*. The product was recrystallized from CH_2Cl_2–EtOH [white microcrystalline powder, R_f = 0.43 (ethyl acetate–hexane, 1:9 v/v)] (7.500 g, 82%), m.p. 180–182 °C (Found: C, 78.95; H, 8.50. $C_{50}H_{66}O_6$ requires C, 78.70; H, 8.70%; M_r = 763.08); $\tilde{\nu}_{max}/cm^{-1}$ (KBr) 3458 (br) (OH) and 1756s (C=O). NMR ($CDCl_3$): ^1H, δ 7.24 (s, 2 H, OH), 7.05 (s, 4 H, *m*-H of aryl–OH), 6.83 (s, 2 H, *m*-H), 6.75 (s, 2 H, *m*-H), 4.68 (s, 2 H, OCH_2CO_2), 4.44 and 3.32 (AB spin system, 4 H, calix CH_2, J = 13.1), 4.32 (q, 2 H, CH_2CH_3, ^3J = 7.1), 4.28 and 3.32 (AB spin system, 4 H, calix CH_2, J = 13.1), 4.10 (q, 2 H, CH_2CH_3, ^3J = 7.1), 1.60 (t, 3 H, CH_2CH_3, ^3J = 7.1), 1.36 (t, 3 H, CH_2CH_3, ^3J = 7.1 Hz), 1.29 (s, 18 H, Bu^t of aryl-OH), 0.99 (s, 9 H, Bu^t) and 0.92 (s, 9 H, Bu^t); ^{13}C-{^1H}, δ 169.17 (s, C=O), 150.87–127.87 (9 × s, aromatic C_{quat}), 125.76, 125.53, 125.23 and 125.06 (4 × s, aromatic CH), 72.60 and 72.14 (2 × s, OCH_2, not assigned), 61.26 (s, $CO_2CH_2CH_3$), 33.99 and 33.90 [2 × s, $C(CH_3)_3$], 31.93 and 31.86 (2 × s, bridge CH_2), 31.77, 31.13 and 31.06 [3 × s, $C(CH_3)_3$], 15.43 (s, CH_2CH_3) and 14.25 (s, CH_2CH_3). FAB mass spectrum: m/z 762 (100%) (M^+).

(−)-5,11,17,23-Tetra-*tert*-butyl-25-ethoxy-26,28-dihydroxy-27-[(1*R*,2*S*,5*R*)menthyloxycarbonylmethoxy]calix[4]arene L[9]. Potassium carbonate (1.9 g, 13.75 mmol) was added to a suspension of 5,11,17,23-tetra-*tert*-butyl-25-ethoxy-26,27,28-trihydroxycalix[4]arene (16.98 g, 25.00 mmol) in acetonitrile (750 cm^3). After stirring for 1 h, (−)-(1*R*,2*S*,5*R*)-menthyl bromoacetate (7.17 g, 25.8 mmol) was added and the mixture refluxed for 12 h. After filtration, the solvent was removed *in vacuo*. The residue was purified by flash chromatography over silica gel 60 (230–400 mesh) with hexane–Et_2O (94:6, v/v), R_f = 0.23 (12.30 g, 56%), m.p. 80 and 195 °C (the observation of two melting points is due to a new phase appearing at *ca.* 148 °C), α −16.9° (589 nm, 20 °C, c = 5 g per 100 cm^3, hexane) (Found: C, 80.00; H, 9.00. $C_{58}H_{80}O_6$ requires C, 79.78; H, 9.25%; M_r = 873.28); $\tilde{\nu}_{max}/cm^{-1}$ (KBr) 3462m (OH), 1757s and 1735s (C=O). NMR ($CDCl_3$): ^1H, δ 7.28 (s, 1 H, OH), 7.25 (s, 1 H, OH), 7.04 (br s, 4 H, *m*-H of aryl–OH), 6.84 (s, 2 H, *m*-H), 6.76 (s, 2 H, *m*-H), 4.88 (dt, 1 H, OCH of menthyl, ^3J = 4.4, ^3J = 10.8), 4.76 and 4.66 (AB spin system, 2 H, OCH_2CO_2, J = 15.8), 4.48 and 3.32 (AB spin system, 2 H, calix CH_2, J = 13.1), 4.46 and 3.32 (AB spin system, 2 H, calix CH_2, J = 13.1), 4.30 and 3.32 (AB spin system, 2 H, calix CH_2, J = 13.0), 4.28 and 3.32 (AB spin system, 2 H, calix CH_2, J = 13.0), 4.10 (q, 2 H, OCH_2CH_3, ^3J = 7.1), 0.77–2.13 (18 H, menthyl), 1.60 (t, 3 H, OCH_2CH_3, ^3J = 7.1 Hz), 1.29 (s, 18 H, Bu^t of aryl–OH), 1.00 (s, 9 H, Bu^t) and 0.94 (s, 9 H, Bu^t); ^{13}C-{^1H}, δ 167.69 (s, C=O), 149.93–126.73 (12 s, aromatic C_{quat}), 124.56, 124.49, 124.34, 124.29, 124.02 and 123.84 (6 × s, aromatic CH), 74.30 (s, OCH of menthyl), 71.44 and 70.87 (2 × s, OCH_2, no exact assignment), 45.86, 30.35 and 25.20 (3 × s, CH of menthyl), 39.74, 33.12 and 22.44 (3 × s, CH_2 of menthyl), 32.80 and 32.69 [3 × s, $C(CH_3)_3$], 30.74 (s, calix CH_2), 30.58, 29.95 and 29.86 [3 × s, $C(CH_3)_3$], 20.83, 19.61, 15.28 and 14.27 (4 × s, CH_3). FAB mass spectrum: m/z 872 (100%) (M^+).

Syntheses of ligands and complexes

5,11,17,23-Tetra-*tert*-butyl-25,27-bis(diphenylphosphinooxy)-26,28-dihydroxycalix[4]arene L[10]. A hexane solution of $LiBu^n$ (5.65 cm^3, 1.53 mol dm^{-3}, 8.64 mmol) was added dropwise to a suspension of *p*-*tert*-butylcalix[4]arene (2.597 g, 4.00 mmol) in thf (80 cm^3) at room temperature. After 0.5 h, a solution of PPh_2Cl (1.892 g, 8.58 mmol) in thf (30 cm^3) was added slowly to the mixture maintained at 0 °C. After stirring for 20 min, the solvent was evaporated to dryness. The residue was treated first with toluene (50 cm^3), then with pentane (50 cm^3). The resulting mixture was filtered over Celite and the filtered solution was concentrated to *ca.* 5 cm^3. After addition of pentane (150 cm^3) and cooling at −20 °C, the product precipitated as a white powder [R_f = 0.22 (thf–pentane, 4:6 v/v)] (2.650 g, 65%), m.p. 220–230 °C. This work up had to be done diligently in order to avoid isomerization of the cone isomer into the partial cone isomer [R_f = 0.86 (thf–pentane, 2:3 v/v); the latter isomer which was not isolated is characterised by (*a*) three Bu^t signals (intensity 2:1:1) at δ 0.79, 0.91 and 1.28 respectively; (*b*) two calix CH_AH_B signals with δ_A 2.56, δ_B 3.74 and $\delta_{A'}$ 3.24, $\delta_{B'}$ 3.67] (Found: C, 80.25; H, 7.35. $C_{68}H_{74}O_4P_2$ requires C, 80.30; H, 7.35%; M_r = 1017.29); $\tilde{\nu}_{max}/cm^{-1}$ (KBr) 3472 (br) (OH). NMR ($CDCl_3$): ^1H, δ 7.93–7.92 and 7.40–7.37 (20 H, PPh_2), 6.96 (s, 4 H, *m*-H), 6.60

(s, 4 H, *m*-H), 6.23 (s, 2 H, OH), 3.96 and 3.01 (AB spin system, 8 H, calix CH_2, J = 13.6 Hz), 1.27 (s, 18 H, Bu^t), 0.84 (s, 18 H, Bu^t); ^{13}C-{^{1}H}, δ 150.63–124.95 (aromatic C_{quat}), 33.86 and 33.79 [2 × s, $C(CH_3)_3$], 32.06 (s, calix CH_2), 31.73 and 30.97 [2 × s, $C(CH_3)_3$]; ^{31}P-{^{1}H}, δ 124.6 (s, $OPPh_2$). CI mass spectrum: m/z 1017 (19%) (M + H$^+$).

5,11,17,23-Tetra-*tert*-butyl-25,27-bis(diphenylphosphinooxy)-26,28-dimethoxycalix[4]arene L[11] (cone). A hexane solution of LiBu^n (7.2 cm^3, 1.65 mol dm^{-3}, 11.88 mmol) was added dropwise to a solution of 5,11,17,23-tetra-*tert*-butyl-25,27-dihydroxy-26,28-dimethoxycalix[4]arene L[2] (4.000 g, 5.91 mmol) in thf (150 cm^3) at −78 °C. After 1 h stirring, a cold (−78 °C) solution of PPh_2Cl (2.610 g, 11.83 mmol) in thf (20 cm^3) was added slowly. The mixture was maintained at −78 °C for 2 h. Then the solvents were removed *in vacuo*. The residue was treated with toluene (100 cm^3) and the resulting suspension was filtered through a glass frit. The filtrate was concentrated under reduced pressure to *ca.* 10 cm^3. Addition of pentane (50 cm^3) afforded a white precipitate which was shown to be analytically pure [R_f = 0.60 (hexane–ethyl acetate, 94:6 v/v)] (5.00 g, 81%), m.p. 255–260 °C (Found: C, 80.25; H, 7.50. $C_{70}H_{78}O_4P_2$ requires C, 80.45; H, 7.50%; M_r = 1045.34). NMR: ^{1}H ($CDCl_3$, 298 K), δ 7.76–7.68 and 7.46–7.43 (20 H, PPh_2), 6.98 (s, 4 H, *m*-H), 6.45 (br s, 4 H, *m*-H), 3.88 and 2.90 (br, AB spin system, 8 H, calix CH_2, J = 13.0 Hz), 3.56 (br s, 6 H, OCH_3), 1.29 (s, 18 H, Bu^t) and 0.89 (s, 18 H, Bu^t); ^{13}C-{^{1}H} ($CDCl_3$, 298 K), δ 155.41–131.16 (aromatic C_{quat}), 132.37, 131.90, 129.85, 128.25, 128.11, 125.86 and 124.92 (aromatic CH), 60.56 (br s, OCH_3), 34.06 and 33.59 [2 × s, $C(CH_3)_3$], 32.79 (br s, calix CH_2), 31.69 and 31.20 [2 × s, $C(CH_3)_3$]; ^{31}P-{^{1}H} (thf–C_6D_6), δ 120.3 (s, $OPPh_2$). CI mass spectrum: m/z 1045 (6%) (M + H$^+$).

5,11,17,23-Tetra-*tert*-butyl-25,27-bis(diphenylphosphinooxy)-26,28-diethoxycalix[4]arene L[12]. A hexane solution of LiBu^n (6.6 cm^3, 1.51 mol dm^{-3}, 10.0 mmol) was added dropwise to a stirred solution of 5,11,17,23-tetra-*tert*-butyl-25,27-diethoxy-26,28-dihydroxycalix[4]arene L[3] (3.525 g, 5.0 mmol) in thf (110 cm^3) at −78 °C. The solution was stirred for 1 h. Then a pre-cooled (−50 °C) solution of PPh_2Cl (2.210 g, 10.0 mmol) in thf (30 cm^3) was added dropwise and the mixture was left at −78 °C for 2 h. The solvents were removed *in vacuo* and to the residue obtained was added toluene–pentane (100 cm^3, 1:1 v/v). The suspension was stirred at 0 °C for 1 h and filtered through Celite in order to remove LiCl. The filtrate and toluene washings of the Celite were combined and evaporated to dryness. The brownish solid was treated with pentane (70 cm^3) and the resulting suspension was filtered. The filtered white solid was washed with pentane and dried *in vacuo* overnight. [R_f = 0.33 (hexane–ethyl acetate, 96:4 v/v)] (3.33 g, 61%), m.p. 255–257 °C (Found: C, 80.45; H, 7.60. $C_{72}H_{82}O_4P_2$ requires C, 80.55; H, 7.70%; M_r = 1073.40). NMR ($CDCl_3$): ^{1}H, δ 7.76–7.68 and 7.43–7.38 (20 H, PPh_2), 7.00 (s, 4 H, *m*-H), 6.34 (s, 4 H, *m*-H), 4.14 and 2.79 (AB spin system, 8 H, calix CH_2, J = 13.0), 4.03 (q, 4 H, OCH_2, ^3J = 7.1), 1.30 (s, 18 H, Bu^t), 1.18 (t, 6 H, OCH_2CH_3, ^3J = 7.1 Hz) and 0.81 (s, 18 H, Bu^t); ^{13}C-{^{1}H}, δ 153.08–133.40 (aromatic C_{quat}), 132.85–124.68 (aromatic CH), 68.64 (s, OCH_2), 34.06 and 33.66 [2 × s, $C(CH_3)_3$], 32.08 (d, calix CH_2, $^4J_{PC}$ = 3 Hz), 31.78 and 31.23 [2 × s, $C(CH_3)_3$], 15.55 (s, OCH_2CH_3); ^{31}P-{^{1}H}, δ 121.9 (s, $OPPh_2$). CI mass spectrum: m/z 1073.5 (82%) (M + H$^+$).

5,11,17,23-Tetra-*tert*-butyl-25,27-bis(diphenylphosphinooxy)-26,28-dipropoxycalix[4]arene L[13]. A hexane solution of LiBu^n (5.2 cm^3, 1.54 mol dm^{-3}, 8.00 mmol) was added dropwise to a stirred solution of 5,11,17,23-tetra-*tert*-butyl-25,27-dihydroxy-26,28-dipropoxycalix[4]arene L[4] (2.933 g, 4.00 mmol) in thf (80 cm^3) at −50 °C. The resulting reddish solution was stirred for 1 h. Then a pre-cooled (−50 °C) solution of PPh_2Cl (1.765 g, 8.00 mmol) in thf (30 cm^3) was added dropwise and the mixture was left at −50 °C for 2 h. The solvents were removed *in vacuo* and to the residue obtained was added toluene (80 cm^3). The suspension was stirred at 0 °C for 1 h and filtered through Celite to remove LiCl. The filtrate and toluene washings of the Celite were combined before concentration to *ca.* 15 cm^3. At this stage the product began to precipitate. The product remaining in solution was precipitated by addition of pentane (50 cm^3), and the precipitate was filtered off and dried *in vacuo* overnight [R_f = 0.74 (hexane–ethyl acetate, 92:8 v/v) (2.81 g, 64%), m.p. 277–280 °C (Found: C, 80.70; H, 7.85. $C_{74}H_{86}O_4P_2$ requires C, 80.60; H, 7.75%; M_r = 1101.45). NMR: ^{1}H ($CDCl_3$), δ 7.76–7.66 and 7.44–7.40 (20 H, PPh_2), 7.00 (s, 4 H, *m*-H), 6.33 (s, 4 H, *m*-H), 4.15 and 2.79 (AB spin system, 8 H, calix CH_2, J = 13.1), 3.90 (AA′ part of an AA′MM′X$_3$ spin system, 4 H, OCH_2), 1.74 (m, 4 H, OCH_2CH_2), 1.30 (s, 18 H, Bu^t) and 0.81 (s, 18 H, Bu^t) and 0.68 (t, 6 H, CH_2CH_3, ^3J = 7.4 Hz); ^{13}C-{^{1}H} ($CDCl_3$), δ 153.62–131.18 (aromatic C_{quat}), 131.26, 132.53, 132.06, 129.82, 128.19, 128.05, 125.75 and 124.67 (aromatic CH), 75.63 (s, OCH_2), 34.07 and 33.65 [2 × s, $C(CH_3)_3$], 32.12 (d, calix CH_2, $^4J_{PC}$ = 3 Hz), 31.78 and 31.22 [2 × s, $C(CH_3)_3$], 22.67 (s, CH_2CH_3) and 9.73 (s, CH_2CH_3); ^{31}P-{^{1}H} (thf–C_6D_6) δ 122.8 (s, $OPPh_2$). CI mass spectrum: m/z 1273.5% [(M + H + 2O)$^+$].

5,11,17,23-Tetra-*tert*-butyl-25,27-bis(diphenylphosphinooxy)-26,28-di(methoxycarbonylmethoxy)calix[4]arene L[14]. To a solution of dry diisopropylamine (1.517 g, 15.00 mmol) in thf (30 cm^3) was added dropwise, at −78 °C, a hexane solution of LiBu^n (10.0 cm^3, 1.51 mol dm^{-3}, 15.1 mmol). After stirring for 0.5 h, the solution was transferred to a solution of 5,11,17,23-tetra-*tert*-butyl-25,27-dihydroxy-26,28-di(methoxycarbonylmethoxy)calix[4]arene L[5] (5.775 g, 7.28 mmol) in thf (120 cm^3). After stirring the mixture for 1 h at −78 °C, a cold (−78 °C) solution of PPh_2Cl (3.212 g, 14.56 mmol) in thf (30 cm^3) was slowly added. The resulting solution was kept at −78 °C for 1 h before raising the temperature to room temperature. The solvents were evaporated and the residue dissolved in toluene–pentane (150 cm^3, 2:1 v/v) and LiCl was removed by filtration through Celite. The filtered solution and toluene washings of the Celite were combined and concentrated nearly to dryness. The yellowish oily residue was treated with pentane (100 cm^3). Filtration of the resulting suspension led to a white powder, which was dried *in vacuo* (4.60 g, 54%), m.p. 267 °C (decomp.) (Found: C, 76.35; H, 6.95. $C_{74}H_{82}O_8P_2$ requires C, 76.55; H, 7.10%; M_r = 1161.42); $\tilde{\nu}_{max}$/cm^{-1} (KBr) 1759s (C=O). NMR: ^{1}H ($CDCl_3$), δ 7.74–7.66 and 7.46–7.40 (20 H, PPh_2), 6.99 (s, 4 H, *m*-H), 6.37 (s, 4 H, *m*-H), 4.85 (s, 4 H, OCH_2), 4.39 and 2.85 (AB spin system, 8 H, calix CH_2, J = 13.4 Hz), 3.35 (s, 6 H, OCH_3), 1.29 (s, 18 H, Bu^t) and 0.83 (s, 18 H, Bu^t); ^{13}C-{^{1}H} ($CDCl_3$), δ 170.46 (s, C=O), 152.60–128.56 (aromatic C_{quat}), 132.27, 131.81, 129.77, 128.23, 128.08, 126.01 and 124.85 (aromatic CH), 69.80 (s, OCH_2), 51.05 (s, OCH_3), 33.98 and 33.59 [2 × s, $C(CH_3)_3$], 32.27 (d, calix CH_2, $^4J_{PC}$ = 4 Hz), 31.65 and 31.11 [2 × s, $C(CH_3)_3$]; ^{31}P-{^{1}H} (thf–C_6D_6), δ 123.0 (s, $OPPh_2$). CI mass spectrum: m/z 1161 (21) (M + H$^+$).

5,11,17,23-Tetra-*tert*-butyl-25,27-bis(diphenylphosphinooxy)-26,28-di(ethoxycarbonylmethoxy)calix[4]arene L[15]. To a solution of dry diisopropylamine (2.024 g, 20.00 mmol) in thf (50 cm^3) was added dropwise, at −78 °C, a hexane solution of LiBu^n (12.60 cm^3, 1.59 mol dm^{-3}, 20.03 mmol). After stirring for 0.5 h, the mixture was transferred *via* cannula to a solution of 5,11,17,23-tetra-*tert*-butyl-25,27-di(ethoxycarbonylmethoxy)-26,28-dihydroxycalix[4]arene L[6] (8.211 g, 10.00 mmol) in thf (200 cm^3). After stirring the mixture for 1 h at −78 °C, a cold (−78 °C) solution of PPh_2Cl (4.412 g, 20.00 mmol) in thf (50 cm^3) was slowly added. The resulting solution was kept at

−78 °C for 1 h before warming to room temperature. The solvents were evaporated and the residue dissolved in toluene–pentane (200 cm^3, 3:1 v/v) and LiCl was removed by filtration through Celite. The filtered solution and toluene washings of the Celite were combined and concentrated nearly to dryness and the yellowish oily residue was treated with 200 cm^3 of pentane. Filtration of the resulting suspension gave a white powder which was dried *in vacuo* (7.70 g, 65%), m.p. 226 °C (slow decomp.) (Found: C, 76.65; H, 7.25. $C_{76}H_{86}O_8P_2$ requires C, 76.75; H, 7.30%; M_r = 1189.47); $\tilde{\nu}_{max}/cm^{-1}$ (KBr) 1762s (C=O). NMR: ^1H ($CDCl_3$), δ 7.74–7.66 and 7.44–7.41 (20 H, PPh_2), 6.97 (s, 4 H, *m*-H), 6.36 (s, 4 H, *m*-H), 4.81 (s, 4 H, OCH_2CO_2), 4.39 and 2.84 (AB spin system, 8 H, calix CH_2, J = 13.1), 3.74 (q, 4 H, CH_2CH_3, ^3J = 7.2), 1.28 (s, 18 H, Bu^t), 1.07 (t, 6 H, CH_2CH_3, ^3J = 7.2 Hz) and 0.81 (s, 18 H, Bu^t); ^{13}C-{^1H} ($CDCl_3$), δ 170.09 (s, C=O), 152.62–131.14 (aromatic C_{quat}), 132.38–124.88 (aromatic CH), 69.90 (s, OCH_2CO_2), 60.12 (s, CH_2CH_3), 33.99 and 33.62 [2 × s, $C(CH_3)_3$], 32.52 (d, calix CH_2, $^4J_{PC}$ = 3 Hz), 31.67 and 31.15 [2 × s, $C(CH_3)_3$] and 13.96 (s, CH_2CH_3); ^{31}P-{^1H} (thf–C_6D_6), δ 123.3 (s, $OPPh_2$). CI mass spectrum: *m/z* 1190 (24%) (M + H^+).

(−)-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[16]. To a solution of dry diisopropylamine (1.166 g, 11.52 mmol) in thf (40 cm^3) was added dropwise, at −78 °C, a hexane solution of $LiBu^n$ (7.8 cm^3, 1.48 mol dm^{-3}, 11.52 mmol). After stirring for 0.5 h, the solution was transferred *via cannula* to a solution of L^7 (6.000 g, 5.76 mmol) in thf (140 cm^3). After the mixture had been stirred for 1 h at −78 °C, a pre-cooled (−78 °C) solution of PPh_2Cl (2.541 g, 11.52 mmol) in thf (30 cm^3) was added. The resulting solution was kept at −78 °C under stirring for 0.5 h, and then warmed to room temperature within 1 h. After evaporation of the solvents under reduced pressure, to the residue obtained was added toluene–pentane (100 cm^3, 1:1 v/v). The suspension was stirred at 0 °C for 1 h and filtered through Celite in order to remove LiCl. The filtrate and toluene washings of the Celite were combined before evaporation to dryness. The residue was treated with pentane (150 cm^3). After stirring for 0.5 h, the suspension was concentrated to *ca.* 100 cm^3 and then filtered through a glass frit. The white solid was dried *in vacuo* overnight (5.3 g, 65%), m.p. 202–207 °C, α = −2.5° (589 nm, 20 °C, c = 2 g per 100 cm^3 toluene) (Found: C, 78.20; H, 8.05. $C_{92}H_{114}O_8P_2$ requires C, 78.40; H, 8.15%; M_r = 1409.88); $\tilde{\nu}_{max}/cm^{-1}$ (KBr) 1758s and 1722s (CO). NMR: ^1H ($CDCl_3$), δ 7.78–7.68 and 7.45–7.32 (20 H, PPh_2), 6.95 (br s, 4 H, *m*-H), 6.41 and 6.37 (AB spin system, 4 H, *m*-H, ^4J = 2.3), 4.90 and 4.80 (AB spin system, 4 H, OCH_2, J = 16.8), 4.42 (dt, 2 H, OCH of menthyl, ^3J = 4.0, ^3J = 10.8), 4.38 and 2.88 (AB spin system, 4 H, calix CH_2, J = 13.2), 4.28 and 2.79 (AB spin system, 4 H, calix CH_2, J = 13.3 Hz), 1.60–0.43 (36 H, menthyl), 1.27 (s, 18 H, Bu^t) and 0.81 (s, 18 H, Bu^t); ^{13}C-{^1H} ($CDCl_3$), δ 169.68 (s, C=O), 151.91–131.00 (aromatic C_{quat}), 132.66–124.72 (aromatic CH), 74.46 (s, OCH of menthyl), 69.66 (s, OCH_2), 46.56, 31.19 and 25.39 (3 × s, CH of menthyl), 39.96, 34.08 and 22.86 (3 × s, CH_2 of menthyl), 33.88 and 33.54 [2 × s, $C(CH_3)_3$], 32.29 (br s, calix CH_2), 31.62 and 31.05 [2 × s, $C(CH_3)_3$], 21.96, 21.07 and 15.67 (3 × s, CH_3 of menthyl); ^{31}P-{^1H} (thf–C_6D_6), δ 123.9 (s, $OPPh_2$). CI mass spectrum: *m/z* 1408 (12%) (M^+).

5,11,17,23-Tetra-*tert*-butyl-25,27-bis(diphenylphosphinooxy)-26-ethoxy-28-ethoxycarbonylmethoxycalix[4]arene L[17]. To a solution of dry diisopropylamine (0.842 g, 8.32 mmol) in thf (30 cm^3) was added dropwise, at −78 °C, a hexane solution of $LiBu^n$ (5.4 cm^3, 1.54 mol dm^{-3}, 8.32 mmol). After stirring for 0.5 h, the mixture was transferred to a solution of L^8 (3.053 g, 4.00 mmol) in thf (50 cm^3). After the mixture had been stirred for 1 h at −78 °C, a pre-cooled (−78 °C) solution of PPh_2Cl (1.765 g, 8.00 mmol) in thf (30 cm^3) was added. The resulting solution was kept at −78 °C under stirring for 0.5 h. The solvents were evaporated and the residue dissolved in toluene–pentane (50 cm^3, 3:2 v/v). Lithium chloride was removed by filtration through Celite and the filtrate and toluene washings of the Celite were combined before evaporation to dryness. The residue was dissolved in CH_2Cl_2 (5 cm^3), then pentane (50 cm^3) was added affording a white precipitate [R_f = 0.45 (hexane–ethyl acetate, 6:1 v/v)] (2.250 g, 50%), m.p. 210–212 °C (Found: C, 78.65; H, 7.15. $C_{74}H_{84}O_6P_2$ requires C, 78.55; H, 7.45%; M_r = 1131.43); $\tilde{\nu}_{max}/cm^{-1}$ (KBr) 1761m (C=O). NMR: ^1H ($CDCl_3$), δ 7.77–7.65 and 7.43–7.40 (20 H, PPh_2), 7.00 (s, 2 H, *m*-H), 6.97 (s, 2 H, *m*-H), 6.35 and 6.33 (AB spin system, 4 H, *m*-H of aryl-$OPPh_2$, $^4J \approx 1$), 5.00 (s, 2 H, OCH_2CO_2), 4.45 and 2.87 (AB spin system, 4 H, calix CH_2, J = 13.5), 4.10 and 2.77 (AB spin system, 4 H, calix CH_2, J = 13.2), 3.91 (q, 2 H, CH_2CH_3, ^3J = 7.1), 3.81 (q, 2 H, CH_2CH_3, ^3J = 7.1), 1.30 (s, 9 H, Bu^t), 1.28 (s, 9 H, Bu^t), 1.10 (t, 3 H, CH_2CH_3, ^3J = 7.1), 1.09 (t, 3 H, CH_2CH_3, ^3J = 7.1 Hz), 0.81 (s, 18 H, Bu^t of aryl-$OPPh_2$); ^{13}C-{^1H} NMR ($CDCl_3$), δ 170.55 (s, C=O), 152.92–124.78 (aromatic C), 69.43 (s, OCH_2), 68.96 (s, OCH_2), 60.12 (s, $CO_2CH_2CH_3$), 34.07, 33.66 and 33.56 [3 × s, $C(CH_3)_3$], 32.76 and 31.80 (2 × s, calix CH_2), 31.76, 31.72 and 31.20 [3 s, $C(CH_3)_3$], 15.50 (s, CH_2CH_3) and 14.06 (s, CH_2CH_3); ^{31}P-{^1H} (thf–C_6D_6), δ 123.2 (s, $OPPh_2$). CI mass spectrum: *m/z* 1131 (1%) (M^+).

(−)-5,11,17,23-Tetra-*tert*-butyl-25,27-bis(diphenylphosphinooxy)-26-ethoxy-28-[(1*R*,2*S*,5*R*)menthyloxycarbonylmethoxy]calix[4]arene L[18]. To a solution of dry diisopropylamine (0.708 g, 7.00 mmol) in thf (30 cm^3) was added dropwise, at − 78 °C, a hexane solution of $LiBu^n$ (4.55 cm^3, 1.54 mol dm^{-3}, 7.00 mmol). After stirring for 0.5 h, the solution was transferred *via* cannula into a solution of L^9 (3.057 g, 3.50 mmol) in thf (50 cm^3). After the mixture had been stirred for 1 h at −78 °C, a pre-cooled (−78 °C) solution of PPh_2Cl (1.540 g, 7.00 mmol) in thf (30 cm^3) was added. The resulting solution was kept at −78 °C under stirring for 0.5 h, and then warmed to room temperature within 1 h. After evaporation of the solvents under reduced pressure, to the residue obtained was added toluene–pentane (50 cm^3, 1:1 v/v). The suspension was stirred at 0 °C for 1 h, filtered through Celite in order to remove LiCl. The filtrate and toluene washings of the Celite were combined before evaporation to dryness. The residue was treated with pentane (100 cm^3). After stirring for 0.5 h, the suspension was concentrated to *ca.* 50 cm^3 and then filtered. The white solid was dried *in vacuo* overnight (3.4 g, 78%), m.p. 238–248 °C, α −9.4° (589 nm, 20 °C, c = 4 g per 100 cm^3, $C_2H_2Cl_4$) (Found: C, 79.25; H, 7.75. $C_{82}H_{98}O_6P_2$ requires C, 79.30; H, 7.95%; M_r = 1241.64); $\tilde{\nu}_{max}/cm^{-1}$ (KBr) 1759s (C=O). NMR: ^1H ($CDCl_3$), δ 7.82–7.59 and 7.42–7.27 (20 H, PPh_2), 7.00 (br s, 2 H, *m*-H), 6.95 (s, 2 H, *m*-H), 6.35 (s, 2 H, *m*-H), 6.33 (br s, 2 H, *m*-H) (in the 400 MHz spectrum the signals at δ 7.00 and 6.33 become respectively an AB spin system), 5.05 (s, 2 H, OCH_2CO_2), 4.53 (dt, 1 H, OCH of menthyl, ^3J = 4.7, ^3J = 10.8), 4.42 and 2.85 (AB spin system, 2 H, calix CH_2, J = 13.5), 4.41 and 2.85 (AB spin system, 2 H, calix CH_2, J = 13.5), 4.11, 4.07 and 2.83, 2.77 (2 AB spin systems, 4 H, calix CH_2, J = 13.0), 3.83 (q, 2 H, OCH_2CH_3, ^3J = 7.1), 1.64–0.49 (18 H, menthyl), 1.30, 1.28, 0.81 and 0.80 (4 × s, 36 H, Bu^t) and 1.05 (t, 3 H, OCH_2CH_3, ^3J = 7.1 Hz); ^{13}C-{^1H} ($CDCl_3$), δ 170.01 (s, C=O), 153.04–124.76 (aromatic C), 74.51 (s, OCH, menthyl), 69.54 and 68.86 (2 × s, OCH_2, not assigned), 46.92, 31.42 and 25.75 (3 × s, CH of menthyl), 40.51, 34.35 and 23.20 (3 × s, CH_2, menthyl), 34.05 [br s, $C(CH_3)_3$], 33.99 and 33.63 [2 × s, $C(CH_3)_3$], 32.70, 32.65, 32.08 and 32.03 (4 × s, calix CH_2), 31.75, 31.48 and 31.19 [3 × s, $C(CH_3)_3$], 22.03 and 21.07 (2 × s, CH_3 of menthyl), 15.94 and 15.53 (2 × s, CH_3); ^{31}P-

{^{1}H} (thf–C_6D_6), δ 123.8 and 123.7 (2 × s, $OPPh_2$). CI mass spectrum: *m/z* 1273.5 (6%) (M + H^+ + 2O).

5,11,17,23-Tetra-*tert*-butyl-25-diphenylphosphinooxy-26,28-di(ethoxycarbonylmethoxy)-27-hydroxycalix[4]arene L[19]. Triethylamine (1.517 g, 15.0 mmol, *ca.* 2.1 cm^3) was added to a solution of 5,11,17,23-tetra-*tert*-butyl-25,27-di(ethoxycarbonylmethoxy)-26,28-dihydroxycalix[4]arene L[6] (4.926 g, 6.00 mmol) in thf (150 cm^3) at −40 °C. After 0.5 h stirring, a solution of PPh_2Cl (2.000 g, 9.00 mmol) in thf (20 cm^3, −40 °C) was added. A white precipitate appeared and the mixture was refluxed for 15 h. The solvent was then evaporated to dryness and the residue dissolved in toluene (70 cm^3). Addition of pentane (150 cm^3) afforded a white precipitate which was removed by filtration. The filtered solution was then concentrated to *ca.* 10 cm^3. Addition of cold pentane (150 cm^3) gave a white powder which was purified by flash chromatography over Kieselgel 60 (Merck, pre-treated with 6% NEt_3 in Et_2O) using thf–pentane (1:9, v/v) as eluent (R_f = 0.4) (4.300 g, 71%), m.p. 177–188 °C (Found: C, 76.50; H, 7.85. $C_{64}H_{77}O_8P$ requires C, 76.45; H, 7.70%; M_r = 1005.29); $\tilde{\nu}_{max}/cm^{-1}$ (KBr) 3445m (OH), 1762s (C=O), 1734s (C=O • • • H). NMR: ^{1}H ($CDCl_3$) δ 7.82–7.76 and 7.44–7.42 (10 H, aromatic H), 6.95 and 6.91 (2s, 4 H, *m*-H), 6.86 (s, 1 H, OH), 6.72 and 6.67 (AB system, 2 H, *m*-H of aryl–OCH_2CO_2Et, ^4J = 2), 4.54 and 3.21 (AB spin system, 4 H, HOarylCH_2arylOCH_2CO_2Et, J = 13), 4.44 and 4.03 (AB system, 4 H, OCH_2CO_2, J = 16), 4.16 and 2.94 (ABX spin system, 4 H, Ph_2POarylCH_2arylOCH_2CO_2Et, J_{AB} = 13, $J_{AP} \approx 2$, J_{BP} = 0), 4.13 (dq, AB part of an ABX_3 spin system, 4 H, OCH_2CH_3, $J_{AX} \approx J_{BX}$ = 7, J_{AB} < 1), 1.24 (t, 6 H, CH_2CH_3, ^3J = 7), 1.23 (s, 9 H, Bu^t), 1.18 (s, 9 H, Bu^t), 0.93 (s, 18 H, Bu^t of arylOCH_2CO_2Et); ^{1}H (C_6D_6), δ 8.06–7.99 and 7.37–7.22 (10 H, aromatic H), 7.11 and 7.08 (2 s, 4 H, *m*-H), 6.93 and 6.91 (AB spin system, 2 H, *m*-H of aryl–OCH_2CO_2Et, ^4J = 2), 7.43 (s, 1 H, OH), 4.96 and 3.33 (AB spin system, 4 H, HOarylCH_2arylOCH_2CO_2Et, J = 13.2), 4.63 and 4.04 (AB spin system, 4 H, OCH_2CO_2, J = 15.7), 4.59 and 3.16 (ABX spin system, 4 H, Ph_2POarylCH_2arylOCH_2CO_2Et, J_{AB} = 13.0, $J_{AP} \approx 2$, J_{BP} = 0), 3.88 (pseudo dq, AB part of an ABX_3 spin system, 4 H, OCH_2CH_3, $J_{AX} \approx J_{BX}$ = 7.0, J_{AB} not determined), 1.37 (s, 9 H, Bu^t), 1.26 (s, 9 H, Bu^t), 1.06 (s, 18 H, Bu^t of arylOCH_2CO_2Et) and 0.91 (t, 6 H, CH_2CH_3, ^3J = 7.0 Hz); ^{13}C-{^{1}H} ($CDCl_3$), δ 169.53 (s, C=O), 151.90–134.00 (aromatic C_{quat}), 132.87–124.77 (aromatic CH), 71.83 (s, OCH_2CO_2Et), 60.69 (s, CH_2CH_3), 33.92, 33.77 and 33.75 [3 × s, $C(CH_3)_3$], 31.63, 31.53 and 31.12 [3 × s, $C(CH_3)_3$], 31.40 and 31.28 (2 × s, calix CH_2) and 14.14 (s, CH_2CH_3); ^{31}P-{^{1}H} (thf–C_6D_6), δ 122.9 (s, $OPPh_2$). CI mass spectrum: *m/z* 1005 (45) (M + H^+).

***p*-*tert*-Butylphenoxydiphenylphosphine L[20].** Triethylamine (1.67 g, *ca.* 2.3 cm^3, 16.5 mmol) was slowly added to a solution of *p*-*tert*-butylphenol (2.104 g, 14.00 mmol) in thf (80 cm^3). After 0.5 h stirring, the mixture was cooled at 0 °C and a solution of PPh_2Cl (3.088 g, 14.00 mmol) in thf (40 cm^3) added. The resulting suspension was stirred at room temperature for an additional hour and then concentrated to *ca.* 50 cm^3. Pentane (50 cm^3) was added and the suspension was filtered to remove $NHEt_3Cl$. The filtrate was evaporated under reduced pressure. After addition under vigorous stirring of cold pentane to the oily residue, the product precipitated as a white powder [R_f = 0.83 (hexane-ethyl acetate, 19:6 v/v)] (4.60 g, 98%), m.p. 57 °C (Found: C, 78.85; H, 6.80. $C_{22}H_{23}OP$ requires C, 79.00; H, 6.95%; M_r = 334.40). NMR: ^{1}H ($CDCl_3$), δ 7.74–7.66 and 7.48–7.44 (m, 10 H, PPh_2), 7.38 and 7.17 (AA'BB'X, 4 H, aryl H, $^3J_{AB}$ = 8.8, $^5J_{AX}$ = 0, $^4J_{BX}$ = 1.6 Hz) and 1.38 (s, 9 H, Bu^t); ^{13}C-{^{1}H} ($CDCl_3$), δ 34.29 [s, $C(CH_3)_3$] and 31.59 [s, $C(CH_3)_3$]; ^{31}P-{^{1}H} (thf–C_6D_6), δ 110.76 (s, $OPPh_2$). CI mass spectrum: *m/z* 335 (44%) (M + H^+).

25,27-*anti*-26,28-*anti*-5,11,17,23-Tetra-*tert*-butyl-25,27-bis(diphenylphosphinooxy)-26,28-dimethoxycalix[4]arene L[21] (1-2 alternate). A hexane solution of LiBu^n (8.4 cm^3, 1.6 mol dm^{-3}, 13.40 mmol) was added dropwise to a solution of 5,11,17,23-tetra-*tert*-butyl-25,27-dihydroxy-26,28-dimethoxycalix[4]arene L[2] (4.320 g, 6.38 mmol) in thf (125 cm^3). After 0.5 h stirring, the yellow solution was cooled to 0 °C and a solution of PPh_2Cl (2.950 g, 13.37 mmol) in thf (20 cm^3) was added slowly. After refluxing for 2 h, the solvents were evaporated to dryness. The residue was treated with toluene (100 cm^3) and the resulting suspension was filtered through a glass frit and the filtered solution was concentrated to *ca.* 10 cm^3. Addition of pentane (50 cm^3) afforded a white precipitate which was shown to be analytically pure [R_f = 0.81(hexane–ethyl acetate, 94:6 v/v)] (3.870 g, 60%), m.p. > 300 °C (Found: C, 80.35; H, 7.65. $C_{70}H_{78}O_4P_2$ requires C, 80.45; H, 7.50%; M_r = 1045.34). NMR ($CDCl_3$): ^{1}H (243 K), δ 7.32–6.61 (28 H, aromatic H), 4.06 and 3.68 (ABX spin system, 4 H, calix CH_2, J_{AB} = 17.7, $^5J_{AP}$ = 0, $^5J_{BP} \approx 4$*), 3.50 and 2.50 (AB spin system, 4 H, calix CH_2, J = 12.7 Hz), 2.61 (s, 6 H, OCH_3), 1.40 (s, 18 H, Bu^t) and 0.91 (s, 18 H, Bu^t); ^{13}C-{^{1}H} (228 K), δ 154.66–123.95 (aromatic C), 59.12 (s, OCH_3), 38.81 (d, *anti*-calix CH_2, $^4J_{PC}$ = 7 Hz), 34.06 and 33.60 [2 s, $C(CH_3)_3$], 31.39 and 30.95 [2 × s, $C(CH_3)_3$] and 29.25 (s, *syn*-calix CH_2); ^{31}P-{^{1}H} δ 113.6 (s, $OPPh_2$). FAB mass spectrum: *m/z* 1077 (100%) (M + H^+ + 2O), 1061 (32) (M + H^+ + O), 1045 (12) (M + H^+); for this measurement, the oxidation of the P atoms could not be avoided.

Important X-ray data for L[21]. $C_{70}H_{78}O_4P_2$, M = 1045.34, monoclinic, space group $P2_1/a$, a = 16.979(9), b = 17.12(2), c = 12.64(1) Å, β = 104.69(9)°, U = 3554(6) $Å^3$, Z = 4, λ(Mo-Kα) = 0.710 73 Å, D_c = 1.954 g cm^{-3}, F(000) = 4172, R = 0.15. Crystals were grown from CH_2Cl_2–hexane for the X-ray study.

***trans*-Dichlorobis{5,11,17,23-tetra-*tert*-butyl-25-diphenylphosphinooxy-26,28-di(ethoxycarbonylmethoxy)-27-hydroxycalix[4]arene}platinum(II) 1.** A solution of L[19] (0.305 g, 0.32 mmol) in thf (20 cm^3) was slowly added to a solution of [$PtCl_2(PhCN)_2$] (0.075 g, 0.16 mmol) in thf (40 cm^3). After 0.5 h, the solution was concentrated to *ca.* 5 cm^3 and pentane (30 cm^3) was added affording an ivory precipitate (0.270 g, 78%), m.p. 268–270 °C (Found: C, 67.20; H, 6.60. $C_{128}H_{154}Cl_2O_{16}P_2Pt$ requires C, 67.55; H, 6.80%; M_r = 2276.58); $\tilde{\nu}_{max}/cm^{-1}$ (KBr) 3463 (br) (OH), 1762s (C=O) and 1734s (C=O • • • H); (Polythene disc) 349 (Pt–Cl). NMR: ^{1}H ($CDCl_3$), δ 7.87–7.84 and 7.32–7.27 (20 H, PPh_2), 7.17 (s, 2 H, OH), 7.14 and 7.05 (AB spin system, 8 H, *m*-H of aryl–OCH_2CO_2Et, ^4J = 2.3), 6.72 (s, 4 H, *m*-H), 6.25 (s, 4 H, *m*-H), 5.24 and 4.60 (AB spin system, 8 H, OCH_2CO_2, J = 16), 4.76 and 3.21 (AB spin system, 8 H, calix CH_2, J = 13.2), 4.28 and 3.28 (AB spin system, 8 H, calix CH_2, J = 13.0), 4.26 (q, 8 H, CH_2CH_3, ^3J = 7.1), 1.32 (s, 36 H, Bu^t of aryl–OCH_2CO_2Et), 1.28 (t, 12 H, CH_2CH_3, ^3J = 7.1 Hz), 1.05 (s, 18 H, Bu^t) and 0.55 (s, 18 H, Bu^t); ^{13}C-{^{1}H} ($CDCl_3$, 100 MHz), δ 170.39 (s, C=O), 153.41–129.71 (aromatic C_{quat}), 131.71, 130.36, 127.31, 126.69, 125.90, 125.43 and 124.39 (aromatic CH), 72.18 (s, OCH_2CO_2), 60.73 (s, CH_2CH_3), 34.11, 33.65 and 33.52 [3 × s, $C(CH_3)_3$], 32.91 and 32.05 (2 × s, calix CH_2), 31.64, 31.28 and 31.19 [3 × s, $C(CH_3)_3$] and 14.26 (s, CH_2CH_3); ^{31}P-{^{1}H} (C_6D_6), δ 102 (s, with Pt satellites, J_{PPt} = 3041 Hz). FAB mass spectrum: *m/z* 2239 (4%) (M − Cl)$^+$.

***cis*-Dichlorobis(*p*-*tert*-butylphenoxydiphenylphosphine)-platinum(II) 3.** A solution of L[20] (0.269 g, 1.61 mmol) in thf (20 cm^3) was slowly added to a solution of [$PtCl_2(PhCN)_2$]

* This coupling constant could be due to a through-space P • • • H interaction: the shortest P • • • H (CH_2) distance found in the preliminary X-ray study was 2.93 Å.

(0.378 g, 0.80 mmol) in thf (10 cm^3). After 0.5 h, the solution was concentrated to *ca.* 5 cm^3 and pentane (30 cm^3) was added affording an ivory precipitate (0.675 g, 90%), m.p. 217–222 °C (Found: C, 56.45; H, 4.80. $C_{44}H_{46}Cl_2O_2P_2Pt$ requires C, 56.55; H, 4.95%; M_r = 934.80); $\tilde{\nu}_{max}/cm^{-1}$ (Polythene disc) 324s and 298s (Pt–Cl). NMR: ^1H ($CDCl_3$), δ 7.69–7.58 and 7.42–7.24 (20 H, PPh_2), 7.12 and 6.52 (AA′BB′XX′ spin system with X = P, 8 H, aryl H, $^3J_{AB}$ = 8.8, $^5J_{AX}$ = 0, $^4J_{BX}$ = 1 Hz) and 1.29 (s, 18 H, Bu^t); ^{13}C-{^1H} ($CDCl_3$), δ 150.88–120.48 (aromatic C), 34.42 [s, $C(CH_3)_3$] and 31.51 [s, $C(CH_3)_3$]; ^{31}P-{^1H} (C_6D_6), δ 84.9 (s, with Pt satellites, J_{PPt} = 4172 Hz). FAB mass spectrum: *m/z* 899 (100%) $(M - Cl)^+$.

***trans*-Dichlorobis{5,11,17,23-tetra-*tert*-butyl-25-diphenylphosphinooxy-26,28-di(ethoxycarbonylmethoxy)-27-hydroxycalix[4]arene}palladium(II) 2.** This complex was obtained by addition of a solution of L^{19} (0.399 g, 0.40 mmol) in thf (20 cm^3) to a suspension of $[PdCl_2(PhCN)_2]$ (0.075 g, 0.20 mmol) in thf (40 cm^3). The mixture turned yellow. After 0.5 h, the solution was filtered and concentrated to *ca.* 5 cm^3. Addition of pentane (30 cm^3) afforded **2** as a yellow powder (0.360 g, 84%), m.p. 240 °C (slow decomp.) (Found: C, 70.05; H, 6.90. $C_{128}H_{154}Cl_2O_{16}P_2Pd$ requires C, 70.25; H, 7.10%; M_r = 2187.89); $\tilde{\nu}_{max}/cm^{-1}$ (KBr) 3467s (OH), 1759s and 1735s (C=O); (Polythene disc), 361 (Pd–Cl). NMR: ^1H ($CDCl_3$), δ 7.85–7.80 and 7.32–7.29 (20 H, PPh_2), 7.18 (s, 2 H, OH), 7.13 and 7.04 (AB spin system, 8 H, *m*-H of aryl-OCH_2CO_2Et, ^4J = 2.3 Hz), 6.71 (s, 4 H, *m*-H), 6.27 (s, 4 H, *m*-H), 5.21 and 4.55 (AB spin system, 8 H, OCH_2CO_2, J = 16), 4.74 and 3.20 (AB spin system, 8 H, calix CH_2, J = 13.1), 4.29 and 3.30 (AB spin system, 8 H, calix CH_2, J = 14.5), 4.25 (q, 8 H, CH_2CH_3, ^3J = 7.1), 1.31 (s, 36 H, Bu^t of aryl-OCH_2CO_2Et), 1.28 (t, 12 H, CH_2CH_3, ^3J = 7.1 Hz), 1.05 (s, 18 H, Bu^t) and 0.56 (s, 18 H, Bu^t); ^{13}C-{^1H} ($CDCl_3$, 100 MHz), δ 170.43 (s, C=O), 153.44–124.39 (aromatic C), 72.19 (s, OCH_2CO_2), 60.72 (s, CH_2CH_3), 34.12, 33.66 and 33.54 [3 × s, $C(CH_3)_3$], 33.02 and 32.05 (2 × s, calix CH_2), 31.65, 31.29 and 31.18 [3 × s, $C(CH_3)_3$], 14.26 (s, CH_2CH_3); ^{31}P-{^1H} (thf–C_6D_6), δ 110 (s, $OPPh_2$). FAB mass spectrum: *m/z* 2152 (1.5%) $(M - Cl + H)^+$, 2114 (3) $(M - 2Cl)^+$.

Important X-ray data for **2**·4$C_2H_2Cl_4$. $C_{128}H_{154}Cl_2O_{16}P_2Pd$·4$C_2H_2Cl_4$, M = 2859.30, monoclinic, space group $P2_1/a$, a = 27.151(6), b = 14.113(6), c = 20.09(1) Å, β = 96.30(3)°, U = 7651(5) Å^3, Z = 2, λ(Mo-Kα) = 0.710 73 Å, D_c = 1.241 g cm^{-3}, $F(000)$ = 2976, space group $P2_1/a$, R = 0.17. Crystals were grown from 1,1,2,2-tetrachloroethane–pentane for the X-ray study.

Tetrameric complex [(*trans*-$PtCl_2L^{15}$)$_4$] 4. This complex was prepared by adding a solution of $[PtCl_2(PhCN)_2]$ (0.100 g, 0.21 mmol) in thf (20 cm^3) to a solution of L^{15} (0.263 g, 0.22 mmol) in thf (20 cm^3). After 0.5 h stirring, the solution was concentrated to *ca.* 5 cm^3. Addition of pentane (30 cm^3) afforded the product as a white powder (0.280 g, 91%), m.p. 254–256 °C (Found: C, 62.65; H, 5.85. $C_{76}H_{86}Cl_2O_8P_2Pt$ requires C, 62.70; H, 5.95%; M_r = 1455.47); $\tilde{\nu}_{max}/cm^{-1}$ (KBr) 1760s and 1733s (C=O); (Polythene disc), 346 (Pt–Cl). NMR: ^1H ($CDCl_3$, 343 K), δ 7.87–7.47 and 7.31–7.26 (20 H, PPh_2), 6.93 (s, 4 H, *m*-H), 6.26 (s, 4 H, *m*-H), 5.14 (br s, 4 H, OCH_2CO_2), 4.50 and 2.93 (AB spin system, br, 8 H, calix CH_2, J = 13.4), 3.86 (br q, 4 H, CH_2CH_3, ^3J = 7.1), 1.30 (s, 18 H, Bu^t), 0.89 (t, 6 H, CH_2CH_3, ^3J = 7.1 Hz) and 0.74 (s, 18 H, Bu^t); ^{13}C-{^1H} ($CDCl_3$, 100 MHz), δ 170.16 (s, C=O), 152.59–132.10 (aromatic C_{quat}), 133.29, 130.46, 127.11, 126.25 and 124.73 (aromatic CH), 70.49 (s, OCH_2CO_2), 60.08 (s, CH_2CH_3), 34.01 and 33.63 [2 × s, $C(CH_3)_3$], 33.11 (s, calix CH_2), 31.72 and 31.17 [2 × s, $C(CH_3)_3$] and 13.96 (s, CH_2CH_3); ^{31}P-{^1H} (thf–C_6D_6), δ 101.8 (s with Pt satellites, J_{PPt} = 3032 Hz). FAB mass spectrum: *m/z* 1419 (8%) $(M_{monomer} - Cl)^+$, 1383 (25) $(M_{monomer} - 2Cl)^+$. Molecular weight (osmometry, CH_2Cl_2) = 5445.

Tetrameric complex [(*trans*-$PdCl_2L^{15}$)$_4$] 5. A solution of L^{15} (0.365 g, 0.31 mmol) in thf (20 cm^3) was added to a suspension of $[PdCl_2(PhCN)_2]$ (0.115 g, 0.30 mmol) in thf (40 cm^3). The mixture instantly turned yellow. After 0.5 h, the solution was filtered and concentrated to *ca.* 5 cm^3. Addition of pentane (30 cm^3) afforded a yellow precipitate (0.370 g, 90%), m.p. 240 °C (decomp.) (Found: C, 66.75; H, 6.35. $C_{76}H_{86}Cl_2O_8P_2Pd$ requires C, 66.80; H, 6.35%; M_r = 1366.78); ν_{max}/cm^{-1} (KBr) 1760s and 1732s (C=O); (Polythene disc), 363 (Pd–Cl). NMR: ^1H ($CDCl_3$, 343 K), δ 7.84–7.81 and 7.29–7.24 (20 H, PPh_2), 6.93 (s, 4 H, *m*-H), 6.25 (s, 4 H, *m*-H), 5.09 (br s, 4 H, OCH_2CO_2), 4.52 and 2.95 (AB spin system, br, 8 H, calix CH_2, J = 13.4), 3.85 (br q, 4 H, CH_2CH_3, ^3J = 7.1), 1.30 (s, 18 H, Bu^t), 0.90 (t, 6 H, CH_2CH_3, ^3J = 7.1 Hz) and 0.74 (s, 18 H, Bu^t); ^{13}C-{^1H} ($CDCl_3$, 100 MHz), δ 170.16 (s, C=O), 152.60–124.78 (aromatic C), 70.48 (s, OCH_2CO_2), 60.03 (s, CH_2CH_3), 34.01 and 33.62 [2 × s, $C(CH_3)_3$], 33.18 (s, calix CH_2), 31.73 and 31.17 [2 × s, $C(CH_3)_3$] and 13.99 (s, CH_2CH_3); ^{31}P-{^1H} (CH_2Cl_2–$CDCl_3$), δ 109.3 (s, $OPPh_2$). FAB mass spectrum: *m/z* 1294 (18%) $(M_{monomer} - 2Cl)^+$. Molecular weight (osmometry, CH_2Cl_2) = 5400.

Tetrameric complex [($PtCl_2L^{12}$)$_4$] 6. A solution of L^{12} (0.580 g, 0.54 mmol) in CH_2Cl_2 (20 cm^3) was added to a stirred solution of $[PtCl_2(cod)_2]$ (0.197 g, 0.53 mmol) in CH_2Cl_2 (30 cm^3). After 15 h the solution was concentrated to *ca.* 5 cm^3. Addition of pentane (30 cm^3) afforded a pale yellow precipitate. Yield 0.505 g, 71%, m.p. 255–260 °C. IR (Polythene disc): 346 (Pt–Cl). Most of the ^1H NMR ($CDCl_3$, 298 K) signals are very broad; only the *m*-H and the Bu^t protons could unambiguously be identified: δ 7.76 and 7.34 (2 × br, 20 H, PPh_2), 7.00 (br s, 4 H, *m*-H), 6.23 (br s, 4 H, *m*-H), 1.34 (s, 18 H, Bu^t) and 0.75 (s, 18 H, Bu^t); ^{31}P-{^1H} NMR ($CDCl_3$), δ 100.8 (s with Pt satellites, J_{PPt} = 2985 Hz). Molecular weight by osmometry = 5600 (CH_2Cl_2) [Found: C, 64.80; H, 6.30. Calc. for $C_{72}H_{82}Cl_2O_4P_2Pt$ (M_r = 1339.40): C, 64.55; H, 6.15%].

Tetrameric complex [($PtCl_2L^{16}$)$_4$] 7. A solution of L^{16} (0.344 g, 0.27 mmol) in CH_2Cl_2 (20 cm^3) was added to a solution of $[PtCl_2(PhCN)_2]$ (0.123 g, 0.30 mmol) in CH_2Cl_2 (30 cm^3). After 1 h the solution was concentrated to *ca.* 5 cm^3 and addition of pentane (30 cm^3) afforded a pale yellow precipitate. Yield 0.344 g, 76%, m.p. 238–242 °C; $\tilde{\nu}_{max}/cm^{-1}$ (KBr) 1750s and 1726s (C=O); (Polythene disc) 347s (Pt–Cl). Most of the ^1H NMR ($CDCl_3$, 298 K) signals are very broad; only the Bu^t protons could unambiguously be identified: δ 1.29 and 0.80 (2 × s, 36 H, Bu^t). ^{31}P-{^1H} NMR (thf–C_6D_6): δ 101.1 (s with Pt satellites, J_{PPt} = 3010 Hz). Molecular weight by osmometry = 6390 (CH_2Cl_2) [Found: C, 65.90; H, 7.10. Calc. for $C_{92}H_{114}Cl_2O_8P_2Pt$ (M_r = 1675.87): C, 65.95; H, 6.85%].

Dimeric complex [(*trans*-$PtCl_2L^{17}$)$_2$] 8. A solution of L^{17} (0.286 g, 0.253 mmol) in thf (20 cm^3) was added to a stirred solution of $[PtCl_2(PhCN)_2]$ (0.118 g, 0.250 mmol) in thf (20 cm^3). The mixture was stirred at room temperature for 0.5 h and then concentrated to *ca.* 5 cm^3. Addition of pentane (30 cm^3) under stirring afforded a yellowish precipitate which was filtered off and dried under reduced pressure overnight (0.307 g, 91%), m.p. 205–210 °C (Found: C, 63.30; H, 5.80. $C_{74}H_{84}Cl_2O_6P_2Pt$ requires C, 63.60; H, 6.05%; M_r = 1397.43); $\tilde{\nu}_{max}/cm^{-1}$ (KBr) 1758s and 1733s (C=O); (Polythene disc) 346 (Pt–Cl). The room-temperature ^1H NMR spectrum is broad. Only Bu^t signals could be identified: δ 1.32, 1.25 and 0.70 (3 × s, 36 H, Bu^t); ^{13}C-{^1H} NMR ($CDCl_3$), δ 170.26 (s, C=O), 145.37–124.55 (aromatic C), 69.45 (OCH_2), 59.98 (OCH_2), 34.00, 33.89, 33.54, 33.15 and 31.29 [these five signals are assigned to $C(CH_3)_3$ or calix CH_2], 31.73, 31.62 and 31.12 [3 × s, $C(CH_3)_3$], 16.15 and 13.80 (2s, CH_2CH_3); ^{31}P-{^1H}

NMR (thf–C_6D_6), δ 101.7 (s with Pt satellites, J_{PPt} = 3026 Hz). FAB mass spectrum: *m/z* 1361 (5%) $(M_{monomer} - Cl)^+$ and 1325 (7) $(M_{monomer} - Cl - HCl)^+$. Molecular weight (osmometry, CH_2Cl_2) = 2920.

Dimeric complex [(*trans*-$PdCl_2L^{18}$)$_2$] 9. A solution of L^{18} (0.450 g, 0.362 mmol) in thf (20 cm^3) was added to a stirred solution of $[PdCl_2(PhCN)_2]$ (0.137 g, 0.357 mmol) in thf (30 cm^3). The mixture was stirred at room temperature for 0.5 h and then concentrated to *ca.* 5 cm^3. Addition of pentane (40 cm^3) under stirring afforded a yellow precipitate which was filtered off and dried under reduced pressure overnight (0.450 g, 89%), m.p. 240 °C (decomp.) (Found: C, 69.40; H, 6.75. $C_{82}H_{98}Cl_2O_6P_2Pd$ requires C, 69.40; H, 6.95%; M_r = 1418.95); $\tilde{\nu}_{max}/cm^{-1}$ (KBr) 1751s and 1718s (C=O); (Polythene disc), 363s (Pd–Cl). The room-temperature ^1H NMR ($CDCl_3$) spectrum displays very broad signals. ^{13}C-{^1H} NMR ($CDCl_3$), δ 169.67 (s, C=O), 154.79–23.99 (aromatic C), 74.49, 70.62 and 69.55 (OCH_2), 34.05, 33.85 and 33.51 [3 × s, $C(CH_3)_3$], 32.40 (br, calix, CH_2), 31.76, 31.61 and 31.05 [3 × s, $C(CH_3)_3$], other signals not assigned; ^{31}P-{^1H} NMR ($CDCl_3$), δ 110.6 and 110.3 (2 × s, PPh_2). FAB mass spectrum: *m/z* 1382 (5%) $(M_{monomer} - Cl)^+$ and 1346 (12) $(M_{monomer} - 2Cl)^+$. Molecular weight (osmometry, CH_2Cl_2) = 3010.

(Cycloocta-1,5-diene){*cis*-5,11,17,23-tetra-*tert*-butyl-25,27-bis(diphenylphosphinooxy)-26,28-bis[(1*R*,2*S*,5*R*)menthyloxycarbonylmethoxy]calix[4]arene}rhodium(I) tetrafluoroborate 10. A solution of $AgBF_4$ (0.092 g, 0.473 mmol) in thf (1 cm^3) was added to a solution of [{RhCl(cod)}$_2$] (0.117 g, 0.237 mmol) in dichloromethane (3 cm^3). Stirring was stopped after 5 min. Then the supernatant solution and dichloromethane washings of the AgCl precipitate were filtered through Celite into a solution of L^{16} (0.670 g, 0.475 mmol) in CH_2Cl_2 (25 cm^3). The solution was concentrated to *ca.* 5 cm^3 and addition of diethyl ether (30 cm^3) afforded a golden precipitate which was filtered off and dried *in vacuo* (0.550 g, 68%), m.p. 197 °C (decomp.) (Found: C, 70.45; H, 7.60. $C_{100}H_{126}BF_4O_8P_2Rh$ requires C, 70.35; H, 7.45%; M_r = 1707.77); $\tilde{\nu}_{max}/cm^{-1}$ (KBr) 1740s and 1722s (C=O). NMR: ^1H ($CDCl_3$, 298 K), δ 7.88–7.64 and 7.10–7.00 (20 H, PPh_2), 6.68 (br s, 4 H, HC=CH of cod), 6.57 (s, 4 H, *m*-H), 5.85 (s, 4 H, *m*-H), 4.78 (br, 6 H, $OCH_2CO_2C_{10}H_{19}$ and OCH of menthyl), 3.63 and 2.86 (2 × br, 8 H, calix CH_2), 3.22 and 1.79 (m, 8 H, CH_2 of cod), 1.61–0.59 (36 H, menthyl), 1.18 (s, 18 H, Bu^t) and 0.57 (s, 18 H, Bu^t); ^{13}C-{^1H} ($CDCl_3$), δ 168.43 (s, C=O), 150.46–124.29 (aromatic C), 100.07 (br s, CH of cod), 75.15 (s, OCH of menthyl), 70.10 (s, OCH_2), 46.76 (s, CH of menthyl), 40.50 (CH_2 of cod), 40.07 (s, CH_2 of menthyl), 33.83 and 33.37 [2 × s, $C(CH_3)_3$], 32.45 (br s, calix CH_2), 31.48 and 30.61 [2 × s, $C(CH_3)_3$]; ^{31}P-{^1H} (CH_2Cl_2–C_6D_6), δ 131.3 (d, PPh_2, J_{PRh} = 175.2 Hz). MS (FAB): *m/z* 1512 (100%) [$(M - BF_4 - cod)^+$] and 1620 (9) [$(M - BF_4)^+$]. Molecular weight by osmometry = 1760 (CH_2Cl_2).

Acknowledgements

We are grateful to Professor Maurice Leroy and the Ecole Européenne de Chimie for providing us with facilities. We thank Professor Anthony Harriman for fruitful discussions.

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Received 7th July 1995; *Paper* 5/04456A