Complexation Studies with a Calix[4]arene-Derived Phosphinite − Divergent Arrays of Cavities Linked by MCl_2 Fragments (M = Pd, Pt)

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A cone-shaped calix[4]arene-derived monophosphinite, 25,27-di(ethoxycarbonylmethoxy)-26-hydroxy-28-(diphenylphosphinooxy)calix[4]arene (**L**^{1}), has been prepared in two steps from calix[4]arene. Treatment of **L**^{1} with [AuCl(tetrahydrothiophene)] in tetrahydrofuran gave the phosphinite complex [AuCl**L**^{1}] (**1**). Reaction of [$PdCl_2(PhCN)_2$] with two equivalents of **L**^{1} gave selectively *trans*-[$PdCl_2$**L**$^1{}_2$] (**2**). Complex **2** · 2 CH_2Cl_2 crystallizes in the triclinic space group $P\bar{1}$. The molecule is centrosymmetric, leading to a divergent array of the two calixarene moieties. The palladium atom resides outside both cones. As a result of steric interactions, the *meta* and *para* carbon atoms of the PPh_2-bearing aryl ring are significantly pushed to the interior of the cavity. The related platinum complex *trans*-[$PtCl_2$**L**$^1{}_2$] (**3**), was obtained similarly from [$PtCl_2(PhCN)_2$] and presents in the solid state a structure which is isomorphous to that of **2**. The diphosphinite 25,27-di(ethoxycarbonylmethoxy)-26,28-bis(diphenylphosphinoxy)calix[4]arene (cone) (**L**^{2}) has also been prepared and reacts with [$PtCl_2(PhCN)_2$] to yield oligomeric material.

The calix[4]arene structural framework has been extensively used as an important building block for the preparation of cavernous multifunctional podands[1][2][3][4][5][6][7]. Many of these ligands appear suitable for the selective recognition and complexation of metal cations[8][9][10][11][12][13][14][15][16][17] and/or for use as sensorial devices for anionic species[18][19]. An important feature which contributes to the valuable binding properties of functionalized calix[4]arenes in the *cone* conformation concerns the plasticity of the calixarene matrix. The flexibility of the cavity allows adoption of numerous geometries ranging from an almost C_4-symmetrical structure[20][21] to that of a so-called "pinched cone"[22][23]. In most structures where the latter shape has been encountered, two of the opposite aryl rings of the calixarene matrix lie almost coparallel, with the other two being essentially perpendicular.

As an extension of our earlier studies on calixarene-derived ligands suitable for transition metal complexation[24][25][26][27][28][29] we now report new examples of bulky calix[4]arene-derived phosphinites that form stable gold(I), palladium(II), and platinum(II) complexes. By reference to X-ray crystallography and NMR data, we describe the unusual structural attributes resulting from coordination of two such bulky ligands to a single metal center and, in particular, the resultant stereochemically-induced modification of the calixarene matrix. The present study complements previous results obtained with somewhat related compounds in which the calixarene ligands bear *tert*-butyl groups in the *para* positions, and for which inadequate X-ray crystallographic data were obtained[23]. In order to isolate the effects of metal complexation on the structural properties of the calixarenes of the macrocycle from steric effects relating to organic substituents, we have focussed our attention on the synthesis of calixarenes with freely accessible cavities. In fact omission of the *t*Bu groups allows intimate structural details to be elucidated. In addition such open cavities being equipped with a metal center at the bottom of the well may provide access to novel catalytic systems based on molecular recognition properties[30][31]. Here we describe the synthesis of open-ended calixarenes bearing two remote ester functions specifically designed to allow complexation of transition metals. Note, that investigations on the complexation properties of calixphosphinite ligands with three[9] and four[9][32][33] phosphorus atoms have recently been published.

Results and Discussion

Monophosphinite **L**^{1}, described here for the first time, was prepared in a two-step synthesis in which the first stage involved blocking of two distal hydroxy groups of calix[4]arene (Scheme 1). Intermediate **L**^{0}, which is a key reactant for the formation of both **L**^{1} and **L**^{2}, was obtained in 55% yield using conventional alkylation procedures[5]. It was deduced that of the four conformations possible for **L**^{0}, the cone conformer was the only species detectable by ^{1}H- and ^{13}C-NMR spectroscopy. In particular, a unique ^{13}C-chemi-

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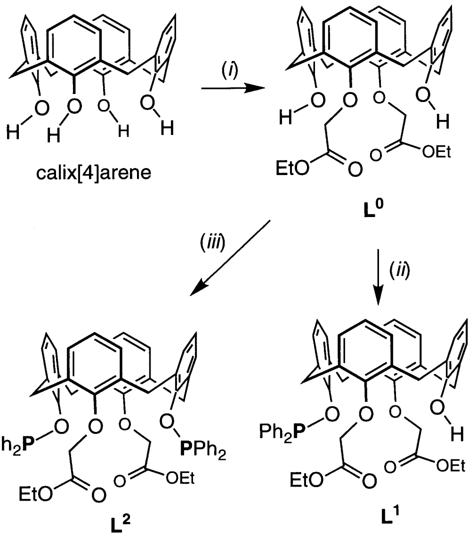
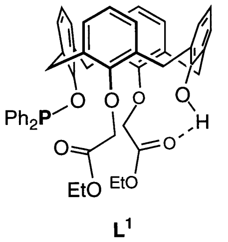
cal shift of $\delta = 31.32$ was observed for the bridging methylene carbon atoms which, according to the diagnostic criteria outlined by Jaime et al. corresponds exactly to that expected for the cone conformation[34]. In fact similar studies made for the other non-metallated calixarene derivatives described here confirmed that these also persisted in the cone conformation.

Scheme 1. (*i*) K_2CO_3 (1 equiv.), RT, 15 h, acetone; then $BrCH_2CO_2Et$ (2 equiv.), 24 h , reflux; (*ii*) NEt_3 (2.5 equiv.), 0°C, in THF, 1 h; then addition of Ph_2PCl (2 equiv.); (*iii*) $LiNiPr_2$ (2 equiv.), 0.5 h, in THF (−78°C); then Ph_2PCl (2 equiv.)



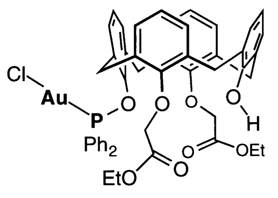
Monophosphination of $\mathbf{L^0}$ was achieved under mild conditions using NEt_3 as base. A signal typical of phosphinite residues is apparent at $\delta = 123.8$ in the ^{31}P-NMR spectrum. The IR (KBr) spectrum of $\mathbf{L^1}$ shows two strong absorption bands in the ester region (1760, 1737 cm^{-1}). The lower-energy band, located at 1737 cm^{-1}, is attributed to an ester having the carbonyl group hydrogen-bonded to a neighbouring hydroxy group. On this basis, the higher-energy band must arise from a non-hydrogen bonded carbonyl group. More surprisingly, precursor $\mathbf{L^0}$ also exhibits two well-resolved carbonyl bands in the IR spectrum (1761, 1742 cm^{-1}). This situation, which we have observed in other functionalized calixarenes bearing appended carbonyl moieties[23], is tentatively interpreted in terms of a mixture of free and hydrogen-bonded esters within the same molecule. X-ray investigations performed on complexes obtained from $\mathbf{L^1}$ corroborate this interpretation (vide infra).



$\mathbf{L^1}$

Despite using forcing conditions, it was not possible to attach two phosphinites to the calixarene using mildly basic reagents (such as NEt_3). Synthesis of the bis-phosphinite $\mathbf{L^2}$ required more basic conditions, but was conveniently accomplished using two equivalents of $LiNiPr_2$ (Scheme 1). The ^{31}P-NMR spectrum of this compound displays a single peak at $\delta = 122.0$, indicating magnetic equivalence of the two phosphinites. The four bridging methylene groups of the macrocycle give a typical AB spectrum, as expected for a cone conformation. Interestingly, the aromatic region of the ^1H-NMR spectrum of $\mathbf{L^2}$ displays an AB_2 signal (6 H, $\delta = 6.21$, *p*-ArH_{calix}, 5.92, *m*-ArH_{calix}) significantly shifted upfield with respect to the other aromatic hydrogen atoms. Presumably, the two bulky phosphino groups cause steric crowding around the ester groups and thereby push the *meta* and *para* hydrogen atoms of two opposite aryl rings into the shielding zone of the other two aromatic rings of the calixarene matrix. These studies however do not allow distinction of which of the two aryl rings, namely those bearing the PPh_2 groups or those connected to the esters, are pinched together.

To show that phosphinite $\mathbf{L^1}$ is suitable for transition metal complexation, we investigated its coordinative properties towards a relatively small metal fragment, namely the "AuCl" unit. Thus, treatment of $\mathbf{L^1}$ with [AuCl(THT)] (THT = tetrahydrothiophene) in tetrahydrofuran gave the gold complex **1** as a white solid. The FAB mass spectrum of **1** shows an intense peak at 977.0 (with the expected isotopic profile) corresponding to the $[M^+ - Cl]$ ion. As for $\mathbf{L^1}$, the ^1H-NMR spectrum of **1** contains two AB patterns for the $ArCH_2Ar$ hydrogen atoms and an AB pattern for the two opposite $OCH_2C(O)$ groups. The ^{31}P-NMR spectrum displays a single peak at $\delta = 118.4$; this chemical shift is in agreement with those reported recently by Puddephatt et al. for other phosphinito-calixarene gold(I) complexes[9].



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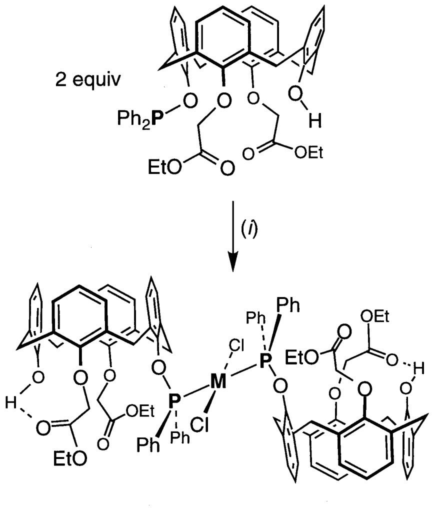
Reaction of $\mathbf{L^1}$ with $[PdCl_2(PhCN)_2]$ resulted in formation of complex **2** with high yield (Scheme 2). The *trans* stereochemistry around the metal center was inferred from the FAR IR spectrum which shows a single ν(Pd−Cl) band at 360 cm^{-1} and was confirmed by an X-ray diffraction study (vide infra). Despite the presence of the bridging P−Pd−P unit, the cone conformation of the two terminal calixarenes is retained. In marked contrast to the behaviour described above for $\mathbf{L^2}$, only a single aryl ring appears to be distorted out of its regular (i.e. non-metallated) position. Thus, NMR studies made with **2** indicate that there is an enhanced shielding effect for the *meta* and *para* hydrogens of only one aryl ring from each calixarene whereas with $\mathbf{L^2}$ two opposite rings are mutually distorted. Presumably, deformation in **2** refers to the aryl rings lying closest to the metal center.

Scheme 2. (*i*) [$MCl_2(PhCN)_2$] (M = Pd, Pt) in CH_2Cl_2



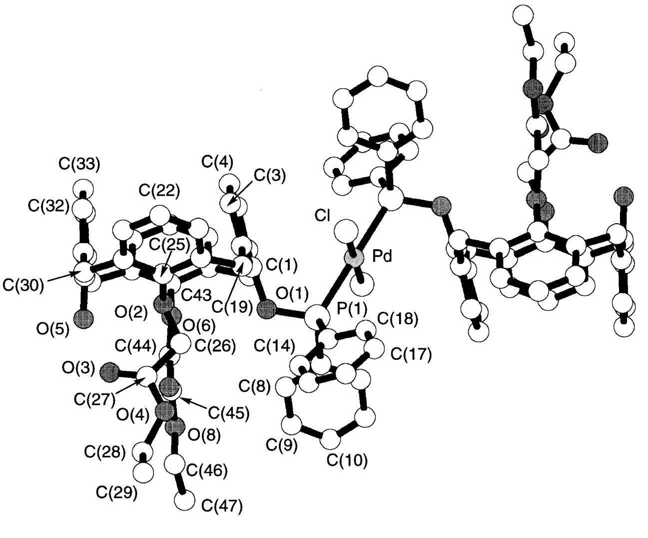
2, M = Pd ; **3**, M = Pt

The corresponding platinum analogue, **3**, also having *trans* sterochemistry [*J*(PPt) = 3006 Hz[35]] was obtained in a similar manner but starting from [$PtCl_2(PhCN)_2$] (Scheme 2). Comparable upfield shifts on *meta* and *para* H atoms of a single aryl ring of each calixarene were observed. In fact, the ^{1}H-NMR properties of **2** and **3** were very similar, suggesting that a common structural feature persists in both metallated calixarenes. It is noteworthy that for complex **1** bearing the relatively small Au−Cl fragment all *m*-ArH hydrogen atoms lie above $\delta = 6.61$ so that it appears reasonable to assign the upfield shifts observed for certain aromatic CH atoms in **2** and **3** to steric effects.

Both metal complexes, **2** and **3**, were fully characterized by X-ray structural analyses, but since these complexes are isomorphous, only one of them, namely the palladium complex **2**, will be described below. A summary of the crystal data is given in Table 1 (complex **2**) and Table 3 (complex **3**). Important distances and angles may be found in Table 2 (complex **2**) and Table 4 (complex **3**) . A view of **2** is represented in Figure 1. Examination of Figure 1 shows that half of the molecule is symmetry-generated since the palladium atom lies at the centre of symmetry. This leads to a solid-state structure with two divergent cavities, as defined by the calixarene units. The overall length of the molecule is ca. 18 Å. The complex exhibits square-planar coordination around the metal center with Pd−Cl and Pd−P bond lengths of 2.3014(6) and 2.3251(6) Å, respectively. The shape of the calixarene units strongly deviates from an ideal cone. In particular, two opposite aryl rings lie nearly perpendicular (dihedral angle $\Delta = 86°$) with the other two making an angle of 12°. Each phosphorus atom is directed away from the cavity defined by the calixarene, the O−P−Pd plane being essentially orthogonal to the corresponding O-aryl ring (dihedral angle ca. 80°).

Several interesting facets emerge from the solid state structure (Fig. 1). Firstly, it is noticeable that the bulky diphenylphosphino groups adopt the position that causes minimal steric perturbation to the terminal calixarene units. Secondly, it is clearly demonstrated that the upper end of the phosphinated aryl ring is pushed towards the center of the cavity. The dihedral angle between the calixarene reference plane and the P-bearing phenoxy ring is 57.7(1)°. This "perturbation" of a single aryl unit was inferred from the NMR studies but is now shown unequivocally to exist in the solid state. Several complementary factors contribute to this effect. Although interactions between the d_{z^2} orbital on the palladium center and the adjacent aryl ring provide some minor repulsive force [Pd···C(1), 3.313 Å], the primary perturbing influence arises from steric interaction with the distant PPh_2 moiety {contacts: H(13)···C′(5) = 3.21 Å and H(13)···C′(6) = 3.33 Å [H(13) on C(18)]}. Thirdly, the above mentioned structural distorsion results in a rather narrow entrance to the cavity. This effect is illustrated by the comparatively short C(4)−C(33) separation of 4.64 Å and is reminiscent of the so-called *bis-roof* structure recently described by Shinkai et al.[36][37][38]. In the latter case, two distal aryl rings are made to approach each other by their involvment in π-complexes with $Cr(CO)_3$ fragments. This is a very different perturbing mode than that outlined for **2** and **3**, since the major structural feature of pinching of the calixarene unit results from mutual attraction of electron-deficient walls. In our case, a *single* wall is forced inwards by external steric influences. Finally, the short O(7)−O(5) distance (2.87 Å) indicates hydrogen bonding between the hydroxy function and the C(45)−O(7) carbonyl group. This finding corroborates our interpretation of the IR spectra.

Figure 1. MolView drawing of complex **2** with partial labeling scheme. The distance between C(4) and C(33) is 4.64 (1) Å



Considerable effort was expended to generate the corresponding cis isomers of **2** and **3**, but to no avail; examination of molecular models suggests that the bulky calixarene fragment provide undue steric barriers to formation of the cis complexes.

Reaction of $\mathbf{L^2}$ with [$PtCl_2(PhCN)_2$] in CH_2Cl_2 gave a sparingly soluble white material in keeping with the overall formulation of [$PtCl_2(\mathbf{L^2})]_n$ to which we assign a polymeric structure. The ^{31}P-NMR spectrum shows a broad peak at δ = 102.8, with a J(PPt) coupling constant of 3009 Hz, indicating that the stereochemistry about platinum is exclusively *trans*. The ^{1}H-NMR spectrum shows broad signals, suggesting the formation of a polymer and/or a mixture of oligomeric compounds. Because of its poor solubility, a molecular weight determination could not be performed. It is worth mentioning here that with previously reported diphosphinites having Bu^t groups occupying the *p*-positions of the calixarene moiety, cyclic tetrameric compounds were obtained[23]. The driving force for formation of oligomeric arrays arises from the fact that each of the phosphino groups in the bis derivative **L^2** is forced to lie outside of the cavity. Formation of bis(phosphinite) complexes with large metallo fragments such as "$PdCl_2$" or "$PtCl_2$" is then most easily accomplished by taking phosphorus from two separate calixarenes. With considerably smaller metallo-fragments such as CuCl, it is feasible that a mononuclear chelate could be generated[32]. Similar behaviour has also recently been observed with smaller phosphorus substituents[33].

In summary, we have described two novel phosphinites having open-ended cavities. Conditions are described which permit the selective attachment of one or two phosphino groups to the lower rim of a 1,3-difunctionalized calix[4]arene. The appended phosphino groups remain accessible for complexation with appropriate metallo-fragments and well-defined complexes have been observed with $PdCl_2$ and $PtCl_2$. In these cases and regardless of the presence of *t*Bu groups on the upper rim, it was only possible to isolate complexes demonstrating *trans* stereochemistry at the metal atom. The bulkyness of the two *trans* arranged phosphinites causes subtle modification to the structure of the calixarene unit, pushing one phenoxy ring into the cavity. In view of the fact that metallocalixarenes **2** or **3** contain two divergent cavities suitable for inclusion of neutral species, such nanostructures may provide further valuable complexation and/or catalytic opportunities.

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Experimental Section

Reagents and Physical Measurements: All manipulations were performed in Schlenk-type flasks under argon. Solvents were dried by conventional methods and distilled immediately prior to use. $CDCl_3$ was eluted from a 5 cm thick alumina column and stored under argon over molecular sieves (0.4 nm). − IR spectra were recorded on a Perkin Elmer 1600 spectrometer (4000−400 cm^{-1}) and a Bruker FIR spectrometer (500−90 cm^{-1}). − ^{1}H-, ^{31}P{^{1}H}-, and ^{13}C{^{1}H}-NMR spectra were recorded with a FT Bruker WP-200 SY instrument. The ^{1}H-NMR data were referenced to residual protiated solvents (7.27 for $CDCl_3$), ^{13}C chemicals shifts are reported relative to deuterated solvents (δ = 77.0 for $CDCl_3$, δ = 67.40 for [D$_8$]THF) while the ^{31}P-NMR data are given relative to external H_3PO_4. − Mass spectra of complexes **2** and **3** were recorded on a ZAB HF VG Analytical instrument with *m*-nitrobenzyl alcohol as a matrix. The mass spectrum of **L^2** was recorded on a TSQ-70 spectrometer. Calix[4]arene[39], [AuCl(THT)] (THT = tetrahydrothiophene)[40], [$PdCl_2(PhCN)_2$][41], and [$PtCl_2(PhCN)_2$][41], were prepared using literature procedures.

Preparations

25,27-Di(ethoxycarbonylmethoxy)-26,28-(dihydroxy)calix[4]-arene (**L^0**): A suspension of calix[4]arene (6.000 g, 14.13 mmol) was treated with K_2CO_3 (2.150 g, 15.55 mmol) in acetone (150 cm^3) for 15 h at room temperature. $BrCH_2CO_2Et$ (4.957 g, 29.68 mmol) was then added and the resultant mixture was heated under reflux for 24 h. After filtration, the solvent was removed in vacuo. The residue was recrystallized from CH_2Cl_2-MeOH, yielding **L^0** as a white analytically pure solid (6.600 g, 78%), R_f = 0.12 (SiO_2, CH_2Cl_2), m.p. 180°C. − IR (KBr): $\tilde{\nu}$ = 3387 br (OH), 1761 (C=O), 1742 (C=O···HO). − ^{1}H NMR ($CDCl_3$): δ = 7.66 (s, 2 H, OH), 7.07 (d, 4 H, *m*-ArH, ^3J = 7.5 Hz), 6.92 (d, 4 H, *m*-ArH, ^3J = 7.5 Hz), 6.75 (t, 2 H, *p*-ArH, ^3J = 7.5 Hz), 6.67 (t, 2 H, *p*-ArH, ^3J = 7.5 Hz), 4.75 (s, 4 H, OCH_2), 4.50 and 3.41 (AB spin system, 8 H, $ArCH_2Ar$, ^2J = 13 Hz), 4.34 (q, 4 H, OCH_2CH_3, ^3J = 7.1 Hz), 1.37 (t, 6 H, CH_3, ^3J = 7.1 Hz). − ^{13}C{^{1}H} NMR ($CDCl_3$): δ = 168.70 (CO), 152.82, 152.20, 132.95, 127.98 (4 C aromatic), 128.97, 128.34, 125.44, 118.95 (4 CH aromatic), 72.29 ($ArOCH_2$), 61.24 (OCH_2CH_3), 31.32 ($ArCH_2Ar$), 13.97 (CH_3). − $C_{36}H_{36}O_8 \cdot 0.5$ MeOH (596.68 + 16.02): calcd. C 71.55; H 6.25; found: C 71.03; H 5.70. The formation of a solvate was confirmed by ^{1}H-NMR spectroscopy.

25,27-Di(ethoxycarbonylmethoxy)-26-hydroxy-28-(diphenylphosphinooxy)calix[4] arene (**L^1**): To a solution of **L^0** (3.320 g, 5.60 mmol) in THF (100 cm^3) at 0°C was added triethylamine (1.420 g, 14.01 mmol). After stirring for 1 h, a solution of Ph_2PCl (1.360 g, 6.16 mmol) in THF (25 cm^3) was added slowly accompanied by formation of Et_3NHCl. The mixture was shaken for a further 24 h and the precipitate was removed by filtration before the solvent was evaporated in vacuo. Recrystallization of the residue from toluene-hexane gave **L^1** as a white solid (3.500 g, 80%), R_f = 0.43 (SiO_2, CH_2Cl_2), m.p. 148−150°C. − IR (KBr): $\tilde{\nu}$ = 3409 (OH), 1760 (C=O), 1737 (C=O···HO). − ^{1}H NMR ($CDCl_3$): δ = 7.80−7.78 and 7.49−7.47 (10 H, $OPPh_2$), 7.05−6.60 (12 H, ArH_{calix}), 4.62 and 3.31 (AB spin system, 4 H, $ArCH_2Ar$, ^2J = 13.5 Hz), 4.51 and 4.08 (AB spin system, 4 H, OCH_2CO_2, ^2J = 15.6 Hz), 4.29 and 3.01 (AB spin system, 4 H, $ArCH_2Ar$, ^2J = 13.2 Hz), 4.13 (q, 4 H,OCH_2CH_3, ^3J = 7.0 Hz), 3.67 (s, 1 H, OH), 1.24 (t, 6 H, OCH_2CH_3 , ^3J = 7.0 Hz). − ^{13}C {^{1}H} NMR ($CDCl_3$): δ = 169.44 (s, CO), 154.26−118.50 (s, C_{arom}), 71.75 (s, OCH_2CO), 60.78 (s, OCH_2CH_3), 31.17 and 30.95 (s, $ArCH_2Ar$), 13.97 (s, OCH_2CH_3). − ^{31}P{^{1}H} NMR ($CDCl_3$): δ = 123.8. − $C_{48}H_{45}O_8P$ (780.86): calcd. C 73.83; H 5.81; found: C 73.57; H 5.55.

25,27-Di(ethoxycarbonylmethoxy)-26,28-bis(diphenylphosphinooxy)calix[4]arene (**L^2**): To a cold (−78°C) solution of BuLi (1.5 M, 4.05 cm^3, 6.07 mmol) in THF (50 cm^3) was added slowly a solution of diisopropylamine (0.614 g, 6.07 mmol) in THF (20 cm^3), pre-cooled at −78°C. The mixture was kept at this temperature for 30 min before slow addition of a solution of the precursor **L^0** (1.800 g, 3.03 mmol) in THF (20 cm^3, −78°C). After 1 h, Ph_2PCl (1.339 g, 6.07 mmol) was added dropwise. The solution was stirred for 2 h, filtered through Celite, and evaporated to dryness. The residue was dissolved in toluene (50 cm^3) and the resulting suspension filtered through Celite in order to remove LiCl. Concentration of the filtrate and addition of hexane precipitated **L^2** as a white solid (2.490 g, 85%), R_f = 0.89 (SiO_2, CH_2Cl_2-MeOH, 95:5, v/v). − IR (KBr): $\tilde{\nu}$ = 1762 (C=O). − ^{1}H NMR ($CDCl_3$): δ = 7.76−6.70 (24H aromatics), 6.20 (t, 2 H, *p*-ArH, ^3J = 7.6 Hz), 5.91 (d, 4 H, *m*-ArH, ^3J = 7.6 Hz), 4.76 (s, 4 H, OCH_2), 4.41 and 2.84 (syst. AB, 8 H, $ArCH_2Ar$, ^2J = 14.5 Hz), 3.99 (q, 4 H, OCH_2CH_3,

^3J = 7.2 Hz), 1.37 (t, 6 H, CH_3, ^3J = 7.2 Hz). − $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ = 122.0 (s, $OPPh_2$). This product is very sensitive to hydrolysis. We detected by NMR the formation of **L**^{1} and **L**^{0} when traces of water were present. − MS (EI); *m/e* (%): 964.2 (10) [M^+]. − $C_{60}H_{54}O_8P_2$ (965.042): calcd. C 74.68; H 5.64; found: C 74.72; H 5.80.

Chlorobis[25,27-di(ethoxycarbonylmethoxy)-26-hydroxy-28-(diphenylphosphinooxy)calix[4]arene]gold(I) (**1**): A solution of [AuCl(THT)] (0.160 g, 0.50 mmol) in THF (15 cm^3) was added to a solution of compound **L**^{1} (0.390 g, 0.50 mmol) in THF (15 cm^3). After 1 h the resultant solution was concentrated to ca. 5 cm^3; addition of pentane gave **1** as a white powder which was recrystallised from THF-pentane (0.380 g, 75%), m.p. 112−114°C (dec.). − IR (KBr): ṽ = 3430 br (OH), 1752 (C=O), 1728 (C=O···HO). − ^1H NMR ([D_8]THF): δ = 8.27−8.17 and 7.74−7.73 (10 H, $OPPh_2$), 7.32−6.57 (12 H, Ar*H*$_{calix}$), 4.68 and 3.13 (AB spin system, 4 H, $ArCH_2Ar$, ^2J = 13.3 Hz), 4.39 and 4.19 (AB spin system, 4 H, OCH_2CO_2, ^2J = 16.0 Hz), 4.31 and 3.32 (AB spin system, 4 H, $ArCH_2Ar$, ^2J = 13.5 Hz), 4.23 (q, 4 H,O*CH*$_2$CH$_3$, ^3J = 7.0 Hz), 3.76 (s, 1 H, OH), 1.30 (t, 6 H, OCH$_2$*CH*$_3$, ^3J = 7.0 Hz). − ^{13}C $\{^1H\}$ NMR ([D_8]THF): δ = 179.90 (s, CO), 154.80−119.18 (s, C_{arom}), 72.70 (s, O*C*H$_2$CO), 61.40 (s, O*C*H$_2$CH$_3$), 32.36 and 31.74 (s, Ar*C*H$_2$Ar), 14.41 (s, OCH$_2$*C*H$_3$). − $^{31}P\{^1H\}$NMR ($CDCl_3$): δ = 118.4. − MS (FAB MS); *m/e* (%): 977 (100) [M^+ − Cl]. − $C_{48}H_{45}AuClO_8P$ (1013.28): calcd. C 56.90; H 4.48; found: C 57.22; H 4.77.

Table 1. Crystallographic data for *trans*-[$PdCl_2$(**L**^{2})$_2$] · 2 CH_2Cl_2 (**2** · 2 CH_2Cl_2)

formula	$C_{96}H_{90}Cl_2O_{16}P_2Pd \cdot 2\ CH_2Cl_2$		
fw	1908.9	T [K]	293
a [Å]	11.393(3)	λ [Å]	0.71073
b [Å]	11.767(3)	space group	$P\bar{1}$
c [Å]	18.933(5)	Z	1
α [deg]	77.16(2)	D_{calcd} [g cm^{-3}]	1.382
β [deg]	87.04(2)	θ range [deg]	2−28
γ [deg]	68.05(2)		
μ [cm^{-1}]	4.720		
V [Å^3]	2294.0	R[a]	0.045
no of data collected	10309	R_w[b]	0.066
no of data with $I > 3\sigma(I)$	7418		

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

Table 2. Selected structural parameters for **2** (lengths in Å, angles in°)

Bond Lengths			
Pd−Cl	2.3014(6)	O2−C26	1.417(3)
Pd−P1	2.3251(6)	C26−C27	1.508(4)
P1−C7	1.811(2)	C27−O4	1.319(4)
P1−C13	1.812(2)	C27−O3	1.211(4)
O1−P1	1.621(2)	O6−C44	1.417(3)
C1−C2	1.396(3)	C44−C45	1.494(4)
C2−C3	1.402(4)	C45−O7	1.186(3)
C3−C4	1.369(4)	C45−O8	1.321(3)
C4−C5	1.388(4)	O8−C46	1.458(3)
C2−C19	1.515(3)	C46−C47	1.455(5)
C5−C6	1.395(3)	O5···O3	2.87(1)
C43−O6	1.397(3)	C4···C33	4.64(1)
C36−O5	1.372(3)	H13···C′5	3.21(1)
C25−O2	1.387(3)	H13···C′6	3.33(1)
Bond Angles			
Cl−Pd−P1	90.67(2)	C6−C48−C42	108.3(2)
O1−P1−C7	101.8(1)	C35−C37−C38	110.2(2)
O1−P1−C13	104.5(1)	C44−C45−O7	126.2(3)
C7−P1−C13	100.3(1)	C26−C27−O3	126.0(3)
C1−O1−P1	118.8(1)	C43−O6−C44	109.3(2)
C2−C19−C20	110.4(2)	C25−O2−C26	114.8(2)

trans-Dichlorobis[25,27-di(ethoxycarbonylmethoxy)-26-hydroxy-28-(diphenylphosphinooxy)calix[4]arene]palladium(II) (**2**): A solution of [$PdCl_2(PhCN)_2$] (0.384 g, 0.310 mmol) in THF (50 cm^3) was added slowly to a solution of **L**^{1} (0.484 g, 0.620 mmol) in THF (40 cm^3). After 2 h the solution was reduced to one-third and hexane was added, yielding **2** as a yellow solid (0.456 g, 84%), R_f = 0.84 (SiO_2, MeOH-CH_2Cl_2, 5/95, v/v), m.p. 238−240°C (dec.). − IR spectrum (KBr): ṽ = 3414 (OH), 1750 (CO) , 1731 (C=O···HO). − Far FT-IR: ṽ = 360 (PdCl). − ^1H NMR ($CDCl_3$): δ = 7.84−6.32 (19 H, CH aromatic), 7.74 (1 H, OH, exchanges with D_2O), 6.21 (t, 1 H, *p*-ArH$_{calix}$, ^3J = 7.5 Hz), 5.92 (d, 2 H, *m*-ArH, 3J = 7.5 Hz), 5.11 and 4.59 (AB spin system, 4 H, OCH_2, ^2J = *16* Hz), 4.67 and 3.22 (AB spin system, 4 H, $ArCH_2$, ^2J = *13* Hz), 4.35 and 3.22 (AB spin system, 4 H, $ArCH_2Ar$, ^2J = 16.8 Hz), 4.24 (q, 8 H, O*CH*$_2$CH$_3$, ^3J = 7.1 Hz), 1.28 (t, 6 H, OCH$_2$*CH*$_3$, ^3J = 7.1 Hz). − ^{13}C $\{^1H\}$ NMR ($CDCl_3$): δ = 171.35 (s, CO), 157.09−119.02 (C aromatic), 71.64 (O*C*H$_2$CO), 60.93 (O*C*H$_2$CH$_3$), 32.57 and 31.97 (2s, ArCH$_2$Ar), 13.97 (OCH$_2$*C*H$_3$). − $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ = 111 (s). − MS (FAB MS); *m/e* (%): 1703 (0.5) [M^+ − Cl]. − $C_{96}H_{90}Cl_2O_{16}P_2Pd$ (1739.03): calcd. C, 66.31; H, 5.22; found: C, 66.34; H, 5.33.

trans-Dichlorobis[25,27-di(ethoxycarbonylmethoxy)-26-hydroxy-28-(diphenylphosphinooxy)calix[4]arene]platinum(II) (**3**): To a solution of **L**^{1} (0.303 g, 0.390 mmol) in THF (40 cm^3) was added slowly a solution of [$PtCl_2(PhCN)_2$] (0.091 g, 0.195 mmol) in THF (50 cm^3). After 2h the solution was concentrated and hexane was added, yielding **3** as a white solid (0.293 g, 82%) which was dried in vacuo overnight, R_f = 0.8 (SiO_2, MeOH/CH_2Cl_2, 5/95, v/v), m.p. 271−275°C. − IR (KBr): ṽ = 3415br (OH), 1756 (C=O), 1731 (C=O···HO). − Far FT-IR: ṽ = 349 (PtCl). − ^1H NMR ($CDCl_3$): δ = 7.86−6.32 (19 H, CH aromatics), 7.72 (s, 1 H, OH, exchanges with D_2O), 6.22 (t, 1 H, *p*-ArH, ^3J = 7.6 Hz), 5.89 (d, 2 H, *m*-ArH, ^3J = 7.6 Hz), 5.14 and 4.65 (AB spin system, 4 H, OCH_2CO_2, ^2J = 16.4 Hz), 4.67 and 3.23 (AB spin system, 4 H, $ArCH_2Ar$, ^3J = 13.7 Hz), 4.42 and 3.20 (AB spin system, 4 H, $ArCH_2Ar$, ^2J = 14.8 Hz), 4.26 (q, 8 H, OCH_2CH_3, ^3J = 7.1 Hz), 1.29 (t, 6 H, OCH$_2$*CH*$_3$, ^3J = 7.1 Hz). − $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 171.39 (CO), 157.20−119.07 (C aromatics), 71.63 (O*C*H$_2$CO$_2$), 60.97(O*C*H$_2$CH$_3$), 32.56 (ArCH$_2$Ar), 31.11 (ArCH$_2$Ar), 14.00 (OCH$_2$*C*H$_3$). − ^{31}P $\{^1H\}$ NMR ($CDCl_3$): δ = 102.7 [s with Pt satellites, ^2J(PPt) = 3006.3 Hz]. − MS (FAB MS); *m/e* (%): 1827 (1) [M^+], 1790 (7) [M^+ − Cl]. − $C_{96}H_{90}Cl_2O_{16}P_2Pt$ (1827.72): calcd C, 63.09; H, 4.96; found: C, 62.79; H, 4.89.

Reaction of [$PtCl_2(PhCN)_2$] with **L**^{2}: A solution of [$PtCl_2(PhCN)_2$] (0.168 g, 3.56 mmol) in CH_2Cl_2 (30 cm^3) was added to a solution of **L**^{2} (0.344 g, 3.56 mmol) in CH_2Cl_2 (20 cm^3). After 1 h the solution was concentrated and hexane was added, yielding a white precipitate (0.329 g, 75%) which was poorly soluble in $CHCl_3$, CH_2Cl_2, and THF, m.p. 263−266°C. − ^1H NMR ($CDCl_3$): δ = 1.19 (t, OCH_2CH_3, ^3J = 7.0 Hz); all other signals are broad probably owing to a fluxional behaviour in solution or to the presence of several oligomeric compounds. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 102.8 [s with Pt satellites, ^2J(P-Pt) = 3009 Hz]. − $C_{60}H_{54}Cl_2O_8P_2Pt$ (1231.04): calcd. C, 58.04; H, 4.42; found: C, 58.11; H, 4.32.

X-ray Crystallographic Studies: Complex **2**: Crystal data are given in Table 1. A suitable crystal of **2** · 2 CH_2Cl_2 was obtained by slow diffusion of hexane into a solution of complex **2** in CH_2Cl_2 at room temperature. Data were collected on an ENRAF-NONIUS MAC3 diffractometer at room temperature with graphite monochromatic Mo-K_α radiation $\lambda = 0.7107$ Å. The cell parameters were obtained by fitting a set of 25 high-theta reflections. The data collection ($\omega/2\theta$ scan type, $2\theta_{max} = 56°$, $+h \pm k \pm l$), intensity controls without appreciable decay (0.2%) gives 10309 reflections from which 7418 were independant with $I>3\sigma(I)$. After Lorenz polarization and absorption (ψ scan) corrections, the structure was solved by direct methods. After refinement of the heavy atoms, a Fourier-difference map revealed maxima of residual electronic density close to the positions expected for hydrogen atoms; they were introduced into structure-factor calculations by their computed coordinates (C−H 0.95 Å) and isotropic thermal parameters such as $B(\mathrm{H}) = 1.3\ B_{eq}(\mathrm{C})$ Å but not refined. Full least squares refinements against F with weights $\omega = 1/\sigma^2(F)$, $\sigma^2(F^2) = \sigma^2\,(\mathrm{counts}) + (pI)^2$. Anisotropic thermal parameters were assigned to all non-hydrogen atoms except for C(28), C(29), C′(28), and C′(29). Final positive and negative electron density residues: 0.81/−0.24 e·Å^{-3}. Atomic scattering factors were from International Tables for X-ray Crystallography (1983)[42]. All calculations were performed on a DEC AXP 3100 computer with the OpenMolEN[43] package (Enraf-Nonius, 1990). The ethyl group of one ester (C28) was found to be disordered over two positions in the ratio 1:1. The plot of **2** was drawn using MolView[44].

Complex **3**$\cdot$*2* CH_2Cl_2*:* Crystal data are given in Table 3. Crystals of **3** · 2 CH_2Cl_2 were obtained by slow diffusion of hexane into a solution of complex **3** in CH_2Cl_2. Data collection as described above. The data collection ($\omega/2\theta$ scan type, $2\theta_{max} = 52°$, $+h \pm k \pm l$), intensity controls without appreciable decay (0.2%) gives 9588 reflections from which 8843 were independant with $I>3\sigma(I)$. After Lorenz polarization and absorption (ψ scan) corrections, the structure was solved by direct methods. After refinement of the heavy atoms, a Fourier-difference map revealed maxima of residual electronic density close to the positions expected for hydrogen atoms; they were introduced into structure-factor calculations by their computed coordinates (C−H 0.95 Å) and isotropic thermal parameters such as $B(\mathrm{H}) = 1.3\ B_{eq}(\mathrm{C})$ Å but not refined. Full least squares refinements against F with weights $\omega = 1/\sigma^2(F)$, $\sigma^2(F^2) = \sigma^2\,(\mathrm{counts}) + (pI)^2$. Anisotropic thermal parameters were assigned to all non-hydrogen atoms. Final positive and negative electron density residues: 0.771/−0.112 e·Å^{-3}. Complete atomic coordinates, thermal parameters and bond lengths and angles for both complexes have been deposited at the Crystallographic Data Centre (CCDC number 100858).

Table 3. Crystallographic data for *trans*-[$PtCl_2(\mathbf{L}^2)_2$] · 2 CH_2Cl_2 (**2** · 2 CH_2Cl_2)

formula	$C_{96}H_{90}Cl_2O_{16}P_2Pt\cdot 2\ CH_2Cl_2$		
fw	1997.59	T [K]	294
a [Å]	11.3891(7)	λ [Å]	0.71073
b [Å]	11.7494(7)	space group	$P\bar{1}$
c [Å]	18.941(1)	Z	1
α [deg]	77.296(5)	D_{calcd} [g cm^{-3}]	1.45
β [deg]	87.064(5)	θ range [deg]	2.5–26
γ [deg]	68.052(5)		
μ [cm^{-1}]	1.819		
V [Å^3]	2291.9 (3)	R[a]	0.029
no of data collected	9588	R_w[b]	0.041
no of data with $I>3\sigma(I)$	8843		

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

Table 4. Selected structural parameters for **3** (lengths in Å, angles in°)

Bond Lengths			
Pt−Cl	2.3066(7)	O2−C26	1.418(4)
Pt−P1	2.3024(7)	C26−C27	1.492(6)
P1−C7	1.815(3)	C27−O4	1.328(5)
P1−C13	1.820(3)	C27−O3	1.203(5)
O1−P1	1.625(2)	O6−C44	1.422(4)
C1−C2	1.386(4)	C44−C45	1.498(4)
C2−C3	1.399(5)	C45−O7	1.172(4)
C3−C4	1.374(5)	C45−O8	1.325(4)
C4−C5	1.381(5)	O8−C46	1.452(4)
C2−C19	1.515(4)	C46−C47	1.464(7)
C5−C6	1.384(4)	O5···O3	2.86(1)
C43−O6	1.398(3)	C4···C33	4.627(6)
C36−O5	1.372(4)	H13···C′5	3.21(1)
C25−O2	1.383(4)	H13···C′6	3.32(1)
Bond Angles			
Cl−Pt−P1	90.78(2)	C6−C48−C42	108.1(2)
O1−P1−C7	101.9(1)	C35−C37−C38	110.2(3)
O1−P1−C13	104.3(1)	C44−C45−O7	127.0(3)
C7−P1−C13	100.2(1)	C26−C27−O3	126.1(4)
C1−O1−P1	118.7(2)	C43−O6−C44	109.2(2)
C2−C19−C20	109.9(3)	C25−O2−C26	115.0(2)

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