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FULL PAPER

Co-ordination chemistry of macrocyclic compounds with dangling phosphines. Unusual NMR shifts in metallo-calix[4]arenes †

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Received 19th July 1999, Accepted 7th October 1999

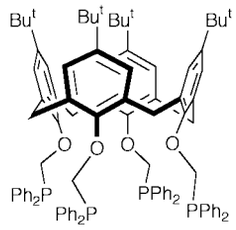
The chelating behaviour of three polyphosphines, *cone*-5,11,17,23-tetra-*tert*-butyl-25,26,27,28-tetrakis(diphenylphosphinomethoxy)calix[4]arene L^1, *cone*-5,11,17,23-tetra-*tert*-butyl-25,26,27-tris(diphenylphosphinomethoxy)-28-methoxycalix[4]arene L^2, and *cone*-5,11,17,23-tetra-*tert*-butyl-25,26-bis(diphenylphosphinomethoxy)-27,28-dihydroxycalix[4]arene L^3, has been investigated. When $[Mo(CO)_3(C_7H_8)]$ and tetraphosphine L^1 are heated together under reflux in tetrahydrofuran (THF) complex $[Mo(CO)_3L^1]$ **1** is formed, for which the calixarene behaves as a *fac*-bonded tridentate ligand with one phosphine remaining free. Similar *fac*-chelating behaviour is found with $[Mo(CO)_3L^2]$ **2**, which is obtained from triphosphine L^2. Formation of this latter complex is accompanied by the calixarene matrix adopting a partially flattened-cone conformation. In contrast, the conventional cone conformation is maintained in the trinuclear complex $[(AuCl)_3L^2]$ **3**, obtained quantitatively by treating L^2 with [AuCl(THT)] (THT = tetrahydrothiophene). Reaction of L^1 with $[RuCl_2(DMSO)_4]$ (DMSO = Me_2SO) in CH_2Cl_2 results in selective formation of the deep purple complex $[RuCl_2L^2]$ **4** built around a *fac*-trigonal bipyramidal $RuCl_2P_3$ structure. Complex **4** reacts reversibly and stepwise with two equivalents of CH_3CN. The calculated stability constants, as determined from a spectrophotometric titration, are $\log \beta_1 = 9.1$ and $\log \beta_2 = 12.4$. The proximally substituted calixarene L^3 reacts with $[PtCl_2(COD)]$ (COD = cycloocta-1,5-diene) to afford the chelate complex *cis*-$[PtCl_2L^3]$ **5**. As revealed by an X-ray diffraction study, the P–Pt vectors point away from the calixarene axis in the solid state. The axial H atom of the $C_6H_2CH_2$ group located between the two phosphine units of L^3 undergoes a significant low-field shift upon complexation (δ 7.32 *vs.* 4.48 for free L^3) presumably due to interaction with the lone pairs of the two neighbouring O-atoms. Complex **5** displays dynamic behaviour in solution, which can be rationalized as follows: (*i*) a fast flip-flop motion of the hydroxyl groups at low temperature, alternately forming hydrogen bonds with each of two neighbouring phenolic oxygens; (*ii*) a reversible inversion of the phenol ring through the lower-rim annulus, triggered by breakage of the hydrogen bonds at higher temperature. Reaction of $[PtCl_2(COD)]$ with one equivalent of L^1, followed by *in situ* oxidation with $NH_2CONH_2{\cdot}H_2O_2$, results in formation of a chelate complex, containing two proximal phosphines bonded to platinum as in **5** and two pending $CH_2P(O)Ph_2$ phosphine oxides. Stepwise reaction of $[PtCl_2(COD)]$ with one equivalent of L^1 and two equivalents of [AuCl(THT)] gives a *cis* complex in which the platinum atom is again bonded to two proximal phosphines and the two AuCl units to the other two phosphine arms. As in **5**, an anomalous low-field shift is observed for the axial C_6H_2CH belonging to the platinocycle of these complexes.

Macrocyclic platforms that contain several phosphino groups attached to their periphery are powerful tools for the construction and study of multimetal species that contain discrete metal centres maintained in close proximity.[1–5] In particular, several recent publications have described the properties of the *p*-*tert*-butylcalix[4]arene-derived tetraphosphine L^1, a ligand containing four pendant CH_2PPh_2 units that can bind up to four transition metal centres.[1,6,7] It has also been reported that, in certain cases, L^1 behaves as a small P_4 surface around which several gold or silver ions can migrate rather easily. These prior studies have revealed that individual metal centres may be bonded to L^1 by way of either a single pendant phosphorus(III) unit or with two adjacent P atoms functioning as *cis* or *trans* chelators. No instance could be found whereby three phosphorus atoms co-ordinate to a single metal centre. Such tripodal co-ordination, which is described here for the first time, results in formation of two adjacent 12-membered metallocycles and in the fixation of a metal centre at the apex of the calixarene cavity. The current study also focuses on the structural implications associated with co-ordination of a metal centre to two adjacent CH_2PPh_2 phosphine units tethered at the lower rim of the calix[4]arene platform. This complements earlier work on distal co-ordination of substituted calix[4]-arenes.[8,9]

† Dedicated to Professor Reinhard Schmutzler on the occasion of his 65th birthday. With our warmest wishes.

Supplementary data available: rotatable 3-D crystal structure diagram in CHIME format. See http://www.rsc.org/suppdata/dt/1999/4139/.

Also available: general experimental details. For direct electronic access see http://www.rsc.org/suppdata/dt/1999/4139/, otherwise available from BLDSC (No. SUP 57667, 3 pp.) or the RSC Library. See Instructions for Authors, 1999, Issue 1 (http://www.rsc.org/dalton).

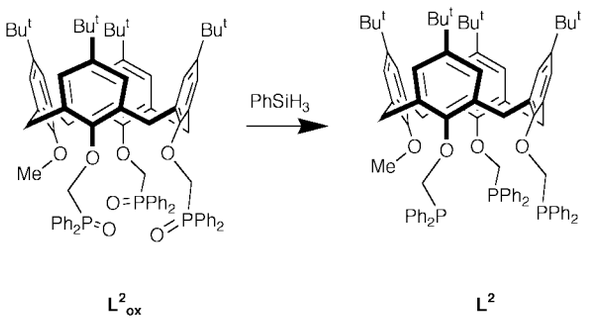


L[1]

Results and discussion

Tripodal behaviour of calix[4]arene polyphosphines

Should we expect tridentate co-ordination to a single transition metal centre by a calix[4]arene substituted at the lower rim by three or four CH_2PPh_2 groups? At first sight such ligation seems unlikely since it requires formation of two 12-membered metallo-macrocycles. To reach a more definitive answer, however, we have examined the co-ordinative properties of two suitably functionalized ligands, namely tetraphosphine L^1 and triphosphine L^2, towards two metal fragments, "$Mo(CO)_3$" and "$RuCl_2$", known to form tris(phosphine) complexes.[10,11] Ligand L^2, which is reported for the first time, was prepared in high yield by reduction of the corresponding tris(phosphine oxide)[6] L^2_{ox} with phenylsilane (Scheme 1) using a known general pro-

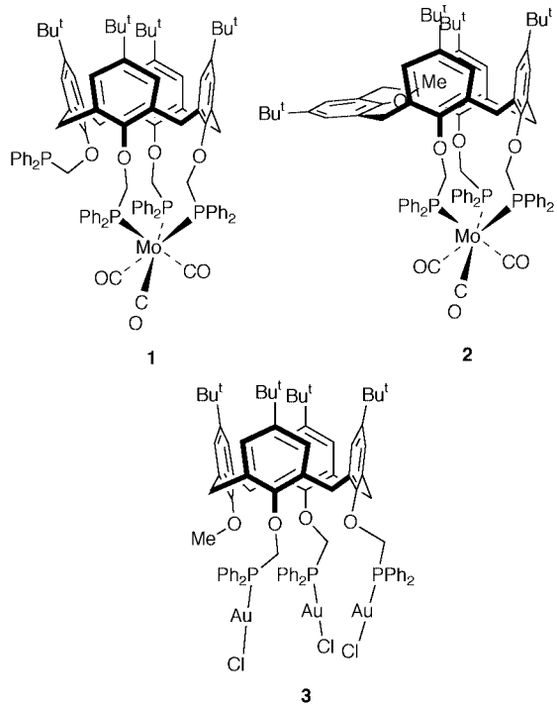


L^2_{ox} L^2

Scheme 1

cedure. Signals for the phosphine units appear at δ −17.3 (2P) and −18.6 (1P) in the ^{31}P NMR spectrum whilst the calixarene fragment adopts a cone conformation as deduced from the ^{13}C NMR spectrum. This latter assignment is based on the following reasoning: CH_2 groups that bridge two aryl rings in a relative *syn* arrangement exhibit chemical shifts in the range δ 29–33[12] whereas the $C_6H_2CH_2$ signal for *anti*-oriented aryl rings in partial-cone conformers appears at higher values (in general δ > *ca.* 37). We are aware that these guidelines, being most helpful for establishing the conformation of calix[4]-arenes, must be applied with care in those cases where the phenolic units of the calixarene are not possessed of bulky substituents.[13] This is because phenolic rings bearing small substituents can undergo fast transannular rotation around the bridging methylene groups or, in certain cases, adopt an orientation that positions the substituent inside the calix cavity. For both situations the chemical shift of the bridging $C_6H_2CH_2$ groups lies between δ 33 and 37. Even so, it seems reasonable to assign a cone conformation to ligand L^2. Relevant spectroscopic data for L^2 are given in the Experimental section.

Reaction of L^1 with $[Mo(CO)_3(C_7H_8)]$ in refluxing tetrahydrofuran (THF) afforded the colourless complex **1** in high yield. The fact that no oligomers are formed, regardless of reaction conditions, is a good indication for the high degree of preorganization of the three podands. The tridentate behaviour of L^1 was inferred from the ^{31}P NMR spectrum which shows two signals of relative intensity 2:1 corresponding to metal-bound phosphines (^2J(PP) = 13 Hz) and a singlet at δ −18.7 (intensity 1P) assignable to an unco-ordinated P^{III} atom. The carbonyl region of the IR spectrum shows two strong absorption bands indicating the presence of a $Mo(CO)_3$ unit with local C_{3v} symmetry.[10] The ^1H and ^{13}C NMR spectral data reveal the presence of two distinct $C_6H_2CH_2$ fragments but the relevant ^{13}C chemical shifts (δ 32.06 and 31.30) are fully consistent with a cone conformation. Similarly, the AB patterns observed for each set of $C_6H_2CH_2$ groups correspond to a splitting of the A and B parts ($\delta_A - \delta_B$ = 1.47 and 1.05) that is further confirmation for a cone conformation:[14] *syn*-oriented aryl rings usually give AB separations > *ca.* 0.7 ppm, while the AB separation is smaller for *anti*-oriented aryl rings.



1 **2**

3

For triphosphine L^2, reaction with $[Mo(CO)_3(C_7H_8)]$ in refluxing THF led to complex **2** (58%), which also contains a *fac*-MoP_3 unit. There was no indication for oligomer formation in this reaction. The FAB mass spectrum of the complex displays peaks at *m*/*z* 1438 and 1410, with the profile exactly matching that expected for the M^+ and $[M - CO]^+$ cations, respectively. The ^{13}C NMR spectrum displays two distinct $C_6H_2CH_2$ signals at δ 30.22 and 35.46. The former value is typical of a CH_2 group bordered by *syn*-arranged aryl rings whereas the latter value lies between those reported for *syn* and *anti* $C_6H_2CH_2C_6H_2$ arrangements. It seems likely, therefore, that the calix matrix adopts a partially flattened conformation with the methoxy group being oriented towards the calix axis and entrapped between two facing aryl units. Indeed, the strong upfield shift experienced by the methoxy protons (δ 0.38, $\Delta\delta$ = −3 ppm) reflects their encapsulation between aromatic rings. Finally, we note that one set of $C_6H_2CH_2$ groups appears as an AB pattern with an AB separation of only 0.50 ppm. No significant structural change was apparent from NMR spectra recorded over the temperature range −80 to +25 °C. It is difficult to explain the different calix conformations adopted by **1** and **2**, especially when allowing for the observation that L^2 reacts with 3 equivalents of [AuCl(THT)] (THT = tetrahydrothiophene) to form the trinuclear species **3** which persists in the cone conformation. The major difference between **2** and **3** is that the P atoms are assembled in one complex *via* a central atom whereas they move as three independent arms in the other. Clearly, a structure with *fac* co-ordinated phosphines results in a more strained calix matrix favouring a partially flattened conformation. The latter was not observed in **1** obviously

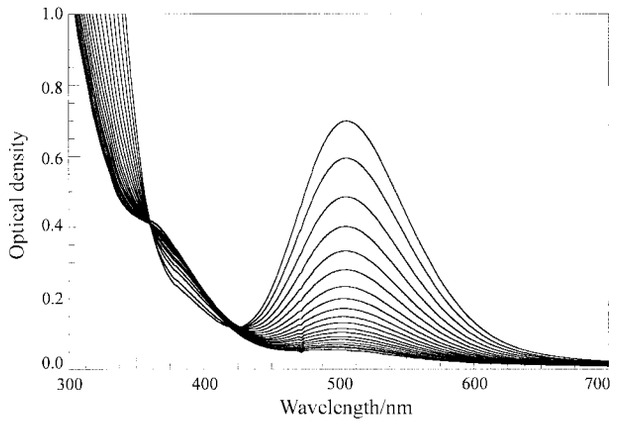
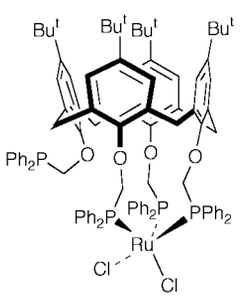


Fig. 1 Spectrophotometric titration of complex **4** by CH_3CN. Conditions: $[\mathbf{4}]_{initial} = 5 \times 10^{-4}$ M. Solvent: CH_2Cl_2.

because the CH_2PPh_2 group is sterically much larger than a Me group. Thus, a subtle balance between the bulk of the non-metallated phenoxy substituent and the strain within the calix backbone explains the different structures adopted by complexes **1**–**3**.

Reaction of L^1 with $[RuCl_2(DMSO)_4]$ (DMSO = Me_2SO) in CH_2Cl_2 (25 °C) is very *slow* but leads to *selective* formation of the deep purple complex **4**. After 15 d the yield reached 60%. The FAB mass spectrum of **4** shows a peak at *m*/*z* 1577 corresponding to the $[M - Cl]^+$ cation. That only a monomeric species is formed was apparent from vapour phase osmometry. In the ^{31}P NMR spectrum the unco-ordinated phosphine appears at δ −20.0 while the three bound phosphorus atoms give rise to an A_2B pattern with $\delta_A = 35.4$ and $\delta_B = 60.3$. The purple colour of the complex is a good indication for a *fac*-trigonal bipyramidal $RuCl_2P_3$ structure.[11,15] Further proof for the mutual *cis* arrangement of the three phosphorus atoms includes: (*i*) the $^2J(P^AP^{A'})$ value, *ca.* 25 Hz, calculated from the ^{13}C NMR signal (a quintet) of the two distal PCH_2 groups and (*ii*) the $^2J(P^AP^B)$ value of 41 Hz as obtained from the ^{31}P NMR spectrum. Note that the overall structure of **4** is reminiscent of that of **1**. There is no indication for fluxional behaviour or isomerization of **4** in solution. In contrast, reaction of triphosphine L^2 with $[RuCl_2(DMSO)_4]$ afforded a mixture of products, presumed to be oligomers, that could not be resolved. The NMR spectra do not change when running them at different concentrations. Thus monomer–oligomer equilibria can be ruled out.



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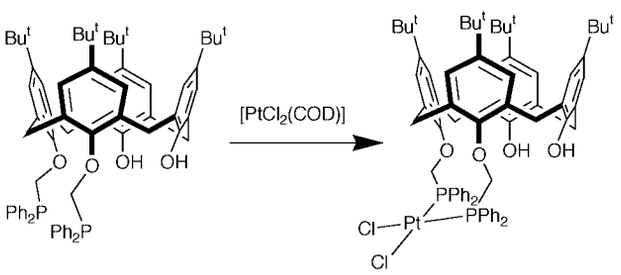
Addition of a few drops of CH_3CN to a solution of complex **4** in CH_2Cl_2 caused an instantaneous change to pale yellow. Evaporation of the solvent fully regenerated **4**. Attempts to isolate a complex formed with CH_3CN were unsuccessful but spectrophotometric titrations (Fig. 1) established that **4** reacts stepwise with two molecules of CH_3CN. The calculated stability constants are $\log \beta_1 = 9.1 \pm 0.2$ and $\log \beta_2 = 12.4 \pm 0.5$, indicating that addition of the first solvent molecule is exceptionally favourable, corresponding to a binding energy of 50 kJ mol^{-1}. Addition of a second acetonitrile molecule is more difficult. Interestingly, the mono-adduct does not absorb in the region 450–650 nm but the bis-adduct absorbs over this range, suggesting different geometries.

Chelating behaviour of two proximally positioned CH_2PPh_2 groups

Tripodal ligation of the type expressed in complexes **1** and **4** forces the metallic centre to reside beneath the lower rim of the calix cavity. Related complexes are known for which the metal centre is chelated by two distally tethered CH_2PPh_2 podands[16] and a logical extension of this work is to design suitable 1,2-disubstituted calixarenes equipped with two proximal CH_2PPh_2 groups. The simplest such representative is the diphosphine L^3, which was obtained in quantitative yield by reduction of the corresponding di(phosphine oxide)[6] L^3_{ox} with $PhSiH_3$. Clear evidence for the cone conformation was obtained from ^1H and ^{13}C NMR spectra. In particular, the ^1H NMR spectrum shows three AB systems for the $C_6H_2CH_2$ groups, with AB separations of 1.39, 1.21 and 0.83 ppm (relative intensity 2 H : 4 H : 2 H). The signal for the two residual OH groups appears at δ 8.91 (*cf.* δ 5.50 for *p-tert*-butylphenol and 10.34 for *p-tert*-butylcalix[4]arene), suggesting their involvement in hydrogen bonding with neighbouring phenolic oxygen atoms.

Reaction of L^3 with $[PtCl_2(COD)]$ (COD = cycloocta-1,5-diene) in dichloromethane afforded complex **5** in 72% yield after chromatography (Scheme 2). To prevent formation of



L^3 **5**

Scheme 2

oligomers, reaction was carried out at modest concentration. In this complex the platinum centre forms part of a 12-membered metallo-macrocycle. The NMR spectral data collected indicate a plane of symmetry. For example, the ^1H NMR spectrum shows three sets of AB patterns for the $C_6H_2CH_2$ groups and two Bu^t signals. The *cis* stereochemistry around platinum was inferred from the *J*(PPt) coupling constant of 3672 Hz. Interestingly, the $C_6H_2CH_2$ group lying between the two phosphines gives rise to an AB system with an exceptionally large splitting of the A and B parts: *ca.* 3.6 ppm (!). The corresponding axial H atom was found at *ca.* δ 7.34. The assignment of this particular AB signal was made on the basis of a two-dimensional ROESY (rotating frame Overhauser enhancement spectroscopy) experiment (at 218 K). We note also that the ^{13}C NMR signal (δ 36.98) for the $C_6H_2CH_2$ group within the metallocycle (as identified by an HETCOR (heteronuclear correlation) experiment) lies considerably outside the range expected for methylene groups bordered by *syn* oriented aryl rings.

Note that Floriani and co-workers[17] have recently reported that the axial C_6H_2CH hydrogen of the *10-membered* metallocycles present in complex **6** undergoes also an anomalous downfield shift (δ_A 5.86) with respect to the "free" ligand. This phenomenon which was attributed to ring current effects generated by the metallomacrocycles is however less important than that observed in **5**. In order to identify other effects that could account for the rather unusual downfield shift observed for **5** and also to clarify the mutual positioning of the metal centre and the cavity (**A** or **B** form), an X-ray diffraction study was

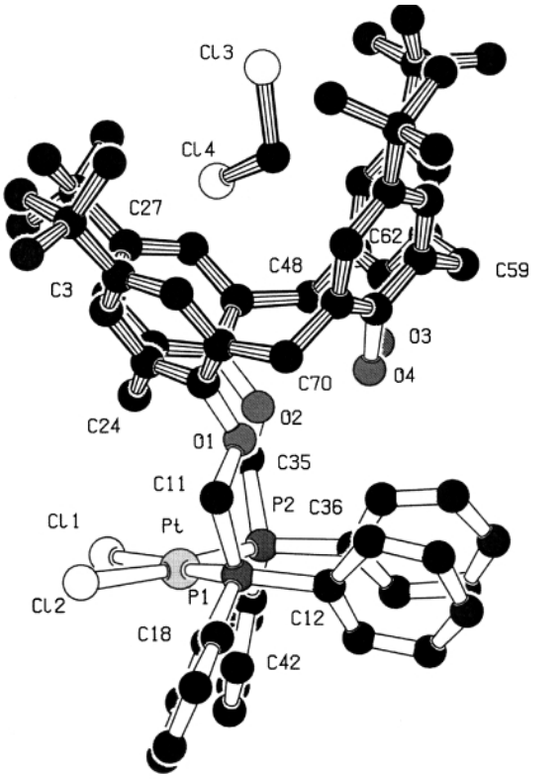
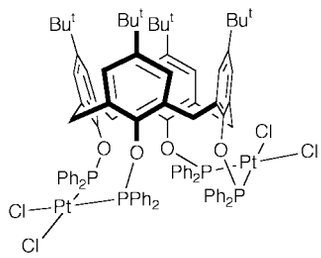


Fig. 2 Molecular structure (PLATON[18]) of complex **5**.



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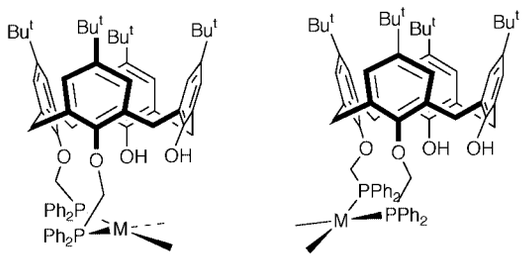


A **B**

carried out for **5**. The result of this investigation is shown in Fig. 2.[18]

The X-ray analysis confirmed the chelating behaviour of L^3 and established the cone conformation. This complex crystallizes with one molecule of water and six molecules of dichloromethane, one of which lies inside the cavity. The two PPt vectors are directed away from the centre of the cavity, so that the two bound chlorides lie well away from the lower rim (**B** form), with the result that the Pt atom lies 2.67 Å beneath the axial C_6H_2CH proton. Note, this distance might be too long for agostic interaction, although in solution shorter separations will abound. It is notable that the axial C_6H_2CH atom, which is located between the two P atoms, resides only 2.42 Å from the two neighbouring phenolic O atoms. Although on the upper limit for hydrogen bonding, we cannot rule out the possibility of weak interactions between these atoms. These

Table 1 Selected bond lengths (Å) and angles (°) for complex **5**

Pt–Cl(1)	2.342(2)	O(1)···O(2)	3.379(7)
Pt–Cl(2)	2.372(2)	O(2)···O(3)	2.780(8)
Pt–P(1)	2.241(2)	O(3)···O(4)	2.668(9)
Pt–P(2)	2.253(2)	O(1)···O(4)	2.897(8)
O(1)···O(3)	4.192(8)	C(24)···Pt	3.546(8)
O(2)···O(4)	4.069(8)		
Cl(1)–Pt–Cl(2)	87.06(8)	C(12)–P(1)–C(18)	101.6(4)
Cl(1)–Pt–P(1)	171.61(8)	C(35)–P(2)–C(36)	103.5(4)
Cl(1)–Pt–P(2)	83.32(8)	C(35)–P(2)–C(42)	102.9(4)
Cl(2)–Pt–P(1)	85.79(9)	C(36)–P(2)–C(42)	103.8(4)
P(1)–Pt–P(2)	103.43(8)	C(30)–O(2)–C(35)	110.0(6)
C(11)–P(1)–C(12)	106.8(4)	C(6)–O(1)–C(11)	109.9(6)
C(11)–P(1)–C(18)	102.2(4)		

Angles between facing phenolic rings: 66.5(2) and 56.0(2)°.

Table 2 Selected bond lengths (Å) and angles (°) for L^3_{ox}

O(1)···O(3)	2.971(6)	O(3)···O(4)	5.339(6)
O(5)···O(3)	2.824(6)	O(5)···O(4)	3.404(6)
O(2)···O(3)	2.710(4)	O(1)···O(5)	3.149(5)
O(4)–C(57)–P(2)	107.2(4)	O(1)–C(11)–P(1)	112.1(4)

Angles between facing phenolic rings: 1.8(2) and 110.8(2)°.

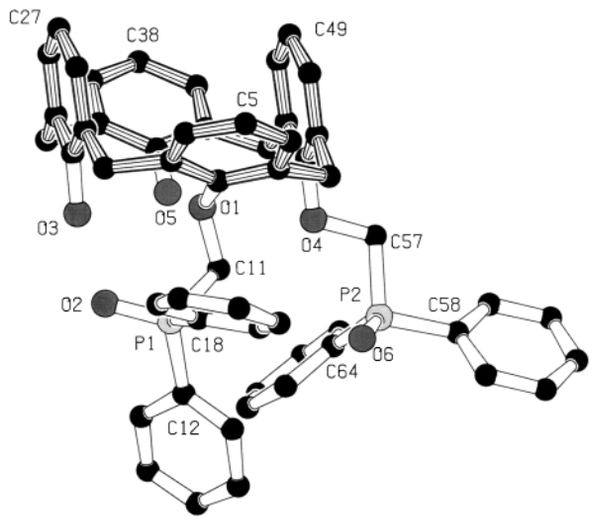


Fig. 3 Molecular structure (PLATON[18]) of L^3_{ox}. The four Bu^t groups have been omitted for clarity.

could then explain the observed low-field shift. The rather short O(1)···O(4), O(3)···O(4) and O(2)···O(3) distances (respectively 2.90, 2.67 and 2.78 Å, Table 1) are indicative of hydrogen bonding between the hydroxy functions and the adjacent phenolic O atoms. The calixarene matrix is close to that found in an ideal cone. This is in marked contrast to the structure of the non-metallated oxidized form of L^3 (Fig. 3, Table 2) which displays the conventional flattened cone shape found in the solid state for most calix[4]arenes. The idealized cone conformation seen for the matrix in **5** probably arises from a combination of effects caused by the presence of the strained metallocycle and the O···HO bridges.

A variable temperature NMR study (CD_2Cl_2, 500 MHz, Fig. 4) carried out between 198 and 308 K revealed that complex **5** undergoes a structural modification in solution on varying the temperature. The low temperature ^1H NMR spectra are fully consistent with a cone conformation (*e.g.* large separations for the $C_6H_2CH_2$ groups at 198 K). On raising the temperature the two sets of AB signals corresponding to the $C_6H_2CH_2$ groups centred on C59 and C(48)/C(70) (for labelling see Fig. 2; for simplification these atoms are respectively labelled # and * in Fig. 4) begin to broaden, reaching a maximum of broadening around 238 K, and eventually reappearing as two new sets of

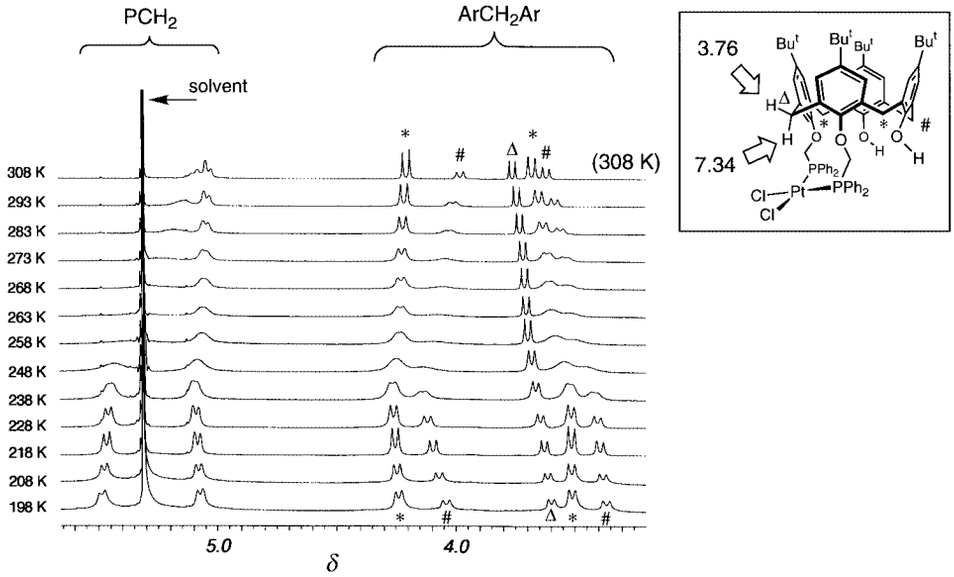
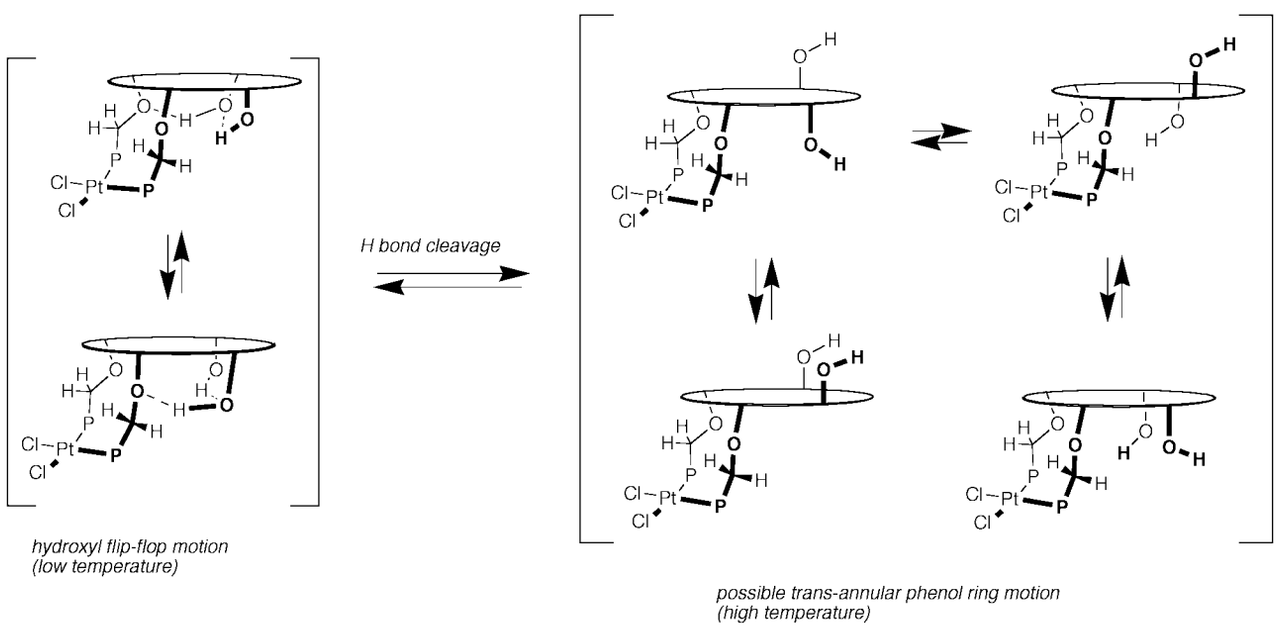
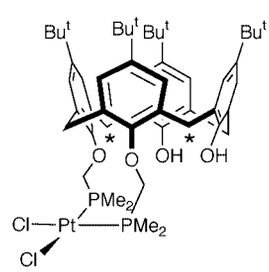


Fig. 4 Variable temperature NMR study (^{1}H NMR, 500 MHz, CD_2Cl_2) for complex **5** (partial view). The spectra show the AB systems corresponding to the PCH_2 and $C_6H_2CH_2C_6H_2$ protons. The symbols *, # and Δ have been used for indexing the bridging $C_6H_2CH_2C_6H_2$ protons. The signal of the axial C_6H_2CH atom belonging to the platinomacrocycle is out of this view (δ 7.34, 308 K).



Scheme 3 Proposed dynamics for complex **5**.

AB signals. At the highest temperature these AB separations are much smaller ($\Delta\delta = 0.56$ and 0.36 ppm, CD_2Cl_2, 308 K) than in the low temperature spectra, thus indicative for the formation of a structurally different isomer. The smaller AB splittings could arise from formation of fast interconverting 1,2-alternate conformers or because of fast equilibration between cone and non-cone species. The third AB system, which corresponds to H atoms bonded to C24 (only the B part, labelled Δ, is shown in Fig. 4) remains essentially unperturbed over this temperature range. To help interpret the high temperature spectra, two-dimensional ROESY experiments‡ were performed on **5** and its PMe_2 analogue **7**. This latter complex is a useful model by which to explain the various NMR spectral changes because the only aromatic hydrogens able to correlate with $C_6H_2CH_2$ protons are those belonging to the calix matrix. In fact the NMR spectrum recorded for **7** shows NOEs between a *m*-CH of the phenol rings and both doubly degenerated $C_6H_2CH_2$ protons (labelled



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*). This observation can be explained only in terms of rapid inversion of the phenol rings.

The spectral modifications observed for complex **5** in the range 198–308 K are reversible and may be rationalized in terms of *disruption* of the hydrogen bonds as the sample is heated, followed by ring inversion at higher temperatures (Scheme 3). Interestingly, on raising the temperature, one of the PCH_2 hydrogen atoms undergoes a significant change in chem-

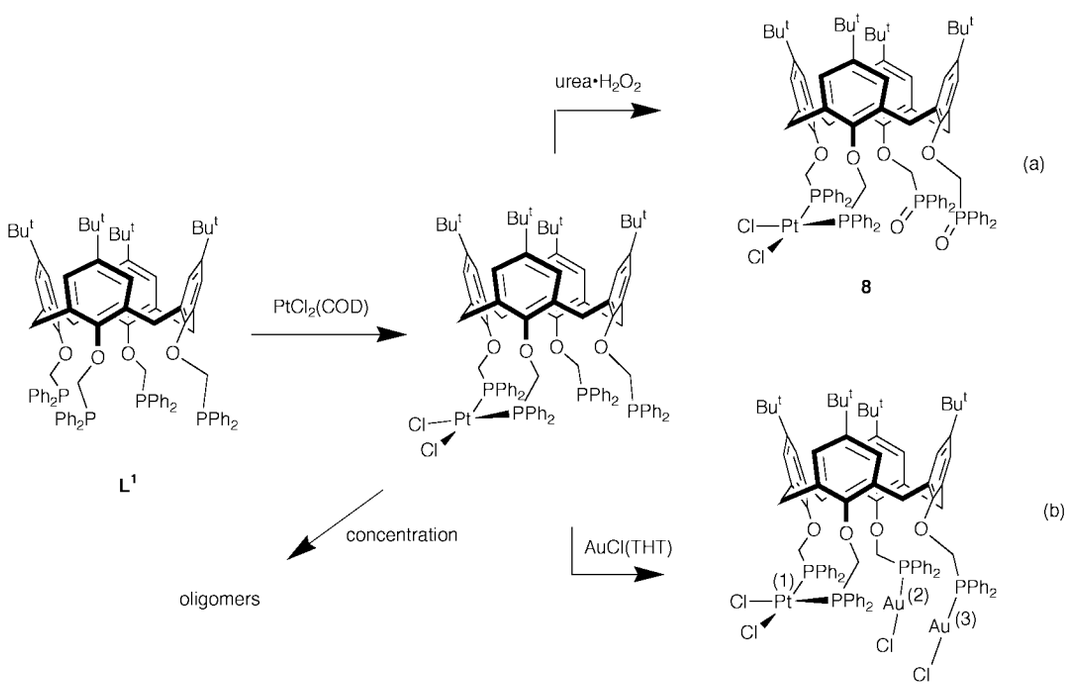
‡ No cross peaks due to dynamic exchange were detected.

ical shift while the other is little affected (Fig. 4). This behaviour would occur if one CH atom is *anti* oriented with respect to the interacting O*H* atom. The low temperature spectra indicate a C_s-symmetrical cone structure with hydrogen bonded OH groups (δ 8.46 at 218 K). Furthermore, two-dimensional ROESY experiments performed at low temperature show that the O*H* atoms correlate with the axial C*H* atoms of both neighbouring $C_6H_2CH_2$ groups. These findings are in agreement with a fast flip-flop motion of the hydroxyl groups, as shown in Scheme 3 (left side). This movement which could not be frozen out is reminiscent of the hydroxyl movement observed in native β-cyclodextrin.[19] The free enthalpy of activation for the interconversion between the isomer containing hydrogen bonds and that obtained after hydrogen bond breaking ($T = 238$ K) is calculated[20] to be 58 kJ mol^{-1}. Note, hydrogen bond breaking involving phenolic OH groups in calixarenes is well documented; for comparison, the energy barrier for cone–cone interconversion of *p-tert*-butylcalix[4]arene, a process that implies the rupture of four hydrogen bonds (followed by inversion of the calix matrix), is 70–75 kJ mol^{-1}.[21,22] Important conformational changes within the metallomacrocycle itself appear unlikely since the AB separation of the endocyclic $C_6H_2CH_2$ group remains essentially unchanged during the temperature variation. However, flipping of the platinum atom under the calix cavity (with exchange between the **A** and **B** forms) cannot strictly be ruled out. In summary, the modification observed in the NMR spectra of complex **5** may be interpreted in terms of hydrogen bond breaking when the temperature is raised. Thus, we observe the reversible conversion of a species "with hydrogen bonds" into an isomer "without hydrogen bonds". Both isomers undergo fast dynamics involving either hydroxyl movement (low temperature species) or phenol ring inversion (high temperature isomer).

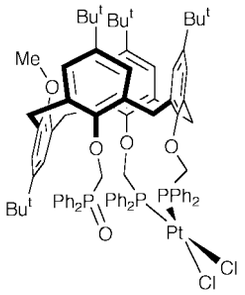
A detailed ^{31}P NMR spectroscopic investigation was made of the reaction between one equivalent of tetraphosphine L^1 and [$PtCl_2$(COD)]. The resultant platinum complex comprises two *cis*-co-ordinated P atoms (δ 8.9, J(PPt) = 3640 Hz) and two free phosphines (δ −19.6). Attempts to isolate this compound were unsuccessful because oligomerization occurred during concentration. To overcome this problem, $NH_2CONH_2{\cdot}H_2O_2$ was added to the reaction mixture after one hour (Scheme 4). This procedure results in mild oxidation of the unco-ordinated phosphine arms and afforded complex **8** in high yield (Scheme 4a). FAB mass spectrometry revealed peaks due to both M^+ and $[M - Cl]^+$ while ROESY, COSY and HETCOR experiments allowing precise assignment of all hydrogen atoms, except those of the PPh groups (see Experimental section). The ^{31}P NMR spectrum recorded for **8** displays a signal centred at δ 8.6 (*cf.* 8.4 for **5**), attributable to the metal-bound phosphines (J(PPt) = 3631 Hz), and a singlet at δ 24.7, due to the phosphine oxides. The NMR data point to a plane of symmetry. Furthermore, the presence of three distinct types of methylenic $C_6H_2CH_2C_6H_2$ groups is strong indication for proximal chelation, rather than distal co-ordination, such that 1,3 complexation seems not to be favourable in the present case. As for **5**, an important downfield shift is observed for a single methylenic $C_6H_2CHC_6H_2$ hydrogen (δ 7.43, $\Delta\delta = 3.97$ ppm) whilst the corresponding ^{13}C NMR signal, identified by a ^{13}C–^{1}H HETCOR experiment, appears far outside of the range expected for a cone conformer (δ 38.88). On the basis of this spectral correspondence, we tentatively assign the conformation of the metallocycle in **8** as being similar to that of **5**.

An alternative method for preventing oligomerization involves complexing the phosphines that remain unco-ordinated after the first step. Thus, addition of two equivalents of [AuCl(THT)] to the product obtained following reaction of one equivalent of L^1 with [$PtCl_2$(COD)] led to the trinuclear complex **9** (Scheme 4b). Again a single C_6H_2CH signal is strongly deshielded (δ(H) = 7.35; δ(C) = 37.15) and can be assigned to the $C_6H_2CH_2$ group of the 12-membered metallacycle. The molecular structure of **9** was confirmed by an X-ray diffraction study which will be reported elsewhere.[23] Surprisingly, reaction of two equivalents of [$PtCl_2$(COD)] with L^1 did not lead to the expected dinuclear complex but gave rise to polymeric products.

The triphosphine L^2 reacts with [$PtCl_2$(COD)] in a manner reminescent of the behaviour described for L^1; isolation of chelate complex **10** requiring oxidation of the phosphine remaining unco-ordinated after the first step. Here, the AB system of the axial C_6H_2CH atom assigned to the metallocycle is characterized by $\delta_A = 7.20$ and $\delta_B = 3.68$. The ^{13}C NMR spectrum displays four $C_6H_2CH_2$ signals, three of which lie slightly under the critical value of δ 37 while the fourth appears at δ 32.10. It seems reasonable to assign a partial cone conform-



Scheme 4 Construction of chelate complexes involving two proximal phosphines of L^1.



10

ation to **10**. Other important characterizing data are given in the Experimental section. Note, in view of the absence of any symmetry element in complex **10**, the latter exists as a mixture of two enantiomers.

The present study demonstrates that calixarenes bearing two proximal CH_2PPh_2 substituents form readily chelate complexes. In particular, [$PtCl_2$(COD)] reacts with each phosphine-based ligand to give a 12-membered metallomacrocycle containing the $PtCl_2$ unit. A characteristic feature of these platinum metallomacrocyclic complexes concerns the anomalous chemical shift observed for the axial C_6H_2CH atom belonging to the macrocycle, possibly due to interaction with the lone pairs of the endocyclic oxygen atoms. The metallomacrocycle in complex **5** appears to weaken pre-existing hydrogen bonds compared to those found in free L^3. Those calixarenes substituted by three or four dangling CH_2PPh_2 groups exhibit P_3-chelating behaviour. This unique type of triple co-ordination leads to formation of *fac*-oriented complexes with incoming "$Mo(CO)_3$" and "$RuCl_2$" fragments, wherein the metal centre is fixed immediately below the calix cavity.

Experimental

General experimental details are given as supplementary data (see SUP 57667). The global binding constants log β_n were determined by UV-visible spectrophotometric titration in dichloromethane (spectroscopic grade). For these measurements a quartz cell was filled under N_2 atmosphere with a solution of complex **4** in dichloromethane (5×10^{-4} M, 3 μL) to which were added multiples of 10 mL of neat acetonitrile solution. The "Ru" : MeCN ratio ranged from 0 to 4 : 1. The spectra were recorded between 190 and 310 nm using a quartz cell (1 cm path length) that was thermoregulated at 25 ± 0.5 °C. The absorbance changes monitored were significant enough to be exploited by multiwavelength numerical treatment based on a Benesi–Hildebrandt type equation (program SPECFIT© [24]), which yielded the desired global binding constants log β_n.

Compounds L^1,[6] L^2_{ox},[6] [AuCl(THT)],[25] [$RuCl_2(DMSO)_4$],[26] [$PtCl_2$(COD)],[27] [$Mo(CO)_3(C_7H_8)$],[28] $Ph_2P(O)CH_2O$-$SO_2C_6H_4$-Me-*p*,[29] and $PhSiH_3$[30] were prepared according to methods reported in the literature. The di(phosphine oxide) L^3_{ox} was synthesized according to an improved procedure (see below). The P-methylated version of L^3 was prepared according to a procedure similar to that described below for L^3, using $Me_2P(O)CH_2O$-$SO_2C_6H_4$Me-*p* as alkylating agent and will be fully described elsewhere (δ ^{31}P: −53.8 (s)).[31]

X-Ray crystallography

Crystal data for L^3_{ox}. $2C_{70}H_{78}O_6P_2 \cdot C_2H_5OC_2H_5$, $M = 2228.82$, triclinic, space group $P\bar{1}$, colourless crystals, $a = 14.9993(8)$, $b = 15.351(1)$, $c = 15.4699(9)$ Å, $\alpha = 102.912(9)$, $\beta = 106.361(9)$, $\gamma = 103.676(9)°$, $U = 3156(1)$ Å^3, $Z = 1$, $D_c = 1.17$ g cm^{-3}, $\mu = 0.116$ mm^{-1}, $F(000) = 1194$. Data were collected on a Nonius KappaCCD diffractometer (graphite Mo-Kα radiation, 0.71073 Å) at −100 °C. 22148 Reflections collected ($2.5 \leq \theta \leq 26.38°$), 5805 data with $I > 3\sigma(I)$. The structure was solved using the Nonius OpenMoleN[32] package and refined by full matrix least-squares with anisotropic thermal parameters for all non-hydrogen atoms. Final results: $R(F) = 0.085$, $wR(F) = 0.109$, goodness of fit = 1.225, 712 parameters, largest difference peak = 1.038 e Å^{-3}.

Crystal data for complex 5. $2C_{70}H_{156}O_{12}P_4Pt \cdot 6CH_2Cl_2 \cdot H_2O$, $M = 3150.30$, orthorhombic, space group $P2_12_12_1$, colourless crystals, $a = 12.571(1)$, $b = 22.5546(3)$, $c = 26.4894(3)$ Å, $V = 7510.6(8)$ Å^3, $Z = 2$, $D_c = 1.39$ g cm^{-3}, $\mu = 2.241$ mm^{-1}, $F(000) = 3212$. Data were collected as above. 50394 Reflections ($2.5 \leq \theta \leq 32.39°$), 9230 data with $I > 3\sigma(I)$. Absolute structure determined refining Flack's x parameter. The structure was solved and refined as above: $R(F) = 0.050$, $wR(F) = 0.068$, goodness of fit = 1.028, 824 parameters, largest difference peak = 1.416 e Å^{-3}.

CCDC reference number 186/1684.

See http://www.rsc.org/suppdata/dt/1999/4139/ for crystallographic files in .cif format.

Syntheses

5,11,17,23-Tetra-*tert*-butyl-25,26,27-tris(diphenylphosphinomethoxy)-28-methoxycalix[4]arene L^2. A suspension of compound L^2_{ox} (6.100 g, 4.67 mmol) in phenylsilane (7.00 mL, 97.80 mmol) was heated at 90–100 °C for 12 d. After evaporation of the solvent *in vacuo* the residue was subjected to flash chromatography using CH_2Cl_2 as eluent. The fraction corresponding to $R_f = 0.67$ (SiO_2, CH_2Cl_2–hexane, 1 : 1, v/v) was concentrated to *ca.* 30 mL. Precipitation with MeOH yielded compound L^2 as a colourless powder. Yield: 5.288 g, 90%; mp 152–154 °C. ^{1}H NMR (300 MHz, 293 K, $CDCl_3$): δ 7.50–7.26 (30 H, PPh_2), 7.06 and 6.90 (2s, 2 H each, *m*-H of aryl), 6.42 and 6.38 (AB quartet, $^4J \approx 2$, 2 H each, *m*-H of aryl), 5.48 (broad s, 2 H, PCH_2O), 4.66 and 4.62 (ABX spin system with X = P, $^2J = 12$, $^2J_{AX} = 3$, $^2J_{BX} = 2$, 2 H each, PCH_2O adjacent to methoxy), 4.51 and 3.01 (AB quartet, $^2J = 13$, 2 H each, $C_6H_2CH_2$), 4.16 and 3.06 (AB quartet, $^2J = 13$ Hz, 2 H each, $C_6H_2CH_2$), 3.33 (s, 3 H, OCH_3), 1.34, 1.32 and 0.83 (3s, 9 H + 9 H + 18 H, *tert*-butyl). ^{13}C-{^{1}H} NMR (50 MHz, 293 K, $CDCl_3$): δ 155.68–131.47 (quat. aryl C), 133.81–124.31 (aryl CH), 77.10 (d, $J_{PC} \approx 10$, PCH_2O), 75.12 (d, $J_{PC} \approx 20$ Hz, PCH_2O), 60.26 (s, OCH_3), 34.10 and 33.60 (3s, $C(CH_3)_3$), 32.61 (s, $C_6H_2CH_2$), 31.76 and 31.15 ($C(CH_3)_3$) (one $C_6H_2CH_2$ signal is probably overlapping with a *tert*-butyl signal). ^{31}P-{^{1}H} NMR (121 MHz, 293 K, $CDCl_3$): δ −17.3 (s, 2P) and −18.6 (s, 1P). Found: C, 80.11; H, 7.35. Calc. for $C_{84}H_{91}O_4P_3$: C, 80.23; H, 7.29%.

(Improved preparation of) 5,11,17,23-tetra-*tert*-butyl-25,26-bis(diphenylphosphinoylmethoxy)-27,28-dihydroxycalix[4]arene L^3_{ox}. To a suspension of *p*-*tert*-butylcalix[4]arene (5.000 g, 7.70 mmol) in DMF (200 mL), cooled at 0 °C, was added in portions NaH (0.647 g, 26.97 mmol). After stirring for 1.5 h, $Ph_2P(O)CH_2O$-$SO_2C_6H_4$Me-*p* (8.920 g, 23.10 mmol) was added and the solution further stirred for 2 h at 0 °C. After 24 h the excess of NaH was decomposed with MeOH (10 mL), then the solvent was removed *in vacuo*. The residue was taken up in CH_2Cl_2 (250 mL) and washed with 1 M HCl (80 mL), then with water (2 × 100 mL). The organic layer was dried with $MgSO_4$ and evaporated to dryness to afford a solid which was purified by flash column chromatography using ethyl acetate–hexane (1 : 1, v/v) as eluent. The fraction eluting first (SiO_2, $R_f = 0.79$, yield 10%), was discarded. Compound L^3_{ox} which is the second compound migrating on the column ($R_f = 0.55$) was obtained as an analytically pure colourless solid (5.475 g, 66%). Spectroscopic data have been published previously.[6]

5,11,17,23-Tetra-*tert*-butyl-25,26-bis(diphenylphosphinomethoxy)-27,28-dihydroxycalix[4]arene L^3. A suspension of compound L^3_{ox} (6.200 g, 5.75 mmol) in toluene (120 mL) was

heated at 90–100 °C in the presence of phenylsilane (2.1 mL, 28.75 mmol) for 7 days. After evaporation of the solvent *in vacuo* the residue was subjected to flash chromatography using CH_2Cl_2–hexane (1 : 1, v/v) as eluent. The fraction obtained with $R_f = 0.23$ (SiO_2) was concentrated to *ca.* 40 mL, and addition of MeOH yielded compound L[3] as a colourless powder. Yield: 5.951 g, 99%; mp 201–203 °C. IR (KBr) ($\tilde{\nu}_{max}/cm^{-1}$): 3362 br (OH). ^1H NMR (300 MHz, 293 K, $CDCl_3$): δ 8.91 (s, 2 H, OH), 7.49–7.32 (20 H, PPh_2), 7.01 and 6.96 (AB system, $^4J = 3$, 2 H each, *m*-H of aryl), 6.93 and 6.86 (AB system, $^4J = 3$, 2 H each, *m*-H of aryl), 5.19 and 4.93 (ABX system with X = P, $^2J_{AB} = 12$, $^2J_{AX} = 2$, $^2J_{BX} = 3$, 2 H each, PCH_2O), 4.59 and 3.20 (AB quartet, $^2J = 13$, 1 H each, $C_6H_2CH_2$), 4.48 and 3.27 (AB quartet, $^2J = 13$, 2 H each, $C_6H_2CH_2$), 4.15 and 3.32 (AB quartet, $^2J = 14$ Hz, 1 H each, $C_6H_2CH_2$), 1.22 and 1.12 (2s, 18 H each, *tert*-butyl). ^{13}C-{^1H} NMR (50 MHz, 293 K, $CDCl_3$): δ 152.81–125.78 (quat. aryl C), 133.58–125.29 (aryl CH), 77.96 (broad s, PCH_2O), 34.06 and 33.94 (2s, $C(CH_3)_3$), 33.26, 32.84 and 32.01 (3s, $C_6H_2CH_2$), 31.63 and 31.33 (2s, $C(CH_3)_3$). ^{31}P-{^1H} NMR (121 MHz, 293 K, $CDCl_3$): δ −20.2 (s). Found: C, 80.20; H, 7.38. Calc. for $C_{70}H_{78}O_4P_2$: C, 80.43; H, 7.52%.

Tricarbonyl{5,11,17,23-tetra-*tert*-butyl-25,26,27,28-tetrakis-(diphenylphosphinomethoxy)calix[4]arene-*P*,*P*′,*P*″} molybdenum(0) 1. A solution of compound L[1] (0.100 g, 0.07 mmol) and [$Mo(CO)_3(C_7H_8)$] (0.019 g, 0.07 mmol) in THF (80 mL) was refluxed for 5 min. The orange solution was evaporated to dryness *in vacuo*. The residue was subjected to flash chromatography using CH_2Cl_2–hexane (1 : 1, v/v) as eluent. The fraction with $R_f = 0.38$ (SiO_2) was precipitated from CH_2Cl_2–hexane (1 : 1, v/v) affording the complex **1** as a colourless solid. Yield: 0.072 g, 64%; mp 235 °C (decomp.). IR (KBr) ($\tilde{\nu}_{max}/cm^{-1}$): 1946s and 1854s (C≡O). ^1H NMR (300 MHz, 293 K, $CDCl_3$): δ 7.90–6.32 (m, 48 H, PPh_2 + *m*-H of aryl), 5.88 and 5.49 (AB quartet, $^2J = 13$, 2 H each, PCH_2O), 4.98 (br s, 2 H, PCH_2O), 4.56 and 3.09 (AB quartet, $^2J = 13$, 2 H each, $C_6H_2CH_2$), 4.49 (br s, 2 H, PCH_2O), 3.67 and 2.62 (AB quartet, $^2J = 13$ Hz, 2 H each, $C_6H_2CH_2$), 1.39, 0.96 and 0.81 (3s, 18 H + 9 H + 9 H, *tert*-butyl). ^{13}C-{^1H} NMR (50 MHz, 293 K, $CDCl_3$): δ 218.91 (m, C≡O), 215.75 (broad d, C≡O), 153.93 and 151.77 (2 broad s, quat. aryl C–O), 150.90 (d, $^3J_{PC} = 11$, quat. aryl C–O), 145.37–126.04 (quat. aryl C), 134.10–124.69 (aryl CH), 78.52 (d, $J_{PC} = 8$, PCH_2O), 75.36 (br s, PCH_2O), 72.77 (d, $J_{PC} = 13$ Hz, PCH_2O), 33.86, 33.73 and 33.53 (3s, $C(CH_3)_3$), 32.06 and 31.30 (2s, $C_6H_2CH_2$), 31.63, 31.17 and 31.04 (3s, $C(CH_3)_3$). ^{31}P-{^1H} NMR (121 MHz, 293 K, $CDCl_3$): δ 21.6 (d) and 20.5 (t) (A_2B system, $^2J(P_A–P_B) = 13$ Hz), −18.7 (s). Found: C, 73.02; H, 6.31. Calc. for $C_{99}H_{100}MoO_7P_4$: C, 73.32; H, 6.21%.

Tricarbonyl{5,11,17,23-tetra-*tert*-butyl-25,26,27-tris-(diphenylphosphinomethoxy)-28-methoxycalix[4]arene-*P*,*P*′,*P*″}-molybdenum(0) 2. A solution of compound L[2] (0.100 g, 0.08 mmol) and [$Mo(CO)_3(C_7H_8)$] (0.026 g, 0.08 mmol) in THF (100 mL) was refluxed for 10 min. The orange solution was evaporated to dryness *in vacuo*. The residue was subjected to flash chromatography using CH_2Cl_2–hexane (3 : 2, v/v) as eluent. The fraction with $R_f = 0.42$ (SiO_2) was precipitated from CH_2Cl_2–hexane (1 : 1, v/v) affording the complex **2** as a colourless solid. Yield: 0.072 g, 58%; mp 235 °C (decomp.). IR (KBr) ($\tilde{\nu}_{max}/cm^{-1}$): 1946s and 1854s (C≡O). ^1H NMR (300 MHz, 293 K, $CDCl_3$): δ 7.86–6.84 (m, 38 H, PPh_2 + *m*-H of aryl), 5.25 (br s, 4 H, PCH_2O), 5.09 and 5.05 (AB quartet, $^2J = 7$ Hz, 2 H each, PCH_2O), 3.61 and 2.89 (AB quartet, $^2J = 13$, 2 H each, $C_6H_2CH_2$), 3.61 and 3.11 (AB quartet, $^2J = 13$ Hz, 2 H each, $C_6H_2CH_2$), 1.46, 1.16 and 1.11 (3s, 9 H + 9 H + 18 H, *tert*-butyl) and 0.38 (s, 3 H, OMe). ^{13}C-{^1H} NMR (50 MHz, 293 K, $CDCl_3$): δ 218.7 (m, C≡O), 155.70 and 154.72 (2 broad s, quat. aryl C–O), 151.77 (d, $^3J_{PC} = 10$, quat. aryl C–O), 146.62–132.78 (quat. aryl C), 134.92–125.02 (aryl CH), 74.41 (pseudo t, PCH_2O), 73.52 (d, $J_{PC} = 26$ Hz, PCH_2O), 59.72 (s, OMe), 35.46 and 30.22 (2s, $C_6H_2CH_2$), 34.09 and 33.82 (2s, $C(CH_3)_3$), 31.69, 31.33 and 30.97 (3s, $C(CH_3)_3$). ^{31}P-{^1H} NMR (121 MHz, 293 K, $CDCl_3$): δ 26.6 (broad s) and 18.2 (t) (A_2B system, $^2J(P_A–P_B) = 25$ Hz). FAB mass spectrum: *m*/*z* 1438 (M^+, 1) and 1410 ([M − CO]$^+$, 6). Found: C, 72.83; H, 6.66. Calc. for $C_{87}H_{91}MoO_7P_3$: C, 72.69; H, 6.38%.

Trichloro{5,11,17,23-tetra-*tert*-butyl-25,26,27-tris(diphenyl-phosphinomethoxy)-28-methoxycalix[4]arene-*P*,*P*′,*P*″}trigold (I) 3. To a stirred solution of compound L[2] (0.100 g, 0.08 mmol) in CH_2Cl_2 (10 mL) was added a solution of [AuCl(THT)] (0.079 g, 0.25 mmol) in CH_2Cl_2 (10 mL). After 0.5 h the solution was filtered over a bed of Celite. Concentration to *ca.* 5 mL and addition of pentane precipitated complex **3** as a colourless powder (SiO_2, $R_f = 0.20$, CH_2Cl_2–hexane, 4 : 1, v/v). Yield: 0.139 g, 89%; mp 200 °C (decomp.). ^1H NMR (200 MHz, 293 K, $CDCl_3$): δ 7.72–7.37 (30H, PPh_2), 7.03 and 6.93 (2s, 2 H each, *m*-H of aryl), 6.44 and 6.23 (AB quartet, $^4J = 2$, 2 H each, *m*-H of aryl), 5.35 (broad s, 2 H, PCH_2O), 4.69 and 4.53 (ABX system with X = P, $^2J_{AB} = 13$, $^2J_{AX} = 0$, $^2J_{BX} = 2$ Hz, 2 H each, PCH_2O adjacent to methoxy), 4.14 and 2.87 (AB quartet, $^2J = 13$, 2 H each, $C_6H_2CH_2$), 4.01 and 3.07 (AB quartet, $^2J = 13$ Hz, 2 H each, $C_6H_2CH_2$), 3.93 (s, 3 H, OCH_3), 1.34, 1.26 and 0.78 (3s, 9 H + 9 H + 18 H, *tert*-butyl). ^{13}C-{^1H} NMR (50 MHz, 293 K, $CDCl_3$): δ 155.01–125.65 (quat. aryl C), 134.52–125.04 (aryl CH), 72.14 (d, $J_{PC} = 46$, PCH_2O), 71.87 (d, $J_{PC} = 41$ Hz, PCH_2O), 61.62 (s, OCH_3), 34.12 and 33.60 (2s, $C(CH_3)_3$), 32.12 (s, $C_6H_2CH_2$), 31.63, 31.56 and 31.01 ($C(CH_3)_3$) (one $C_6H_2CH_2$ signal is probably overlapping with a *tert*-butyl signal). ^{31}P-{^1H} NMR (81 MHz, 293 K, $CDCl_3$): δ 22.7 (s, 2P) and 20.5 (s, 1P). Found: C, 51.77; H, 4.87. Calc. for $C_{84}H_{91}Au_3Cl_3O_4P_3$: C, 51.61; H, 4.69%.

Dichloro{5,11,17,23-tetra-*tert*-butyl-25,26,27,28-tetrakis-(diphenylphosphinomethoxy)calix[4]arene-*P*,*P*′,*P*″}ruthenium(II) 4. A solution of compound L[1] (0.915 g, 0.63 mmol) and [$RuCl_2(DMSO)_4$] (0.323 g, 0.66 mmol) in CH_2Cl_2 (150 mL) was stirred for 15 d. The deep purple solution was filtered over a bed of Celite (5 cm) and concentrated to *ca.* 5 mL. Addition of Et_2O precipitated complex **4** as a deep purple powder. Yield: 0.610 g, 60%; mp 255 °C (decomp.); ^1H NMR (500 MHz, 293 K, CD_2Cl_2): δ 7.97–6.19 (m, 48 H, PPh_2 + *m*-H of aryl), 6.08 and 5.42 (d of filled-in d, AA′BB′XX′ system with X,X′ = P, $^2J_{AB} = 14$, 2 H each, PCH_2O), 5.17 (d, $^2J_{PH} = 4$, 2 H, PCH_2O), 4.64 (d, $^2J_{PH} = 2$, 2 H, PCH_2O), 4.52 and 3.15 (AB quartet, $^2J = 13$, 2 H each, $C_6H_2CH_2$), 3.78 and 2.85 (AB quartet, $^2J = 13$ Hz, 2 H each, $C_6H_2CH_2$), 1.32, 0.97 and 0.65 (3s, 18 H + 9 H + 9 H, *tert*-butyl). ^{13}C-{^1H} NMR (125 MHz, 293 K, CD_2Cl_2): δ 154.14 and 151.43 (2 broad s, quat. aryl C–O), 150.81 (d, $^3J_{PC} = 12$, quat. aryl C-O), 146.09–131.43 (quat. aryl C), 132.10–125.55 (aryl CH), 77.09 (d, $J_{PC} = 9$ Hz, PCH_2O), 77.98 (quintet, $J_{PC} = 29$, $J_{P'C} \approx 1$, $J_{PP'} = 25$, PCH_2O), 70.20 (d, $J_{PC} = 51$ Hz, PCH_2O free), 34.11, 34.03 and 33.72 (3s, $C(CH_3)_3$), 33.44 and 33.15 (2s, $C_6H_2CH_2$), 31.62, 31.12 and 31.08 (3s, $C(CH_3)_3$). ^{31}P-{^1H} NMR (202 MHz, 293 K, CD_2Cl_2): δ 60.3 (t) and 35.4 (d) (A_2B system, $^2J(P_A–P_B) = 41$ Hz), −20.0 (s). FAB mass spectrum: *m*/*z* 1577 ([M − Cl]$^+$, 32). Found: C, 71.72; H, 6.31. Calc. for $C_{96}H_{100}Cl_2O_4P_4Ru$: C, 71.45; H, 6.25%.

***cis*-(*P*,*P*)-Dichloro{5,11,17,23-tetra-*tert*-butyl-25,26-bis(di-phenylphosphinomethoxy)-27,28-dihydroxycalix[4]arene-*P*,*P*′}-platinum(II) 5.** To a solution of L[3] (0.100 g, 0.09 mmol) in CH_2Cl_2 (400 mL) was added a solution of [$PtCl_2$(COD)] (0.036 g, 0.09 mmol) in CH_2Cl_2 (50 mL). After 1 h the solution was evaporated to dryness *in vacuo*. The residue was subjected to flash chromatography using ethyl acetate–hexane (3 : 7, v/v) as eluent. The fraction with $R_f = 0.48$ (SiO_2) was recrystallized from ethyl acetate–hexane (1 : 1, v/v) yielding the complex **5** as a colourless solid. Yield: 0.085 g, 72%; mp >250 °C (decomp.). IR (KBr) ($\tilde{\nu}_{max}/cm^{-1}$): 3454(br) (OH). ^1H NMR (500 MHz,

218 K, CD_2Cl_2): δ 8.46 (s, OH), 7.45–6.97 (m, 28 H, *m*-H of aryl + PPh_2), 7.32 and 3.63 (AB quartet, ^2J = 13, 1 H each, $C_6H_2CH_2$), 5.46 and 5.08 (AB quartet, ^2J = 12, 2 H each, PCH_2O), 4.25 and 3.51 (AB quartet, ^2J = 13, 2 H each, $C_6H_2CH_2$), 4.09 and 3.39 (AB quartet, ^2J = 13 Hz, 1 H each, $C_6H_2CH_2$), 1.15 and 1.14 (2s, 18 H + 18 H, *tert*-butyl). ^{1}H NMR (500 MHz, 308 K, CD_2Cl_2): δ 7.44–6.98 (m, 28 H, *m*-H of aryl + PPh_2), 7.34 and 3.76 (AB quartet, ^2J = 13, 1 H each, $C_6H_2CH_2$), 5.08 and 5.03 (broad AB quartet, ^2J = 12, 2 H each, PCH_2O), 4.20 and 3.64 (AB quartet, ^2J = 13, 2 H each, $C_6H_2CH_2$), 3.97 and 3.61 (AB quartet, ^2J = 13 Hz, 1 H each, $C_6H_2CH_2$), 1.26 and 1.20 (2s, 18 H + 18 H, *tert*-butyl). ^{1}H NMR (300 MHz, 293 K, $CDCl_3$): δ 7.46–7.03 (m, 20 H, PPh_2), 7.20 and 3.85 (AB quartet, ^2J = 13, 1 H each, $C_6H_2CH_2$), 6.75–6.68 (m, 8H, *m*-H of aryl), 4.96 and 4.70 (AB quartet, ^2J = 10, 2 H each, PCH_2O), 4.06 and 3.85 (AB quartet, ^2J = 13, 2 H each, $C_6H_2CH_2$), 3.85 and 3.68 (AB quartet, ^2J = 13 Hz, 1 H each, $C_6H_2CH_2$), 1.28 and 1.20 (2s, 18 H + 18 H, *tert*-butyl). ^{13}C-{^{1}H} NMR (50 MHz, 293 K, $CDCl_3$): δ 153.67–129.90 (quat. aryl C), 133.80–125.31 (aryl CH), 71.85 (d, J_{PC} = 52 Hz, PCH_2O), 36.38 and 35.92 (2s, $C_6H_2CH_2$), 34.28 and 33.92 (2s, $C(CH_3)_3$), 32.45 (s, $C_6H_2CH_2$), 31.53 and 31.37 (2s, $C(CH_3)_3$). ^{31}P-{^{1}H} NMR (121 MHz, 293 K, $CDCl_3$): δ 8.4 (s with Pt satellites, $J_{P\text{-}Pt}$ = 3672 Hz). Found: C, 64.31; H, 5.99. Calc. for $C_{70}H_{78}Cl_2O_4P_2Pt$: C, 64.12; H, 5.99%.

***cis*-Dichloro{5,11,17,23-tetra-*tert*-butyl-25,26-bis(dimethylphosphinomethoxy)-27,28-dihydroxycalix[4]arene-*P*,*P*′}platinum(II) 7.** This complex was prepared according to a method similar to that used for the preparation of **5**, but starting from the PMe_2 analogue of phosphine L^3. Yield: 0.146 g, 55%; mp = 212 °C (decomp.). IR (KBr) ($\tilde{\nu}_{max}$/cm^{-1}): 3450(br) (OH). ^{1}H NMR (500 MHz, 293 K, CD_2Cl_2): δ 7.26–7.06 (m, 8H, *m*-H of aryl), 5.62 and 3.65 (AB quartet, ^2J = 13, 1 H each, $C_6H_2CH_2$), 4.62 (broad s, 4 H, PCH_2O), 4.20 and 3.58 (AB quartet, ^2J = 13, 2 H each, $C_6H_2CH_2$), 4.09 and 3.51 (AB quartet, ^2J = 13, 1 H each, $C_6H_2CH_2$), 1.85 (d with Pt satellite not resolved, J_{PH} = 13 Hz, 12 H, PMe), 1.25 and 1.21 (2s, 18 H + 18 H, *tert*-butyl). ^{13}C-{^{1}H} NMR (125 MHz, 293 K, CD_2Cl_2): δ 152.69–125.86 (aryl C), 75.85 (m, PCH_2O), 34.61 and 34.31 (2s, $C(CH_3)_3$), 32.49 and 32.15 (s, $C_6H_2CH_2$), 31.72 and 31.45 (2s, $C(CH_3)_3$), 14.00 (m, PMe_2). ^{31}P-{^{1}H} NMR (121 MHz, 293 K, CD_2Cl_2): δ −14.1 (s with Pt satellites, $J_{P\text{-}Pt}$ = 3535 Hz). Found: C, 56.22; H, 6.59. Calc. for $C_{50}H_{70}Cl_2O_4P_2Pt$: C, 56.49; H, 6.64%.

***cis*-Dichloro{5,11,17,23-tetra-*tert*-butyl-25,26-bis(diphenylphosphinoylmethoxy)-27,28-bis(diphenylphosphinomethoxy)-calix[4]arene-*P*,*P*′}platinum(II) 8.** To a solution of compound L^1 (0.100 g, 0.06 mmol) in THF (3 mL) was added a solution of [$PtCl_2$(COD)] (0.026 g, 0.07 mmol) in THF (2 mL). After 1 h an excess of H_2O_2–urea adduct (0.050 g) was added, and the solution stirred vigorously for 1 h. The solution was filtered and evaporated to dryness *in vacuo*. The residue was subjected to flash chromatography using ethyl acetate–hexane (65 : 35, v/v) as eluent. The fraction with R_f = 0.42 (SiO_2) was recrystallized from ethyl acetate–hexane (1 : 1, v/v) yielding the complex **8** as a colourless solid. Yield: 0.092 g, 88%; mp 250 °C (decomp.). IR (KBr) ($\tilde{\nu}_{max}$/cm^{-1}): 1192s (P=O, tentative assignment). ^{1}H NMR (400 MHz, 293 K, CD_2Cl_2): δ 7.85–7.81 and 7.53–7.14 (m, 40 H, PPh_2), 7.43 and 3.46 (AB quartet, ^2J = 13, 1 H each, $C_6H_2CH_2$), 7.07 and 7.01 (AB quartet, ^4J = 6, 2 H each, *m*-H of aryl), 6.66 and 6.62 (AB quartet, ^4J = 5, 2 H each, *m*-H of aryl), 6.06 and 4.91 (ABX system with X = P, $^2J_{AB}$ = 13, $^2J_{AX}$ = $^2J_{BX}$ ≈ 0, 2 H each, PCH_2O), 5.12 and 4.79 (AB quartet, ^2J = 13, 2 H each, PCH_2O), 4.77 and 2.81 (AB quartet, ^2J = 13, 1 H each, $C_6H_2CH_2$), 4.63 and 2.94 (AB quartet, ^2J = 13 Hz, 2 H each, $C_6H_2CH_2$), 1.22 and 1.04 (2s, 18 H + 18 H, *tert*-butyl). ^{1}H NMR (500 MHz, 293 K, C_6D_6): δ 8.05–6.57 (m, 48 H, *m*-H of aryl + PPh_2), 7.36 and 3.59 (AB quartet, ^2J = 13, 1 H each, $C_6H_2CH_2$), 6.51 and 5.30 (broad AB quartet, $^2J_{AB}$ = 13, 2 H each, $PtPCH_2O$), 5.14 and 4.68 (ABX system with X = P, $^2J_{AB}$ = 13, $^2J_{AX}$ = 2, $^2J_{BX}$ = 1, 2 H each, PCH_2O), 4.86 and 3.00 (AB quartet, ^2J = 13, 1 H each, $C_6H_2CH_2$), 4.75 and 2.86 (AB quartet, ^2J = 13 Hz, 2 H each, $C_6H_2CH_2$), 1.24 and 1.05 (2s, 18 H + 18 H, *tert*-butyl). ^{13}C-{^{1}H} NMR (50 MHz, 293 K, CD_2Cl_2): δ 154.46 and 153.91 (2s, quat. aryl C–O), 146.71–132.81 (quat. aryl C), 134.50–125.61 (aryl CH), 73.72 (d, J_{PC} = 78, PCH_2O), 73.83 (d, J_{PC} = 48 Hz, PCH_2O), 38.88 (s, $C_6H_2CH_2$), 34.36 and 34.21 (2s, $C(CH_3)_3$), 31.75 (s, 2 × $C_6H_2CH_2$), 31.53 and 31.52 (2s, $C(CH_3)_3$). ^{31}P-{^{1}H} NMR (121 MHz, 293 K, CD_2Cl_2): δ 24.7 (s), 8.6 (s with Pt satellites, $J_{P\text{-}Pt}$ = 3631 Hz). FAB mass spectrum: *m*/*z* 1739 ([*M* + H]$^+$, 3), 1703 ([*M* − Cl]$^+$, 65) and 1667 ([*M* − 2Cl]$^{2+}$, 50%). Found: C, 66.11; H, 5.82. Calc. for $C_{96}H_{100}Cl_2O_6P_4Pt$: C, 66.28; H, 5.79%.

Tetrachloro{5,11,17,23-tetra-*tert*-butyl-25,26,27,28-tetrakis(diphenylphosphinomethoxy)calix[4]arene-1κ^2*P*,*P*′; 2κ*P*″,3κ*P*‴}digold(I)platinum(II) 9. To a solution of compound L^1 (0.100 g, 0.07 mmol) in THF (5 mL) was added a solution of [$PtCl_2$(COD)] (0.026 g, 0.07 mmol) in THF (5 mL). After 1 h a solution of [AuCl(THT)] (0.044 g, 0.14 mmol) in THF (5 mL) was added. The solution was filtered over a bed of Celite after 10 min, and evaporated to dryness *in vacuo*. The residue was subjected to flash chromatography using MeOH–CH_2Cl_2 (4 : 96, v/v) as eluent. The fraction with R_f = 0.42 (SiO_2) was recrystallized from ethyl acetate–hexane (1 : 1, v/v) precipitating complex **9** as a colourless solid. Yield: 0.092 g, 88%; mp 250 °C (decomp.). ^{1}H NMR (400 MHz, 293 K, $CDCl_3$): δ 7.81–6.40 (m, 48 H, *m*-H of aryl + PPh_2), 7.35 and 3.63 (AB quartet, $^2J_{AB}$ = 13, 1 H each, $C_6H_2CH_2$), 5.83 and 4.85 (AB quartet, $^2J_{AB}$ = 13, 2 H each, PCH_2O), 5.12 and 4.90 (ABX system with X = P, $^2J_{AB}$ = 13, $^2J_{AX}$ = 0, $^2J_{BX}$ = 4, 2 H each, PCH_2O), 4.98 and 3.07 (AB quartet, ^2J = 13, 1 H each, $C_6H_2CH_2$), 4.15 and 3.35 (AB quartet, ^2J = 13 Hz, 2 H each, $C_6H_2CH_2$), 1.21 and 0.94 (2s, 18 H + 18 H, *tert*-butyl). ^{13}C-{^{1}H} NMR (50 MHz, 293 K, $CDCl_3$): δ 153.23 and 151.77 (2s, quat. aryl C-O), 146.55–125.09 (quat. aryl C), 134.41–125.76 (aryl CH), 75.02 (d, J_{PC} = 64, PCH_2O), 73.73 (d, J_{PC} = 40 Hz, PCH_2O), 37.15 (s, $C_6H_2CH_2$), 34.09 and 33.92 (2s, $C(CH_3)_3$), 31.86 (s, $C_6H_2CH_2$) and 31.45 (s, $C(CH_3)_3$). ^{31}P-{^{1}H} NMR (121 MHz, 293 K, CD_2Cl_2): δ 21.9 (s) and 8.1 (s with Pt satellites, $J_{P\text{-}Pt}$ = 3634 Hz). Found: C, 53.16; H, 4.56. Calc. for $C_{96}H_{100}Au_2Cl_4O_4P_4Pt$: C, 53.07; H, 4.64%.

***cis*-Dichloro{5,11,17,23-tetra-*tert*-butyl-25,26-bis(diphenylphosphinomethoxy)-27-(diphenylphosphinoylmethoxy)-28-methoxycalix[4]arene-*P*,*P*′}platinum(II) 10 and its enantiomer.** To a solution of L^2 (0.150 g, 0.12 mmol) in CH_2Cl_2 (3 mL) was added a solution of [$PtCl_2$(COD)] (0.045 g, 0.12 mmol) in CH_2Cl_2 (3 mL). After 1 h an excess of H_2O_2–urea adduct (0.050 g) was added, and the solution stirred vigorously for 1 h. The solution was filtered and evaporated to dryness *in vacuo*. The residue was subjected to flash chromatography using ethyl acetate–hexane (65 : 35, v/v) as eluent. The fraction with R_f = 0.58 (SiO_2) was recrystallized from ethyl acetate–hexane (1 : 1, v/v) affording the complex *rac*-**10** as a colourless solid. Yield: 0.101 g, 68%; mp >250 °C (decomp.). IR (KBr) ($\tilde{\nu}_{max}$/cm^{-1}): 1192s (P=O, tentative assignment). ^{1}H NMR (500 MHz, 293 K, CD_2Cl_2): δ 8.05–7.95 and 7.56–6.56 (m, 38 H, *m*-H of aryl + PPh_2), 7.20 and 3.68 (AB quartet, ^2J = 13, 1 H each, $C_6H_2CH_2$), 6.26 and 5.24 (ABX system with X = P, $^2J_{AB}$ = 11, $^2J_{AX}$ = 0, $^2J_{BX}$ = 4, 1 H each, PCH_2O), 4.75 and 2.93 (AB quartet, ^2J = 13, 1 H each, $C_6H_2CH_2$), 4.64 and 4.47 (ABX system with X = P, $^2J_{AB}$ = 13, $^2J_{AX}$ = 3, $^2J_{BX}$ = 4, 1 H each, PCH_2O), 4.35 and 3.88 (ABX system with X = P, $^2J_{AB}$ = 10, $^2J_{AX}$ = 3, $^2J_{BX}$ = 0, 1 H each, PCH_2O), 4.32 and 3.62 (AB quartet, ^2J = 13, 1 H each, $C_6H_2CH_2$), 3.67 and 3.53 (AB quartet, ^2J = 13 Hz, 1 H each, $C_6H_2CH_2$), 1.34, 1.25, 1.11 and

1.04 (4s, 9 H + 9 H + 9 H + 9 H, *tert*-butyl). ^{13}C-{^1H} NMR (50 MHz, 293 K, CD_2Cl_2): δ 158.43, 155.41, 155.16 and 155.05 (4s, quat. aryl C–O), 147.30–130.71 (quat. aryl C), 135.42–126.14 (aryl CH), 72.30 (d, $J_{PC} = 77$, PCH_2O), 72.37 (d, $J_{PC} = 28$, PCH_2O), 71.37 (d, $J_{PC} = 29$ Hz, PCH_2O), 59.40 (s, OMe), 36.92, 36.68 and 36.59 (3s, $C_6H_2CH_2$), 34.23, 34.20, 34.03 and 33.90 (4s, $C(CH_3)_3$), 32.10 (s, $C_6H_2CH_2$), 31.51, 31.41 and 31.11 (3s, $C(CH_3)_3$). ^{31}P-{^1H} NMR (121 MHz, 293 K, CD_2Cl_2): δ 23.8 (s), 13.5 (br s with Pt satellites, $J_{P\text{-}Pt} = 3752$) and 5.76 (d with Pt satellites, $J_{P\text{-}Pt} = 3574$ Hz). Found: C, 65.69; H, 5.89. Calc. for $C_{84}H_{91}Cl_2O_5P_3Pt$: C, 65.53; H, 5.96%.

Acknowledgements

We are indebted to Johnson Matthey for a generous loan of platinum.

References

1 C. B. Dieleman, D. Matt, I. Neda, R. Schmutzler, H. Thönessen, P. G. Jones and A. Harriman, *J. Chem. Soc.*, *Dalton Trans.*, 1998, 2115.
2 C. Wieser, C. B. Dieleman and D. Matt, *Coord. Chem. Rev.*, 1997, **165**, 93.
3 S. Pellet-Rostaing, J.-B. Regnouf de Vains and R. Lamartine, *Tetrahedron Lett.*, 1995, **36**, 5745.
4 W. Xu, R. J. Puddephatt, L. Manojlovic-Muir, K. W. Muir and C. S. Frampton, *J. Incl. Phenom.*, 1994, **19**, 277.
5 C. Floriani, D. Jacoby, A. Chiesi-Villa and C. Guastini, *Angew. Chem.*, *Int. Ed. Engl.*, 1989, **28**, 1376.
6 C. B. Dieleman, D. Matt and P. G. Jones, *J. Organomet. Chem.*, 1997, **454–456**, 461.
7 C. Dieleman, C. Loeber, D. Matt, A. De Cian and J. Fischer, *J. Chem. Soc.*, *Dalton Trans.*, 1995, 3097.
8 C. Wieser, D. Matt, J. Fischer and A. Harriman, *J. Chem. Soc.*, *Dalton Trans.*, 1997, 2391.
9 C. Loeber, D. Matt, A. De Cian and J. Fischer, *J. Organomet. Chem.*, 1994, **475**, 297.
10 P. Stössel, H. A. Mayer, C. Maichle-Mössmer, R. Fawzi and M. Steimann, *Inorg. Chem.*, 1996, **35**, 5860.
11 P. Barbaro, C. Bianchini and A. Togni, *Organometallics*, 1997, **16**, 3004.
12 C. Jaime, J. de Mendoza, P. Prados, P. M. Nieto and C. Sánchez, *J. Org. Chem.*, 1991, **56**, 3372.
13 J. O. Magrans, J. de Mendoza, M. Pons and P. Prados, *J. Org. Chem.*, 1997, **62**, 4518.
14 K. Ito, A. Kida, Y. Ohba and T. Sone, *Chem. Lett.*, 1998, 1221.
15 G. Jia, I.-M. Lee, D. W. Meek and J. C. Galluci, *Inorg. Chim. Acta*, 1990, **177**, 81.
16 C. Wieser and D. Matt, *Platinum Met. Rev.*, 1998, **42**, 2.
17 M. Stolmàr, C. Floriani, A. Chiesi-Villa and C. Rizzoli, *Inorg. Chem.*, 1997, **36**, 1694.
18 PLATON, A Multipurpose Crystallographic Tool, version 1999, Utrecht University, Utrecht, 1999.
19 V. Zabel, W. Saenger and S. Mason, *J. Am. Chem. Soc.*, 1986, **108**, 3664.
20 H. Günther, *NMR-Spektroskopie*, Georg Thieme, Stuttgart, 3rd edn., 1992, pp. 306–312.
21 T. Kusano, M. Tabatabai, Y. Okamoto and V. Böhmer, *J. Am. Chem. Soc.*, 1999, **121**, 3789.
22 C. D. Gutsche, *Calixarenes Revisited*, The Royal Society of Chemistry, Cambridge, 1998.
23 C. Dieleman and D. Matt, unpublished work.
24 R. A. Binstead and A. D. Zuberbühler, SPECFIT v. 2.1, Spectrum Software Associates, Chapel Hill, NC, 1994.
25 R. Uson, A. Laguna and M. Laguna, *Inorg. Synth.*, 1989, **26**, 85.
26 I. P. Evans, A. Spencer and G. Wilkinson, *J. Chem. Soc.*, *Dalton Trans.*, 1973, 204.
27 D. Drew and J. R. Doyle, in *Inorg. Synthesis*, ed. R. J. Angelici, Wiley, New York, 1990, vol. 28, pp. 350–352.
28 G. Brauer, *Handbuch der preparativen Anorganischen Chemie*, F. Enke Verlag, Stuttgart, 3rd edn., 1981, p. 1885.
29 W. Z. Wegener, *Z. Chem.*, 1971, **11**, 262.
30 K. L. Marsi, *J. Org. Chem.*, 1974, **39**, 265.
31 C. Dieleman, Thèse de Doctorat, Université Louis Pasteur, Strasbourg, 1999.
32 OpenMoleN, Interactive Structure Solution, Nonius B.V., Delft, 1997.

Paper 9/05814A