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Heterofunctionalised phosphites built on a calix[4]arene scaffold and their use in 1-octene hydroformylation. Formation of 12-membered P,O-chelate rings

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The calixarene phosphites L^1–L^4 were obtained in high yield through reaction of PCl_3/NEt_3 with the mono-functionalised *cone*-calixarenes *p-tert*-butylcalix[4]arene$(OH)_3OR$, in which the R substituents bear an oxygen donor ligand [R = $CH_2P(O)Ph_2$ (L^1), CH_2CO_2Et (L^2), $CH_2C(O)NEt_2$ (L^3), CH_2CH_2OMe (L^4)]. The calixarene core of the four ligands adopts a cone conformation and, hence, the phosphites become potential P,O-chelating systems. Phosphite L^1 is remarkably stable towards aqueous NaOH, but the presence of slightly acidic water results in phosphonate formation. Slow oxidation of L^1 in air afforded the corresponding mixed phosphine oxide–phosphate. In the complexes $[RuCl_2(p\text{-cymene})L^1]$, [*cis*-$PtCl_2(L^1)_2$] (**9**), *trans*-$[PdCl_2(L^1)_2]$, $[Pd(8\text{-mq})Cl(L^n)]$ (8-mqH = 8-methyl-quinoline, n = 1–3), $[Pd(dmba)Cl(L^1)]$ (dmbaH = *N,N*-dimethylbenzylamine), $[Pd(\eta^3\text{-}C_4H_7)Cl(L^2)]$, $[Rh(acac)(CO)L^n]$ (n = 1–3) and $[RhCl(CO)(L^1)_2]$, the phosphites behave as a monodentate phosphorus donor ligands. Owing to their steric crowding, the two *cis*-disposed ligands of complex **9** cannot freely rotate about their coordination axis. In the solid state, the calixarene backbones of complex **9** display a so-called 'up-up-out-up' conformation. Chelating phosphite behaviour was found in the cationic complexes $[Pd(8\text{-mq})L^n]BF_4$ (n = 1–3). In solution, the large, chelating P,O-loop of the latter complexes swings from one side of the metal plane to the other, the dynamics possibly being facilitated by the flexibility of the calixarene backbone. The four oxo-functionalised phosphites were tested as catalysts for 1-octene hydroformylation. The observed reaction rates lie in the range reported for other medium-bulky phosphites. Furthermore, the hydroformylation rate decreases as the donor strength of the side group increases, suggesting binding of the O-donor during catalysis. The L/B ratios lie in the range 1.4–3.6, the highest linear aldehyde selectivity being observed with the phosphite ester L^3.

Ligands which combine a P(III) centre with an oxygen-donor functionality have been intensively investigated over the last twenty years.[1–6] Prominent applications for such ligands are, *e.g.* the nickel-catalysed oligomerisation of ethylene with enolato-phosphine complexes[7–9] or the hydroformylation of propene with rhodium complexes made water-soluble with sulfonato-phosphines.[10] Hybrid P,O-ligands offer distinct advantages over conventional phosphines or diphosphines. For example, they may act towards naked d^8 metal ions as unsymmetrical chelates capable of directing an incoming substrate specifically towards one of the two opposite coordination sites, *i.e. trans* to P or *trans* to O.[11] Another important feature of mixed P,O-ligands concerns their ability to display hemilabile behaviour, a property which is frequently observed for neutral P,O-chelators in which the oxygen atom is a weak donor (*e.g.* an ether group) and, therefore, may reversibly be substituted.[12–16] Such bidentate ligands have proved useful for increasing the rate of catalytic reactions by stabilisation of transient key inter-mediates.[17,18] It should also be mentioned that P,O-ligands in which the oxygen atom is part of a water-solubilising fragment have attracted much attention in recent years owing to their potential utility in biphasic catalysis. Interestingly, to date, most mixed P,O-ligands are based on tertiary phosphines, while phosphite ligands comprising additional oxygen donors have scarcely been studied.[19–21] This is rather surprising considering the above-mentioned industrial applications of P,O-phosphine ligands.

The present work deals with the synthesis, characterisation and co-ordinative properties of phosphite ligands that contain a secondary 'oxygen' function (amide, ester, phosphine oxide, ether). The new ligands are based on a calix[4]arene scaffold on which the auxiliary function has been introduced prior to P-functionalisation. This work also reports the first example of a structurally characterised chelate complex derived from a calixarene-based phosphite. The new P,O-phosphites, which may form 12-membered chelate complexes, were used in octene hydroformylation and the influence of the side group was determined. Phosphites based on a calix[4]arene scaffold were first reported by Lattman *et al.*[22] Recent publications by the groups of Pringle,[23,24] van Leeuwen[25,26] and Röper[27] report the coordination and catalytic chemistry of other calix[*n*]arene phosphites (n = 4, 6), but none of these ligands is suitable for the formation of an unsymmetrical chelate.

Results and discussion

Synthesis and stability of the ligands

In this work, the nomenclature '*m*-H' specifically refers to aromatic protons in *meta* positions on phenolic rings of the

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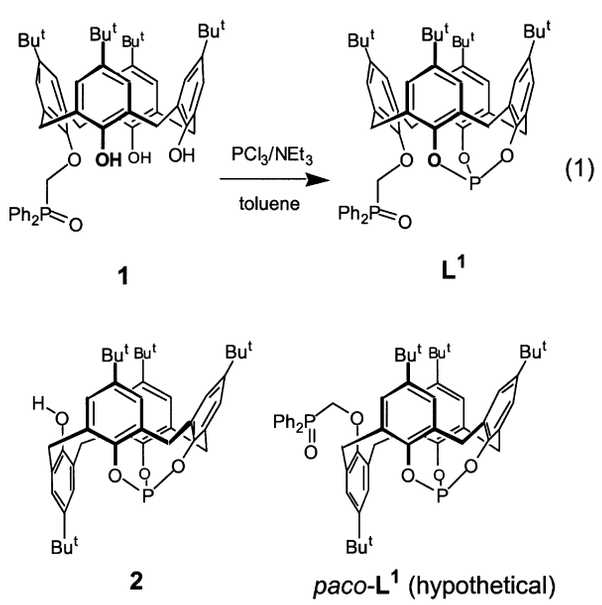
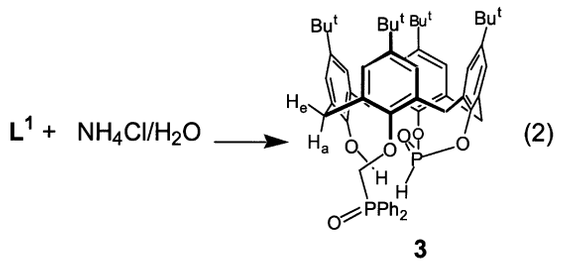
calixarene backbone. The following results illustrate how a calix[4]arene bearing a single substituent tethered at the lower rim can be used for the preparation of functional phosphites. All calixarene phosphites presented herein adopt a cone conformation.

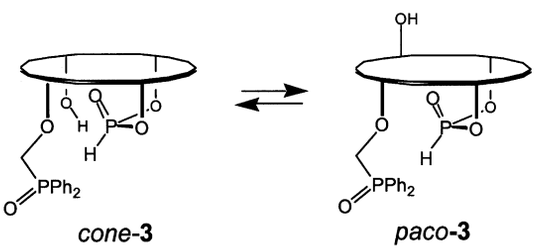
Reaction of the mono-functionalised calixarene **1**[28] with PCl_3/NEt_3 in toluene afforded phosphite L^1 in quantitative yield (eqn. 1). Compound L^1 is highly soluble in all common organic solvents, a property that makes recrystallisation difficult. It turned out that after careful elimination of NEt_3HCl and NEt_3 from the reaction mixture (see Experimental section), the product did not require further purification. The ^{31}P NMR spectrum of L^1 shows two signals, at 107 and 26.1 ppm, corresponding to the phosphite and phosphine oxide fragments, respectively (*cf.* 128 ppm for $P(OPh)_3$ and 23 ppm for $O{=}PPh_3$). The ^1H NMR spectrum, which displays three Bu^t signals of relative intensity 1:1:2 and two AB patterns for the ArCH_2 groups, is consistent with the existence of a symmetry plane. As revealed by 2D ROESY experiments, the '*m*-H' protons of the calixarene unit correlate exclusively with *equatorial* ArCH_2Ar atoms. This observation unambiguously establishes the cone structure of L^1. Note that this conformation contrasts with that of Lattman's calixarene **2**, obtained by reacting *p-tert*-butylcalix[4]arene with hexamethylphosphorus triamide/CF_3CO_2H.[22] Clearly, the steric crowding of the phosphine oxide group in precursor **1** prevents *trans* annulus inversion and, hence, leads to the selective formation of a cone conformer. It should be stressed that the use of PCl_3/NEt_3 for the preparation of *cone*-L^1 does not result in the formation of a second (isomeric) product, in contrast to the observations made by Parlevliet *et al*., who applied the same methodology to the synthesis of other calix-phosphites.[26] Thus, starting from a monoprotected calixarene appears to be advantageous for synthesising calix[4]arene-based phosphites. Molecular mechanics calculations have shown that the calixarene core of *cone*-L^1 is significantly more strained than the hypothetical partial-cone analogue, *paco*-L^1.[29] Corroborating the observations made by Pringle *et al*. for another calixarene phosphite,[23] we found that dichloromethane solutions of L^1 were quite stable towards aqueous NaOH. However, L^1 decomposes instantly on treatment with slightly acidic water (*vide infra*).



Treatment of a dichloromethane solution of L^1 with aqueous NH_4Cl results in cleavage of a P–O bond and selective formation of phosphonate **3** (eqn. 2). This compound was characterised by ^1H, ^{13}C, ^{31}P and IR spectroscopy. The phosphonate signal appears at 1.4 ppm in the ^{31}P NMR spectrum, while the



PH proton gives a characteristic doublet at 6.01 ppm [J(PH) = 792 Hz]. The ^1H NMR spectrum shows four distinct AB patterns for the ArCH_2 bridging units. All AB separations were found to be ≥ 0.7 ppm, suggesting a cone conformation. However, 2D NOESY experiments clearly indicate that a cone ⇔ partial cone exchange, as shown in Scheme 1, takes place.



Scheme 1 Proposed dynamics for compound **3**.

This was easily deduced from the number of correlations involving the two methylene groups bordering the phenol ring; indeed, both possess a CH atom correlating with two aromatic '*m*-H' protons of the calixarene core, while the other CH correlates with a single '*m*-H' (Fig. 1). The other two methylene

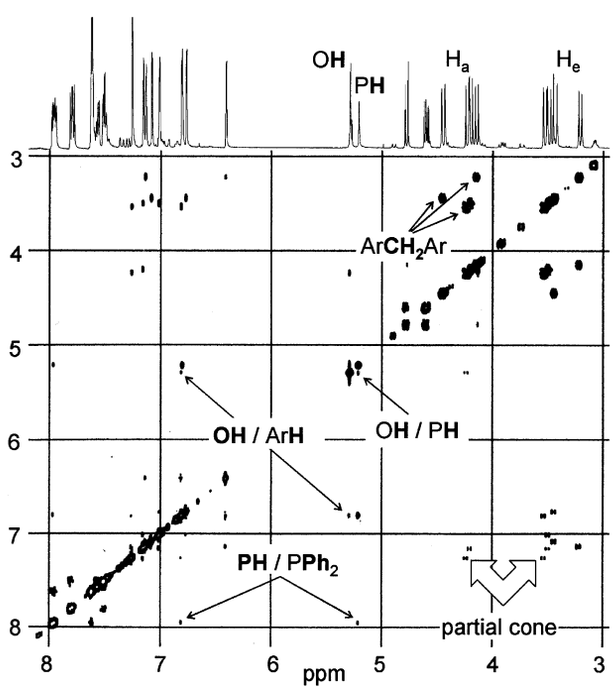
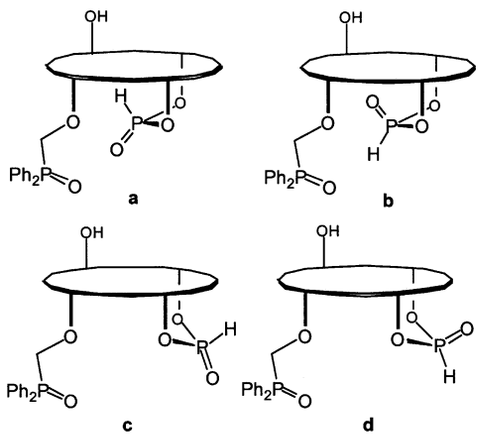


Fig. 1 ROESY spectrum of phosphonate **3** ($CDCl_3$).

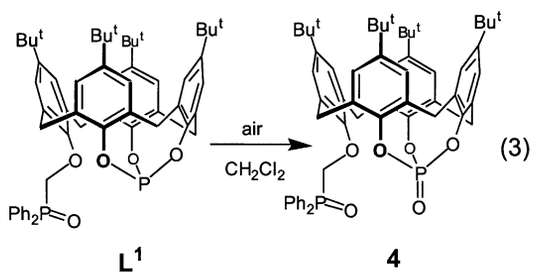
groups show NOEs, exactly as expected for CH_2 groups linking *syn*-oriented aryl rings (*i.e.* the equatorial CH_e atoms correlate with two '*m*-H' protons, while no cross-peaks involving axial CH_a atoms are observed). The same 2D experiment also revealed a spatial proximity between the PH group and the hydroxy group, indicating that the phosphorus atom

is positioned below the cavity. Finally, the 2D spectrum established a proximity between the PH group and the PPh_2 protons. These data allow assignment of structure b (Scheme 2). Note, **3** is a chiral molecule and therefore exists as a mixture of two enantiomers (not drawn).



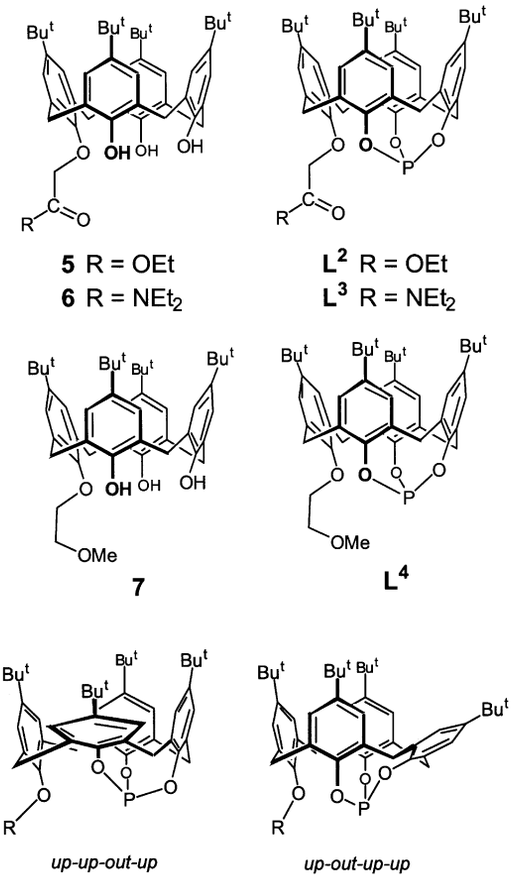
Scheme 2 The four possible orientations of the phosphonate group in *paco*-**3**.

Slow oxidation occurred when a solution of L^1 was allowed to stand in air for several days, affording the mixed phosphine oxide–phosphate **4** (eqn. 3). The phosphate unit is characterised by a peak at −23.3 ppm in the ^{31}P NMR spectrum. As expected, the IR spectrum of **4** shows a strong phosphate band near 1300 cm^{-1} [ν(P=O)].



The related ligands L^2, L^3 and L^4 were prepared by a method similar to that outlined for L^1, but starting from the mono-functionalised *cone*-calixarenes **5**,[30] **6** and **7**,[31] respectively (see Experimental section). As for L^1, the three $^{31}P\{^1H\}$ NMR spectra show a phosphite signal near 106 ppm and the ^1H NMR spectra are in keeping with cone conformations. The IR spectrum of L^2 displays a strong absorption band at 1760 cm^{-1}, typical for an ester function, while the amide strech vibration of L^3 appears at 1653 cm^{-1}.

As already mentioned, the four calixarenes L^1–L^4 possess a conical shape. Many studies have established that, for *syn* *Ar*CH_2*Ar* arrangements, the ^{13}C chemical shift of the bridging methylene carbon lies between *ca.* 29 and 33 ppm, while for an *anti* arrangement, the methylene signal appears in the 37–39 ppm region.[31,32] Interestingly, for each of the four C_s-symmetrical ligands described in this work, one Ar*C*H_2 signal lies exactly between these two regions (near 36.5 ppm), while the other one appears in the range expected for *syn*-arranged *Ar*CH_2*Ar* moieties (*ca.* 33 ppm). The observation of a signal with an 'intermediate' chemical shift may be interpreted in terms of partial flattening of the calix core as a consequence of the strain imposed by the very short μ_3-P capping unit. Shape modification of calixarenes through μ_3-P caps has already been described in detail, including for larger calixarenes.[23,26,33] In fact, the observed ^{31}P chemical shifts, near 106 ppm, suggest that calixarenes L^1–L^4 adopt a so-called *up-up-out-up* rather than an *up-out-up-up* conformation (Scheme 3). As shown by van Leeuwen *et al.*, higher δ values are expected (*ca.* 116 ppm) for the latter conformation.[26]

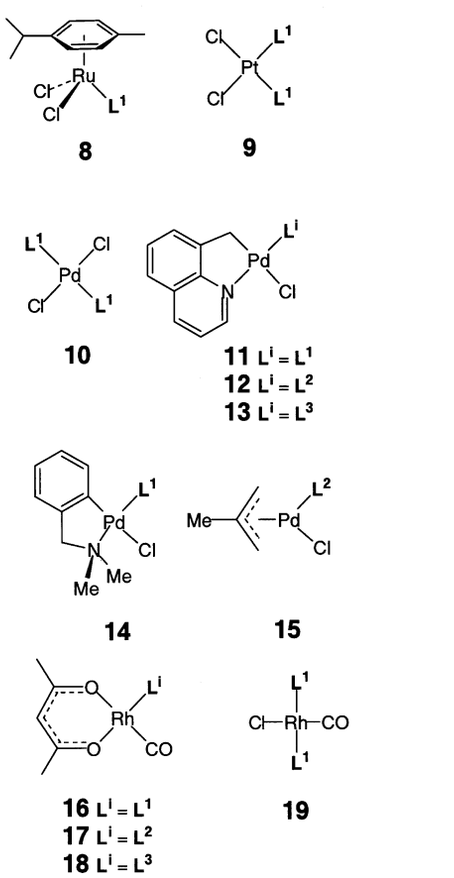


Scheme 3 The two known cone conformations of calix[4]arene phosphites.

Complexes obtained from phosphites L^1–L^3

L^1 reacts with $[RuCl_2(p\text{-cymene})]_2$ to quantitatively afford the red phosphite complex **8** characterised by a singlet at 92.6 ppm in the ^{31}P NMR spectrum. This signal is *highfield*-shifted with respect to that of free L^1 (107 ppm), but this is not unusual for coordinated phosphites.[34] Furthermore, no significant shift was observed for the phosphine oxide signal upon complexation, hence ruling out bonding of the phosphoryl unit.

Reaction of L^1 with $[PtCl_2(1,5\text{-cyclooctadiene})]$ afforded complex **9** in high yield. Its ^{31}P NMR spectrum shows a singlet at 32.7 ppm with the corresponding Pt satellites. The observed J(PPt) coupling constant, 6736 Hz, is nearly identical to the value (6629 Hz) recently reported by Pringle *et al.* for *cis*-$[PtCl_2(paco\text{-}\mathbf{2}')]$ (**2′** is the non-butylated analogue of **2**).[23] An X-ray diffraction study (*vide infra*) confirmed the *cis* stereochemistry. Unlike that of L^1, the ^1H NMR spectrum of **9** shows four distinct AB patterns for the bridging methylene units, as well as an AB spectrum for the PCH_2 protons, in keeping with two calixarene subunits that are no longer C_s-symmetric. This observation reflects the important steric crowding of the two calixarene fragments, preventing the *cis*-arranged phosphites freely rotating about the MP bonds. Fig. 2 shows the solid state structure of the complex. The platinum centre has, as expected, a planar coordination environment, the metal lying only *ca.* 0.010 Å out of the least-squares P_2Cl_2 plane. The PPtP angle lies 6° over the ideal 90° value. The Pt–P bond lengths [2.218(2) and 2.224(2) Å] are comparable to those found in other $[PtCl_2(phosphite)_2]$ complexes.[35,36] Both calixarene cores adopt a cone conformation, but are highly distorted with respect to calix[4]arenes containing uncapped phenol units. Thus, as



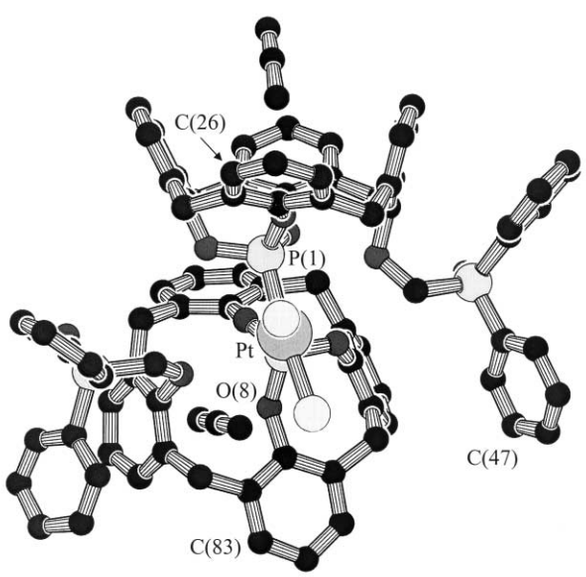


Fig. 2 Molecular structure of *cis*-[$PtCl_2(L^1_2)$]. Each calixarene contains an acetonitrile molecule (other solvents not shown). The Bu^t groups have been ommitted for clarity. The most inclined phenol units are those containing C(26) and C(83). Selected bond lengths (Å): Pt–Cl(1) 2.342(1), Pt–Cl(2) 2.339(1), Pt–P(1) 2.217(1), Pt–P(3) 2.224(1)

anticipated, each calixarene contains an aryl–OP ring whose orientation approaches that of the calixarene reference plane [dihedral angles 26.2(2) and 27.9(3)°], resulting in an *up-up-out-up*[26] conformation (Fig. 2). The fact that rotation of a particular phosphite about its Pt–P axis is hindered by the neighbouring ligand becomes obvious if one considers the spatial expansion of the ligands. The latter is particularly important in the region containing the phosphine oxide arm. For example, the P(1)–Pt–C(47) angle is 123°. Thus, virtual rotation of the ligands about their coordination axis generates a cone having an opening angle (Ω) larger than 180°, hence implying mutual steric hindrance between the phosphites. Finally, we note that both calixarene cavities contain an acetonitrile guest. This is not unusual with calix[4]arenes that are somewhat flattened.[37] The molecule crystallises with three further CH_3CN molecules as well as a water molecule.

Reaction of L^1 with [$PdCl_2$(1,5-cyclooctadiene)] yielded complex *trans*-**10** quantitatively. The assignment of a *trans* stereochemistry was inferred from the NMR spectra which show that the calixarene fragments retain a C_s-symmetrical structure upon complexation. Obviously, owing to the large separation between the two calixarene fragments, there is, in this case, no barrier to rotation about the M–P bond.

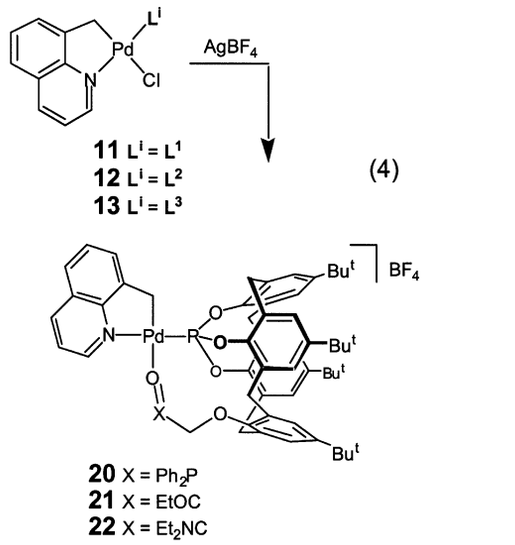
Further examples where the ligand symmetry remains unaffected upon complexation are the complexes **11**–**13**, obtained by reaction of $[Pd(8\text{-mq})Cl]_2$ (8-mqH = 8-methylquinoline) with L^1, L^2 and L^3, respectively, and complex **14** resulting from the reaction of L^1 with the cyclometallated Pd(II) complex $[PdCl(o\text{-}C_6H_4CH_2NMe_2)]_2$.

Reaction of L^2 with [$PdCl(\eta^3\text{-}C_4H_7)$] afforded the allylic complex **15**. The metal plane is not a symmetry element of this molecule, hence the corresponding ^{1}H NMR spectrum exhibits four distinct ArCH_2Ar groups and an AB pattern for the methylenic OCH_2CO_2Et protons.

Reaction of [$Rh(acac)(CO)_2$] with one equiv. of L^1–L^3 gave the highly soluble complexes **16**, **17** and **18**, respectively. Phosphite bonding in these complexes was deduced from the presence of a doublet in their ^{31}P NMR spectra [J(PRh) = *ca.* 305 Hz]. The corresponding IR spectra show a strong ν(CO) carbonyl band near 2000 cm^{-1}. The bis-phosphite **19** was obtained in high yield by reaction of $[RhCl(CO)_2]_2$ with 4 equiv. of L^1. Characterisation data are reported in the Experimental section. It is worth mentioning here that small amounts of **19** were formed in hydroformylation experiments (*vide infra*) when using insufficiently purified samples of L^1, *i.e.* containing residual amounts of NEt_3HCl.

In order to force bonding of the auxiliary groups, the three complexes **11**–**13** were treated with silver tetrafluroborate (eqn. 4). These reactions afforded the cationic complexes **20**–**22**, respectively, which were authenticated by elemental analysis and mass and multinuclear NMR spectroscopies. Coordination of the carbonyl functions of **21** and **22** was inferred from their IR spectra. Thus, the ν(C=O) stretching vibrations of these two complexes are lowered by more than 50 cm^{-1} when compared to the corresponding starting complexes, **12** and **13**, respectively. In the ^{13}P NMR spectrum of complex **20**, the phosphine oxide signal underwent a downfield shift of *ca.* 5 ppm upon complexation, in accord with bonding of the phosphoryl fragment. Owing to the presence of broad calixarene bands in the ν(P=O) region, we were unable to confirm by IR the coordination of the phosphoryl unit.

The ultimate proof for chelate formation in complex **22** came from a single crystal X-ray diffraction study. The molecular structure of the complex is shown in Fig. 3. Again, the calixarene core adopts an *up-up-out-up* cone conformation ['*out*' refers to the phenol ring bearing O(3)], but the deviation from a typical cone is more pronounced than in **9**, as revealed by the dihedral angle of only 10° between the O(3) phenol ring and the calix reference plane. The coordination plane is strongly inclined with respect to the calix reference plane (dihedral angle *ca.* 68°). All metal–ligand bond distances are normal, but, as frequently observed in chelate complexes, the palladium stereochemistry deviates somewhat from an ideal square planar coordination geometry. Thus, the P–Pd–O angle is 7° greater than 90°, reflecting the strain imposed on the P,O-chelate by amide coordination. In fact, Pd–O bond formation forces the amide plane to be nearly perpendicular to the coordination plane, so as to optimise overlap of an oxygen lone pair with the in-plane metal d-orbital. Incidently, the particular orientation



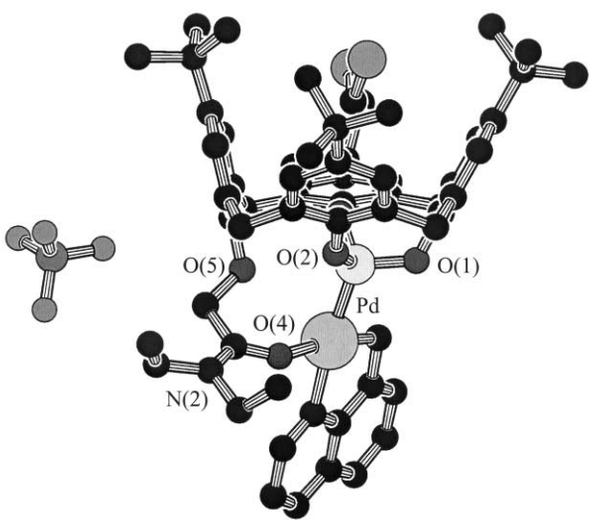
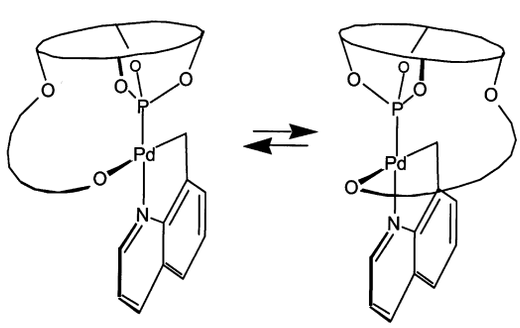


Fig. 3 Molecular structure of the chelate complex **22**. The calixarene contains a CH_2Cl_2 guest. The O(3) atom is opposite to O(2). Selected bond lengths (Å): Pd–N(1) 2.089(3), Pd–O(4) 2.148(3), Pd–P 2.2041(11).

of the amide induces an increased distortion of the calixarene shape, as revealed by the strong inclination of the O(5) phenol plane with respect to the calix reference plane (dihedral angle *ca.* 80° *vs.* 61° for the O(1) phenol plane). Complex **22** displays an apparent C_s symmetry in solution, in keeping with the dynamics shown in Scheme 4, in which the chelate loop rapidly



Scheme 4 Swinging of the P–O(amide) loop from one side of the metal plane to the other.

swings from one side of the metal plane to the other. This motion implies restricted rotation of the two chelate ends about the Pd–P and Pd–O(4) bonds, respectively, as well as a structural rearrangement of the calixarene core, rendering the O(2) and O(3) phenol rings equivalent on the NMR timescale. It is noteworthy that equilibrating *up-up-out-up*/*out-up-up-up* conformations of calix[4]arenes have already been evidenced by van Leeuwen *et al.*[26] It appears very plausible that this fluxionality induces the displacement of the amide arm from one side of the coordination plane to the other. As verified by IR spectroscopy (in CH_2Cl_2 and CH_3CN), there is no amide labilisation during this process, ruling out hemilabile[38] ligand behaviour.

Hydroformylation with heterodifunctional calix phosphites

In the present study, 1-octene was hydroformylated in toluene at 80 °C under 22 bar CO–H_2 pressure (initial pressure at 80 °C). The phosphite:metal:substrate ratio was 10:1:5000. The results obtained for the four phosphites are summarised in Table 1 and Fig. 4. It should be emphasised that these experiments were

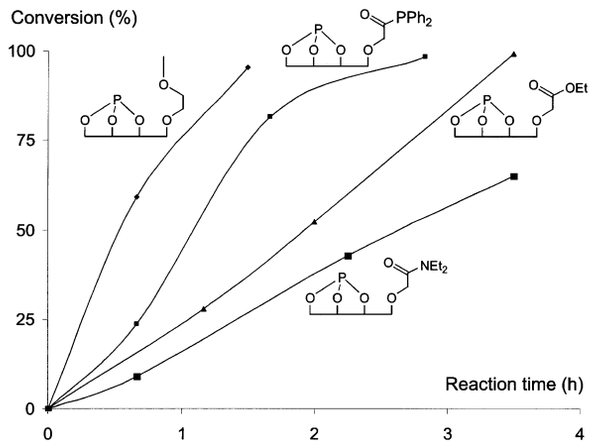


Fig. 4 Conversion of 1-octene as a function of time using phosphites L^1–L^4.

carried out with rigorously pure samples of phosphites, free of NEt_3HCl in particular. The presence of the latter in ligand samples resulted in the formation of undesirable side products, *e.g.* **19** (when starting from L^1).

As expected for bulky phosphites, the reaction rates were higher than those observed using $P(OPh)_3$. The higher activity is generally explained by a lower number of coordinated phosphites. The fastest catalysis occurred with the ether phosphite L^4. The corresponding activity (TOF *ca.* 4500) is, however, 1.6 times lower than that recently reported by van Leeuwen *et al.* for the related phosphite **23** bearing an ^{i}Pr group instead of –CH_2CH_2OMe. For comparison, the TOF found for PPh_3 under similar conditions is 2200 (L/B = 2.8), while the highest rates reported to date were those for the bulky phosphite **24** (*ca.* 40000 mol Rh^{-1} h^{-1}; L/B = 1.9).[39] Interestingly, the activity decreases in the order $L^4 > L^1 > L^2 > L^3$, that is, with increasing donor strength of the oxygen-containing side group. The aldehyde selectivity also changes significantly, those of ligands L^1–L^3 being higher than those observed for **23** and L^4. The reason for these variations is a matter for discussion. A logical explanation for an activity decrease is that conformational changes within the calixarene backbone occur during catalysis which incidently change the electronic and steric properties of the ligand. Such a shape modification appears, however, questionable since ligands **23** and L^4 have similar structures but different activities. Note in particular that both ligands adopt an *up-up-out-up* conformation, at least at room temperature.[26] The observed changes could also arise from the formation of P,O-chelate † complexes during catalysis.

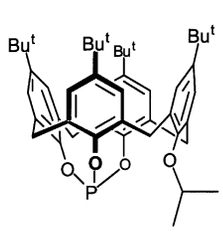
† Molecular mechanics calculations show that for a hypothetical chelate complex [RhH(CO)$_2$(P–O)] with tbp structure, the bisequatorial P,O-coordination (ee) is favored over equatorial apical (ae) coordination.[29] For this calculation, the calixarene was maintained in an *up-up-out-up* conformation.

Table 1 Hydroformylation of 1-octene with calixarene phosphites[a]

Ligand	TOF[b]	L/B[c]	L/all products[d] (%)	Isomerisation[e] (%)
PPh_3	2200	2.8		1.5
$P(OPh)_3$	—	2.8[f]		—
Alkylphosphite **23**	7300	1.4	54	6
Ether phosphite L^4	4400	1.4	53	3.5
$P^V(O)$-phosphite L^1	2450	2.4	58	11.2
Ester phosphite L^2	1300	3.6	57	9.6
Amide phosphite L^3	950	2.7	57	13.6

[a] Conditions: L/Rh = 10, 1-octene/Rh = 5000, [Rh] = *ca.* 0.11 mM, initial pressure (at 20 °C) P = 20 bar CO–H_2 (1:1), T = 80 °C, toluene–*n*-decane (15 cm^3, 0.5 cm^3). [b] Turnover frequency, determined at *ca.* 30% conversion. [c] The L/B ratio takes into account all possible branched aldehydes. [d] At *ca.* 95% conversion. [e] Isomerised 1-octene/all octenes. [f] At 40 bar. See also Experimental section.

Indeed, it should be recalled that, as shown by Lindner and Norz, ether phosphines may act as transient chelate ligands when used in methanol carbonylation.[17] Furthermore, Alper *et al.* recently established that phosphine oxides may coordinate to rhodium centres during olefin hydroformylation.[40] Note that the L/B variation (Table 1) does not rigorously parallel the donor strength of the side group (ether < phosphine oxide < ester < amide). The reason why ester L^2 gives a higher L/B ratio than amide L^3 (the amide is a stronger donor than the ester group) remains unclear and suggests that other factors (probably steric) have to be taken into account. At the end of the catalytic runs performed with L^1, the reaction mixture contained, beside unmodified L^1, trace amounts of compounds **3** and **4**.



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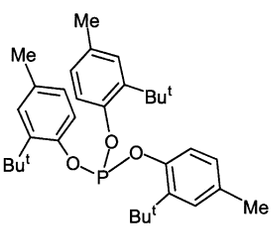

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Conclusion

In the present study we have described the high yield synthesis of four new heterofunctionalised P,O-phosphites based on a calix[4]arene backbone. The mixed phosphine oxide–phosphite L^1 is stable towards aqueous NaOH, but decomposes instantly in the presence of slightly acidic water. All calixarenes adopt a cone conformation, making the phosphites potential chelating systems. The ability to behave as a P,O-chelate was unambiguously demonstrated for three of them, L^1–L^3, which form 12-membered palladacycles with the '$Pd(8\text{-mq})^+$' unit. In the latter complexes, the chelating P,O-loop swings from one side of the metal plane to the other, the whole dynamics possibly being facilitated by the flexibility of the calixarene. In keeping with their steric crowding, the rates of hydroformylation for the ligands are higher than those observed for $P(OPh)_3$, but remain lower than that found for the bulky phosphite $P\{O(2\text{-}Bu^t,4\text{-}MeC_6H_3)\}_3$. The activity decreases with the donor strength of the oxo side group, suggesting that, during catalysis, P,O-chelates are formed. Furthermore, with the 'good' O-donors, the L/B ratios are significantly higher than with the ether phosphite L^4. However, the observed selectivities cannot be explained solely in terms of the donor properties of the side group and further experiments, including IR studies under CO/H_2, with other heterofunctionalised phosphites need to be performed to ascertain the reasons for these observations.

Experimental

General procedures

Unless otherwise stated, materials were obtained from commercial suppliers and used without further purification. Solvents were dried over suitable reagents and freshly distilled under dry nitrogen before use. $CDCl_3$ was passed through a 5 cm thick alumina column and stored under N_2 over molecular sieves (4 Å). All reactions were carried out using modified Schlenk tube techniques under a dry nitrogen atmosphere. IR spectra were recorded on a Perkin-Elmer 1600 spectrometer (4000–400 cm^{-1}). Routine ^1H, $^{13}C\{^1H\}$ and $^{31}P\{^1H\}$ NMR spectra were recorded on Bruker AC-200 (^1H: 200.1 MHz; ^{13}C: 50.3 MHz), AC-300 (^1H: 300.1 MHz; ^{31}P: 121.5 MHz) and ARX-500 (^1H: 500.1 MHz) spectrometers. The 2D (^1H–^1H NOESY and ROESY) NMR spectra were recorded on a Bruker ARX-500 using a standard pulse sequence and Bruker software for treatment of the acquired data. Proton chemical shifts are reported relative to residual protiated solvents ($CHCl_3$, δ 7.26). The ^{13}C chemical shifts are referenced relative to deuterated solvents ($CDCl_3$, δ 77.00) and the ^{31}P NMR data are given relative to external H_3PO_4. A positive sign denotes a value downfield from the reference. Abbreviations used are s = singlet, d = doublet, t = triplet, q = quartet, br = broad. The mass spectra were recorded on a ZAB HF VG analytical spectrometer using *m*-nitrobenzyl alcohol as a matrix. For column chromatography, Geduran SI (E. Merck, 0.040–0.063 mm) was used. Routine thin layer chromatographic analyses were carried out using plates coated with Merck Kieselgel 60 GF_{254}. Elemental analyses were performed by the Service de Microanalyse, Centre de Recherche Chimie, Université Louis Pasteur, Strasbourg. Melting points were determined with a Büchi 535 capillary melting point apparatus and are uncorrected. The abbreviation 8-mq stands for the 8-methylquinolinyl fragment.

Syntheses

5,11,17,23-Tetra-*tert*-butyl-25-(diphenylphosphinoylmethoxy)-26,27,28-(μ_3-phosphorustrioxy)calix[4]arene (L^1). To a cold (−40 °C) solution of **1** (1.000 g, 1.16 mmol) in a NEt_3–toluene mixture (2 cm^3, 14.35 mmol NEt_3; 100 cm^3 toluene) was added dropwise a solution of PCl_3 (0.1 cm^3, 1.16 mmol) in toluene (5 cm^3) maintained at *ca.* −40 °C. The mixture was then heated at 80 °C for 20 h. The NEt_3HCl salt formed was removed by filtration, first through a bed of Celite, then through a 2 cm layer of SiO_2 and finally washed with cold toluene (2 × 10 cm^3). Filtration over SiO_2 was required for complete removal of the ammonium salt. The filtrate and washing solutions were evaporated under vacuum. Drying under vacuum for 2 h is sufficient for complete removal of the remaining amine. Yield: 1.000 g, 1.12 mmol, 97%. Mp 105 °C. IR (KBr) ν_{max}/cm^{-1}: 1194 (s, P=O, tentative assignment). ^1H NMR (500 MHz, $CDCl_3$): δ 8.11–8.07 and 7.45–7.37 [10 H, $P(O)Ph_2$], 7.10 and 7.01 (AB q, ^4J = 2.5, 2H each, *m*-ArH), 7.02 (s, 2H, *m*-ArH), 6.66 (s, 2H, *m*-ArH),

4.58 [d, ^2J = 7.7, 2H, P(O)CH_2], 4.38 and 3.45 (AB q, ^2J = 14.7, 4H, ArCH_2Ar), 4.11 and 3.34 (AB q, ^2J = 14.4 Hz, 4H, ArCH_2Ar), 1.36 [s, 18H, C$(CH_3)_3$], 1.16 [s, 9H, C$(CH_3)_3$], 0.86 [s, 9H, C$(CH_3)_3$]. $^{13}C\{^1H\}$ NMR (50 MHz, $CDCl_3$): δ 153.38–124.56 (aryl C), 73.48 [d, J(PC) 83 Hz, P(O)CH_2], 36.42 (s × 2, ArCH_2Ar), 34.23 [s, C$(CH_3)_3$], 34.03 [s × 2, C$(CH_3)_3$], 33.86 [s, C$(CH_3)_3$], 33.11 (s × 2, ArCH_2Ar), 31.42 [s × 3, C$(CH_3)_3$)], 30.94 [s, C$(CH_3)_3$]. $^{31}P\{^1H\}$ NMR (121 MHz, $CDCl_3$): δ 107.0 [s, P$(OAr)_3$], 26.1 [s, P(O)Ph_2]. Found: C, 76.04; H, 7.44; calc. for $C_{57}H_{64}O_5P_2\cdot H_2O$ (M_r = 900.07): C, 76.06; H, 7.28%.

Racemic mixture of 5,11,17,23-tetra-*tert*-butyl-25-(diphenylphosphinoylmethoxy)-(μ_2-26,27-phosphonato)-28-hydroxycalix[4]arene and 5,11,17,23-tetra-*tert*-butyl-25-(diphenylphosphinoylmethoxy)-26-hydroxy-(μ_2-27,28-phosphonato)calix[4]arene (3). A solution of L^1 (1.000 g, 1.13 mmol) in CH_2Cl_2 (20 cm^3) was shaken in the presence of a 0.1 M solution of NH_4Cl in water (20 cm^3). After 0.5 h, the organic component was separated and washed twice with water (2 × 10 cm^3). The organic phase was then dried over $MgSO_4$. After filtration, the solution was evapored to dryness. Recrystallisation from CH_2Cl_2–pentane at −78 °C afforded **3** as a white, analytically pure solid. Yield: 0.803 g, 0.88 mmol, 78%. Mp 175–182 °C. IR (KBr) ν_{max}/cm^{-1}: 1194 (P=O, tentative assignment). ^1H NMR (500 MHz, $CDCl_3$): δ 8.00–7.93, 7.83–7.77 and 7.64–7.33 [10H, P(O)Ph_2], 7.27 and 7.16 (AB q, ^4J = 2.2, 2H, m-ArH), 7.14 and 7.08 (AB q, ^4J = 2.0, 2H, m-ArH), 7.02 and 6.42 (AB q, ^4J = 2.2, 2H, m-ArH), 6.82 and 6.77 (AB q, ^4J = 2.4, 2H, m-ArH), 6.01 [d, J(PH) 792, 1H, P$(OAr)_2$(O)H], 5.27 (s, 1H, OH, exchanges with D_2O), 4.79 and 4.60 [ABX system with X = P, $^2J_{AB}$ = 13.2, $^2J_{AX}$ = 7.6, $^2J_{BX}$ = 0, 2H, P(O)CH_2], 4.47 and 3.45 (AB q, ^2J = 14.7, 2H, ArCH_2Ar), 4.25 and 3.54 (AB q, ^2J = 14.0, 2H, ArCH_2Ar), 4.20 and 3.50 (AB q, ^2J = 14.0, 2H, ArCH_2Ar), 4.16 and 3.22 (AB q, ^2J = 14.4 Hz, 2H, ArCH_2Ar), 1.33 [s, 9H, C$(CH_3)_3$], 1.25 [s, 9H, C$(CH_3)_3$], 1.06 [s, 9H, C$(CH_3)_3$], 0.84 [s, 9H, C$(CH_3)_3$]. $^{13}C\{^1H\}$ NMR (50 MHz, $CDCl_3$): δ 152.98–125.06 (aryl C), 73.92 [d, J(PC) = 82 Hz, P(O)CH_2], 35.83 (s × 2, ArCH_2Ar), 34.19 [s, C$(CH_3)_3$], 34.03 (s, ArCH_2Ar), 33.93, 33.83, 33.76 [s × 3, C$(CH_3)_3$], 33.53 (s, ArCH_2Ar), 31.60, 31.40, 31.11, 30.79 [s × 4, C$(CH_3)_3$)]. $^{31}P\{^1H\}$ NMR (121 MHz, $CDCl_3$): δ 25.8 [s, P(O)Ph_2], 1.4 [s, P$(OAr)_2$(O)H]. ^{31}P NMR (121 MHz, $CDCl_3$): δ 25.9 [br s, P(O)Ph_2], 1.4 [d, J(PH) 792 Hz, P$(OAr)_2$(O)H]. Found: C, 75.12; H, 7.48; calc. for $C_{57}H_{64}O_6P_2$ (M_r = 909.08): C, 75.31; H, 7.44%.

5,11,17,23-Tetra-*tert*-butyl-25-(diphenylphosphinoylmethoxy)-26,27,28-(μ_3-phosphato)calix[4]arene (4). A CH_2Cl_2–ethanol solution (1:1, v/v, 50 cm^3) of L^1 (3.000 g, 3.37 mmol) was left standing in air for 4 days. The solvent was then evaporated and the residue was subjected to flash chromatography using AcOEt–hexane (40:60, v/v) as eluent. Unreacted L^1 eluted first (R_f = 0.50, AcOEt–hexane, 40:60, v/v) followed by **4** (R_f = 0.30, AcOEt–hexane, 40:60, v/v). Analytically pure **4** (white solid) was obtained by recrystallisation in CH_2Cl_2–pentane. Yield: 0.600 g, 0.66 mmol, 19%. Mp > 240 °C. IR (KBr) ν_{max}/cm^{-1}: 1307 (s, P=$O_{phosphate}$), 1187 (s, P=$O_{phosphine\ oxide}$, tentative assignment). ^1H NMR (300 MHz, $CDCl_3$): δ 8.37–8.31 and 7.50–7.48 [10 H, P(O)Ph_2], 7.10 and 7.06 (AB q, ^4J = 2.2, 4H, m-ArH), 7.06 (s, 2H, m-ArH), 6.48 (s, 2H, m-ArH), 4.55 [d, ^2J = 7.7, 2H, P(O)CH_2], 4.53 and 3.51 (AB q, ^2J = 14.6, 4H, ArCH_2Ar), 4.24 and 3.27 (AB q, ^2J = 14.8 Hz, 4H, ArCH_2Ar), 1.35 [s, 18H, C$(CH_3)_3$], 1.15 [s, 9H, C$(CH_3)_3$], 0.71 [s, 9H, C$(CH_3)_3$]. $^{13}C\{^1H\}$ NMR (50 MHz, $CDCl_3$): δ 155.11–124.72 (aryl C), 74.08 [d, J(PC) 84 Hz, P(O)CH_2], 35.36 (s × 2, ArCH_2Ar), 34.38 [s, C$(CH_3)_3$], 34.16 [s × 2, C$(CH_3)_3$], 33.76 [s, C$(CH_3)_3$], 32.31 (s × 2, ArCH_2Ar), 31.36 [s × 3, C$(CH_3)_3$)], 30.82 [s, C$(CH_3)_3$]. $^{31}P\{^1H\}$ NMR (121 MHz, $CDCl_3$): δ 24.9 [s, P(O)Ph_2], −23.3 [s, P$(OAr)_3$]. Found: C, 75.67; H, 7.35; calc. for $C_{57}H_{64}O_6P_2$ (M_r = 907.06): C, 75.48; H, 7.11%.

5,11,17,23-Tetra-*tert*-butyl-25-(ethoxycarbonylmethoxy)-26,27,28-(μ_3-phosphorustrioxy)calix[4]arene (L^2). PCl_3 (0.17 cm^3, 1.94 mmol) was added dropwise to a solution of **5** (1.420 g, 1.93 mmol) and NEt_3 (2.0 cm^3, 14.35 mmol) in toluene (100 cm^3). The mixture was stirred at room temperature for 4 days. The NEt_3HCl salt formed was filtered off using a bed of Celite and washed with toluene (2 × 10 cm^3). The filtrate and washing solutions were evaporated under vacuum. Analytically pure L^2 was obtained as a white solid by recrystallisation from CH_2Cl_2–methanol at −78 °C. Yield: 0.984 g, 1.29 mmol, 67%. Mp > 240 °C. IR (KBr) ν_{max}/cm^{-1}: 1760 (m s, C=O). ^1H NMR (300 MHz, $CDCl_3$): δ 7.17–7.10 (m, 4H, m-ArH), 7.04 (s, 2H, m-ArH), 6.77 (s, 2H, m-ArH), 4.73 and 3.56 (AB q, ^2J = 14.4, 4H, ArCH_2Ar), 4.56 (s, 2H, OCH_2CO_2), 4.39 and 3.44 (AB q, ^2J = 14.3, 4H, ArCH_2Ar), 4.25 (q, ^3J = 7.1, 2H, CH_2CH_3), 1.36 [s, 18H, C$(CH_3)_3$], 1.30 (t, ^3J = 7.1 Hz, 3H, CH_2CH_3), 1.19 [s, 9H, C$(CH_3)_3$], 0.94 [s, 9H, C$(CH_3)_3$]. $^{13}C\{^1H\}$ NMR (50 MHz, $CDCl_3$): δ 169.44 (s, CO_2), 148.13–124.60 (aryl C), 72.04 (s, OCH_2CO_2), 61.00 (s, CH_2CH_3), 36.57 (s × 2, ArCH_2Ar), 34.32 [s, C$(CH_3)_3$], 34.09 [s × 2, C$(CH_3)_3$], 33.99 [s, C$(CH_3)_3$], 33.86 [s, C$(CH_3)_3$], 33.86 (s × 2, ArCH_2Ar), 31.51 [s × 3, C$(CH_3)_3$)], 31.14 [s, C$(CH_3)_3$], 14.29 (s, CH_2CH_3); $^{31}P\{^1H\}$ NMR (121 MHz, $CDCl_3$): δ 106.3 [s, P$(OAr)_3$]. Found: C, 75.61; H, 7.88; calc. for $C_{48}H_{59}O_6P$ (M_r = 762.95): C, 75.56; H, 7.79%.

5,11,17,23-Tetra-*tert*-butyl-25-(diethylcarbamoylmethoxy)-26,27,28-trihydroxycalix[4]arene (6). A suspension of *p-tert*-butylcalix[4]arene (1.000 g, 1.54 mmol) and K_2CO_3 (0.115 g, 0.83 mmol) in acetonitrile (50 cm^3) was refluxed for 2 h. 2-Bromo-*N*,*N*-diethylacetamide (1.000 g, 5.15 mmol) was then added and the mixture refluxed for a further 10 days. After cooling, the solvent was removed under reduced pressure. The residue was taken up in CH_2Cl_2 (30 cm^3) and washed with 1 M HCl (30 cm^3), then with water (30 cm^3). The organic layer was dried over $MgSO_4$, filtered and evaporated. The crude product was purified by column chromatography using AcOEt–hexane (30:70, v/v) as eluent. Unreacted *p-tert*-butylcalix[4]arene eluted first followed by **6** (SiO_2, R_f = 0.38, AcOEt–hexane, 30:70, v/v). After evaporation, the residue was taken up in CH_2Cl_2. Addition of ethanol at −78 °C afforded the product as a white powder. Yield: 0.274 g, 0.36 mmol, 23%. Mp 149 °C. IR (KBr) ν_{max}/cm^{-1}: 1653 (s, C=O). ^1H NMR (300 MHz, $CDCl_3$): δ 10.43 (s, 1H, OH, exchanges with D_2O), 9.73 (s, 2H, OH, exchanges with D_2O), 7.08 (s, 2H, m-ArH), 7.04 (m, 4H, m-ArH), 6.95 (d, ^4J = 2.4, 2H, m-ArH), 4.96 (s, 2H, OCH_2), 4.60 and 3.37 (AB q, ^2J = 12.9, 4H, ArCH_2Ar), 4.34 and 3.40 (AB q, ^2J = 13.6, 4H, ArCH_2Ar), 3.55 (q, ^3J = 7.2, 2H, NCH_2CH_3), 3.29 (q, ^3J = 7 Hz, 2H, NCH_2CH_3), 1.29–1.20 [overlapping signals, 42H, C$(CH_3)_3$ and NCH_2CH_3]; $^{13}C\{^1H\}$ NMR (50 MHz, $CDCl_3$): δ 168.85 (s, C=O), 148.31, 142.76, 134.03, 127.95 (s × 4, aromatic C_{quat}), 126.34–125.61 (aryl C), 72.26 (s, OCH_2CO), 40.68 and 40.42 (s × 2, CH_2CH_3), 33.96 [s, C$(CH_3)_3$], 33.16 (s × 2, ArCH_2Ar), 32.94 (s × 2, ArCH_2Ar), 31.50 [s, C$(CH_3)_3$)], 31.33 [s, C$(CH_3)_3$], 14.06 and 12.94 (s × 2, CH_2CH_3). Only one C$(CH_3)_3$ signal could be detected. Found: C, 78.71; H, 8.83; N, 1.77; calc. for $C_{50}H_{67}NO_5$ (M_r = 762.07): C, 78.80; H, 8.86; N, 1.84%.

5,11,17,23-Tetra-*tert*-butyl-25-(diethylcarbamoylmethoxy)-26,27,28-(μ_3-phosphorustrioxy)calix[4]arene (L^3). To a solution of **6** (0.611 g, 0.802 mmol) in an NEt_3–toluene mixture (NEt_3, 1 cm^3, 7.17 mmol; toluene, 50 cm^3) was added dropwise PCl_3 (0.070 cm^3, 0.802 mmol) under stirring. After 3 h, the NEt_3HCl salt formed was removed by filtration through a bed of Celite and washed with toluene (2 × 15 cm^3). The filtrate and washing solutions were evaporated under vacuum. Yield: 0.620 g, 0.79 mmol, 98%. Mp 88–90 °C. IR (KBr) ν_{max}/cm^{-1}: 1653 (s, C=O). ^1H NMR (300 MHz, $CDCl_3$): δ 7.16 (m, 2H, m-ArH), 7.09 (d, ^4J = 2.5 Hz, 2H, m-ArH), 7.04 (s, 2H, m-ArH), 6.77 (s, 2H, m-ArH), 4.64 and 3.43 (AB q, ^2J = 14.1, 2H each, ArCH_2Ar),

4.55 (s, 2H, OCH_2), 4.39 and 3.56 (AB q, ^2J = 14.3, 2H each, ArCH_2Ar), 3.58 (q, ^3J = 6.9, 2H, NCH_2CH$_3$), 3.45 (q, ^3J = 7.1, 2H, NCH_2CH$_3$), 1.35 [s, 18H, C$(CH_3)_3$], 1.24 (t, ^3J = 6.9, 3H, NCH$_2$CH_3), 1.18 [s, 9H, C$(CH_3)_3$], 1.17 (t, ^3J = 6.9 Hz, 3H, NCH$_2$CH_3), 0.95 [s, 9H, C$(CH_3)_3$]. ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ 167.15 (s, C=O), 155.43–124.54 (aryl C), 74.36 (s, OCH_2CO), 41.54 and 39.90 (s × 2, CH_2CH$_3$), 36.49 (s × 2, ArCH_2Ar), 34.23, 34.00 and 33.90 [s × 3, $C(CH_3)_3$], 33.82 (s × 2, ArCH_2Ar), 31.40 and 31.06 [s × 2, C$(CH_3)_3$], 14.40 and 12.83 (s × 2, CH_2CH_3). ^{31}P{^{1}H} NMR (121 MHz, $CDCl_3$): δ 106.1 [s, P$(OAr)_3$]. Found: C, 76.22; H, 8.65; N, 1.51; calc. for $C_{50}H_{64}NO_5P$ (M_r = 790.02): C, 76.02; H, 8.17; N, 1.77%.

5,11,17,23-Tetra-*tert*-butyl-25-(3-oxabutyloxy)-26,27,28-(μ_3-phosphorustrioxy)calix[4]arene (L^4). PCl_3 (0.027 cm^3, 0.31 mmol) was added dropwise to a toluene (100 cm^3) solution containing **7** (0.217 g, 0.31 mmol) and NEt_3 (0.5 cm^3, 3.59 mmol). The mixture was stirred at room temperature for 18 h. The NEt_3HCl salt formed was filtered off using a bed of Celite and washed with toluene (2 × 10 cm^3). The filtrate and washing solutions were evaporated under vacuum. Yield: 0.194 g, 0.264 mmol, 86%. Mp 91–92 °C. ^{1}H NMR (200 MHz, $CDCl_3$): δ 7.18 and 7.11 (AB q, ^4J = 2.2 Hz, 4H, *m*-ArH), 7.06 (s, 2H, *m*-ArH), 6.80 (s, 2H, *m*-ArH), 4.67 and 3.52 (AB q, ^2J = 14.5, 4H, ArCH_2Ar), 4.45 and 3.48 (AB q, ^2J = 14.3 Hz, 4H, ArCH_2Ar), 4.03 (m, 2H, OCH_2), 3.78 (m, 2H, OCH_2), 3.47 (s, 3H, OCH_3), 1.51 [s, 18H, C$(CH_3)_3$], 1.20 [s, 9H, C$(CH_3)_3$], 0.98 [s, 9H, C$(CH_3)_3$]. ^{13}C{^{1}H} NMR (50 MHz, $CDCl_3$): δ 152.22–143.00 and 134.15–124.40 (aryl C), 74.26 (s, OCH_2), 71.67 (s, OCH_2), 59.39 (s, OCH_3), 36.56 (s × 2, ArCH_2Ar), 34.27 [s, $C(CH_3)_3$], 34.04 [s, $C(CH_3)_3$], 33.62 (s × 2, ArCH_2Ar), 31.47 [s × 3, C$(CH_3)_3$], 31.17 [s, C$(CH_3)_3$]. ^{31}P{^{1}H} NMR (121 MHz, $CDCl_3$): δ 105.6 [s, P$(OAr)_3$]. Found: C, 76.95; H, 8.24; calc. for $C_{47}H_{59}O_5P$ (M_r = 734.942): C, 76.81; H, 8.09%.

(η^6-*p*-Cymene)dichloro{5,11,17,23-tetra-*tert*-butyl-25-(diphenylphosphinoylmethoxy)-26,27,28-(μ_3-phosphorustrioxy)calix[4]arene}ruthenium(II) (8). L^1 (0.250 g, 0.28 mmol) was added to a solution of $[RuCl_2(p\text{-cymene})]_2$ (0.086 g, 0.14 mmol) in CH_2Cl_2 (40 cm^3). After stirring for 2 h, the solvent was removed under vacuum. Recrystallisation from AcOEt–hexane. Yield: 0.190 g, 0.16 mmol, 57%. Mp 219–223 °C (slow decomp.). IR (KBr) ν_{max}/cm^{-1}: 1195 (P=O, tentative assignment). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.78–7.71 and 7.52–7.42 [10 H, P(O)Ph_2], 7.10 (s, 2H, *m*-ArH), 7.05 (s, 2H, *m*-ArH), 6.88 (s, 2H, *m*-ArH), 6.21 (s, 2H, *m*-ArH), 5.82 and 5.70 (AA'BB' system, ^3J = 5.9, 2H each, C_6H_4 of *p*-cymene), 4.90 and 3.50 (AB q, ^2J = 14.3, 2H each, ArCH_2Ar), 4.82 [s, 2H, P(O)CH_2], 4.76 and 3.23 (AB q, ^2J = 15, 2H each, ArCH_2Ar), 2.76 [m, 1H, C$H(CH_3)_2$ of *p*-cymene], 1.80 (s, 3H, ArCH_3 of *p*-cymene), 1.33 [s × 2, 18H, C$(CH_3)_3$], 1.13 [s, 9H, C$(CH_3)_3$], 1.05 [d, ^3J = 6.9 Hz, 6H, CH$(CH_3)_2$ of *p*-cymene], 0.59 [s, 9H, C$(CH_3)_3$]. ^{13}C{^{1}H} NMR (50 MHz, $CDCl_3$): δ 148.29–123.87 (aryl C), 108.99 and 96.54 (s × 2, C_{quat} of *p*-cymene), 91.69, 91.56, 87.33 and 87.16 (s × 4, aryl CH of *p*-cymene), 73.28 [d, J(PC) = 80.3 Hz, P(O)CH_2], 35.99 (s, ArCH_2Ar), 34.16 [s, $C(CH_3)_3$], 33.80 [s, $C(CH_3)_3$], 33.27 (s, ArCH_2Ar), 31.31 [s, C$(CH_3)_3$)], 31.21 [s × 2, C$(CH_3)_3$)], 30.74 [s, C$(CH_3)_3$], 21.27 [s, CH$(CH_3)_2$ of *p*-cymene], 17.93 (s, ArCH_3 of *p*-cymene). ^{31}P{^{1}H} NMR (121 MHz, $CDCl_3$): δ 92.56 [s, P$(OAr)_3$], 24.75 [s, P$(O)Ph_2$]. Found: C, 67.47; H, 7.64; calc. for $C_{67}H_{78}Cl_2O_5P_2Ru$ (M_r = 1197.29): C, 67.21; H, 6.57%. Despite several purifications (recrystallisation followed by chromatography), the samples always contained free *p*-cymene.

***cis*-Dichlorobis{5,11,17,23-tetra-*tert*-butyl-25-(diphenylphosphinoylmethoxy)-26,27,28-(μ_3-phosphorustrioxy)calix[4]arene}platinum(II) (9).** L^1 (0.143 g, 0.16 mmol) was added to a solution of $[PtCl_2$(1,5-cyclooctadiene)] (0.030 g, 0.08 mmol) in CH_2Cl_2 (30 cm^3). After stirring for 1 h, the solution was concentrated under vacuum. Addition of pentane and cooling to −20 °C afforded **9** as a white solid. Yield: 0.130 g, 0.06 mmol, 79%. Mp > 240 °C. IR (KBr) ν_{max}/cm^{-1}: 1179.2 (P=O, tentative assignment). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.89–7.68 and 7.46–7.31 [20 H, P(O)Ph_2], 7.06–6.98 (6H, *m*-ArH), 6.91 (4H, *m*-ArH), 6.70 (s, 2H, *m*-ArH), 6.57 (s, 2H, *m*-ArH), 6.45 (s, 2H, *m*-ArH), 5.78 and 5.54 [ABX system with X = P, $^2J_{AB}$ = 12.9, $^2J_{AX}$ = 0, $^2J_{BX}$ = 6.5, 4H, P(O)CH_2], 4.89 and 3.34 (AB q, ^2J = 12.8, 4H, ArCH_2Ar), 4.60 and 3.22 (AB q, ^2J = 13.9, 4H, ArCH_2Ar), 4.60 and 2.90 (AB q, ^2J = 12.8, 4H, ArCH_2Ar), 3.98 and 2.49 (AB q, ^2J = 12.2 Hz, 4H, ArCH_2Ar), 1.28 [s, 18H, C$(CH_3)_3$], 1.23 [s, 18H, C$(CH_3)_3$], 1.20 [s, 18H, C$(CH_3)_3$], 0.96 [s, 18H, C$(CH_3)_3$]. ^{13}C{^{1}H} NMR (50 MHz, $CDCl_3$): δ 150.75–124.07 (aryl C), 71.69 [d, J(PC) = 72.6 Hz, P(O)CH_2], 37.76 (s, ArCH_2Ar), 35.40 [s, $C(CH_3)_3$], 34.81 [s, $C(CH_3)_3$], 33.27 (s, ArCH_2Ar), 32.27 [s, C$(CH_3)_3$], 32.07 [s, C$(CH_3)_3$]. ^{31}P{^{1}H} NMR (121 MHz, $CDCl_3$): δ 32.7 [s with Pt satellites, J(PPt) = 6736 Hz, P$(OAr)_3$], 26.5 [s, P$(O)Ph_2$]. Found: C, 66.70; H, 6.52; calc. for $C_{114}H_{128}Cl_2O_{10}P_4Pt$ (M_r = 2048.11): C, 66.85; H, 6.30%.

***trans*-Dichlorobis{5,11,17,23-tetra-*tert*-butyl-25-(diphenylphosphinoylmethoxy-26,27,28-(μ_3-phosphorustrioxy)calix[4]arene}palladium(II) (10).** L^1 (0.150 g, 0.168 mmol) was added to a solution of $[PdCl_2$(1,5-cyclooctadiene)] (0.024 g, 0.08 mmol) in CH_2Cl_2 (15 cm^3). After stirring for 1 h, the solution was concentrated under vacuum. Addition of pentane and cooling to −20 °C afforded **10** as a pale yellow solid. Yield: 0.224 g, 0.11 mmol, 68%. Mp > 240 °C. IR (KBr) ν_{max}/cm^{-1}: 1183.1 (P=O, tentative assignment). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.90–7.84 and 7.23–7.18 [20 H, P(O)Ph_2], 7.05 (s, 4H, *m*-ArH), 7.00 (d, ^4J = 2.9, 4H, *m*-ArH), 6.93 (s, 4H, *m*-ArH), 6.60 (s, 4H, *m*-ArH), 5.56 [s, 4H, P(O)CH_2], 4.82 and 3.26 (AB q, ^2J = 14.1, 2H, ArCH_2Ar), 4.45 and 3.18 (AB q, ^2J = 14.3 Hz, 2H, ArCH_2Ar), 1.28 [s, 36H, C$(CH_3)_3$], 1.20 [s, 18H, C$(CH_3)_3$], 0.93 [s, 18H, C$(CH_3)_3$]. ^{13}C{^{1}H} NMR (50 MHz, $CDCl_3$): δ 146.43–124.63 (aryl C), 72.88 [d, J(PC) = 74 Hz, P(O)CH_2], 36.42 (s, ArCH_2Ar), 35.66 [s, $C(CH_3)_3$], 34.45 [s, $C(CH_3)_3$], 33.99 [s, $C(CH_3)_3$], 33.83 [s, ArCH_2Ar], 31.40 [s × 3, C$(CH_3)_3$], 31.17 [s, C$(CH_3)_3$]. ^{31}P{^{1}H} NMR (121 MHz, $CDCl_3$): δ 58.8 [s, P$(OAr)_3$], 27.6 [s, P$(O)Ph_2$]. Found: C, 69.56; H, 6.58; calc. for $C_{114}H_{128}Cl_2O_{10}P_4Pd$ (M_r = 1959.45): C, 69.88; H, 6.58%.

Chloro(8-methylquinolinylmethyl-*C*,*N*){5,11,17,23-tetra-*tert*-butyl-25-(diphenylphosphinoylmethoxy)-26,27,28-(μ_3-phosphorustrioxy)calix[4]arene}palladium(II) (11). L^1 (0.151 g, 0.169 mmol) was added to a solution of $[Pd(8\text{-mq})Cl]_2$ (0.048 g, 0.08 mmol) in CH_2Cl_2 (15 cm^3). After stirring for 1 h, the solution was concentrated under vacuum. Addition of pentane and cooling to −20 °C afforded **11** as a pale yellow solid. Yield: 0.160 g, 0.136 mmol, 60%. Mp > 168–169 °C (decomp). IR (KBr) ν_{max}/cm^{-1}: 1187.3 (P=O, tentative assignment). ^{1}H NMR (200 MHz, $CDCl_3$): δ 9.60–9.54 (1H, arom. H of 8-mq), 8.31–8.26 (1H, arom H of 8-mq), 7.65–7.43 and 7.13–6.99 [20 H, P(O)Ph_2, arom. H of 8-mq and *m*-ArH of calix], 6.51 (s, 2H, *m*-ArH), 4.95 [d, ^2J = 1.7, 2H, P(O)CH_2], 4.82 and 3.45 (AB q, ^2J = 14, 4H, ArCH_2Ar), 4.65 and 3.41 (AB q, ^2J = 14.1 Hz, 4H, ArCH_2Ar), 1.36 [s, 18H, C$(CH_3)_3$], 1.18 [s, 9H, C$(CH_3)_3$], 0.82 [s, 9H, C$(CH_3)_3$]. ^{13}C{^{1}H} NMR (50 MHz, $CDCl_3$): δ 154.16–121.09 (aryl C), 72.82 [d, J(PC) = 80 Hz, P(O)CH_2], 35.99 (s × 2, ArCH_2Ar), 34.35 [s, $C(CH_3)_3$], 34.03 [s, $C(CH_3)_3$], 33.70 (s × 2, ArCH_2Ar), 31.40 [s, C$(CH_3)_3$], 31.01 [s, C$(CH_3)_3$], 26.39 (s, CH_2 8-mq); ^{31}P{^{1}H} NMR (121 MHz, $CDCl_3$): δ 89.8 [s, P$(OAr)_3$], 26.3 [s, P$(O)Ph_2$]. Found: C, 64.52; H, 6.17; calc. for $C_{67}H_{72}ClNO_5P_2Pd.CH_2Cl_2$ (M_r = 1260.04): C, 64.82; H, 6.17%.

Chloro(8-methylquinolinylmethyl-*C*,*N*){5,11,17,23-tetra-*tert*-butyl-25-(ethoxycarbonylmethoxy)-26,27,28-(μ_3-phosphorustrioxy)calix[4]arene}palladium(II) (12). L^2 (0.175 g, 0.23 mmol) was added to a solution of $[Pd(8\text{-mq})Cl]_2$ (0.065 g, 0.114 mmol) in CH_2Cl_2 (50 cm^3). After stirring for 24 h, the solution was

concentrated under vacuum. Addition of MeOH and cooling to −78 °C afforded **12** as a pale yellow solid. Yield: 0.163 g, 0.156 mmol, 68%. Mp > 240 °C. IR (CH_2Cl_2) ν_{max}/cm^{-1}: 1755 (C=O). ^1H NMR (300 MHz, $CDCl_3$): δ 9.64–9.60 (m, 1H, arom. H of 8-mq), 8.28 (d, ^3J = 7.1, 1H, arom. H of 8-mq), 7.61–7.44 (m, 4H, arom. H of 8-mq), 7.21–7.05 (m, 6H, *m*-ArH), 6.77 (s, 2H, *m*-ArH), 5.07 and 3.54 (AB q, ^2J = 13.9, 4H, ArCH_2Ar), 4.71 and 3.49 (AB q, ^2J = 14.0, 4H, ArCH_2Ar), 4.71 (s, 2H, OCH_2CO_2), 3.84 (s, 2H, CH_2 of 8-mq), 3.66 (q, ^3J = 7.2 Hz, 2H, CH_2CH$_3$), 1.36 [s, 18H, C(CH_3)$_3$], 1.22 [s, 9H, C(CH_3)$_3$], 0.96 [s, 9H, C(CH_3)$_3$], 0.88 (t, ^3J = 7.1 Hz, 3H, CH$_2$CH_3); $^{13}C\{^1H\}$ NMR (50 MHz, $CDCl_3$): δ 169.77 (s, CO), 153.25–121.19 (aryl C), 71.62 (s, OCH_2CO_2), 60.25 (s, CH_2CH_3), 36.12 (s, ArCH_2Ar), 34.42 [s, C(CH$_3$)$_3$], 34.12 [s, ArCH_2Ar and C(CH$_3$)$_3$], 33.93 [s × 2, C(CH$_3$)$_3$], 31.40 [s × 3, C(CH$_3$)$_3$], 31.11 [s, C(CH$_3$)$_3$], 13.80 (s, CH$_2$$CH_3$), the CH_2 signal of 8-mq was not detected. $^{31}P\{^1H\}$ NMR (121 MHz, $CDCl_3$): δ 88.7 [s, P(OAr)$_3$]. Found: C, 66.80; H, 6.43; N, 1.42; calc. for $C_{58}H_{67}ClNO_6PPd$ (M_r = 1047.00): C, 66.53; H, 6.45; N, 1.34%.

Chloro(8-methylquinolinylmethyl-*C*,*N*){5,11,17,23-tetra-*tert*-butyl-25-(diethylcarbamoylmethoxy)-26,27,28-(μ$_3$-phosphorustrioxy)calix[4]arene}palladium(II) (13). L^3 (0.175 g, 0.22 mmol) was added to a solution of [Pd(8-mq)Cl]$_2$ (0.063 g, 0.111 mmol) in CH_2Cl_2 (20 cm^3). After stirring for 24 h, the solution was concentrated under vacuum. Addition of hexane and cooling to −78 °C afforded **13** as a pale yellow solid. Yield: 0.170 g, 0.158 mmol, 71%. Mp > 233 °C (decomp.). IR (CH_2Cl_2) ν_{max}/cm^{-1}: 1655 (C=O). ^1H NMR (300 MHz, $CDCl_3$): δ 9.66–9.62 (m, 1H, arom. H of 8-mq), 8.29–8.26 (m, 1H, arom. H of 8-mq), 7.61–7.44 (m, 4H, arom. H of 8-mq), 7.20 (br s, 2H, *m*-ArH), 7.12 (s, 2H, *m*-ArH), 7.10 (s, 2H, *m*-ArH), 6.75 (s, 2H, *m*-ArH), 5.10 and 3.56 (AB q, ^2J = 13.9, 4H, ArCH_2Ar), 4.79 (s, 2H, OCH$_2$-CON), 4.70 and 3.49 (AB q, ^2J = 14.0, 4H, ArCH_2Ar), 3.82 (s, 2H, CH$_2$Pd), 3.07 (q, ^3J = 7.1, 2H, CH_2CH$_3$), 2.87 (q, ^3J = 7.1 Hz, 2H, CH_2CH$_3$), 1.36 [s, 18H, C(CH$_3$)$_3$], 1.21 [s, 9H, C(CH$_3$)$_3$], 0.95 [s, 9H, C(CH$_3$)$_3$], 0.67 (t, ^3J = 7.1 Hz, 3H, CH$_2$CH_3), 0.48 (t, ^3J = 7.1 Hz, 3H, CH$_2$CH_3). $^{13}C\{^1H\}$ NMR (50 MHz, $CDCl_3$): δ 167.64 (s, CO), 153.71–121.19 (aryl C), 72.86 (s, OCH_2), 41.35 and 39.89 (s × 2, CH_2CH_3), 36.16 (s, ArCH_2Ar), 34.45 [s, C(CH$_3$)$_3$], 34.31 (s, ArCH_2Ar), 34.10 [s × 2, C(CH$_3$)$_3$], 33.93 [s, C(CH$_3$)$_3$], 31.48 [s × 3, C(CH$_3$)$_3$], 31.15 [s, C(CH$_3$)$_3$], 27.12 (s, CH_2 of 8-mq), 13.77 and 12.61 (s × 2, CH_2CH_3); $^{31}P\{^1H\}$ NMR (121 MHz, $CDCl_3$): δ 88.1 [s, P(OAr)$_3$]. Found: C, 67.14; H, 6.60; N, 2.48; calc. for $C_{60}H_{72}ClN_2O_5PPd$ (M_r = 1074.07): C, 67.09; H, 6.79; N, 2.61%.

Chloro(*o*-dimethylaminomethylphenyl-*C*,*N*){5,11,17,23-tetra-*tert*-butyl-25-(diphenylphosphinoylmethoxy)-26,27,28-(μ$_3$-phosphorustrioxy)calix[4]arene}palladium(II) (14). L^1 (0.107 g, 0.12 mmol) was added to a solution of [Pd(*o*-$C_6H_4CH_2$-NMe_2)Cl]$_2$ (0.031 g, 0.06 mmol) in CH_2Cl_2 (10 cm^3). After stirring for 1 h, the solvent was removed under vacuum. Recrystallisation from CH_2Cl_2–hexane at −78 °C gave **14** as a pale yellow solid. Yield: 0.072 g, 0.062 mmol, 52%. Mp > 186 °C (decomp). IR (KBr) ν_{max}/cm^{-1}: 1185 (P=O, tentative assignment). ^1H NMR (200 MHz, $CDCl_3$): δ 7.64–7.38, 7.28–7.19 and 7.06–6.62 (20 H, arom. H), 6.41 (s, 2H, *m*-ArH of calix), 5.17 (s, 2H, P(O)CH_2), 4.77–4.70 (m, 4H, ArCH_2Ar), 3.93 (s, 2H, NCH_2), 3.44 (d, ^2J = 14, 2H, ArCH_2Ar), 3.01 (d, ^2J = 14, 2H, ArCH_2Ar), 2.76 [d, ^4J(PH) = 4.2 Hz, 6H, N(CH$_3$)$_2$], 1.31 [s, 18H, C(CH$_3$)$_3$], 1.19 [s, 9H, C(CH$_3$)$_3$], 0.86 [s, 9H, C(CH$_3$)$_3$]. $^{13}C\{^1H\}$ NMR (50 MHz, $CDCl_3$): δ 153.90–122.60 (aryl C), 72.90 [d, ^3J(PC) = 4.9 Hz, NCH_2], 72.65 [d, J(PC) = 80.8 Hz, P(O)CH_2], 50.38 [s × 2, N(CH$_3$)$_2$], 36.16 (s × 2, ArCH_2Ar), 34.32 [s, C(CH$_3$)$_3$], 33.93 [s, C(CH$_3$)$_3$], 33.67 (s × 2, ArCH_2Ar), 31.34 [s × 3, C(CH$_3$)$_3$], 31.01 [s, C(CH$_3$)$_3$]. $^{31}P\{^1H\}$ NMR (121 MHz, $CDCl_3$): δ 82.3 [s, P(OAr)$_3$], 26.5 [s, P(O)Ph$_2$]. Found: C, 68.10; H, 6.86; N, 1.24; calc. for $C_{66}H_{76}ClNO_5P_2Pd$ (M_r = 1167.13): C, 67.92; H, 6.56; N, 1.20%.

Chloro(η^3-2-methylallyl){5,11,17,23-tetra-*tert*-butyl-25-(ethoxycarbonylmethoxy)-26,27,28-(μ$_3$-phosphorustrioxy)-calix[4]arene}palladium(II) (15). L^2 (0.186 g, 0.244 mmol) was added to a solution of [Pd(η^3-C_4H_7)Cl]$_2$ (0.048 g, 0.12 mmol) in CH_2Cl_2 (10 cm^3). After stirring for 15 h, the solution was concentrated to *ca.* 50%. Addition of hexane and cooling to −78 °C gave **15** as a white powder. Yield: 0.160 g, 0.167 mmol, 68%. Mp > 240 °C. IR (nujol) ν_{max}/cm^{-1}: 1734 (C=O). ^1H NMR (400 MHz, $CDCl_3$): δ 7.22–7.19 and 7.11–7.10 (2 overlapping AB q, 4H, *m*-ArH), 7.07 (s, 2H, *m*-ArH), 6.73 and 6.71 (AB q, 2H, *m*-ArH), 5.01 and 3.54 (AB q, ^2J = 14.4, 2H, ArCH_2Ar), 5.00 and 4.72 (AB q, ^2J = 16.4, 2H, OCH_2CO_2), 4.93 and 3.56 (AB q, ^2J = 15.0, 2H, ArCH_2Ar), 4.45 and 3.46 (AB q, ^2J = 13.6, 2H, ArCH_2Ar), 4.43 (br s, 1H, H-allyl), 4.41 and 3.49 (AB q, ^2J = 13.2, 2H, ArCH_2Ar), 4.14 (q, ^3J = 7.2, 2H, OCH_2CH$_3$), 3.47 (br s, 1H, H-allyl), 3.16 (br s, 1H, H-allyl), 2.55 (br s, 1H, H-allyl), 1.85 (s, 3H, CH_3-allyl), 1.37 [s, 9H, C(CH$_3$)$_3$], 1.36 [s, 9H, C(CH$_3$)$_3$], 1.25 (t, ^3J = 7.2 Hz, OCH_2CH_3), 1.18 [s, 9H, C(CH$_3$)$_3$], 0.90 [s, 9H, C(CH$_3$)$_3$]; $^{13}C\{^1H\}$ NMR (50 MHz, $CDCl_3$): δ 170.73 (s, CO_2), 153.77–124.60 (aryl C and C_{quat}-allyl), 78.62 and 77.54 (s × 2, CH_2-allyl), 71.95 (s, OCH_2CO_2), 60.73 (s, OCH_2CH_3), 36.31 and 35.99 (s × 2, ArCH_2Ar), 34.45 [s × 2, C(CH$_3$)$_3$], 34.18 [s × 2, C(CH$_3$)$_3$], 33.98 (s × 2, ArCH_2Ar), 31.49 [s × 3, C(CH$_3$)$_3$], 31.11 [s, C(CH$_3$)$_3$], 23.27 (s, CH_3-allyl), 14.24 (s, OCH_2CH_3); $^{31}P\{^1H\}$ NMR (121 MHz, $CDCl_3$): δ 107.0 [s, P(OAr)$_3$]. Found: C, 67.23; H, 7.10; calc. for $C_{52}H_{66}ClO_6PPd$ (M_r = 959.92): C, 67.06; H, 6.93%.

Acetylacetonatocarbonyl{5,11,17,23-tetra-*tert*-butyl-25-(diphenylphosphinoylmethoxy)-26,27,28-(μ$_3$-phosphorustrioxy)-calix[4]arene}rhodium(I) (16). L^1 (0.134 g, 0.15 mmol) was added‡ to a solution of [Rh(acac)(CO)$_2$] [acac = MeC(O)-CHC(O)Me] (0.040 g, 0.151 mmol) in CH_2Cl_2 (30 cm^3). After stirring for 12 h, the volatiles were evaporated under vacuum to give **16** as a yellow powder. Owing to its high solubility in all common organic solvents, **16** was not purified further. Yield: 0.156 g, 0.139 mmol, 92%. Mp 76–78 °C. IR (CH_2Cl_2) ν_{max}/cm^{-1}: 2004s (CO), 1182 (s, P=O, tentative assignment). ^1H NMR (300 MHz, $CDCl_3$): δ 8.00–7.93 and 7.53–7.44 [10 H, P(O)Ph$_2$], 7.05 (s, 4H, *m*-ArH), 7.02 (s, 2H, *m*-ArH), 6.35 (s, 2H, *m*-ArH), 5.37 (s, 1H, CH-acac), 4.79 [d, ^2J = 4.4, 2H, P(O)CH_2], 4.52 and 3.40 [AB q, ^2J = 14.6, 4H, ArCH_2Ar], 4.52 and 3.29 [AB q, ^2J = 14.9 Hz, 4H, ArCH_2Ar], 1.99 (s, 3H, CH_3-acac), 1.36 (s, 3H, CH_3-acac), 1.33 [s, 18H, C(CH$_3$)$_3$], 1.17 [s, 9H, C(CH$_3$)$_3$], 0.70 [s, 9H, C(CH$_3$)$_3$]. $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 187.23 and 187.00 (s × 2, CO), 146.29–124.13 (aryl C), 101.65 (s, CH-acac), 73.21 [d, J(PC) = 56 Hz, P(O)CH_2], 35.83 and 35.34 (s × 2, ArCH_2Ar), 34.08 [s × 2, C(CH$_3$)$_3$], 33.63 [s × 2, C(CH$_3$)$_3$], 33.11 (s × 2, ArCH_2Ar), 31.42 [s × 3, C(CH$_3$)$_3$], 31.33 [s, C(CH$_3$)$_3$], 26.94 (CH_3-acac), 25.46 (CH_3-acac). $^{31}P\{^1H\}$ NMR (121 MHz, $CDCl_3$): δ 104.0 [d, J(PRh) = 300 Hz, P(OAr)$_3$], 28.0 [s, P(O)Ph$_2$]. Found: C, 67.66; H, 6.53; calc. for $C_{63}H_{71}O_8P_2Rh$ (M_r = 1121.09): C, 67.49; H, 6.38%.

Acetylacetonatocarbonyl{5,11,17,23-tetra-*tert*-butyl-25-(ethoxycarbonylmethoxy)-26,27,28-(μ$_3$-phosphorustrioxy)calix-[4]arene}rhodium(I) (17). L^2 (0.111 g, 0.15 mmol) was added to a solution of [Rh(acac)(CO)$_2$] (0.040 g, 0.15 mmol) in CH_2Cl_2 (30 cm^3). After stirring for 12 h, the volatiles were evaporated under vacuum to give **17** as a yellow powder. Yield: 0.135 g, 0.136 mmol, 90%. Mp 109–111 °C. IR (CH_2Cl_2) ν_{max}/cm^{-1}: 2001s (CO), 1755m (C=O ester). ^1H NMR (200 MHz, $CDCl_3$): δ 7.18 and 7.07 (AB q, ^2J = 2.4, 4H, *m*-ArH), 7.05 (s, 2H, *m*-ArH), 6.59 (s, 2H, *m*-ArH), 5.36 (s, 1H, CH-acac), 4.98 and 3.57 (AB q, ^2J = 14.6, 4H, ArCH_2Ar), 4.64 (s, 2H, OCH_2CO_2), 4.58 and 3.43 (AB q, ^2J = 14.6, 4H, ArCH_2Ar), 4.19 (q, ^3J = 7.1, OCH_2CH$_3$), 2.03 (s, 3H, CH_3-acac), 1.45 (s, 3H,

‡ L^1 needs to be free of NEt_3HCl. The presence of the latter leads to formation of complex **19**.

CH_3-acac), 1.35 [s, 18H, $C(CH_3)_3$], 1.28 (t, ^3J = 7.1 Hz, OCH_2-CH_3), 1.18 [s, 9H, $C(CH_3)_3$], 0.79 [s, 9H, $C(CH_3)_3$]. $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 186.91 and 185.70 (s × 2, CO), 170.00 (s, CO_2), 153.61–124.20 (aryl C), 100.85 (s, CH-acac), 71.52 (s, OCH_2CO_2), 60.80 (s, OCH_2CH_3), 36.31 and 36.00 (s × 2, $ArCH_2Ar$), 34.42 [s × 2, $C(CH_3)_3$], 34.09 [s × 2, $C(CH_3)_3$], 33.77 (s × 2, $ArCH_2Ar$), 31.47 [s × 3, $C(CH_3)_3$], 31.04 [s, $C(CH_3)_3$], 26.94 (CH_3-acac), 25.58 (CH_3-acac), 14.25 (s, OCH_2CH_3). $^{31}P\{^1H\}$ NMR (121 MHz, $CDCl_3$): δ 103.1 [d, J(PRh) = 309 Hz, $P(OAr)_3$]. Found: C, 65.48; H, 6.85; calc. for $C_{54}H_{66}O_9PRh$ (M_r = 992.98): C, 65.32; H, 6.70%.

Acetylacetonatocarbonyl{5,11,17,23-tetra-*tert*-butyl-25-(diethylcarbamoylmethoxy)-26,27,28-(μ$_3$-phosphorustrioxy)calix[4]arene}rhodium(I) (18). L[3] (0.119 g, 0.15 mmol) was added to a solution of [Rh(acac)$(CO)_2$] (0.040 g, 0.15 mmol) in CH_2Cl_2 (30 cm^3). After stirring for 12 h, the volatiles were evaporated under vacuum to afford **18** as a yellow powder. Yield: 0.143 g, 0.14 mmol, 93%. Mp 90–92 °C. IR (CH_2Cl_2) ν_{max}/cm^{-1}: 2000s (CO), 1634 (C=O amide). ^1H NMR (300 MHz, $CDCl_3$): δ 7.17 and 7.07 (AB q, ^2J = 2.5, 4H, *m*-ArH), 7.05 (s, 2H, *m*-ArH), 6.57 (s, 2H, *m*-ArH), 5.36 (s, 1H, CH-acac), 4.83 and 3.43 (AB q, ^2J = 14.3, 4H, $ArCH_2Ar$), 4.60 (s, 2H, OCH_2), 4.58 and 3.55 (AB q, ^2J = 14.6, 4H, $ArCH_2Ar$), 3.77 (q, ^3J = 7.1, 2H, NCH_2CH_3), 3.41 (q, ^3J = 7.3 Hz, 2H, NCH_2-CH_3), 2.02 (s, 3H, CH_3-acac), 1.40 (s, 3H, CH_3-acac), 1.35 [s, 18H, $C(CH_3)_3$], 1.24–1.16 [m, 15H, $C(CH_3)_3$ and NCH_2CH_3], 0.79 [s, 9H, $C(CH_3)_3$]. $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 187.23 and 186.74 (s × 2, CO), 167.69 [s, C(O)N], 153.69–124.12 (aryl C), 101.59 (s, CH-acac), 73.90 (s, OCH_2CONEt_2), 41.92 and 39.90 (s × 2, CH_2CH_3), 35.89 (s × 2, $ArCH_2Ar$), 34.36 [s, $C(CH_3)_3$], 34.04 [s × 2, $C(CH_3)_3$], 33.73 [s, $C(CH_3)_3$], 33.57 (s × 2, $ArCH_2Ar$), 31.40 [s × 3, $C(CH_3)_3$], 30.99 [s, $C(CH_3)_3$], 26.92 and 25.43 (s × 2, CH_3-acac), 14.26 and 12.88 (s × 2, CH_2CH_3). $^{31}P\{^1H\}$ NMR (121 MHz, $CDCl_3$): δ 102.7 [d, J(PRh) = 306 Hz, $P(OAr)_3$]. Found: C, 66.22; H, 7.15; N, 1.21; calc. for $C_{56}H_{71}NO_8PRh$ (M_r = 1020.04): C, 65.94; H, 7.02; N, 1.37%.

Chlorocarbonylbis{5,11,17,23-tetra-*tert*-butyl-25-(diphenylphosphinoylmethoxy)-26,27,28-(μ$_3$-phosphorustrioxy)calix[4]arene}rhodium(I) (19). L[1] (0.200 g, 0.11 mmol) was added to a solution of $[RhCl(CO)_2]_2$ (0.022 g, 0.056 mmol) in CH_2Cl_2 (30 cm^3). After stirring for 1 h, hexane was added to precipitate the product. Yield: 0.189 g, 0.097 mmol, 88%. Mp 235–237 °C. IR (KBr) ν_{max}/cm^{-1}: 1989s (CO). ^1H NMR (300 MHz, $CDCl_3$): δ 7.87–6.93 (m, 32H, PPh_2 and *m*-ArH), 6.58 (s, 4H, *m*-ArH), 5.40 (br s, 4H, PCH_2), 4.70 and 3.26 (AB q, ^2J = 13.9, 8H, $ArCH_2Ar$), 4.45 and 3.23 (AB q, ^2J = 14.1 Hz, 8H, $ArCH_2Ar$), 1.27 [s, 36H, $C(CH_3)_3$], 1.21 [s, 18H, $C(CH_3)_3$], 0.91[s, 18H, $C(CH_3)_3$]. $^{13}C\{^1H\}$ NMR (50 MHz, $CDCl_3$): δ 152.72–124.46 (aryl C), 72.53 [d, J(PC) = 77 Hz, $P(O)CH_2$], 36.12 (s × 2, $ArCH_2Ar$), 34.49 [s, $C(CH_3)_3$], 34.25 (s × 2, $ArCH_2Ar$), 34.00 [s × 2, $C(CH_3)_3$], 33.85 [s, $C(CH_3)_3$], 31.37 [s × 3, $C(CH_3)_3$], 31.14 [s, $C(CH_3)_3$]. $^{31}P\{^1H\}$ NMR (121 MHz, $CDCl_3$): δ 93.4 [d, J(PRh) = 223 Hz, $P(OAr)_3$], 26.9 [s, $P(O)Ph_2$]. FAB mass spectrum: *m*/*z* 1021.3 ([M − L^1 − Cl]$^+$, 73%), 1884.8 ([M − CO − Cl + H]$^+$, 75%), 1919.7 ([M − Cl + H]$^+$, 9%). Found: C, 71.05; H, 6.84; calc. for $C_{115}H_{129}O_{11}P_4Rh$ (M_r = 1948.49): C, 70.89; H, 6.62%.

(8-Methylquinolinylmethyl-*C*,*N*){5,11,17,23-tetra-*tert*-butyl-25-(diphenylphosphinoylmethoxy)-26,27,28-(μ$_3$-phosphorustrioxy)calix[4]arene}palladium(II) tetrafluoroborate (20). A solution of $AgBF_4$ (0.016 g, 0.082 mmol) in THF (1 cm^3) was added to a solution of **11** (0.100 g, 0.085 mmol) in CH_2Cl_2 (20 cm^3). After stirring for 5 min, the solution was filtered through Celite and evaporated to dryness. **20** Was obtained as a pale yellow powder by recrystallisation from an ethyl acetate–hexane mixture at −78 °C. Yield: 0.53 g, 0.043 mmol, 51%. Mp > 163–164 °C (decomp). IR (KBr) ν_{max}/cm^{-1}: 1197.5 (P=O, tentative assignment). ^1H NMR (200 MHz, $CDCl_3$): δ 9.60–9.54 (1H, arom. H of 8-mq), 8.31–8.26 (1H, arom. H of 8-mq), 7.65–7.43 and 7.13–6.99 [20 H, $P(O)Ph_2$, arom. H of 8-mq and *m*-ArH], 6.51 (s, 2H, *m*-ArH), 4.95 [d, ^2J = 1.7 Hz, 2H, $P(O)CH_2$], 4.82 and 3.45 (AB q, ^2J = 14, 2H each, $ArCH_2Ar$), 4.65 and 3.41 (AB q, ^2J = 14.1 Hz, 2H each, $ArCH_2Ar$), 1.36 [s × 2, 18H, $C(CH_3)_3$], 1.18 [s, 9H, $C(CH_3)_3$], 0.82 [s, 9H, $C(CH_3)_3$]. $^{13}C\{^1H\}$ NMR (50 MHz, $CDCl_3$): δ 154.16–121.09 (aryl C), 72.82 [d, J(PC) = 80 Hz, $P(O)CH_2$], 35.99 (s × 2, $ArCH_2Ar$), 34.35 [s, $C(CH_3)_3$], 34.03 [s, $C(CH_3)_3$], 33.70 (s × 2, $ArCH_2Ar$), 31.40 [s, $C(CH_3)_3$], 31.01 [s, $C(CH_3)_3$], 26.39 (s, CH_2-8-mq). $^{31}P\{^1H\}$ NMR (121 MHz, $CDCl_3$): δ 88.5 [s, $P(OAr)_3$], 31.0 [br s, $P(O)Ph_2$]. Found: C, 63.30; H, 5.96; calc. for $C_{67}H_{72}ClNO_5P_2Pd{\cdot}CH_2Cl_2$ (M_r = 1283.09) C, 63.34; H, 5.76%.

(8-Methylquinolinylmethyl-*C*,*N*){5,11,17,23-tetra-*tert*-butyl-25-(ethoxycarbonylmethoxy)-26,27,28-(μ$_3$-phosphorustrioxy)-calix[4]arene}palladium(II) tetrafluoroborate (21). A solution of $AgBF_4$ (0.017 g, 0.09 mmol) in THF (1 cm^3) was added to a solution of **12** (0.093 g, 0.09 mmol) in CH_2Cl_2 (20 cm^3). After stirring for 5 min, the solution was filtered through Celite and concentrated under vacuum. Addition of hexane afforded **21** as a pale yellow powder. Yield: 0.080 g, 0.073 mmol, 81%. Mp > 196–197 °C (decomp.). IR (CH_2Cl_2) ν_{max}/cm^{-1}: 1685 (C=O). ^1H NMR (300 MHz, $CDCl_3$): δ 8.95–8.93, (m, 1H, arom. H of 8-mq), 8.35 (d, ^3J = 8.2 Hz, 1H, arom. H of 8-mq), 7.65 (d, ^3J = 8.0 Hz, 1H, arom. H of 8-mq), 7.45–7.30 (m, 3H, arom. H of 8-mq), 7.21 and 7.19 (AB q, ^4J = 0, 4H, *m*-ArH), 7.13 (s, 2H, *m*-ArH), 6.77 (s, 2H, *m*-ArH), 4.70 (s, 2H, OCH_2CO_2), 4.61 and 3.61 (AB q, ^2J = 14.5, 4H, $ArCH_2Ar$), 4.56 and 3.61 (AB q, ^2J = 14.5, 4H, $ArCH_2Ar$), 4.44 (q, ^3J = 6.8, 2H, CH_2CH_3), 3.51 (s, 2H, CH_2 of 8-mq), 1.35 (t, ^3J = 6.8 Hz, 3H, CH_2CH_3), 1.35 [s, 18H, $C(CH_3)_3$], 1.21 [s, 9H, $C(CH_3)_3$], 0.94 [s, 9H, $C(CH_3)_3$]. $^{13}C\{^1H\}$ NMR (50 MHz, $CDCl_3$): δ 150.36–122.89 (aryl C), 71.95 (s, OCH_2CO_2), 63.53 (s, CH_2CH_3), 36.02 (s × 2, $ArCH_2Ar$), 34.45 [s, $C(CH_3)_3$], 34.16 [s × 2, $C(CH_3)_3$], 33.96 [s, $C(CH_3)_3$], 33.70 (s × 2, $ArCH_2Ar$), 31.27 [s × 3, $C(CH_3)_3$], 30.98 [s, $C(CH_3)_3$], 14.90 (s, CH_2CH_3), the CH_2 signal of 8-mq was not detected. $^{31}P\{^1H\}$ NMR (121 MHz, $CDCl_3$): δ 87.8 [s, $P(OAr)_3$]. FAB mass spectrum: *m*/*z* 1010.4 ([M − BF_4]$^+$, 100%). Found: C, 63.21; H, 6.43; N, 1.32; calc. for $C_{58}H_{67}BF_4NO_6PPd$ (M_r = 1098.354): C, 63.42; H, 6.15; N, 1.28%.

(8-Methylquinolinylmethyl-*C*,*N*){5,11,17,23-tetra-*tert*-butyl-25-(diethylcarbamoylmethoxy)-26,27,28-(μ$_3$-phosphorustrioxy)-calix[4]arene}palladium(II) tetrafluoroborate (22). A solution of $AgBF_4$ (0.017 g, 0.09 mmol) in THF (1 cm^3) was added to a solution of **13** (0.095 g, 0.09 mmol) in CH_2Cl_2 (20 cm^3). After stirring for 5 min, the solution was filtered through Celite and concentrated under vacuum. Addition of hexane afforded **22** as a pale yellow powder. Yield: 0.094 g, 0.08 mmol, 95%. Mp > 229 °C (decomp.). IR (CH_2Cl_2) ν_{max}/cm^{-1}: 1603 (C=O). ^1H NMR (300 MHz, $CDCl_3$): δ 8.68–8.64, 8.34–8.31, 7.90–7.85, 7.65–7.61 and 7.44–7.36 (6H, arom. H of 8-mq), 7.19 and 7.15 (AB q, ^4J = 2.4, 4H, *m*-ArH), 7.17 (s, 2H, *m*-ArH), 6.98 (s, 2H, *m*-ArH), 4.93 [s, 2H, $OCH_2C(O)N$, 4.62 and 3.62 (AB q, ^2J = 13.9, 4H, $ArCH_2Ar$), 4.49 and 3.55 (AB q, ^2J = 13.5, 4H, $ArCH_2Ar$), 3.72 (q, ^3J = 7.2 Hz, 2H, CH_2CH_3), 3.58 (m, 4H, CH_2CH_3 and CH_2 of 8-mq), 1.31 (t, 6H, CH_2CH_3), 1.31 [s, 18H, $C(CH_3)_3$], 1.24 [s, 9H, $C(CH_3)_3$], 1.13 [s, 9H, $C(CH_3)_3$]. $^{13}C\{^1H\}$ NMR (50 MHz, $CDCl_3$): δ 171.04 (s, CO), 151.47–123.36 (aryl C), 71.14 [s, $OCH_2C(O)N$], 42.84 and 42.26 (s × 2, CH_2CH_3), 36.32 (s × 2, $ArCH_2Ar$), 34.60 (s × 2, $ArCH_2Ar$), 34.50 [s, $C(CH_3)_3$], 34.22 [s, $C(CH_3)_3$], 34.15 [s × 2, $C(CH_3)_3$], 31.32 [s, $C(CH_3)_3$], 31.24 [s × 3, $C(CH_3)_3$], 20.02 (s, CH_2-8-mq), 13.87 and 13.14 (s × 2, CH_2CH_3). $^{31}P\{^1H\}$ NMR (121 MHz, $CDCl_3$): δ 87.0 [s, $P(OAr)_3$]. Found: C, 63.82; H, 6.46; N, 2.47; calc. for $C_{60}H_{72}BF_4N_2O_5PPd$ (M_r = 1124.424): C, 64.03; H, 6.45; N, 2.49%.

Hydroformylation experiments

The hydroformylation experiments were carried out in a glass-lined, 100 cm^3 stainless steel autoclave containing a magnetic stirring bar. In a typical run, the autoclave was charged under nitrogen with 0.5 cm^3 of a 4 mM toluene solution of [Rh(acac)$(CO)_2$], 10 equiv. of ligand (0.02 mmol) and 14.5 cm^3 of toluene. Once closed, the autoclave was flushed twice with syngas (CO–H_2 1:1 v/v), then pressurised with 15 bar of the CO–H_2 mixture and heated for 2 h at 80 °C. The autoclave was then allowed to cool to room temperature and depressurised. A mixture of internal standard (decane, 0.5 cm^3, 2.56 mmol) and 1-octene (1.57 cm^3, 10 mmol) was then added to the catalyst mixture. The autoclave was pressurised to 20 bar, then heated to 80 °C (leading to a 22 bar pressure). Progress of the reaction was checked by monitoring the pressure decrease. During the experiments, several samples were taken, which were diluted with toluene and analysed by GC. In view of the relatively low isomerisation observed, the reaction was not quenched with $P(OBu^n)_3$ at the end of the catalytic run.

X-Ray crystallography

Crystal data for 9. Crystals suitable for X-ray diffraction were obtained by slow evaporation of an acetonitrile solution of the complex: $C_{114}H_{128}Cl_2O_{10}P_4Pt\cdot5CH_3CN\cdot H_2O$, M = 2271.46, triclinic, space group $P\bar{1}$, colourless, a = 16.3979(1), b = 17.5637(1), c = 24.1629(1) Å, α = 71.905(6), β = 84.340(6), γ = 65.213(6)°, U = 6001.5(1) $Å^3$, D_c = 1.26, Z = 2, μ = 1.325 mm^{-1}, $F(000)$ = 2368. Data were collected on a Nonius KappaCCD diffractometer (graphite Mo-Kα radiation, λ = 0.71073 Å) at −100 °C. 37 630 Reflections collected with ($2.5 < \theta < 27.53°$), 22 183 data with $I > 3\sigma(I)$. The structure was solved by direct methods and refined anisotropically on F^2 using the Open-MoleN package.[41] Hydrogen atoms were included using a riding model or rigid methyl groups. No hydrogen atoms were located by Fourier difference for either the acetonitrile or the water molecules. Some atoms were refined isotropically [C(108)–C(113), C(117), C(118), N(2), O(11)]. The molecule crystallises with 5 acetonitrile molecules, two of which are located inside the two calixarene cavities, and one water molecule. Final results: $R(F)$ = 0.060, $wR(F)$ = 0.074, goodness of fit = 1.077, 1256 parameters, largest difference peak = 1.3 e $Å^{-3}$.

Crystal data for 22. Crystals suitable for X-ray diffraction were obtained by slow diffusion of hexane into a dichloromethane solution of the complex: $C_{60}H_{72}BF_4N_2O_5PPd\cdot3CH_2Cl_2\cdot0.5C_6H_{14}$, M = 1423.24, triclinic, space group $P\bar{1}$, pale yellow, a = 13.7230(4), b = 14.6378(4), c = 18.4221(6) Å, α = 87.411(2), β = 88.7070(13), γ = 78.6180(13)°, U = 3623.70(19) $Å^3$, D_c = 1.304, Z = 2, μ = 0.555 mm^{-1}, $F(000)$ = 1478. Data were collected on a Nonius KappaCCD diffractometer (graphite Mo-Kα radiation, λ = 0.71073 Å) at −90 °C. 21 214 Reflections collected with ($1.02 < \theta < 27.48°$), 9432 data with $I > 2\sigma(I)$. The structure was solved by direct methods and refined anisotropically on F^2 using the SHELXL-97 procedure.[42] Hydrogen atoms were included using a riding model or rigid methyl groups. The hexane molecule has been idealised. Final results: $R(F^2)$ = 0.063, $wR(F^2)$ = 0.176, goodness of fit = 1.048, 773 parameters, largest difference peak = 1.56 e $Å^{-3}$.

CCDC reference numbers 184801 and 184802.

See http://www.rsc.org/suppdata/dt/b2/b204604k/ for crystallographic data in CIF or other electronic format.

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