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Bis-phosphites and bis-phosphinites based on distally-functionalised calix[4]arenes: coordination chemistry and use in rhodium-catalysed, low-pressure olefin hydroformylation

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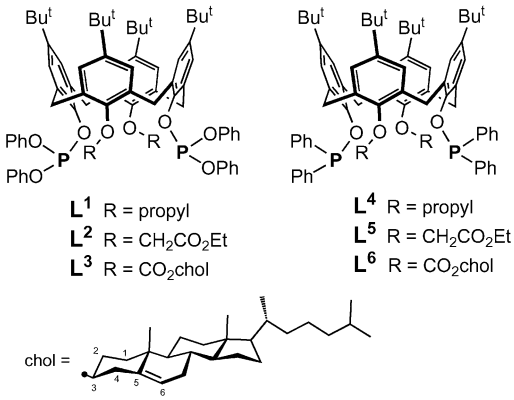
Six calix[4]arenes each bearing two non-cyclic PR_2 units attached at distal phenolic oxygen atoms, *p*-Bu^t-calix[4]arene-25,27-$(OPR_2)_2$-26,28-$(OR')_2$ (R = OPh; R′ = Pr^n, **L**^{1}; R = OPh; R′ = CH_2CO_2Et, **L**^{2}; R = OPh; R′ = CO_2cholesteryl, **L**^{3}; R = Ph; R′ = Pr^n, **L**^{4}; R = Ph; R′ = CH_2CO_2Et, **L**^{5}; R = Ph; R′ = CO_2cholesteryl, **L**^{6}) have been synthesized and their coordinative properties investigated. The diphosphites **L**^{1}–**L**^{3}, where the P centres are separated by 12 bonds, readily form chelate complexes provided the complexation reaction is achieved either by using a starting complex that possesses good leaving groups or by operating under high dilution in order to avoid oligomer formation. Thus, the cationic complexes [Rh(COD)**L**^{1}]BF_4 and [Rh(COD)**L**^{3}]BF_4 were both formed in high yield by reacting the appropriate diphosphite with either [Rh(COD)$(THF)_2$]BF_4 or [Rh$(COD)_2$]BF_4. At high dilution, reaction of **L**^{3} with the neutral complex [$PdCl_2$(COD)] afforded the chelate complex [$PdCl_2$**L**^{3}] in 90% yield. The reaction of one equiv. of **L**^{1} with [Rh(acac)$(CO)_2$] resulted in the formation of [Rh(acac)**L**^{1}] without requiring high dilution conditions. When the latter reaction was carried out with 0.5 equiv. of **L**^{1}, the bimetallic complex [{Rh(acac)(CO)}$_2$(η^1-*P*,η^1-*P*′-**L**^{1})] was formed instead. Reaction at high dilution of **L**^{2} with the cyclometallated complex [Pd(*o*-$C_6H_4CH_2NMe_2$)$(THF)_2$]BF_4 gave the expected chelate complex [Pd(*o*-$C_6H_4CH_2NMe_2$)**L**^{2}]BF_4. The latter slowly converts in solution to an oligomer in which the ligand behaves as a (η^1-*P*,η^1-*P*′) bridging ligand, thus leading to a less strained structure. All six ligands, when mixed with [Rh(acac)$CO)_2$], effectively catalyse the hydroformylation of octene and styrene. In the hydroformylation of octene, the linear aldehyde selectivities observed with **L**^{2} and **L**^{3} are significantly higher (linear : branched = *ca.* 10) than those obtained with the other 4 ligands of this study and also with respect to PPh_3. Molecular modelling shows that the lower rim substituents of **L**^{2} and **L**^{3} form tighter pockets about the metal centre than do the other ligands and so sterically favour the formation of Rh(*n*-alkyl) intermediates over that of Rh(*i*-alkyl) ones. In styrene hydroformylation, all ligands result in the formation of unusually high amounts of the linear aldehyde, the b : l ratios being all close to 65 : 35. The highest activities were found when using an L/Rh ratio of 1/1.

Introduction

The calix[4]arene platform allows several ligating moieties to be assembled in a convergent manner about one metal centre, thereby forming a complex with a well-defined coordination environment.[1–3] Although there are now numerous examples of multiply P(III)-substituted calixarenes,[4–7] catalytic chemistry with such ligands is only at its beginning. Among the most striking contributions in this field are some recent studies dealing with the use of calixarene-phosphites in rhodium-catalysed olefin hydroformylation.[8–12] The importance of phosphites and especially of bulky phosphites in hydroformylation arises from the higher reaction rates they usually produce in comparison to triphenylphosphine.[13] In the present study, we report the synthesis and coordinative properties of calix[4]arenes in which two non-cyclic PR_2 groups have been tethered at distal phenolic oxygen atoms, the other two phenolic functions being substituted either by a non-coordinating group (*e.g.* *n*-Pr as in **L**^{1}) or by a podand arm containing a moderately strong coordinating function (CH_2CO_2Et, **L**^{2}; CO_2cholesteryl, **L**^{3}). The resulting phosphites were assessed in the hydroformylation of octene and styrene and also compared to the related diphosphinites **L**^{4}–**L**^{6}.



The present study complements an interesting catalytic study recently reported by Schmutzler and Börner, based on the use of the related ligands **A**–**C**,[11,12] in which the P centres, as part of a ring, are sterically considerably more demanding that those of the phosphite centers in **L**^{1}–**L**^{3}.[14] The catalysts reported by these authors were shown to be highly active in the hydroformylation of 1-octene and to lead to lower linear aldehyde selectivities than conventional Rh/PPh_3 systems. Paciello and Röper reported on another chelating calixarene-diphosphite, **D**, which displays remarkably high nonanal selectivities (99.5%) in octene hydroformyation.[8] Here again, the P atoms are part of a ring. Finally, we wish to mention that calixarene-monophosphites in which the phosphorus atom acts as a triple μ_3-*O*,*O*,*O* bridge were also used recently in olefin hydroformylation. These phosphites were found to be quite robust and to provide highly active hydroformylation catalysts.[9,10,15] It should be recalled that diphosphites are usually preferred over monophosphites in octene hydroformylation since they lead to higher linear : branched (l : b) ratios.[13]

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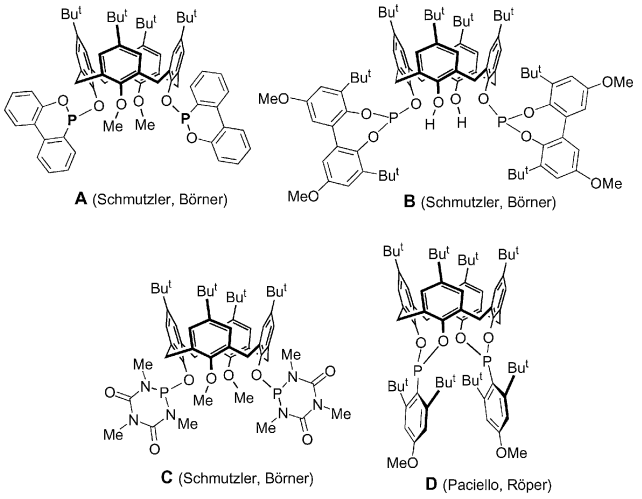


Results and discussion

Ligand syntheses

The present study required the synthesis of the 1,3-difunctionalized calixarenes **1**–**3**. Precursors **1** and **2** were prepared according to reported procedures, while calixarene **3** was obtained in good yield by reacting *p-tert*-butyl-calix[4]arene with cholesteryl chloroformate in the presence of NEt_3. Unlike **1** and **2**, which adopt a stable cone conformation, compound **3** is conformationally mobile, the two unsubstituted phenol rings flipping quickly through the calixarene annulus. This conclusion was inferred from a 2D-NMR study which established a spatial proximity between the *m*-H of the ArOH rings and both methylenic protons of the Ar*CH*$_2$ groups (Fig. 1). Note that **3** contains 16 asymmetric carbon atoms.

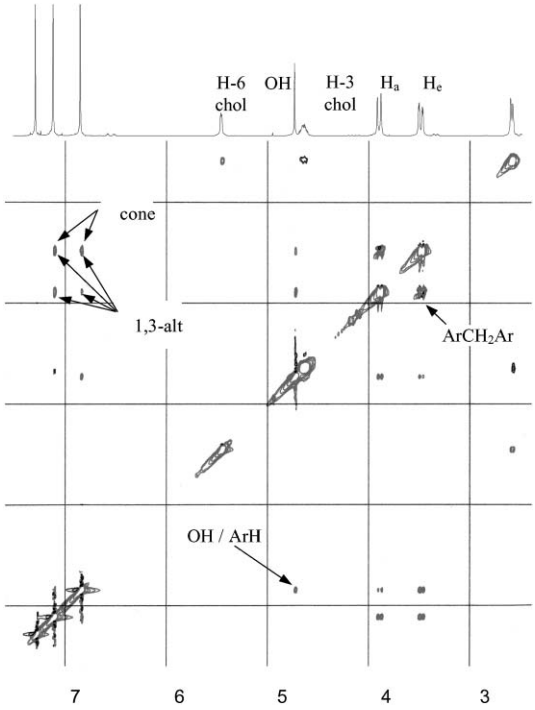
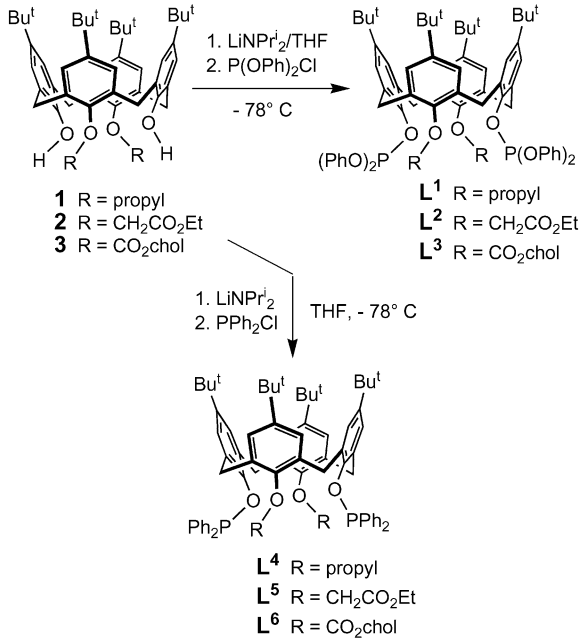
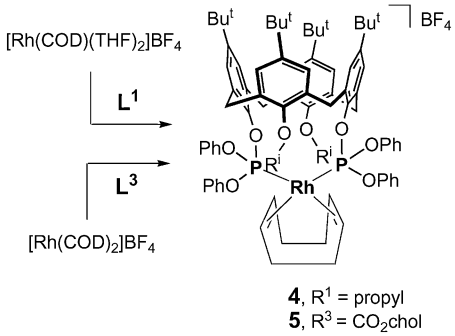


Fig. 1 NOESY spectrum (500 MHz, $CDCl_3$) of **3**.

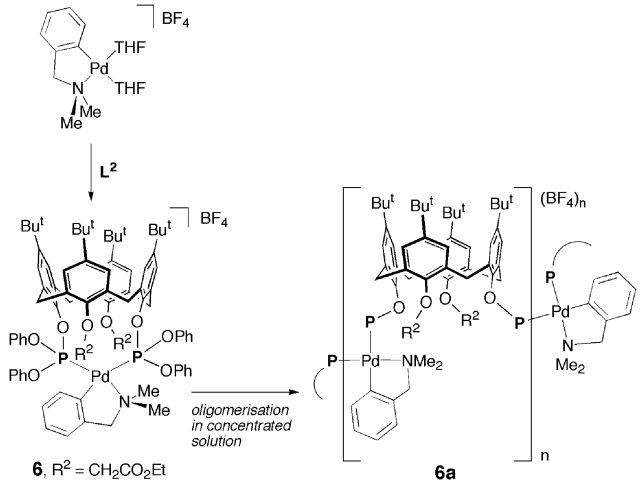
The three diphosphites $\mathbf{L}^1$–$\mathbf{L}^3$ were obtained by reacting the appropriate di-hydroxy precursor with $LiNPr^i_2$ and chlorodiphenylphosphite in THF. All three ligands are highly soluble in alkanes. Typically for triarylphosphites, each ^{31}P NMR spectrum displays a peak near 130 ppm.[16] In the corresponding ^{1}H NMR spectra, the bridging Ar*CH*$_2$Ar groups appear as AB patterns with AB separations larger than 1 ppm (Δ_{AB} = 1.48 ($\mathbf{L}^1$), 1.71 ($\mathbf{L}^2$), 1.34/1.36 ($\mathbf{L}^3$)), hence allowing unambiguous assignment of a cone conformation to all three calixarenes.[17] This geometry was further confirmed by the ^{13}C NMR spectra that display Ar*C*H$_2$Ar signals in the range expected for *syn*-oriented phenolic neighbours (≈ 29–33 ppm).[18] It is interesting to note that despite the dynamic behaviour of **3**, anchoring of two "P(OPh)$_2$" units to this precursor selectively resulted in the formation of a conical species rather than a 1,3-alternate or a partial cone conformer. For the catalytic study (*vide infra*), the related phosphinites $\mathbf{L}^4$–$\mathbf{L}^6$ were also prepared. These were obtained in a similar fashion using the same precursors, but with Ph_2PCl as reagent and like the related phosphites, all three adopt a cone conformation. They are characterised by phosphinite signals near 122 ppm in the corresponding ^{31}P NMR spectra. As already observed for $\mathbf{L}^1$–$\mathbf{L}^3$, the three phosphinites display high solubility in alkanes.



Our earlier studies have shown that certain 1,3-diphosphinito-calix[4]arenes are suitable for chelation, provided that the complexation reaction is carried out with a labile, cationic species that allows fast complexation.[19] In the present study, the chelating ability of the phosphites $\mathbf{L}^1$–$\mathbf{L}^3$ was assessed by their reactions with square planar Rh(I) or Pd(II) precursors. Thus, reaction of $\mathbf{L}^1$ with one equiv. of $[Rh(COD)(THF)_2]BF_4$ (COD = 1,5-cyclooctadiene) afforded complex **4** in high yield, while reaction of $\mathbf{L}^3$ with $[Rh(COD)_2]BF_4$ readily gave the related complex **5**. The ^{31}P NMR spectra of these complexes are characterised by a doublet with a J(PRh) coupling constant of *ca.* 250 Hz (**4**: 101.0 ppm, J(PRh) = 252 Hz; **5**: 99.7 ppm, J(PRh) = 254 Hz). Chelate formation was inferred from the corresponding FAB MS spectra, which both show the expected $(M - BF_4)^+$ peak.

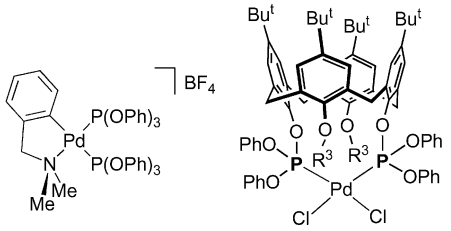


Reaction at high dilution of $\mathbf{L}^2$ with the cyclometallated complex $[Pd(o\text{-}C_6H_4CH_2NMe_2)(THF)_2]BF_4$ afforded in high yield the chelate complex **6**. Its MS spectrum (electrospray) shows an intense peak at m/z 1492 corresponding to the $[M - BF_4]^+$ ion. The ^{31}P NMR spectrum of **6** is characterised by an AB system with $\delta_A = 141.6$ and $\delta_B = 115.2$ ppm. The observed $J(PP')$ coupling constant, 54 Hz, is not unusual for *cis*-disposed phosphites (such coupling constants can reach values as high as 150 Hz)[20,21] and hence, no conclusion about the ligand's bite angle in **6** can be drawn from this value. Upon standing complex **6** slowly converts irreversibly into another species, **6a**, characterised by an AB spectrum as well, with $J(PP') = 86$ Hz, but in this case the AB separation is only 9 ppm. It is likely that **6a**, which was not isolated, has an oligomeric structure in which the diphosphite behaves as a bridging unit. Its formation is probably favoured by the strong *trans* influence of the metallated carbon atom which by labilising the *trans*-positioned P atom results in formation of a less strained structure.



6, $R^2 = CH_2CO_2Et$ **6a**

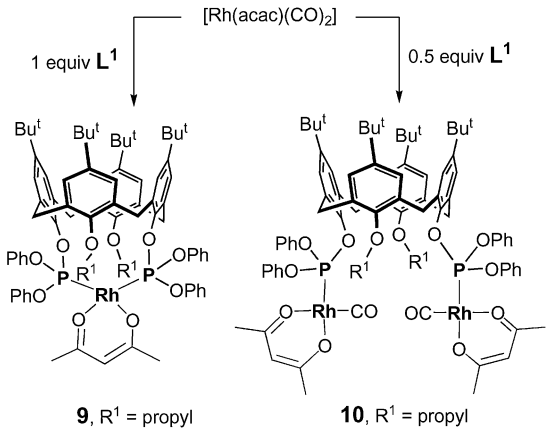
We propose that due to the strain release resulting from chelate opening, the PPdP′ angles of **6a** would come closer to 90°. The ^{31}P NMR spectrum of **6a** was therefore compared to that of the bis-triphenylphosphite complex $[Pd(o\text{-}C_6H_4CH_2NMe_2)\{P(OPh)_3\}_2]BF_4$ **7**, which was prepared *in situ*. The shape and position of the corresponding AB pattern is indeed very close to that of **6a** (AB separation: 11 ppm; $J(PP') = 89$ Hz). Finally, we note that the ^1H NMR spectrum of **6** reveals that the molecule has a C_1-symmetrical structure (reflected, *e.g.* in inequivalence of the Bu^t groups), an observation which suggests that the coordination plane of this chelate complex is inclined with respect to the calixarene axis.



7 **8**, $R^3 = CO_2chol$

Neutral chelate complexes of the phosphites could also be synthesised. Thus for example, reaction of $[PdCl_2(COD)]$ with $\mathbf{L}^3$ afforded complex **8** in high yield, but this reaction needed to be carried out at medium to high dilution conditions in order to avoid oligomer formation. The formation of a chelate was established by an osmometric molecular weight determination (see Experimental section).

The mononuclear complex **9** was formed by reacting one equiv. of diphosphine $\mathbf{L}^1$ with $[Rh(acac)(CO)_2]$. As a result of fast CO displacement, this reaction did not need to be carried out at high dilution. When the reaction was repeated with only 0.5 equiv. of $\mathbf{L}^1$, the binuclear complex **10** was formed quantitatively. As shown by an NMR study, **10** is an intermediate in the synthesis of the chelate **9**.



9, R^1 = propyl **10**, R^1 = propyl

Catalytic studies

The beneficial role of P(III)-ligands in rhodium-catalysed hydroformylation is well established and many sophisticated P-ligands have been designed over the last 40 years which have illustrated how the performance of rhodium-P(III) complexes depends on both the electronic and steric factors of the ligand. In the early 1990s, it became apparent that diphosphines having a natural bite angle larger than 90° may lead to high l : b ratios in the hydroformylation of alkenes.[22] This behaviour was attributed to the greater stabilisation of reaction intermediates when the diphosphine can chelate in a diequatorial rather than equatorial–axial mode, the former favouring the formation of the linear aldehyde. However, recently several authors[23,24] convincingly demonstrated that bis-equatorial coordination is not a prerequisite for high linearity. In view of these recent results, it appears that predicting the outcome of catalytic hydroformylation reactions still remains a difficult task, many parameters contributing to the formation of a major compound. One aspect of ligand design that certainly deserves more attention concerns the use of ligand systems that locate the metal in a "pocket", the walls of which may sterically interact with the coordinated olefin or the corresponding metal alkyl.

The bulky phosphite and phosphinite ligands described above were tested in the rhodium-catalysed hydroformylation of 1-octene and styrene. All runs were carried out at 80 °C under a CO/H_2 pressure of 20 bar. Unless otherwise specified, the catalyst precursors were prepared *in situ*, in toluene at 80 °C, from $[Rh(acac)(CO)_2]$ and the appropriate ligand under CO/H_2. The metal : olefin ratio applied during catalysis was 1 : 2500 in all cases. The ligand : metal ratio was between 1 : 1 and 4 : 1.

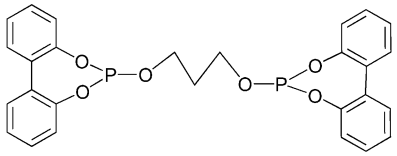
Hydroformylation of octene. The phosphites $\mathbf{L}^1$–$\mathbf{L}^3$ were investigated first. All three ligands, when mixed with $[Rh(acac)CO)_2]$, effectively catalyse the hydroformylation of octene. It turned out that long activation periods (15 h) resulted in activities significantly better than those observed when the activation was stopped after 2 h (Table 1). Similar long activation periods have been used by other authors.[9] However, we found that the 2 h activations could be made more efficient by adding NEt_3 to the $[Rh(acac)(CO)_2]$ solution. The highest TOF, 1204 mol (mol Rh)$^{-1}$ h^{-1}, was observed with the dipropyl derivative $\mathbf{L}^1$ and by using a L : Rh ratio of 1 : 1 (Table 1). For all three diphosphites, the activity dropped, as expected, on increasing the L : Rh ratio, while the selectivity for nonanal increased (*vide infra*). The observed activities are not unusual and fall in the range reported for other diphosphites.[13] As found with other diphosphites, olefin isomerisation occured during catalysis, but in the present runs the amounts of internal olefins did not exceed 12%. The l : b ratios (Table 1) observed with $\mathbf{L}^1$–$\mathbf{L}^3$, when present in excess, were higher than those obtained

Table 1 1-Octene hydroformylation with phosphites $\mathbf{L^1}$–$\mathbf{L^3}$

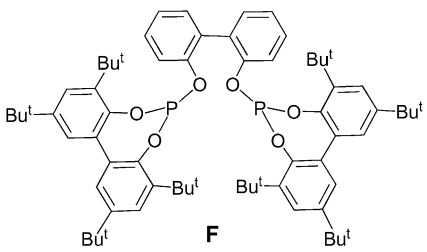
Ligand	L/Rh	Activation period	TOF[b]	l : b[c]	Isomerisation[d] (%)
$P(OPh)_3$	20		—	2.8	—
$\mathbf{L^1}$	1	2 h	632	2.59	6.97
$\mathbf{L^1}$	1	15 h	1204	2.35	9.15
$\mathbf{L^1}$	1	2 h (+ 30 NEt_3)	816	2.61	8.41
$\mathbf{L^1}$	2	2 h	120	5.02	5.15
$\mathbf{L^1}$	2	15 h	156	4.99	4.29
$\mathbf{L^1}$	2	2 h (+ 30 NEt_3)	129	5.33	5.50
$\mathbf{L^1}$	4	2 h	124	5.33	1.85
$\mathbf{L^2}$	1	2 h	416	2.82	4.34
$\mathbf{L^2}$	1	15 h	629	3.17	8.03
$\mathbf{L^2}$	1	2 h (+ 30 NEt_3)	707	2.85	12.00
$\mathbf{L^2}$	2	2 h	60	9.57	6.98
$\mathbf{L^2}$	2	15 h	247	9.56	3.09
$\mathbf{L^2}$	2	2 h (+ 30 NEt_3)	211	8.99	6.66
$\mathbf{L^2}$	4	2 h	62	9.66	6.78
$\mathbf{L^3}$	1	2 h	328	2.86	5.50
$\mathbf{L^3}$	1	15 h	1045	2.70	11.64
$\mathbf{L^3}$	1	2 h (+ 30 NEt_3)	580	2.71	12.28
$\mathbf{L^3}$	2	2 h	39	10.61	8.57
$\mathbf{L^3}$	2	15 h	65	10.65	4.86
$\mathbf{L^3}$	2	2 h (+ 30 NEt_3)	55	10.70	8.00
$\mathbf{L^3}$	4	2 h	38	9.23	6.32

[a] 1-Octene/Rh = 2500. Initial pressure (at 80 °C) $P = 20$ bar CO/H_2 (1/1), $T = 80$ °C, toluene/*n*-decane (20 cm^3/0.5 cm^3). [b] Determined at *ca.* 30% conversion. [c] The l : b ratio takes into account branched aldehydes when observed. [d] Isomerised 1-octene/all octenes.

with the moderately bulky diphosphites **E** and **F**, although the activities of the latter were higher. The most striking results are the rather high l : b ratios, *ca.* 10, observed with ligands $\mathbf{L^2}$ and $\mathbf{L^3}$, both bearing side groups that incorporate a carbonyl function (*cf.* l : b = 5 for the dipropylated calixarene $\mathbf{L^1}$, l : b = 2.2 for **E**, l : b = 1.2 for **F**, and l : b = 2.8 for $P(OPh)_3$).



E



F

The origin of the higher aldehyde selectivity of $\mathbf{L^1}$–$\mathbf{L^3}$, when compared to that of **E**, could of course arise from a bite angle significantly larger than 90°, hence favouring equatorial–equatorial binding of the diphosphite and accordingly driving the catalysis preferentially towards the linear aldehyde. Molecular mechanics calculations carried out with SPARTAN[25] indicate that this angle is close to 113° in the square planar complex **8**. Note that in a silver complex obtained from a related diphosphite, a bite angle as high as 134° was found in the solid state, thus illustrating the high flexibility of such diphosphites.[19] A possible explanation for the significantly higher l : b ratios obtained with $\mathbf{L^2}$ and $\mathbf{L^3}$ compared to $\mathbf{L^1}$ is the marked confinement of the metal inside the pocket constituted by the four OPh groups and the two auxiliary substituents of these calixarenes, a confinement which for steric reasons would favour the formation of a "Rh(*n*-alkyl)" intermediate over that of an "Rh(*iso*-alkyl)" one, whenever the reaction is under thermodynamic control. Note that hydroformylation studies have shown that olefin insertion into the Rh–H bond occurs reversibly with rhodium *phosphite* complexes.[13] The presence of C=O functions in $\mathbf{L^2}$ and $\mathbf{L^3}$ that may coordinate in a hemilabile fashion is another factor that may regulate the form of the pocket. Thus, the outcome of the reaction is possibly controlled by the shape of the pocket. Molecular mechanics calculations show that in the corresponding phosphinites $\mathbf{L^4}$–$\mathbf{L^6}$, like in the Börner/Schmutzler systems **A** and **B**, the pocket about the metal is considerably more open, the auxiliary OR^i substituents here being pushed outwards by the PPh_2 groups (this is mainly due to the larger cone angles of the individual phosphinite units) (Fig. 2). In keeping with these geometrical features, $\mathbf{L^4}$–$\mathbf{L^6}$ lead to lower selectivities for linear aldehyde (Table 2). It is worth mentioning that these latter selectivities compare with those reported for the 1,3-diphosphonito-2,4-dimethoxy-calixarene **A**. Finally, we found that using complex **4** as catalyst precursor instead of a $[Rh(acac)(CO)_2]$–$\mathbf{L^1}$ mixture did not change the outcome of the catalytic runs (same activity and same aldehyde selectivity).

Hydroformylation of styrene. Hydroformylation of styrene with P-ligands, phosphites and phosphines as well, usually gives high amounts of branched aldehyde. Typically, diphosphite **G** results in a 2-phenylpropanal : 3-phenylpropanal ratio of 96 : 4. For all ligands $\mathbf{L^1}$–$\mathbf{L^6}$, the proportion of the linear aldehyde considerably increases (Table 3) in comparison with **G**, be the ligand a phosphite or a phosphinite. For example, with the diester-diphosphite $\mathbf{L^2}$, b : l = 66/34 while for the

Table 2 1-Octene hydroformylation with phosphinites $\mathbf{L^4}$–$\mathbf{L^6}$

Ligand	L/Rh	TOF[b]	l : b[c]	Isomerisation[d] (%)
$\mathbf{L^4}$	1	2625	1.59	5.84
$\mathbf{L^4}$	2	1660	1.61	2.90
$\mathbf{L^5}$	1	1032	2.49	10.18
$\mathbf{L^5}$	2	110	3.08	5.74
$\mathbf{L^6}$	1	1219	2.19	1.22
$\mathbf{L^6}$	2	1087	2.00	1.60

[a] 1-Octene/Rh = 2500, initial pressure (at 80 °C) $P = 20$ bar CO/H_2 (1/1), $T = 80$ °C, toluene/*n*-decane (20 cm^3/0.5 cm^3), incubation overnight. [b] Determined at *ca.* 30% conversion. [c] The l : b ratio takes into account branched aldehydes when observed. [d] Isomerized 1-octene/all octenes.

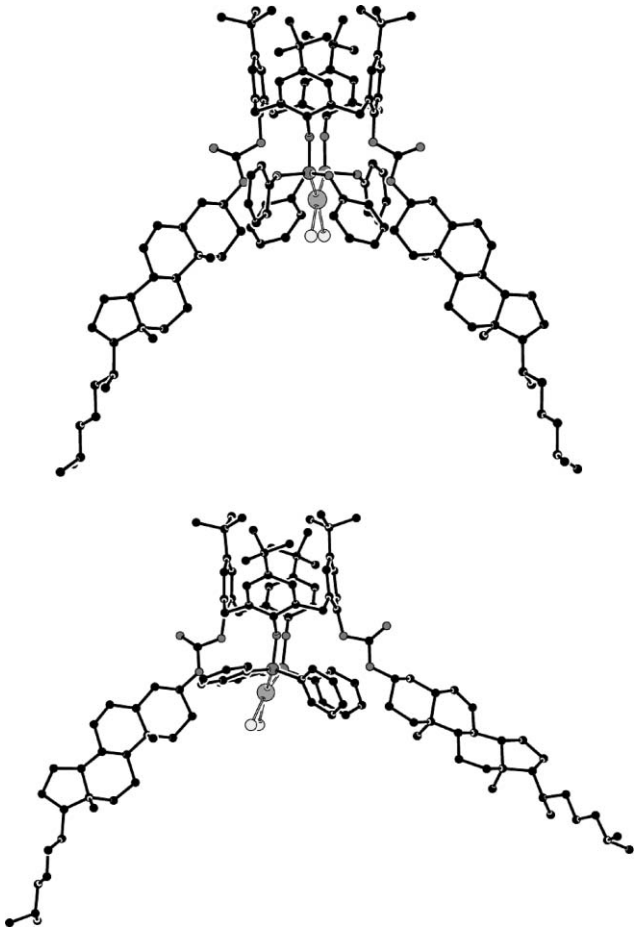


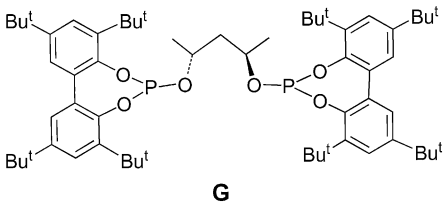
Fig. 2 Molecular modelling structures of $[PdCl_2{\cdot}\mathbf{L}^3]$ (**8**) (top) and $[PdCl_2{\cdot}\mathbf{L}^6]$ (bottom) showing the pockets about the metal centre.

Table 3 Styrene hydroformylation with $\mathbf{L}^1$–$\mathbf{L}^6$

Ligand	L/Rh	TOF[b]	b : l	Ligand	L/Rh	TOF[b]	b : l
$\mathbf{L}^1$	1	2033	67/33	$\mathbf{L}^4$	1	854	66/34
$\mathbf{L}^1$	2	1975	63/37	$\mathbf{L}^4$	2	240	74/26
$\mathbf{L}^2$	1	140	66/34	$\mathbf{L}^5$	1	891	64/36
$\mathbf{L}^2$	2	28	88/12	$\mathbf{L}^5$	2	86	64/36
$\mathbf{L}^3$	1	789	73/27	$\mathbf{L}^6$	1	210	59/41
$\mathbf{L}^3$	2	587	75/25	$\mathbf{L}^6$	2	22	67/33

[a] Styrene/Rh = 2500, initial pressure (at 80 °C) $P = 20$ bar CO/H_2 (1/1), $T = 80$ °C, toluene/*n*-decane (20 cm^3/0.5 cm^3), incubation overnight. [b] Determined at *ca.* 30% conversion.

diester-diphosphinite $\mathbf{L}^5$, b : l = 64/36. The increased linear aldehyde selectivity corroborates the trend that was found in the hydroformylation of octene. Styrene being sterically more demanding than octene, the substrate sensitivity to the presence of a pocket is possibly enhanced in this case. Finally, we wish to mention that styrene hydroformylation using the preformed cationic complex [Rh(norbornadiene)$\mathbf{L}^4$]SbF_6[26] resulted in b : l ratios similar to those obtained with a $[Rh(acac)(CO)_2]/\mathbf{L}^4$ 1 : 1 mixture, hence showing that it is not mandatory to use a pre-formed complex.



G

Conclusion

In conclusion, we have shown that the calix[4]arene-derived phosphites and phosphinites used in the present study are suitable for the formation of 14-membered chelate rings and effectively catalyse the hydroformylation of olefins. The unexpected linear selectivities observed in the hydroformylation of octene and styrene are likely to arise from a combination of a bite angle larger than 90° and the existence of a pocket at the metal centre which favours the formation of "Rh-*n*-alkyl" intermediates, although we have not proved that the reaction is under thermodynamic control (however, this is usually the case with phosphites[13]). The relevance of pocket formation about the metal centre in the outcome of hydroformylation reactions has emerged recently and was formulated on the basis of studies exploiting the particular properties of other diphosphites.[27] In these systems, the pockets are generated by large P-substituents, contrasting with the present where the pockets arise mainly from the presence of appropriate side groups supported by the macrocyclic platform. Variation of these auxiliary groups should result in the formation of optimised pockets.

Experimental

All manipulations involving phosphites and phosphinites were performed in Schlenk-type flasks under dry nitrogen. Solvents were dried by conventional methods and distilled immediately prior to use. $CDCl_3$ was passed down a 5 cm-thick alumina column and stored under nitrogen over molecular sieves (4 Å). Routine ^1H, $^{13}C\{^1H\}$ and $^{31}P\{^1H\}$ spectra were recorded with Bruker FT instruments (AC-200, AC-300, ARX-500). ^1H NMR spectra were referenced to residual protonated solvents (7.26 ppm for $CDCl_3$ and 5.32 for CD_2Cl_2), ^{13}C chemical shifts are reported relative to deuterated solvents (77.0 ppm for $CDCl_3$ and 53.8 ppm for CD_2Cl_2), and the ^{31}P NMR data are given relative to external H_3PO_4. Mass spectra were recorded either on a ZAB HF VG analytical spectrometer using *m*-nitrobenzyl alcohol as matrix or on a MicroTOF Bruker Daltonic spectrometer (MALDI) using CH_2Cl_2 or CH_3CN as solvant. *n*-BuLi/hexane solutions were titrated according to a conventional method.[28] 5,11,17,23-Tetra-*tert*-butyl-25,26,27,28-tetrahydroxycalix[4]arene (abbreviated *p*-Bu^t-calix[4]-$(OH)_4$),[29] 5,11,17,23-tetra-*tert*-butyl-25,27-dihydroxy-26,28-dipropoxy-calix[4]arene (**1**),[30] 5,11,17,23-tetra-*tert*-butyl-25,27-di(ethoxy-carbonylmethoxy)-26,28-dihydroxycalix[4]arene (**2**),[31] 5,11,17,23-tetra-*tert*-butyl-25,27-dipropoxy-26,28-bis(diphenylphosphanyloxy)calix[4] arene ($\mathbf{L}^4$),[32] 5,11,17,23-tetra-*tert*-butyl-25,27-bis-(ethoxycarbonylmethoxy)-26,28-bis(diphenylphosphanyloxy)-calix[4]arene ($\mathbf{L}^5$),[32] $(PhO)_2PCl$,[33,34] $[PdCl_2(COD)]$,[35] $[Pd(o\text{-}C_6H_4NMe_2)Cl]_2$,[36] were prepared using literature procedures. The abbreviation dmba stands for *N*,*N*-dimethylbenzylamine.

5,11,17,23-Tetra-*tert*-butyl-25,27-bis(cholesteryloxycarbonyloxy)-26,28-dihydroxycalix[4]arene (3)

A mixture of *p*-Bu^t-calix[4]-$(OH)_4$ (3.245 g, 5.00 mmol), cholesteryl chloroformate (5.614 g, 12.50 mmol) and NEt_3 (5 cm^3) in CH_2Cl_2 (100 cm^3) was stirred for 12 h at room temperature. The solution was then treated with 50 cm^3 HCl (1 M) and water (2 × 50 cm^3). The organic layer was dried over $MgSO_4$ then filtered and evaporated to dryness. The residue was purified by flash chromatography using AcOEt–hexane (25 : 75, v/v) as eluent. Some unidentified cholesteryl derivatives eluted first followed by **3** (SiO_2, $R_f = 0.25$, AcOEt–hexane, 25 : 75, v/v). After evaporation, the residue was taken up in CH_2Cl_2. Addition of methanol afforded the product as a white microcrystalline powder. Yield: 6.047 g, 4.102 mmol, 82%; mp: 170–177 °C. IR (KBr, cm^{-1}): ν(C=O) = 1763. ^1H NMR (300 MHz, $CDCl_3$): δ 7.08 (s, 4H, *m*-ArH), 6.82 (s, 4H, *m*-ArH), 5.42 (d, 2H, H-6, $^3J = 4$ Hz), 4.70 (s, 2H, OH, exchange with D_2O), 4.60 (m, 2H,

H-3), 3.87 and 3.45 (AB spin system, 8H, ArCH_2Ar, ^2J = 14 H z), 2.58–0.69 (86H, 2 × cholesteryl), 1.35 (s, 18H, C(CH_3)$_3$), 0.97 (s, 18H, C(CH_3)$_3$). ^{13}C{^{1}H} NMR (50 MHz, $CDCl_3$): δ 153.31–142.28 (aryl C), 139.38 (C-5 tentative assignment), 131.87–125.90 (aryl C), 123.16 (s, C-6), 79.22 (s, C-3), 56.79 (s, C-14), 56.25 (s, C-17), 50.09 (s, C-9), 42.41 (s, C-13), 39.83 (s, C-12), 39.61 (s, C-1 tentative assignment), 38.03 (s, CH_2), 36.99 (s, CH_2), 36.68 (s, C-10), 36.29 (s, CH_2), 35.88 (s, CH), 34.01 (s, C(CH_3)$_3$), 33.2 (s, ArCH_2Ar), 31.98 (s, C-7), 31.78 and 31.12 (2s, C(CH_3)$_3$), 28.32 (s, C-16), 28.09 (s, CH), 27.71 (s, CH_2), 24.38 (s, CH_2), 23.93 (s, CH_2), 22.91 (s, CH_3), 22.66 (s, CH_3), 21.16 (s, C-11), 19.36 (s, CH_3), 18.82 (s, CH_3), 11.96 (s, CH_3). Found: 81.52, H 9.80%. Calc. for $C_{100}H_{144}O_8$ (M_r = 1474.21): C 81.47, H 9.84%.

5,11,17,23-Tetra-*tert*-butyl-25,27-dipropoxy-26,28-bis(diphenoxyphosphanyloxy)calix[4]arene (L^1)

The reaction was carried out at −78 °C. To a solution of **1** (1.990 g, 2.70 mmol) in THF (150 cm^3) was added a 1.3 M solution of *n*-BuLi/hexane (4.2 cm^3, 5.40 mmol). After 0.5 h, $(PhO)_2PCl$ (1.364 g, 5.40 mmol, *ca.* 1.1 cm^3) was added. The resulting mixture was stirred for 2 h and then warmed to room temperature (30 min). After evaporation to dryness the residue was taken up with toluene (50 cm^3). The lithium salt was removed by filtration through a bed of Celite and washed with toluene (2 × 10 cm^3). The filtered solution was evaporated to dryness upon which the residue was then redissolved in CH_2Cl_2. Addition of pentane and cooling at −78 °C afforded L^1 as a white powder. Yield: 1.521 g, 1.305 mmol, 48%; mp 210–211 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.27–7.22 and 7.08–6.97 (m, 24H, *m*-ArH and P(OPh)$_2$), 6.66 (s, 4H, *m*-ArH), 4.64 and 3.16 (AB spin system, 8H, ArCH_2Ar, ^2J = 12.9 Hz), 3.92 (t, 4H, OCH_2, J = 8.2 Hz), 2.08 (m, 4H, CH_2CH$_3$), 1.25 (s, 18H, C(CH_3)$_3$), 0.96 (s, 18H, C(CH_3)$_3$), 0.78 (t, 6H, CH$_2$CH_3, ^3J = 7.4 Hz). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ 154.34–133.97 (C_{quat}), 129.52–120.10 (aryl C), 76.86 (s, OCH_2), 33.98 (s, C(CH$_3$)$_3$), 33.77 (s, C(CH$_3$)$_3$), 32.31 (s, ArCH_2Ar), 31.62 (s, C(CH$_3$)$_3$), 31.43 (s, C(CH$_3$)$_3$), 22.96 (s, CH_2CH$_3$), 9.94 (s, CH_2CH$_3$). ^{31}P{^{1}H} NMR (121 MHz, $CDCl_3$): δ 135.26 (s, P(OPh)$_2$). Found: C 73.79, H 7.58%. Calc. for $C_{74}H_{86}O_8P_2$·0.5 CH_2Cl_2 (M_r = 1165.45 + 42.47): C, 74.08; H, 7.26%.

5,11,17,23-Tetra-*tert*-butyl-25,27-bis(ethoxycarbonylmethoxy)-26,28-bis(diphenoxy phosphanyloxy)calix[4]arene (L^2)

To a solution of diisopropylamine (0.63 cm^3, 4.80 mmol) in THF (20 cm^3) was added, at −78 °C, a 1.6 M solution of *n*-BuLi/hexane (3.0 cm^3, 4.80 mmol). After stirring for 0.5 h, the solution was transferred *via* canula to a solution of **2** (1.935 g, 2.36 mmol) in THF (100 cm^3). After stirring for 1 h, $(PhO)_2PCl$ (1.192 g, 4.72 mmol, *ca.* 1.0 cm^3) was added and the resulting mixture stirred for a further hour at −78 °C. The mixture was then allowed to reach room temperature. The solvent was evaporated and the residue taken up with toluene (50 cm^3). The insoluble lithium salt was filtered off using Celite and washed with toluene (2 × 10 cm^3). The filtrate and washing solutions were evaporated under vacuum to afford L^2 as a white powder. Yield: 2.325 g, 1.85 mmol, 78%; mp 39–40 °C, IR (KBr, cm^{-1}): ν(C=O) = 1761. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.26–7.21 and 7.07–6.99 (m, 24H, *m*-ArH and P(OPh)$_2$), 6.63 (s, 4H, *m*-ArH), 4.95 and 3.24 (AB spin system, 8H, ArCH_2Ar, ^2J = 13.4 Hz), 4.95 (s, 4H, OCH_2CO$_2$), 3.99 (q, 4H, CH_2CH$_3$, ^3J = 7.1 Hz), 1.26 (s, 18H, C(CH_3)$_3$), 1.12 (t, 6H, CH$_2$CH_3, ^3J = 7.1 Hz), 0.95 (s, 18H, C(CH_3)$_3$). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ 170.51 (s, CO_2), 153.40–129.70 (C_{quat}), 129.52–120.43 (aryl C), 70.52 (s, OCH_2CO_2), 60.27 (s, CH_2CH_3), 34.03 (s, C(CH$_3$)$_3$), 33.79 (s, C(CH$_3$)$_3$), 33.02 (s, ArCH_2Ar), 31.61 (s, C(CH$_3$)$_3$), 31.18 (s, C(CH$_3$)$_3$), 14.05 (s, CH_2CH_3). ^{31}P{^{1}H} NMR (121 MHz, $CDCl_3$): δ 130.54 (s, P(OPh)$_2$). Found: C 72.18, H 6.96%. Calc. for $C_{76}H_{86}O_{12}P_2$ (M_r = 1253.44): C 72.82, H 6.92%.

5,11,17,23-Tetra-*tert*-butyl-25,27-bis(cholesteryloxycarbonyloxy)-26,28-bis(dipheno xyphosphanyloxy)calix[4]arene (L^3)

To a solution of diisopropylamine (0.63 cm^3, 4.80 mmol) in THF (20 cm^3) was added, at −78 °C, a 1.6 M solution of *n*-BuLi/hexane (3.0 cm^3, 4.80 mmol). After stirring for 0.5 h, the solution was transferred *via* canula to a solution of **3** (3.538 g, 2.40 mmol) in THF (100 cm^3). After stirring for 1 h, $(PhO)_2PCl$ (1.213 g, 4.80 mmol, *ca.* 1.0 cm^3) was added and the resulting mixture stirred for an additional hour. The mixture was allowed to reach room temperature (2 h). The solvent was removed *in vacuo* and the residue was taken up with toluene (50 cm^3). The insoluble lithium salt was filtered off using Celite and washed with toluene (2 × 10 cm^3). The filtrate and washing solutions were evaporated to dryness to afford L^3 as a white powder. Yield: 3.853 g, 2.02 mmol, 84%; mp 93–95 °C, IR (KBr, cm^{-1}): ν(C=O) = 1756 s, 1727 sh. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.24–7.11 and 7.01–6.89 (m, 24H, *m*-ArH and P(OPh)$_2$), 6.60 (s, 4H, *m*-ArH), 5.20 (d, 2H, H-6 of cholesteryl, ^3J = 4.9 Hz), 4.58 and 3.24 (AB spin system, 4H, ArCH_2Ar, ^2J = 13.1 Hz), 4.60 and 3.24 (AB quartet, ^2J = 13.2 Hz, 4H, ArCH_2Ar), 4.23 (m, 2H, H-3 of cholesteryl), 2.36–0.67 (86H, cholesteryl), 1.36 (s, 18H, C(CH_3)$_3$), 0.90 (s, 18H, C(CH_3)$_3$). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ 154.69–143.77 (aryl C_{quat}), 139.88 (s, C-5 or aryl C), 135.25–125.05 (aryl C_{quat}), 123.04 (C-6 tentative assignment), 122.36–120.83 (aryl C), 78.59 (s, C-3), 56.69 (s, C-14), 56.15 (s, C-17), 49.92 (s, C-9), 42.33 (s, C-13), 39.75 (s, C_{quat}-12), 39.54 (s, C-1, tentative assignment), 37.43 (s, CH_2), 37.00 (s, CH_2), 36.53 (s, C-10), 36.20 (s, CH_2), 35.82 (s, CH), 34.21 (s, C(CH$_3$)$_3$), 33.84 (s, C(CH$_3$)$_3$), 32.30 (s, ArCH$_2$Ar), 31.85 (s, ArCH$_2$Ar), 31.69 (s, C(CH$_3$)$_3$), 31.11 (s, C(CH$_3$)$_3$), 28.25 (s, C-16), 28.04 (s, CH), 27.08 (s, CH_2), 24.31 (s, CH_2), 23.86 (s, CH_2), 22.85 (s, CH_3), 22.58 (s, CH_3), 21.04 (s, C-11), 19.53 (s, CH_3), 18.74 (s, CH_3), 11.87 (s, CH_3); ^{31}P{^{1}H} NMR (121 MHz, $CDCl_3$): δ 127.62 (s, P(OPh)$_2$). Found: C 78.47 H 8.31%. Calc. for $C_{124}H_{162}O_{12}P_2$ (M_r = 1906.55): C 78.12, H 8.56%.

5,11,17,23-Tetra-*tert*-butyl-25,27-bis(cholesteryloxycarbonyloxy)-26,28-bis(diphenylphosphanyloxy)calix[4]arene (L^6)

To a solution of diisopropylamine (0.73 cm^3, 5.60 mmol) in THF (20 cm^3) was added, at −78 °C, a 1.6 M solution of *n*-BuLi/hexane (3.5 cm^3, 5.60 mmol). After stirring for 30 minutes, the solution was transferred *via* a canula to a solution of **3** (4.080 g, 2.77 mmol) in THF (100 cm^3). After stirring for 1 h, Ph_2PCl (1.222 g, 5.54 mmol, *ca.* 1.0 cm^3) was added and the resulting mixture stirred for an additional hour. The mixture was warmed to room temperature (2 h). The solvent was evaporated and the residue was redissolved in toluene (50 cm^3). The lithium salt 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 to afford L^6 as a white powder. Yield: 4.08 g, 2.22 mmol, 80%; mp 138–140 °C, IR (KBr, cm^{-1}): ν(C=O) = 1771 and 1742. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.79–7.74 and 7.41–7.17 (m, 20H, PPh_2), 7.01 (s, 4H, *m*-ArH), 6.44 (s, 4H, *m*-ArH), 5.26 (d, 2H, H-6, ^3J = 4.5 Hz), 4.55 (m, 2H, H-3), 3.95 and 2.81 (AB spin system, 4H, ArCH_2Ar, ^2J = 13.3 Hz), 3.92 and 2.81 (AB spin system, 4H, ArCH_2Ar, ^2J = 13.3 Hz), 2.37–0.70 (86H, 2 × cholesteryl), 1.29 (s, 18H, C(CH_3)$_3$, 0.84 (s, 18H, C(CH_3)$_3$. ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ 152.24–140.63 (quaternary aryl C), 140.25 (s, C-5 or aryl C), 134.90–125.05 (aryl C), 122.28 (s, C-6 tentative assignment), 78.07 (s, C-3), 56.83 (s, C-14), 56.23 (s, C-17), 50.07 (s, C-9), 42.39 (s, C-13), 39.85 (s, C-12), 39.56 (s, C-1 tentative assignment), 37.88 (s, CH_2), 37.18 (s, CH_2), 36.61 (s, C-10), 36.24 (s, CH_2), 35.85 (s, CH), 34.17 (s, C(CH$_3$)$_3$), 33.68 (s, C(CH$_3$)$_3$), 32.04 (s, ArCH$_2$Ar), 31.94 (s, ArCH$_2$Ar), 31.62 (s, C(CH$_3$)$_3$), 31.17 (s, C(CH$_3$)$_3$), 30.98 (s, C_{quat}), 30.77 (s, C_{quat}), 28.30 (s, C-16), 28.06 (s, CH), 27.55 (s, CH_2), 24.37 (s, CH_2), 23.89 (s, CH_2), 22.87 (s, CH_3), 22.61

(s, CH_3), 21.50 (s, C-11), 19.54 (s, CH_3), 18.78 (s, CH_3), 11.92 (s, CH_3). $^{31}P\{^1H\}$ NMR (121 MHz, $CDCl_3$): δ 122.47 (s, PPh_2). Found: C 80.09, H 8.86%. Calc. for $C_{124}H_{162}O_8P_2$ (M_r = 1842.56): C 80.83, H 8.86%.

cis-*P*,*P*′-{[5,11,17,23-Tetra-*tert*-butyl-25,27-dipropoxy-26,28-bis(diphenoxyphosphanyloxy)calix[4]arene]-1,5-cyclooctadiene}rhodium(I) tetrafluoroborate (4)

A solution of $AgBF_4$ (0.052 g, 0.266 mmol) in THF (1 cm^3) was added to a solution of [{Rh(cyclooctadiene)Cl}$_2$] (0.066 g, 0.133 mmol) in CH_2Cl_2 (10 cm^3). Stirring was stopped after 5 minutes and the solution was decanted to eliminate AgCl. The supernatant was filtered through Celite and added to a solution of **L**[1] (0.155 g, 0.133 mmol) in CH_2Cl_2 (50 cm^3). After 1 h the solution was concentrated to *ca.* 5 cm^3 and addition of hexane afforded **4** as an orange precipitate. Yield: 0.105 g, 0.154 mmol, 79%; mp 123 °C (decomp.). ^1H NMR (300 MHz, $CDCl_3$): δ 7.26–7.17 (20H, $P(OPh)_2$), 7.13 (s, 4H, *m*-ArH), 6.78 and 6.77 (2s, 8H, *m*-ArH), 6.40 (s, 4H, *m*-ArH), 5.39 (broad signal, 4H, HC=CH of COD), 4.86 and 3.23 (AB spin system, 8H, $ArCH_2Ar$, ^2J = 13.2 Hz,), 3.98 (t, 4H, OCH_2, ^3J = 7.9 Hz), 2.27 (m, 2H, CH_2 of COD), 1.61 (m, 4H, OCH_2CH_2), 1.35 (s, 18H, $C(CH_3)_3$), 0.83 (s, 18H, $C(CH_3)_3$), 0.75 (t, 6H, CH_2CH_3, ^3J = 7.5 Hz). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 151.47–130.08 (quaternary aryl C), 129.88–119.58 (aryl C), 101.96 (s, CH of COD), 78.01 (s, OCH_2), 34.24 (s, $C(CH_3)_3$), 33.67 (s, $C(CH_3)_3$), 32.83 (s, $ArCH_2Ar$), 31.45 (s, $C(CH_3)_3$), 30.98 (s, $C(CH_3)_3$), 30.20 (s, CH_2 of COD), 21.77 (s, CH_2CH_3), 9.79 (s, CH_2CH_3). $^{31}P\{^1H\}$ NMR (121 MHz, $CDCl_3$): δ 101.0 (d, J(P–Rh) = 252 Hz, $P(OPh)_2$). FAB mass spectrum: *m*/*z* (%) 1375.5 (25) [$(M - BF_4)^+$, expected isotopic profile], 1267.4 [$(M - BF_4 - COD)^+$, expected isotopic profile]. Found: C 67.58, H 6.56%. Calc for $C_{82}H_{98}BF_4O_8P_2Rh$ (M_r = 1463.35): C 67.31, H 6.75%.

cis-*P*,*P*′-{[5,11,17,23-Tetra-*tert*-butyl-25,27-bis(cholesteryloxycarbonyloxy)-26,28-bis(diphenoxyphosphanyloxy)calix[4]arene]-1,5-cyclooctadiene}rhodium(I) tetrafluoroborate (5)

A solution of **L**[3] (0.235 g, 0.123 mmol) in THF (100 cm^3) was dropwise added to a cold (−78 °C) solution of $[Rh(COD)_2]BF_4$ (0.050 g, 0.123 mmol) in THF (100 cm^3). After 3 h the solution was allowed to reach room temperature and stirred for another 12 h. The solvent was removed *in vacuo* and the residue was redissolved in CH_2Cl_2. Addition of pentane and cooling at −78 °C afforded **5** as a yellow powder. Yield: 0.234 g, 0.106 mmol, 86%; mp 109–111 °C, IR (KBr, cm^{-1}): ν(CO) = 1756. ^1H NMR (300 MHz, $CDCl_3$): δ 7.23–7.19 and 6.84–6.77 (m, 24H, *m*-ArH and $P(OPh)_2$), 6.47 (s, 4H, *m*-ArH), 5.58 (m, 4H, CH of COD), 5.37 (d, 2H, H-6, ^3J = 4.9 Hz), 4.64 (m, 2H, H-3), 4.55 and 3.19 (AB quartet, ^2J = 13.6 Hz, 4H, $ArCH_2Ar$), 4.52 and 3.20 (AB quartet, ^2J = 13.5 Hz, 4H, $ArCH_2Ar$), 2.49–0.67 (86H, cholesteryl), 2.37 (m, 2H, CH_2 of COD), 1.39 (s, 18H, $C(CH_3)_3$, 0.86 (s, 18H, $C(CH_3)_3$). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 152.94–143.78 and 135.98 (quaternary aryl C), 138.62 (s, C-5 or aryl C), 130.11–123.64 (s, aryl C), 121.05 (s, C-6 tentative assignment), 119.96 (s, aryl C), 115.37 (s, CH of COD), 79.70 (s, C-3), 56.60 (s, C-14), 56.07 (s, C-17), 49.89 (s, C-9), 42.27 (s, C-13), 39.60 (s, C-12), 39.46 (s, C-1 tentative assignment), 37.86 (s, CH_2), 36.69 (s, C-10), 36.14 (s, CH_2), 35.73 (s, CH), 34.31 (s, $C(CH_3)_3$), 33.83 (s, $C(CH_3)_3$), 32.78 (s, $ArCH_2Ar$), 32.30 (s, CH_2 of COD), 31.85 (s, $ArCH_2Ar$), 31.75 (s, CH), 31.43 (s, $C(CH_3)_3$), 30.85 (s, $C(CH_3)_3$), 28.17 (s, C-16), 27.96 (s, CH), 27.56 (s, CH_2), 24.22 (s, CH_2), 23.77 (s, CH_2), 22.78 (s, CH_3), 22.52 (s, CH_3), 20.99 (s, C-11), 19.31 (s, CH_3), 18.67 (s, CH_3), 11.81 (s, CH_3). $^{31}P\{^1H\}$ NMR (121 MHz, $CDCl_3$): δ 99.7 (d, J(P–Rh) = 254 Hz, $P(OPh)_2$). ESI TOF mass spectrum *m*/*z* 2117.1 ([M − BF_4]$^+$, expected isotopic profile). Found: C 65.11, H 7.20%. Calc. for $C_{132}H_{174}BF_4O_{12}P_2Rh{\cdot}3CH_2Cl_2$ (M_r = 2204.5 + 3 × 84,93): C 65.93, H 7.38%.

cis-*P*,*P*′-(*o*-Dimethylaminomethylphenyl-*C*,*N*)-{5,11,17,23-tetra-*tert*-butyl-25,27-bis(ethoxycarbonylmethoxy)-26,28-bis(diphenoxyphosphanyloxy)calix[4]arene}palladium(II) tetrafluoroborate (6)

A solution of $AgBF_4$ (0.032 g, 0.165 mmol) in THF (1 cm^3) was added to a solution of $[Pd(o\text{-}C_6H_4NMe_2)Cl]_2$ (0.046 g, 0.083 mmol) in CH_2Cl_2 (20 cm^3). Stirring was stopped after 5 minutes and the solution was decanted to eliminate AgCl. The supernatant was filtered through Celite and added to a solution of **L**[2] (0.209 g, 0.167 mmol) in CH_2Cl_2 (50 cm^3). The solution was stirred overnight and concentrated to *ca.* 5 cm^3. Addition of pentane afforded a pale yellow solid **6**. Yield: 0.227 g, 0.140 mmol, 84%; mp 118–119 °C, IR (KBr, cm^{-1}): ν(CO) = 1758. ^1H NMR (300 MHz, $CDCl_3$) (assignment using COSY): δ 8.10–8.04 and 7.35–6.43 (m, 32H, C_6H_4 of dmba, *m*-ArH and $P(OPh)_2$), 5.33 and 3.42 (AB spin system, 2H, $ArCH_2Ar$, ^2J = 13.4 Hz), 5.21 and 3.38 (AB spin system, ^2J = 12.5 Hz, 2 × 2H, $ArCH_2Ar$), 5.04 and 3.47 (AB spin system, ^2J = 14.2 Hz, 2H, $ArCH_2Ar$), 4.50 and 4.30 (AB spin system, ^2J = 16.9 Hz, 4H, OCH_2CO_2), 3.96 (q, ^3J = 7.0 Hz, 2H, CH_2CH_3), 3.81 (q, ^3J = 7.1 Hz, 2H, CH_2CH_3), 3.34 and 3.08 (ABX (with X = P), ^2J(HH) = 13.1 Hz, ^4J(PH) = 3.1 Hz, ^4J(PH) = 4.5 Hz, 2H, NCH_2), 2.45 (d, ^4J(PH) = 4.3 Hz, 3H, $N(CH_3)$, 2.36 (d, ^4J(PH) = 4.5 Hz, 3H, $N(CH_3)$, 1.44 (s, 9H, $C(CH_3)_3$), 1.38 (s, 9H, $C(CH_3)_3$), 1.10 (t, ^3J = 7.0 Hz, 3H, CH_2CH_3), 0.99 (t, ^3J = 7.1 Hz, 3H, CH_2CH_3), 0.88 (s, 9H, $C(CH_3)_3$), 0.84 (s, 9H, $C(CH_3)_3$); $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 169.73 (s, CO_2), 169.49 (s, CO_2), 153.11–120.01 (aryl C), 73.04 (s, OCH_2CO_2), 71.09 (s, OCH_2CO_2), 65.22 (d, ^3J(PC) = 3 Hz, NCH_2), 60.63 (s, CH_2CH_3), 60.45 (s, CH_2CH_3), 43.56 (s, $N(CH_3)_2$), 43.11 (s, $N(CH_3)_2$), 34.38 (s, $C(CH_3)_3$), 34.29 (s, $C(CH_3)_3$), 33.79 (s, $C(CH_3)_3$), 33.75 (s, $C(CH_3)_3$), 32.87 (s, $ArCH_2Ar$), 32.63 (s, $ArCH_2Ar$), 31.61 (s, $C(CH_3)_3$), 31.06 (s, $C(CH_3)_3$), 14.18 (s, CH_2CH_3), 13.98 (s, CH_2CH_3); $^{31}P\{^1H\}$ NMR (121 MHz, $CDCl_3$): δ 141.6 and 115.2 (AB system, J(PP′) = 54 Hz). ES mass spectrum (CH_2Cl_2): *m*/*z* 1492.5 ([M − BF_4]$^+$, 100%). Found: C 63.95, H 6.41, N 0.62%. Calc for $C_{85}H_{98}BF_4NO_{12}P_2Pd{\cdot}0.25CH_2Cl_2$ (M_r = 1580.86 + 21.23): C 63.91, H 6.20, N 0.87%. The isomerisation product **6a** was obtained quantitatively after 24 h from a concentrated (*ca.* 2 × 10^{-3} mmol cm^{-3}) solution of **6**. $^{31}P\{^1H\}$ NMR (121 MHz, $CDCl_3$): δ 105.3 and 96.4 (AB system, J(PP′) = 86 Hz). As observed for **6**, the ^1H NMR spectrum of **6a** reveals a C_1-symmetrical structure.

In situ preparation of {[*o*-(dimethylaminomethyl)phenyl-*C*,*N*]-bis(triphenylphosphite)}palladium(II) tetrafluoroborate (7)

A solution of $AgBF_4$ (0.035 g, 0.180 mmol) in THF (1 cm^3) was added to a solution of $[Pd(o\text{-}C_6H_4CH_2NMe_2)Cl]_2$ (0.050 g, 0.091 mmol) in CH_2Cl_2 (20 cm^3). Stirring was stopped after 5 minutes and the solution was decanted to eliminate AgCl. The supernatant was filtered through Celite and added to a solution of $P(OPh)_3$ (70 μL, 0.083 g, 0.282 mmol) in CH_2Cl_2 (50 cm^3). The solution was stirred overnight and the volatiles removed. $^{31}P\{^1H\}$ NMR (121 MHz, $CDCl_3$): δ 112.2 and 101.4 (AB quartet, J(P–P) = 89 Hz, $(P(OAr)_3)_2$).

cis-*P*,*P*′-Dichloro{5,11,17,23-tetra-*tert*-butyl-25,27-bis(cholesteryloxycarbonyloxy)-26,28-bis(diphenoxyphosphanyloxy)calix[4]arene}palladium(II) (8)

A solution of **L**[3] (0.200 g, 0.105 mmol) in THF (75 cm^3) was added dropwise to a cold (−78 °C) solution of $[PdCl_2(COD)]$ (0.030 g, 0.105 mmol) in THF (75 cm^3). After stirring for

3 h the solution was allowed to reach room temperature and stirred for a further 12 h. Solvent evaporation afforded **8** as a pale yellow powder. The complex was then recrystallized in a CH_2Cl_2–pentane mixture at −78 °C. Yield: 0.199 g, 0.095 mmol, 90%; mp 168–169 °C, IR (KBr, cm^{-1}): ν(CO) = 1758. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.32–7.07 and 6.79–6.78 (m, 24H, *m*-ArH and P(OPh)$_2$), 6.47 (s, 4H, *m*-ArH), 5.30 (d, 2H, H-6, ^3J = 4.7 Hz), 4.74 and 3.34 (AB spin system, 4H, ArCH_2Ar, ^2J = 13.8 Hz), 4.74 and 3.32 (AB spin system, 4H, ArCH_2Ar, ^2J = 13.8 Hz), 4.60 (m, 2H, H-3), 2.72 (broad t, 2 × 1H, H-cholest not assigned), 2.38–0.68 (86H, cholesteryl), 1.44 (s, 18H, C(CH_3)$_3$), 0.88 (s, 18H, C(CH_3)$_3$). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ 154.35–143.98 (quaternary aryl C), 139.95 (s, C-5 or aryl C), 136.65–124.82 (aryl C), 122.33 (s, C-6 tentative assignment), 80.29 (s, C-3), 56.73 (s, C-14), 56.12 (s, C-17), 49.93 (s, C-9), 42.29 (s, C-13), 39.73 (s, C-12), 39.49 (s, C-1 tentative assignment), 37.84 (s, CH_2), 37.07 (s, CH_2), 36.66 (s, C-10), 36.16 (s, CH_2), 35.76 (s, CH), 34.33 (s, *C*(CH$_3$)$_3$), 33.83 (s, *C*(CH$_3$)$_3$), 32.79 (s, Ar*C*H$_2$Ar), 31.92 (s, Ar*C*H$_2$Ar), 31.80 (s, CH), 31.50 (s, C(*C*H$_3$)$_3$), 30.98 (s, C(*C*H$_3$)$_3$), 28.21 (s, C-16), 27.98 (s, CH), 27.42 (s, CH_2), 24.25 (s, CH_2), 23.80 (s, CH_2), 22.80 (s, CH_3), 22.54 (s, CH_3), 21.02 (s, C-11), 19.43 (s, CH_3), 18.69 (s, CH_3), 11.82 (s, CH_3). ^{31}P{^{1}H} NMR (121 MHz, $CDCl_3$): δ 75.91 (s, P(OPh)$_2$). MALDI TOF mass spectrum: *m*/*z* 2010.1 ([M − 2 Cl]$^+$, 100%). Molecular weight determination by osmometry (CH_2Cl_2): 1990 ± 100, corresponding to a monomer. Found: C 70.25, H 7.71%. Calc. for $C_{124}H_{162}Cl_2O_{12}P_2Pd{\cdot}0.5CH_2Cl_2$ (M_r = 2083.88 + 42.46): C 70.33, H 7.73%.

Acetylacetonato-{5,11,17,23-tetra-*tert*-butyl-25,27-dipropoxy-26,28-bis(diphenoxy phosphanyloxy)calix[4]arene}rhodium(I) (9)

L[1] (0.136 g, 0.117 mmol) was added to a solution of [Rh(acac)(CO)$_2$] (acac = MeCOCHCOMe) (0.030 g, 0.116 mmol) in CH_2Cl_2 (50 cm^3). The solution turned from green to yellow within a few minutes. After 12 h, the solvent was evaporated to dryness to afford **9** as a yellow solid which was washed quickly with small amounts of cold (−78 °C) pentane. Yield: 0.132 g, 0.096 mmol, 83%; mp > 173–175 °C (decomp.), IR (KBr, cm^{-1}): ν = 1593s, 1580sh, 1518s (acac). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.34–7.21 and 7.11–6.94 (24H, *m*-ArH and P(OPh)$_2$), 6.44 (s, 4H, *m*-ArH), 5.13 and 3.18 (AB spin system, 8H, ArCH_2Ar, ^2J = 13.1 Hz,), 4.94 (s, 1H, C*H*-acac), 3.86 (t, 4H, OCH$_2$, ^3J = 7.8 Hz), 1.93 (m, 4H, OCH$_2$CH_2), 1.44 (s, 18H, C(CH_3)$_3$), 1.19 (s, 6H, CH_3-acac), 0.88 (s, 18H, C(CH_3)$_3$), 0.80 (t, 6H, CH$_2$CH_3, ^3J = 7.4 Hz). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ 184.52 (s, CO), 153.33–129.78 (quaternary aryl C), 127.90–120.07 (aryl C), 99.30 (s, *C*H-acac), 77.67 (s, OCH$_2$), 34.18 (s, *C*(CH$_3$)$_3$), 33.65 (s, *C*(CH$_3$)$_3$), 33.16 (s, ArCH$_2$Ar), 31.69 (s, C(*C*H$_3$)$_3$), 31.22 (s, C(*C*H$_3$)$_3$), 25.40 (s, *C*H$_3$-acac), 22.34 (s, *C*H$_2$CH$_3$), 10.42 (s, CH$_2$*C*H$_3$). ^{31}P{^{1}H} NMR (121 MHz, $CDCl_3$): δ 115.4 (d, *J*(P–Rh) = 325 Hz, P(OPh)$_2$). MALDI TOF mass spectrum: *m*/*z* 1366.00 ([M]$^+$, 100%). Found: C 69.55, H 6.93%. Calc for $C_{79}H_{93}O_{10}P_2Rh$ (M_r = 1367.43): C 69.39, H 6.86%.

Bis(acetylacetonato)biscarbonyl{5,11,17,23-tetra-*tert*-butyl-25,27-dipropoxy-26,28-bis(diphenoxyphosphanyloxy)-calix[4]arene}dirhodium(I) (10)

L[1] (0.124 g, 0.106 mmol) was added to a solution of [Rh(CO)$_2$acac] (acac = MeCOCHCOMe) (0.055 g, 0.213 mmol) in CH_2Cl_2 (50 cm^3). After stirring for one night at room temperature, the solvent was evaporated affording **10** as a green microcrystalline powder which was dried under vacuum. The complex was washed quickly with small amounts of cold pentane. Yield: 0.151 g, 0.093 mmol, 88%; mp 98.5–100 °C, IR (KBr, cm^{-1}): ν = 1591s, 1581sh, 1521s (acac). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.37–7.13 and 7.07–7.02 (m, 24H, *m*-ArH and P(OPh)$_2$), 6.54 (s, 4H, *m*-ArH), 5.36 (s, 2H, C*H*-acac), 4.83 and 3.34 (AB spin system, 8H, ArCH_2Ar, ^2J = 13.1 Hz), 4.19 (t, 4H, OCH_2, ^2J = 8.4 Hz), 2.45 (m, 4H, OCH$_2$CH_2), 2.01 (s, 6H, CH_3-acac), 1.70 (s, 6H, CH_3-acac), 1.38 (s, 18H, C(CH_3)$_3$), 0.87 (s, 18H, C(CH_3)$_3$), 0.81 (t, 6H, CH$_3$, ^3J = 7.5 Hz). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ 187.14 (s, CO), 185.38 (s, CO), 154.97–132.45 (quaternary aryl C), 132.40–121.08 (aryl C), 100.62 (s, *C*H-acac), 76.90 (s, OCH$_2$), 34.17 (s, *C*(CH$_3$)$_3$), 33.76 (s, *C*(CH$_3$)$_3$), 33.01 (s, ArCH$_2$Ar), 31.82 (s, C(*C*H$_3$)$_3$), 31.08 (s, C(*C*H$_3$)$_3$), 27.43 (d, *C*H$_3$-acac, *J* = 8.6 Hz), 26.49 (s, CH$_3$-acac), 23.68 (s, *C*H$_2$CH$_3$), 9.83 (s, CH$_2$*C*H$_3$). ^{31}P{^{1}H} NMR (121 MHz, $CDCl_3$): δ 123.79 (d, *J*(P–Rh) = 288 Hz, P(OPh)$_2$). Found: C 63.27, H 6.31%. Calc. for $C_{86}H_{100}O_{14}P_2Rh_2$ (M_r = 1625.46): C 63.55, H 6.20%.

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