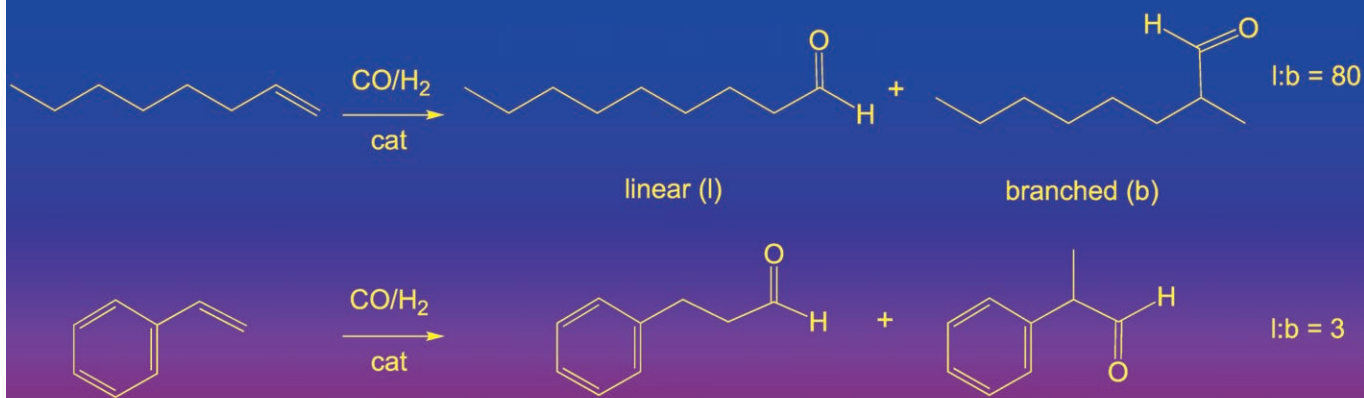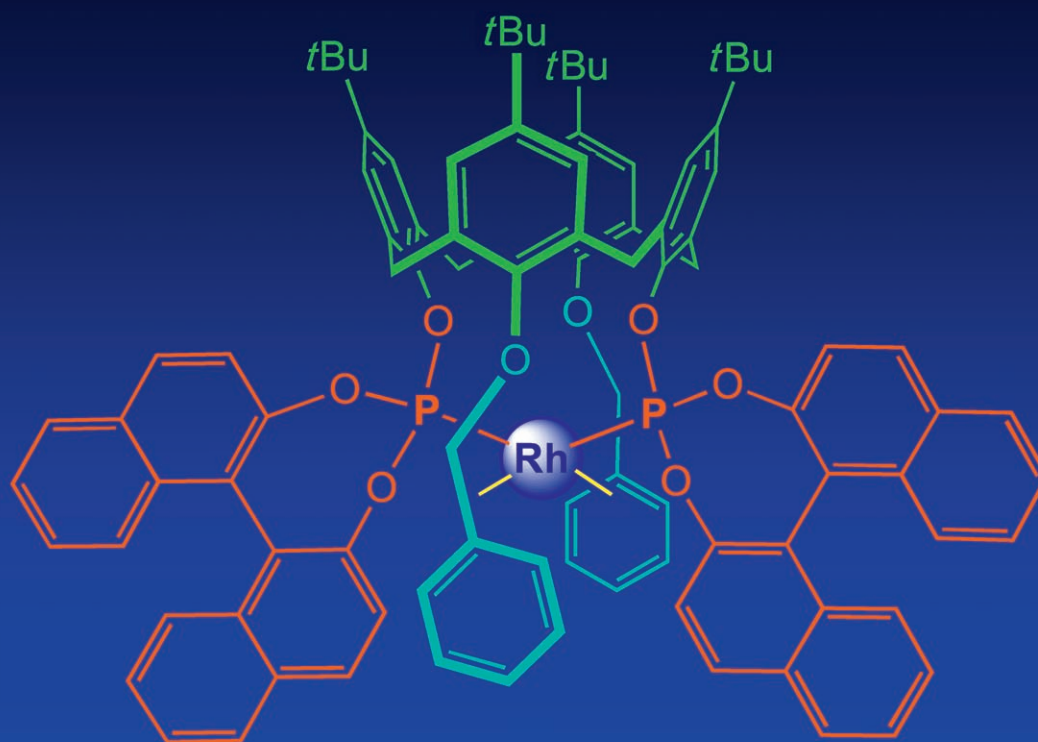VIP

Highly Regioselective Hydroformylation with Hemispherical Chelators

David Sémeril,*[a] Dominique Matt,*[a] and Loïc Toupet[b]

Abstract: The hemispherical diphosphites (*R,R*)- or (*S,S*)-5,11,17,23-tetra-*tert*-butyl-25,27-di(OR)-26,28-bis(1,1′-binaphthyl-2,2′-dioxyphosphanyloxy)-calix[4]arene (R = OPr, OCH$_2$Ph, OCH$_2$-naphtyl, O-fluorenyl; R = H, R′ = OPr) (L^R), all with C_2 symmetry, have been synthesised starting from the appropriate di-*O*-alkylated calix[4]-arene precursor. In the presence of [Rh(acac)(CO)$_2$], these ligands straightforwardly provide chelate complexes in which the metal centre sits in a molecular pocket defined by two naphthyl planes related by the C_2 axis and the two apically situated R groups. Hydroformylation of octen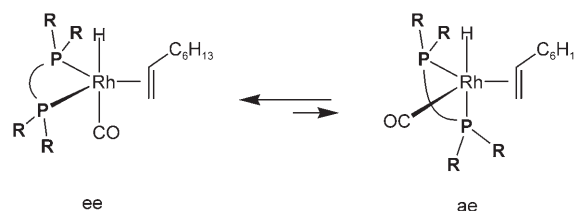e with the L^{Pr}/Rh system turned out to be highly regioselective, the linear-to-branched (l:b) aldehyde ratio reaching 58:1. The l:b ratio significantly increased when the propyl groups were replaced by -CH$_2$Ph (l:b = 80) or -CH$_2$naphthyl (l:b = 100) groups, that is, with substituents able to sterically interact with the apical metal sites, but without inducing an opening of the cleft nesting the catalytic centre. The trend to preferentially form the aldehyde the shape of which fits with the shape of the catalytic pocket was further confirmed in the hydroformylation of styrene, for which, in contrast to catalysis with conventional diphosphanes, the linear aldehyde was the major product (up to ca. 75% linear aldehyde). In the hydroformylation of *trans*-2-octene with the L^{benzyl}/Rh system, combined isomerisation/hydroformylation led to a remarkably high l:b aldehyde ratios of 25, thus showing that isomerisation is more effective than hydroformylation. Unusually large amounts of linear products were also observed with all the above diphosphites in the tandem hydroformylation/amination of styrene (l:b of ca. 3:1) as well as in the hydroformylation of allyl benzyl ether (l:b ratio up to 20).

Keywords: calixarenes · homogeneous catalysis · hydroformylation · phosphites · rhodium

Introduction

Catalytic olefin hydroformylation with CO/H$_2$ mixtures currently constitutes the main route for the production of linear C$_3$–C$_{18}$ aldehydes. In most plants, these are subsequently converted into plasticiser and detergent alcohols, as well as acids and other derivatives.[1–4] The world production of oxo chemicals today reaches almost 10 million tons. Most of the aldehydes are produced by low-pressure hydroformylation with Rh^I, which, when starting from terminal alkenes, affords mainly linear aldehydes when the catalyst is based on triarylphosphane ligands, for example, PPh$_3$. Owing to the increasing importance of oxo products, considerable efforts have been devoted in recent years to improving the regioselectivity of hydroformylation reactions. In particular, research has focussed on the design and use of diphosphanes characterised by a large natural bite angle.[5–12] Chelators of this type are known to favour the formation of trigonal-bipyramidal hydrido–carbonyl species in which the phosphorus atoms both occupy equatorial sites (ee configuration in Scheme 1). Such a conformation often increases the linear aldehyde selectivity, but does not constitute a *must* for high regioselectivity. The latter is in fact controlled by the ligand bite angle, which, if having the proper value, may drive the hydride-transfer step towards the formation of a linear rhodium–alkyl intermediate, which in turn leads to a linear aldehyde.[1]

In the last decade, calixarenes have proved to be valuable scaffolds for the synthesis of diphosphanes with strong chelation properties.[13–16] Of particular interest are calix[4]arenes bearing two phosphite units distally located at the lower rim,[17] here termed 1,3-calix[4]diphosphites (Scheme 2). X-ray studies have revealed that these ligands may give chelate complexes in which the P-M-P angles are significantly larger than those observed in related complexes with non-chelating ligands.[18, 19]

In a recent preliminary communication, we reported that the use of 1,3-calix[4]diphosphites in which both phosphorus atoms are substituted by the bulky 1,1′-binaphthalene-2,2′-dioxy ("bino") group led to a high proportion of linear aldehydes in the hydroformylation of octene. This effect is mark-
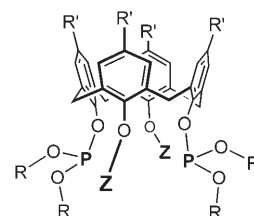

Scheme 1. Trigonal-bipyramidal intermediates in the rhodium-catalysed octene hydroformylation by using chelating diphosphanes with large bite angles (ee and ae stand for equatorial–equatorial and axial–equatorial configurations, respectively).

Scheme 2. General formula of 1,3-calix[4]diphosphites bearing secondary Z groups.

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edly stronger than with related calixarenes containing P-(OPh)$_2$ substituents.[19] The high regioselectivity may be attributed to the ability of the phosphorus substituents to form a tight pocket about the rhodium centre, which, in line with van Leeuwen's proposals,[20,21] favours the formation of linear products. Having four phenolic oxygen atoms at the lower rim of the calixarene platform enables the tethering of two further substituents (Z) so as to create, together with the two P(OR)$_2$ moieties, a hemispherical ligand environment that may then result in a greater "embrace" of the metal. In the present contribution, we describe a series of binol-derived 1,3-calix[4]diphosphites bearing various Z side groups and show that these may be used efficiently in various olefin hydroformylations. The results presented herein illustrate how the introduction of properly chosen Z groups may significantly improve the regioselectivity of the reaction.

Results and Discussion

Synthesis of diphosphites: The double deprotonation with NaH of the appropriate, distally *O*-dialkylated precursor (**1**–**5**) followed by reaction with (*S*)- or (*R*)-(1,1′-binaphthalene-2,2′-diyl)chlorophosphite (Scheme 3) led to the diphosphites **6**–**12**. The compounds were obtained after workup (see Experimental Section) in yields between 14 and 75%. As expected, identical NMR spectra were obtained for the diastereoisomeric pairs **6** and **7** as well as for **8** and **9**. The "cone" form of the calixarenes was inferred from the corresponding ^{13}C NMR spectra, which show Ar*CH$_2$*Ar signals in a range typical for this conformation (observed chemical shifts between $\delta = 31.43$ and 33.55 ppm).[22] In keeping with a C_2-symmetrical structure, each ^{1}H NMR spectrum displays two distinct AB patterns for the diastereotopic Ar*CH$_2$*Ar pro-

tons, while the ^{31}P NMR spectra exhibit a single signal in the phosphite region ($\delta = 118.7$–134.4 ppm). The conical structure of the backbone was further confirmed by a single-crystal X-ray diffraction study of diphosphite **12** (Figure 1), al-
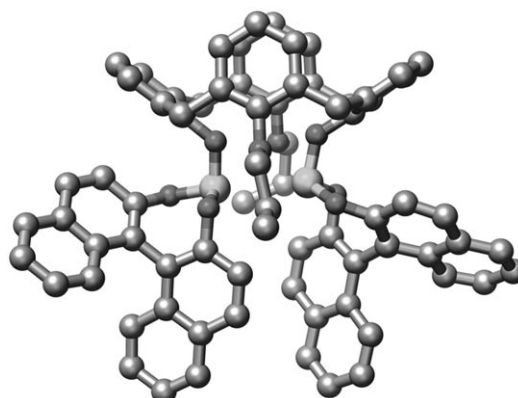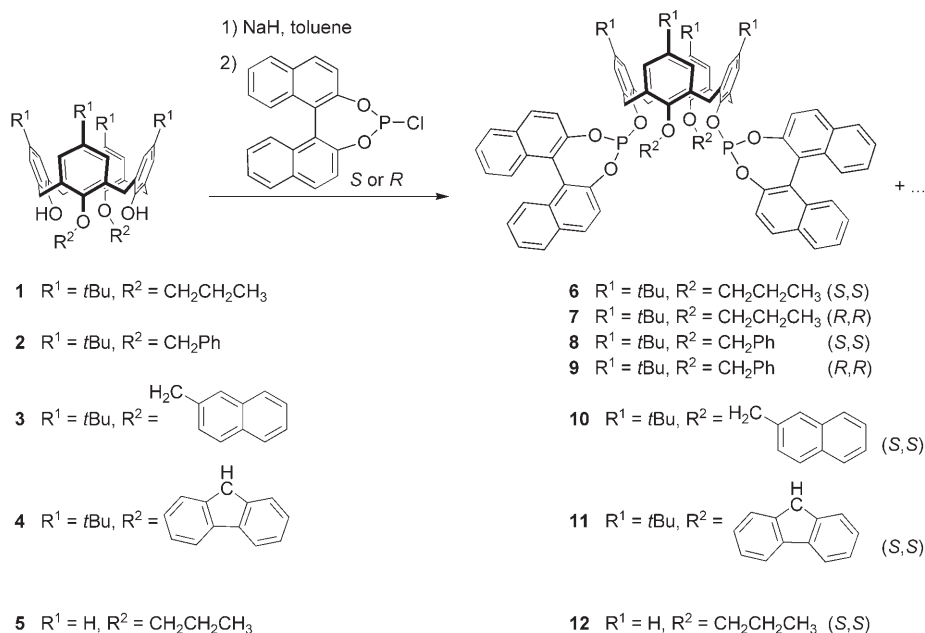

Figure 1. Molecular structure of **12** (*S*,*S*). Interplanar angle between connected naphthyl moieties: 24.8°; dihedral angles between facing phenoxy rings of the calixarene: 72.6° (O1/O2), 24.7° (O3/O4). The molecule crystallises with a molecule of toluene lying out of the cavity (not shown).

though the cone is flattened so that the *O*-propyl groups of **12** are pushed towards the calixarene axis and form with the two naphthyl groups a molecular pocket. Careful examination of the crude reaction mixtures revealed for all of them, except for that leading to **12**, the presence of a minor by-product, namely a "partial cone" isomer (vide infra), which could be separated straightforwardly by fractional crystallisation. In the case of **12**, several by-products were formed that were not identified. Two partial cone conformers, **13** and **14**, could be isolated as pure products.

The assignment of a partial cone conformation was made on the basis of the corresponding ^{13}C NMR spectra, which each shows four Ar*CH$_2$*Ar signals, two being typical for CH$_2$ groups bridging *anti*-oriented phenol rings, the other two in accord with methylene groups linking *syn*-oriented rings. The ^{31}P NMR spectra both display two distinct phosphite signals separated by about 10 ppm. A single-crystal X-ray diffraction study was carried out for diphosphite **14**, which confirmed the proposed conformation and revealed that the phosphorus atoms belong to *anti*-oriented phenol rings (Figure 2) of two distal phenol rings.

The ability of the conical 1,3-calixdiphosphites described above to form chelate complexes with rhodium was proved by reacting **8** with [Rh-
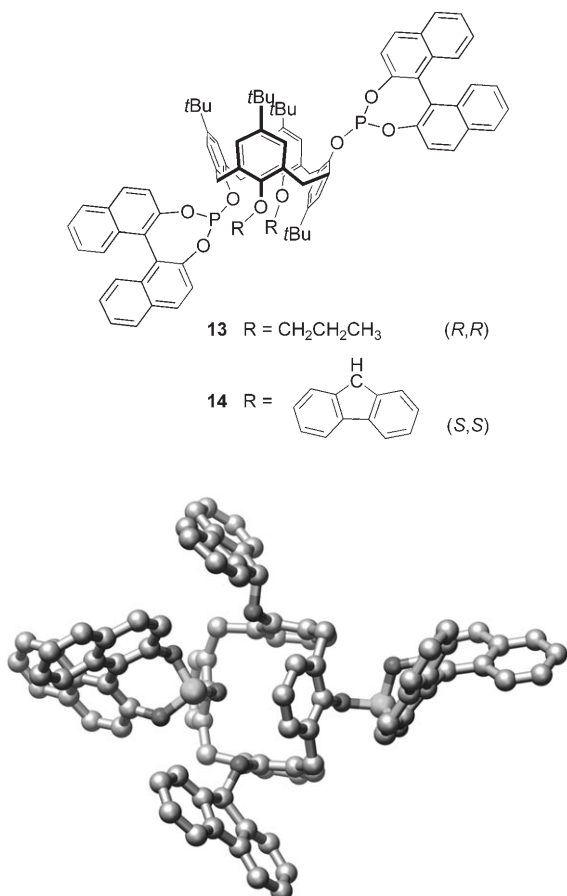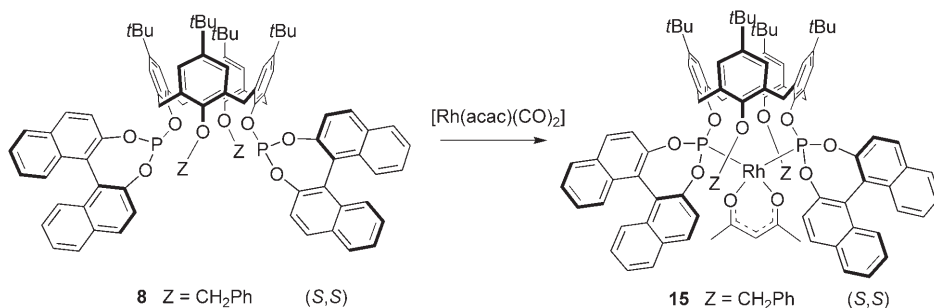

Scheme 3. Synthesis of calixarenes **6**–**12**.

1) NaH, toluene

1 R^1 = *t*Bu, R^2 = CH$_2$CH$_2$CH$_3$

2 R^1 = *t*Bu, R^2 = CH$_2$Ph

3 R^1 = *t*Bu, R^2 =

4 R^1 = *t*Bu, R^2 =

5 R^1 = H, R^2 = CH$_2$CH$_2$CH$_3$

6 R^1 = *t*Bu, R^2 = CH$_2$CH$_2$CH$_3$ (*S*,*S*)
7 R^1 = *t*Bu, R^2 = CH$_2$CH$_2$CH$_3$ (*R*,*R*)
8 R^1 = *t*Bu, R^2 = CH$_2$Ph (*S*,*S*)
9 R^1 = *t*Bu, R^2 = CH$_2$Ph (*R*,*R*)

10 R^1 = *t*Bu, R^2 = (*S*,*S*)

11 R^1 = *t*Bu, R^2 = (*S*,*S*)

12 R^1 = H, R^2 = CH$_2$CH$_2$CH$_3$ (*S*,*S*)

good crystals, but is likely to be close to that of its analogue in [Pd(η³-allyl)(**6**)]PF₆,[19] in which the metal centre sits on the calixarene axis in a kind of cleft formed by two symmetrically situated naphthyl units that are perpendicular to the P-M-P plane. In this complex, the ligand bite angle is 107.5°. MM2 calculations[23] caried out for [Rh(**8**)] reveal that the two benzyl side groups delineate together with the two "P-bino" moieties a hemispherical pocket (Figure 3). As in the palladium complex, the naphthyl units forming the cleft are inclined by about 45° with respect to the orientation defined by the d_{z^2} orbital.

13 R = CH₂CH₂CH₃ (*R,R*)

14 R = (*S,S*)

Figure 2. Molecular structure of **14**. The *t*Bu groups have been omitted for clarity. Interplanar angle between connected naphthyl moieties: 31.1° and 32.1°. The molecule crystallises with a molecule of toluene (not shown).
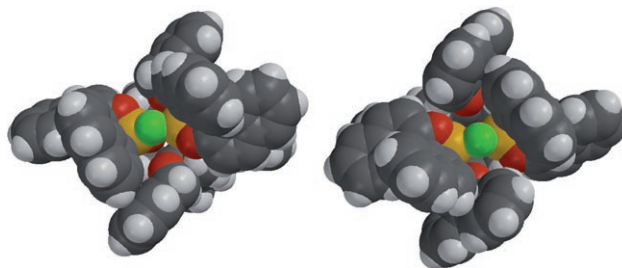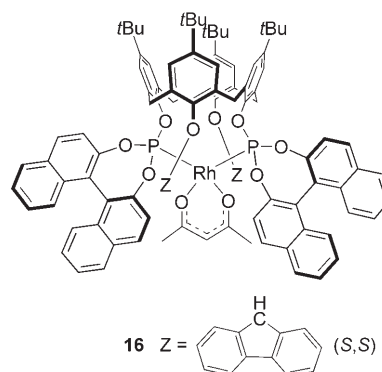

Figure 3. Calculated MM2 structures of the Rh·**8** moiety. The calculations were carried out with metal parameters for a square-planar (left) and a trigonal-bipyramidal (right) coordination geometry.

Finally, we checked that the presence of the sterically encumbered fluorenyl substituents in **16** (obtained by reacting [Rh(acac)(CO)₂] with **11**) have no impact on the stability of the complex.

(acac)(CO)₂] (Scheme 4). This reaction afforded **15** in high yield (75% after workup). Complex **15** is highly soluble in hexane. Its mass spectrum shows a strong peak at 1659.59 corresponding to the [*M*]⁺ ion. All NMR spectra of **15** are consistent with a C_2-symmetrical molecule. For example, the ³¹P NMR spectrum shows a doublet centred at $\delta =$ 126.4 ppm (*J*(Rh,P) = 327 Hz), while the corresponding ¹H NMR spectrum displays two AB systems for the ArC*H*₂Ar methylenic protons. The solid-state structure of the M·**8** moiety could not be determined because of lack of

16 Z = (*S,S*)

Catalytic hydroformylation: Only those diphosphites with a conical calixarene skeleton, namely the hemispherical ligands **6–12**, were assessed in hydroformylation reactions (Scheme 5). The olefins tested were octene, *trans*-2-octene, styrene, allyl benzyl ether and norbornene. The catalysts were generated in situ.

8 Z = CH₂Ph (*S,S*) → [Rh(acac)(CO)₂] → **15** Z = CH₂Ph (*S,S*)

Scheme 4. Synthesis of complex **15**.
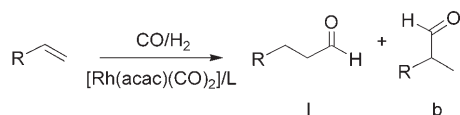
Scheme 5. Rhodium-catalysed hydroformylation of olefins.

1-Octene hydroformylation: These tests were carried out at 80 °C under 20 bar of CO/H$_2$ using [Rh(acac)(CO)$_2$] as precursor. With the exception of **11** (see below), all ligands gave remarkably high linear-to-branched (l:b) aldehyde ratios (l:b = 34–102) provided an excess of diphosphite was used (Table 1, see e.g., entries 1–4). As observed by other

Table 1. Rhodium-catalysed hydroformylation of 1-octene using diphosphites **6, 8–12**.[a]

	L	L/Rh	t [h]	Conv[b] [%]	TOF[c]	Product distribution Olefins[d] [%]	Aldehydes[e] [%]	l:b[f]
1	**6**	10	1.2	34.5	1440	17.0	17.5	58.0
			8	98.5	620	46.7	51.8	56.3
2	**6**	1	1	13.2	660	3.8	9.4	3.9
			8	76.2	480	22.4	53.8	2.5
3	**8**	10	1	23.9	1190	3.0	20.9	>100[g]
			4	53.3	670	3.5	49.8	78.3
			24	87.3	180	12.1	75.2	80.1
4	**8**	1	1	23.1	1150	2.6	20.5	7.2
			24	95.5	200	22.6	72.9	1.9
5	**9**	10	1	24.2	1200	1.8	22.4	>100[g]
			24	94.5	200	13.6	80.9	71.0
6	**10**	10	1	14.4	720	6.3	8.1	>100[g]
			4	48.5	600	29.5	19.0	101.6
7	**11**	10	4	28.8	360	2.0	26.8	3.3
8	**12**	10	1	19.7	980	7.9	11.8	91.6
			4	51.0	640	22.2	28.8	86.9
			24	98.5	205	44.4	54.1	34.0

[a] 1-octene (10 mmol), 1-octene/Rh = 5000, P(CO/H$_2$) = 20 bar, T = 80 °C, toluene/n-decane (15 mL/0.5 mL), incubation overnight at 80 °C under P(CO/H$_2$) = 15 bar. [b] Conversion: determined by GC using decane as standard. [c] mol(converted 1-octene)mol(Rh)$^{-1}$h^{-1}. [d] Isomerised 1-octene/initial 1-octene. [e] Aldehydes/initial 1-octene. [f] The l:b aldehyde ratio takes into account branched aldehydes (which consist mainly of 2-methyloctanal). [g] Exact value not determined because of a very low amount of branched aldehydes.

authors, excess of ligand is necessary to prevent the formation of "naked" rhodium, which behaves as an unselective catalyst.[24] Changing the pendant auxiliary groups induced considerable variations in both reactivity and regioselectivity. As a general trend, larger Z substituents led to lower reaction rates (Table 1, see, e.g., entries 1 and 6), the highest turnover frequency (TOF) being found with the propyl-substituted calixarene **6** (TOF = 1440 mol(olefin) mol(Rh)$^{-1}$h^{-1}). A considerable selectivity increase with respect to **6** (l:b = 58) was observed for the ligands with Z = CH$_2$Ph (**8**) and CH$_2$–naphthyl (**10**), both resulting in a l:b > 100 (Table 1, entries 1, 3 and 6). Thus, substituents which seemingly increase the metal confinement favour the formation of the linear aldehyde. However, there is no simple relationship between the size of the Z group and the selectivity, as can

be seen when considering the poor selectivity (l:b = 3.3) obtained with ligand **11** with two fluorenyl units. In fact, these modify the metal confinement as a result of strong steric interactions with both the calixarene backbone and the naphthyl groups, thereby modifying the degree of confinement of the metal olefin unit (vide infra). We found that the high preference obtained for the linear product with **8** and **10** was maintained until the end of the reaction; for example, the l:b ratio was still 80 after 24 h reaction time with diphosphite **8** (Table 1, entry 3). The presence of four *tert*-butyl substituents on the upper rim of the calixarene turned out to have a beneficial influence on the activity and on the regioselectivity. Thus, in contrast to the reactions carried out with the tetrabutylated calixarene ligands, those performed with diphosphite **12** resulted in a decrease of aldehyde selectivity with time (l:b = 91.6 at 19.7 % conversion, l:b = 34.0 at 98.5 % conversion; Table 1, entry 8), the only branched aldehyde produced being 2-methyl octanal. A similar l:b decrease has already been observed by Börner et al. with other phosphorus-containing calixarenes.[25] The reason for the selectivity decrease with **12** remains unclear. Possibly ligand **12** displays a weaker chelating power and therefore decoordinates gradually, hence leading to a less selective catalyst. The fact that 2-methyl octanal is the only branched aldehyde seen suggts that under the conditions used, this aldehyde originates directly from 1-octene rather than from 2-octene, since hydroformylation of the latter was shown to result also in 2-ethyl heptanal.

In all the tests in which L:Rh ratios of ten were applied internal olefins were produced, the proportion of 1-octene converted to internal olefins being in some instances almost as important as that transformed into aldehydes. The only calixarenes for which olefin isomerisation remained relatively low with respect to hydroformylation were the benzyl-substituted calixarenes **8** and **9** (Table 1, entries 3 and 5). It is worth mentioning here that no octane was detected in these reactions. As expected, no significant differences were observed between the two diastereoisomeric diphosphites (*S,S*)-**8** and (*R,R*)-**9** (Table 1, entries 3 and 5).

trans-2-Octene hydroformylation: Given that the systems described above may act as isomerisation catalysts, we decided to extend our investigations to the hydroformylation of *trans*-2-octene, with the expectation that this would produce appreciable amounts of nonanal. The selective formation of linear aldehydes starting from internal alkenes is still an important challenge in industrial hydroformylation. The tests were carried out at 120 °C with the diphosphites **6, 8, 10** and **12** (Table 2), namely with those giving the best regioslectivities in the hydroformylation of 1-octene. As there, the hydroformylation rate of 2-octene decreased with the calixarene ligands with the larger auxiliary groups, while the corresponding regioselectivity increased. The highest l:b ratio, 25.3, was obtained with diphosphite **10**, which bears two CH$_2$–naphthyl groups (Table 2, entry 3). The observation of such a high regioselectivity implies that at the temperature of the reaction (120 °C), isomerisation of *trans*-2-octene to

Table 2. Rhodium-catalysed hydroformylation of *trans*-2-octene using diphosphites **6**, **8**, **10** and **12**.[a]

	L	t [h]	Conv[b] [%]	TOF[c]	Product distribution		1:b[f]
					Isomerisation[d] [%]	Aldehydes[e] [%]	
1	**6**	2	41.6	170	1.9	39.7	4.3
2	**8**	2	30.6	120	1.8	28.8	21.7
3	**10**	2	17.3	70	0.7	16.6	>25[g]
		4	24.6	50	1.0	23.6	25.3
4	**12**	2	25.6	100	2.3	23.3	5.5
		8	52.1	50	5.5	46.6	3.5
		24	67.9	20	14.7	53.2	2.3

[a] *trans*-2-Octene (3.2 mmol), *trans*-2-octene/Rh = 800, L/Rh = 10, $P(CO/H_2)$ = 20 bar, T = 120 °C toluene/*n*-decane (15 mL/0.5 mL), incubation overnight at 80 °C under $P(CO/H_2)$ = 15 bar. [b] Conversion: Determined by GC using decane as standard. [c] mol(converted *trans*-2-octene) mol(Rh)$^{-1}$h^{-1}. [d] Isomerised 2-octene/initial 2-octene. [e] Aldehydes/initial 2-octene. [f] The l:b aldehyde ratio takes into account all branched aldehydes (which consist mainly of 2-methyloctanal). [g] Exact value not determined because of the very small amount of branched aldehydes.

Table 3. Rhodium-catalysed hydroformylation of styrene using diphosphites **6–8** and **10–12**.[a]

	L	L/ Rh	$P(CO/H_2)$ [bar]	t [h]	Conv[b] [%]	TOF[c]	Branched[b] [%]	Linear[b] [%]	1:b[d]
1	**6**	10	20	5	18.3	180	41.2	58.8	1.4
2	**6**	1	20	4	24.0	300	61.2	38.8	0.6
3	**6**	10	10	5	21.7	220	34.8	65.2	1.9
				24	58.7	120	32.6	67.4	2.0
4	**7**	10	10	4	24.2	300	34.5	65.5	1.9
5	**8**	10	10	5.5	21.4	200	23.9	76.1	3.2
6	**10**	10	10	4	25.7	320	23.2	76.8	3.3
				8	35.7	220	22.9	77.1	3.4
				24	71.4	150	23.2	76.8	3.3
7	**11**	10	10	4	21.5	270	78.9	21.1	0.3
8	**12**	10	10	1	11.3	700	11.3	88.7	7.8
				4	34.3	430	18.2	81.8	4.5
				8	63.1	390	23.8	76.2	3.2
				24	70.5	150	25.2	74.8	3.0

[a] Styrene (10 mmol), styrene/Rh = 5000, T = 80 °C, toluene/*n*-decane (15 mL/0.5 mL), incubation overnight at 80 °C under $P(CO/H_2)$ = 15 bar. [b] Determined by GC using decane as internal standard. [c] mol(converted styrene) mol(Rh)$^{-1}$h^{-1}. [d] l:b aldehyde ratio.

1-octene takes place efficiently. The remarkably high regioselectivity observed for **10** slightly surpasses that obtained with the to date most effective ligand (l:b = 24.7) for this reaction, van Leeuwen's 4,5-bis(9-dibenzo[b,d]phospholyl)phenoxazine, a ligand with a calculated natural bite angle of 128.9°.[26] In comparison, the l:b ratio obtained with PPh$_3$[8] in the hydroformylation of *trans*-2-octene does not exceed 0.9. Calixarene **12**, with no *tert*-butyl groups on the upper rim, is the sole ligand for which the l:b ratio decreased during catalysis, as already observed when using this ligand in the hydroformylation of 1-octene (Table 2, entry 4). This could be a further indication that this ligand tends to decoordinate with time.

Styrene hydroformylation: It is known that with usual rhodium catalysts (e.g., Rh/PPh$_3$), styrene gives mainly the corresponding branched aldehyde, 2-phenylpropanal.[27] Thus, the major isomer is the inverse of that observed for alkyl-monosubstituted olefins. The most plausible explanation for this regioselectivity is the ready formation of a η^3-complex as shown in Scheme 6.[28]
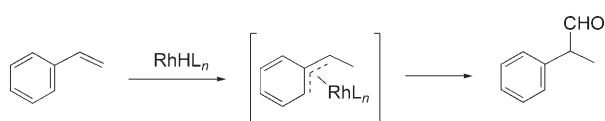
Scheme 6. Hydroformylation of styrene.

Remarkably, for all the ligands tested, except for **11** (Table 3, entry 7), hydroformylation of styrene gave the linear aldehyde as the major product. Changes in the CO/H$_2$ pressure induced changes in the regioselectivity, but the activity was little affected. For example, on decreasing the pressure from 20 to 10 bar in tests carried out with **6**, the selectivity for linear aldehyde rose from 58.8 to 65.2 % (Table 3, entries 1 and 3). The most striking result is that the proportion of linear aldehyde dramatically increased on replacing the propyl groups of **6** (l:b = 1.9) by benzyl groups (ligand **8**, l:b = 3.2) for reactions at 10 bar. This effect was also observed with calixarene **10**, bearing the somewhat longer methyl-2-naphtalenyl groups (l:b = 3.4). These observations suggest that with these particular Z substituents, the shape of the pocket no longer allows the formation of an η^3-complex with styrene, but only that of a conventional σ-alkyl complex involving the terminal carbon atom of the styrene moiety. Note that these high selectivities persisted after 24 h (Table 3, entries 3 and 6). Ligand **12**, which is the "debutylated" version of **6**, also resulted in high proportions of linear aldehyde, but the selectivity slightly dropped with time (88.7 % linear aldehyde after 1 h vs. 74.8 % after 24 h; Table 3, entry 8), as already seen during the hydroformylation of octene. Again, no significant differences were observed between the two diastereoisomic diphosphites (*S,S*)-**1** and (*R,R*)-**2** (Table 3, entries 3 and 4). The behaviour of ligand **11**, which is not selective, resembles that of usual phosphanes (Table 3, entry 7), suggesting again that this ligand dissociates as the reaction proceeds.

Styrene hydroaminovinylation: The hydroaminovinylation of olefins is an atom-economical domino reaction composed of two steps: 1) hydroformylation of an olefin and 2) in situ condensation of the resulting aldehyde with a secondary amine to yield an enamine.[29, 30] Surprisingly, this reaction is not well-developed to date, even though it allows the direct synthesis of unsaturated products under hydrogenation conditions.[31–34] Encouraged by the performance of 1,3-calixdiphosphites in the hydroformylation of styrene, we repeated this reaction, at 80 °C, in the presence of dibutylamine or piperidine (Scheme 7). GC analysis revealed the formation of enamines, aldehydes and amines, the linear regioisomer being the major product within each category. The propor-
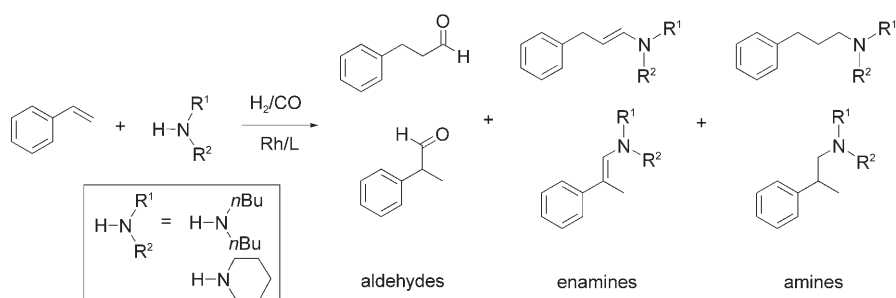
Scheme 7. Rhodium-catalysed hydroaminovinylation of styrene.

tion of enamines present was between 51 and 98 % (Table 4). As expected, the proportion of linear product increased in the order aldehyde < enamine < amine, this variation corresponding to the higher reactivity of the linear product both in the condensation with the amine and in the hydrogenation steps (Table 4, entry 4). Increasing the temperature from 80 °C to 130 °C favoured hydrogenation and consequently led to a lower proportion of enamines. At higher temperatures, the proportion of linear regioisomer was comparable for the three types of product (Table 4, entries 2–4). With all the diphosphites tested (**6**, **8**, **10**–**12**), the proportion of enamines was higher with piperidine than with dibutylamine, this difference reflecting both an easier condensation of piperidine with the aldehydes formed and a more difficult hydrogenation step. The highest linear enam-
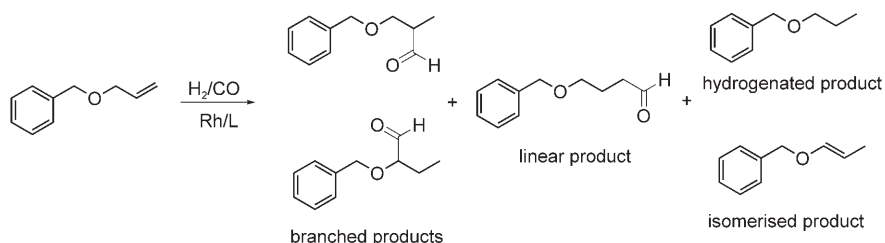
ine regioselectivity was obtained by using diphosphite **12**: 82.8 % with dibutylamine and 83.4 % with piperidine, the proportion of enamine being 69.4 and 83.8 %, respectively (Table 4, entries 11 and 12). The fluorenyl ligand **11** produced high amounts of enamine (ca. 98 %; Table 4, entries 9 and 10), but, as already seen in styrene hydroformylation with this ligand, the branched product was the major compound.

Allyl benzyl ether hydroformylation: 1,4-Butanediol is an important chemical intermediate used industrially as solvent and for the manufacture of plastics and fibers. A possible synthesis of this intermediate consists of hydroformylating an allyl ether. Butanediol is then produced after aldehyde reduction followed by a deprotection step.[35] In this synthetic route, the key step is the formation of the linear aldehyde with a high regioselectivity. Considering the excellent regioslectivities observed for 1,3-calixdiphosphites in the hydroformylation of octenes and styrene, we investigated the chemo- and regioselective hydroformylation of allyl benzyl ether. The products formed in this reaction are shown in Scheme 8.

Table 4. Rhodium-catalysed hydroaminovinylation of styrene using diphosphites **6**, **8**, **10**–**12**.[a]

	L	HNR₂	T [°C]	Conv[b] [%]	Aldehydes[b] [%] (l:b)	E-Enamines[b] [%] (l:b)	Amines[b] [%] (l:b)	PhEt[b] [%]
1	**6**	HNC₅H₁₀	130	100	3.9 (59.8:40.2)	80.5 (71.9:28.1)	13.1 (72.3:27.7)	2.5
2	**6**	HNBu₂	130	100	13.0 (76.8:23.2)	53.2 (75.8:24.2)	29.2 (75.1:24.9)	4.6
3	**6**	HNBu₂	105	99.5	13.6 (75.0:25.0)	62.5 (76.8:23.2)	19.2 (78.8:21.2)	4.2
4	**6**	HNBu₂	80	97.9	14.1 (67.4:32.6)	63.3 (71.4:28.6)	18.6 (80.4:19.4)	1.9
5	**8**	HNBu₂	130	92.6	11.8 (67.1:32.9)	51.5 (66.0:34.0)	9.4 (67.3:32.7)	19.9
6	**8**	HNC₅H₁₀	130	98.6	3.8 (71.1:28.9)	82.5 (68.9:31.1)	8.2 (80.1:19.9)	4.1
7	**10**	HNBu₂	130	99.4	8.7 (71.9:28.1)	80.3 (81.0:19.0)	6.7 (85.3:14.7)	3.7
8	**10**	HNC₅H₁₀	130	99.4	4.9 (78.7:21.3)	81.9 (79.0:21.0)	10.7 (92.9:7.1)	1.9
9	**11**	HNBu₂	130	99.0	traces	97.6 (28.9:71.1)	traces	1.4
10	**11**	HNC₅H₁₀	130	99.4	traces	98.4 (25.3:74.7)	traces	1.0
11	**12**	HNBu₂	130	99.7	7.5 (84.7:15.3)	69.4 (82.8:17.2)	21.8 (85.5:14.5)	1.0
12	**12**	HNC₅H₁₀	130	99.5	traces	83.8 (83.4:16.6)	13.4(85.0:15.0)	2.3

[a] Styrene (2.0 mmol), amine (2.4 mmol), L/Rh = 10, Rh(CO)₂(acac) (2 μmol, 0.1 mol %), toluene 30 mL, P(CO/H₂) = 8 bar, 24 h, incubation overnight at 80 °C under P(CO/H₂) = 10 bar. [b] Determined by GC and ¹H NMR spectroscopy.

As previously observed by Lazzaroni et al. using [Rh₄(CO)₁₂] as catalyst,[36] the proportion of linear hydroformylation products increased on raising the temperature. Thus, by using **8**, the 1:b ratio increased from 2.5 to 7.4 when the temperature was brought from 60 to 120 °C (Table 5, entries 2–5). A similar effect was observed by decreasing the reaction pressure (Table 5, entries 5, 6 and 9). Interestingly, the total amount of by-products (i.e. isomerised and hydrogenated allyl benzyl ether) did not change on varying the pressure, the temperature, or the reaction time (Table 5, entries 2–9). Under optimised conditions (120 °C, 10 bar CO/H₂), the linear aldehyde selectivity observed for the various diphosphites parallels the trend already observed in the hydroformylation of 1-octene, that is, the 1:b increases in the order **6** (5.0) < **8** (10.0) < **10** (15.7)

Scheme 8. Rhodium-catalysed hydroformylation of allyl benzyl ether.

Table 5. Rhodium-catalysed hydroformylation of allyl benzyl ether using diphosphites **6**, **8**, **10–12**.[a]

	L	T [°C]	$P(CO/H_2)$ [bar]	Conv[b] [%]	Product distribution[b]			1:b[c]
					Isomer. [%]	Hydrogen. [%]	Aldehydes [%]	
1	**6**	120	10	100	traces	1.2	98.8	5.0
2	**8**	60	20	100	4.9	8.4	86.7	2.5
3	**8**	80	20	100	3.1	7.3	89.6	3.7
4	**8**	100	20	100	2.6	8.8	88.6	5.7
5	**8**	120	20	100	traces	11.2	88.8	7.4
6	**8**	120	30	100	1.9	11.6	86.5	5.3
7[d]	**8**	120	10	95	7.9	4.1	83	9.9
8[e]	**8**	120	10	100	4.1	8.1	87.8	10.0
9	**8**	120	10	100	traces	11.8	88.2	9.9
10	**10**	120	10	100	16.2	13.8	70	15.7
11	**11**	120	10	100	traces	20.8	79.2	6.5
12	**12**	120	10	100	traces	traces	100	19.8
13	PPh$_3$	120	10	100	traces	–	100	1.6

[a] Allyl benzyl ether (0.8 mmol), L/Rh = 10, allyl benzyl ether/Rh = 400, toluene 15 mL, 24 h, incubation overnight at 80 °C under $P(CO/H_2)$ = 15 bar. [b] Conversion determined by ^{1}H NMR spectroscopy. [c] The 1:b aldehyde ratio takes into account all branched aldehydes, determined by ^{1}H NMR spectroscopy. [d] 2 h. [e] 4 h.

(Table 5, entries 1, 9 and 10). The most chemo- and regioselective tested ligand was the debutylated diphosphite **12**, for which only traces of by-products and a 1:b ratio of 19.8 were observed (Table 5, entry 12). This value compares with those obtained by Claver with tris-(o-tert-butylphenyl)phosphite.[37] For comparison, under similar catalytic conditions with PPh$_3$ as ligand, an 1:b ratio of 1.6 (Table 5, entry 13) was obtained.

Norbornene asymmetric hydroformylation: All the phosphites prepared in this study were optically pure compounds. We therefore assessed some of them, namely those in which the naphthyl units have an *S* conformation, in the asymmetric hydroformylation of norbornene. With only one exception reported by Huang,[38] rhodium-catalysed hydroformylation of norbornene with chiral ligands is known to give low optical induction (enantiomeric excess (*ee*) below 25 %),[39,40] the major compound being, in general, the *exo*-aldehyde. At 80 °C and under 20 bar of CO/H$_2$, the diphos-

Table 6. Rhodium-catalysed asymmetric hydroformylation of norbornene using diphosphites **6**, **8**, **10–12**.[a]

	L	T [°C]	$P(CO/H_2)$ [bar]	Conv[b] [%]	exo[b] [%]	endo[b] [%]	ee(exo)[c] [%]
1	**6**	80	20	100	99.0	1.0	6 (S)
2	**8**	80	20	100	82.7	17.3	16 (S)
3	**10**	80	20	100	91.3	8.7	18 (S)
4	**11**	80	20	100	100	traces	52 (R)
5	**11**	55	20	100	100	–	61 (R)
6	**11**	30	20	71.1	100	–	51 (R)
7	**11**	80	10	100	100	traces	22 (R)
8	**11**	55	10	57.9	100	–	41 (R)
9	**11**	30	10	35.7	100	–	5 (R)
10	**12**	80	20	100	97.5	2.5	6 (S)

[a] Norbornene (0.8 mmol), L/Rh = 10, norbornene/Rh = 200, toluene 12 mL, 24 h, incubation overnight at 80 °C under $P(CO/H_2)$ = 15 bar. [b] Conversion: determined by ^{1}H NMR spectroscopy. [c] Determined by GC using a chiral column (Chirasil-DEX CB, 25 m × 0.25 mm) after reduction into the alcohols.

phites **6**, **8**, **10** and **12** gave low *ee*'s (< 18 %; Table 6, entries 1–3 and 10). We noted that the *ee*'s increased on increasing the size of the secondary substituent (propyl < benzyl < methylnaphtalenyl). A marked *ee* increase was observed with the fluorenyl-substituted calixarene **11**; the *ee* here reaching 52 %. In this particular case, the absolute conformation (*R*) is opposite to the one obtained in all other tests (Table 6, entry 4). Lowering the temperature to 55 °C improved the *ee* to 61 % (Table 6, entry 5). Lower temperatures or operating at lower pressures led to lower *ee*'s (Table 6, entries 6–9).

Structure–regioselectivity relationship: Whatever the type of hydroformylation considered, all the diphosphites **6–10** resulted in remarkably high linear aldehyde regioselectivities. According to van Leeuwen, regioselectivity correlates essentially with the bite angle of the diphosphane used, rather than their mode of chelation (axial–axial or equatorial–axial), in the corresponding catalytic trigonal-bipyramidal intermediates (Scheme 1). For the ligands of the present study, the calixarene backbone imposes a separation between the two phosphorus-bonded oxygen atoms that leads to ligand bite angles close to 110°. A preliminary study revealed that reaction of [Rh(acac)(**8**)] with CO/H$_2$ (5 bar) led selectively to the [RhH(CO)$_2$(**8**)] complex, with both phosphorus atoms occupying equatorial sites.[41] MM2 calculations further showed that in such complexes, the rhodium centre is roughly sandwiched between two symmetrically situated naphthyl groups (Figure 3, right), thus creating a directional constraint for the incoming olefin. Note, the two planes forming the cleft that nests the metal are approximately parallel, but inclined by about 45° with respect to the apical axis of the metal centre. The high degree of metal embrace thus generated by the flat naphthyl substituents was confirmed by an X-ray diffraction study of the structurally related complex [Pd(η^3-allyl)(**6**)]PF$_6$ (P-M-P angle 107.5°).[19] The reason why the regioselectivity observed in octene hydroformylation may be significantly enhanced upon replacement of the propyl side groups by -CH$_2$Ph or -CH$_2$–naphthyl groups, that is, on increasing the hemispherical character of the ligand, is a matter of debate. Possibly these substituents favourably interact with the apical hydrido ligand so as to drive the hydride-transfer step towards a Rh–*n*-alkyl intermediate. They may also shape the pocket about the metal centre and thus favourably orientate the coordinated olefin. In contrast, the presence of fluorenyl groups (in ligand **11**) leads to a loss of selectivity. Clearly, in this case, the bulkiness of the secondary groups modifies the

shape of the naphthyl clip, which opens slightly (in keeping with MM2 calculations) as a result of steric interactions with the calixarene backbone as well as the binaphthyl groups. Overall, secondary substituents larger than a propyl group that can sterically interact only with the axial positions effectively increase the selectivity, while bulkier ones that induce a widening of the naphthyl pocket lead to a loss of selectivity. A remarkable result of this study concerns the hydroformylation of styrene, for which, unexpectedly, unusually large amounts of linear aldehyde were formed. The observed ligand behaviour parallels that obtained with **6–12** in the hydroformylation of octene and therefore suggest a late transition state for all these reactions. In the case of styrene, the formation of a Rh–allyl intermediate as drawn in Scheme 6 seems difficult to achieve for steric reasons. Thus, styrene probably coordinates the metal by forming a conventional π-complex before giving the "linear" alkyl complex [Rh(CO)$_2$(diphosphane)(PhCH$_2$CH$_2$)]. It is worth mentioning here that the embrace created by the hemispherical ligands **6–10** in the hydroformylation of styrene is particularly restrictive compared to that reported for other diphosphanes, notably Xantphos derivatives, and this may explain why somewhat higher regioselectivities were obtained with the former ligands.[10, 42]

Conclusion

In conclusion, the binol-derived calixphosphites **6–10** provide examples of hemispherical chelators able to efficiently drive olefin hydroformylation reactions towards the formation of "linear" products. Our findings hold for octenes (terminal and internal ones), styrene and allyl benzyl ether. The observed high regioselectivities essentially result from a combination of large ligand bite angles and the presence of phosphorus substituents able to form a cleft about the metal centre, hence creating in the catalytic intermediates the right structural constraint for the incoming olefin and/or the apical hydrido ligand. The presence of secondary calixarene substituents able to sterically interact with the apical positions of bipyramidal [RhH(CO)(olefin)(diphosphane)] intermediates can improve the regioselectivity, provided the substituents remain of moderate bulkiness; too large groups giving rise to strong steric interactions with the naphthyl groups and/or the calixarene backbone and therefore opening the cleft that entraps the olefin. The results obtained in asymmetric norbornene hydroformylation indicate that, unlike the regioselectivity, enantioselectivity cannot be directly correlated with a strong metal embrace. Nevertheless, it must be emphasised that the performance of the fluorenyl-substituted ligand **11**, giving *ee*'s reaching 61%, is to date only surpassed by a restricted number of diphosphanes. A logical extension of this work could consist in introducing chiral centres in the secondary groups and assessing if this has an impact on the enantioselectivity. Overall, this study shows, for the first time, that the use of hemispherical ligands, which may be regarded as ligands providing a "three-dimensional" metal embrace, can increase the regioselectivity in hydroformylation with respect to more classical diphosphanes having a large bite angle.

Experimental Section

5,11,17,23-Tetra-*tert*-butyl-25,27-di-9-fluorenyloxy-26,28-dihydroxycalix[4]arene (4: cone): 9-Bromofluorene (6.000 g, 24.5 mmol) was added to a suspension of *p-tert*-butylcalix[4]arene (7.564 g, 11.7 mmol) and K$_2$CO$_3$ (3.383 g, 24.5 mmol) in CH$_3$CN (150 mL). The reaction mixture was refluxed for 16 h, then the solvent was evaporated to dryness. The residue was dissolved in CH$_2$Cl$_2$ (200 mL) and the resulting suspension was treated with HCl (2 N, 200 mL). The aqueous layer was extracted with CH$_2$Cl$_2$ (2 × 100 mL). The organic layers were dried over MgSO$_4$, concentrated and the product was precipitated with methanol. The precipitate was filtered off and dried under vacuum to afford **4** as a white solid (9.080 g, 80%). ^{1}H NMR (300 MHz, CDCl$_3$): $\delta = 7.69$ (d, $^3J = 7.5$ Hz, 4H; *CH* arom), 7.43 (d, $^3J = 7.9$ Hz, 4H; *CH* arom), 7.42 (t, $^3J = 7.6$ Hz, 4H; *CH* arom), 7.14 (t, $^3J = 7.2$ Hz, 4H; *CH* arom), 7.01 (s, 4H; *CH* arom), 6.92 (s, 2H; O*H*), 6.85 (s, 4H; *CH* arom), 5.96 (s, 2H; OC*H*), 4.24 and 3.17 (AB system, $^2J = 13.1$ Hz, 8H; ArC*H$_2$*Ar), 1.26 (s, 18H; C-(C*H$_3$*)$_3$), 1.00 ppm (s, 18H; C(C*H$_3$*)$_3$); ^{13}C{^{1}H} NMR (75 MHz, CDCl$_3$): $\delta = 150.52$–119.78 (arom C's), 84.76 (s, O*C*H), 33.99 (s, *C*(CH$_3$)$_3$), 33.75 (s, *C*(CH$_3$)$_3$), 32.26 (s, Ar*C*H$_2$Ar), 31.66 (s, C(*C*H$_3$)$_3$), 31.04 ppm (s, C-(*C*H$_3$)$_3$); elemental analysis calcd (%) for C$_{70}$H$_{72}$O$_4$·0.5 MeOH (977.32 + 16.02): C 85.24, H 7.51; found: C 85.22, H 7.76.

(*S,S*)-5,11,17,23-Tetra-*tert*-butyl-25,27-dipropoxy-26,28-bis(1,1'-binaphthyl-2,2'-dioxyphosphanyloxy)calix[4]arene (6: cone): A suspension of calixarene **1** (1.760 g, 2.41 mmol) and NaH (60% dispersion in oil, 0.250 g, 6.25 mmol) in toluene (40 mL) was heated under reflux for 16 h. [(*S*)-(1,1'-Binaphthalene-2,2'-diyl)]chlorophosphite (1.750 g, 5.00 mmol) in toluene (20 mL) was added at 0°C and the reaction mixture was stirred for 2 h at room temperature. The crude reaction mixture was filtered through aluminium oxide. The aluminium oxide was washed with toluene (2 × 30 mL). The filtered solution was concentrated to about 5 mL. Addition of hexane (30 mL) gave a precipitate containing **6** and its partial cone isomer (^{31}P{^{1}H} NMR (121 MHz, C$_6$D$_6$) of partial cone calix: $\delta = 133.0$ (s) and 121.2 (s)). The mother liquor was then evaporated to dryness, affording **6** as pure white powder (1.690 g, 52%). ^{1}H NMR (300 MHz, C$_6$D$_6$): $\delta = 7.69$–7.27 (m, 15H; *CH* arom), 7.18–6.98 (m, 10H; *CH* arom), 6.95–6.75 (m, 7H; *CH* arom), 5.10 and 3.52 (AB system, $^2J = 13.0$ Hz, 4H; ArC*H$_2$*Ar), 5.00 and 3.00 (AB system, $^2J = 13.0$ Hz, 4H; ArC*H$_2$*Ar), 4.00–3.79 (m, 4H; OC*H$_2$*), 2.06–1.85 (m, 4H; CH$_2$C*H$_2$*), 1.26 (s, 18H; C-(C*H$_3$*)$_3$), 1.23 (s, 18H; C(C*H$_3$*)$_3$), 0.39 ppm (t, $^3J = 7.4$ Hz, 6H; CH$_2$C*H$_3$*); ^{13}C{^{1}H} NMR (75 MHz, C$_6$D$_6$): $\delta = 154.10$–121.98 (arom C's), 77.34 (s, O*C*H$_2$), 33.81 (s, *C*(CH$_3$)$_3$), 33.79 (s, *C*(CH$_3$)$_3$), 33.30 (s, Ar*C*H$_2$Ar), 31.96 (s, Ar*C*H$_2$Ar), 31.43 (s, C(*C*H$_3$)$_3$), 31.40 (s, C(*C*H$_3$)$_3$), 22.96 (s, *C*H$_2$CH$_3$), 9.44 ppm (s, CH$_2$*C*H$_3$); ^{31}P{^{1}H} NMR (121 MHz, C$_6$D$_6$): $\delta = 133.8$ ppm (s, O*P*(OAr)$_2$); elemental analysis calcd (%) for C$_{90}$H$_{90}$O$_8$P$_2$·2 toluene (1361.62 + 184.28): C 80.79, H 6.92; found: C 80.58, H 7.15.

FULL PAPER

(R,R)-5,11,17,23-Tetra-*tert*-butyl-25,27-dipropoxy-26,28-bis(1,1′-binaphth-yl-2,2′-dioxyphosphanyloxy)calix[4]arene (7: cone and 13: partial cone): A suspension of calixarene **1** (1.760 g, 2.41 mmol) and NaH (60% dispersion in oil, 0.250 g, 6.25 mmol) in toluene (40 mL) was heated under reflux for 16 h. [(R)-(1,1′-Binaphthalene-2,2′-diyl)]chlorophosphite (1.750 g, 5.00 mmol) in toluene (20 mL) was added at 0°C and the reaction mixture was stirred for 2 h at room temperature. The crude reaction mixture was filtered through aluminium oxide. The aluminium oxide was then washed with toluene (2×30 mL). The filtered solution was then concentrated to 5 mL and hexane (30 mL) was added precipitating **13** (0.295 g, 9%). The mother liquor was then evaporated to dryness, affording pure **7** as a white powder (2.034 g, 62%).

Cone calixarene 7: ^{1}H NMR (300 MHz, C$_6$D$_6$): $\delta = 7.66$–7.35 (m, 15 H; CH arom), 7.28 (d, $^3J = 8.8$ Hz, 2 H; CH arom), 7.14–6.99 (m, 8 H; CH arom), 6.91–6.77 (m, 7 H; CH arom), 5.10 and 3.51 (AB system, $^2J = 13.0$ Hz, 4 H; ArCH$_2$Ar), 5.00 and 3.00 (AB system, $^2J = 12.8$ Hz, 4 H; ArCH$_2$Ar), 3.97–3.81 (m, 4 H; OCH$_2$), 2.01–1.91 (m, 4 H; CH$_2$CH$_3$), 1.26 (s, 18 H; C(CH$_3$)$_3$), 1.23 (s, 18 H; C(CH$_3$)$_3$), 0.39 ppm (t, $^3J = 7.4$ Hz, 6 H; CH$_2$CH$_3$); ^{13}C{^{1}H} NMR (75 MHz, C$_6$D$_6$): $\delta = 154.09$–121.98 (arom C's), 77.34 (s, OCH$_2$), 33.79 (s, C(CH$_3$)$_3$), 33.29 (s, ArCH$_2$Ar), 31.95 (s, ArCH$_2$Ar), 31.40 (s, C(CH$_3$)$_3$), 22.96 (s, CH$_2$CH$_3$), 9.43 ppm (s, CH$_2$CH$_3$); ^{31}P{^{1}H} NMR (121 MHz, C$_6$D$_6$): $\delta = 133.7$ ppm (s, OP(OAr)$_2$); elemental analysis calcd (%) for C$_{90}$H$_{90}$O$_8$P$_2$·1.5 toluene (1361.62+138.21): C 80.48, H 6.85; found: C 80.52, H 6.97.

Partial cone calixarene 13: ^{1}H NMR (300 MHz, C$_6$D$_6$): $\delta = 7.83$–7.73 (3 H; CH arom), 7.67–7.50 (10 H; CH arom), 7.45–6.99 (12 H; CH arom), 6.91 (br t, $^3J = 7.7$ Hz, 2 H; CH arom), 6.79 (br t, $^3J = 7.5$ Hz, 1 H; CH arom), 6.74 (d, $^3J = 8.8$ Hz, 1 H; CH arom), 6.66 (br t, $^3J = 7.3$ Hz, 2 H; CH arom), 6.53 (d, $^4J = 2.1$ Hz, 1 H; m-ArH), 5.13 and 3.42 (AB system, $^2J = 12.5$ Hz, 2 H; ArCH$_2$Ar), 4.83 and 2.60 (AB system, $^2J = 13.0$ Hz, 2 H; ArCH$_2$Ar), 4.39 and 4.08 (AB system, $^2J = 14.0$ Hz, 2 H; ArCH$_2$Ar), 4.02 and 3.31 (AB system, $^2J = 13.4$ Hz, 2 H; ArCH$_2$Ar), 3.90–3.69 (3 H; OCH$_2$), 3.60–3.52 (m, 1 H; OCH$_2$), 2.12–2.04 (m, 2 H; CH$_2$CH$_3$), 1.89–1.82 (m, 2 H; CH$_2$CH$_3$), 1.70 (s, 9 H; C(CH$_3$)$_3$), 1.38 (s, 9 H; C(CH$_3$)$_3$), 1.32 (s, 9 H; C(CH$_3$)$_3$), 1.24 (s, 9 H; C(CH$_3$)$_3$), 0.80 (t, $^3J = 7.4$ Hz, 3 H; CH$_2$CH$_3$), 0.70 ppm (t, $^3J = 7.4$ Hz, 3 H; CH$_2$CH$_3$); ^{13}C{^{1}H} NMR (75 MHz, C$_6$D$_6$): $\delta = 154.19$–121.67 (arom C's), 76.60 (s, OCH$_2$), 76.35 (s, OCH$_2$), 39.25 (s, ArCH$_2$Ar), 36.76 (s, ArCH$_2$Ar), 34.16 (s, C(CH$_3$)$_3$), 34.01 (s, C(CH$_3$)$_3$), 33.75 (s, C(CH$_3$)$_3$), 33.07 (s, ArCH$_2$Ar), 32.12 (s, C(CH$_3$)$_3$), 31.93 (s, ArCH$_2$Ar), 31.51 (s, C(CH$_3$)$_3$), 31.47 (s, C(CH$_3$)$_3$), 31.42 (s, C(CH$_3$)$_3$), 23.82 (CH$_2$CH$_3$), 23.69 (CH$_2$CH$_3$), 10.18 (CH$_2$CH$_3$), 9.82 ppm (CH$_2$CH$_3$); ^{31}P{^{1}H} NMR (121 MHz, C$_6$D$_6$): $\delta = 133.1$ (s, OP(OAr)$_2$), 121.17 ppm (s, OP(OAr)$_2$); elemental analysis calcd (%) for C$_{90}$H$_{90}$O$_8$P$_2$·0.5 C$_6$H$_{14}$ (1361.62+43.09): C 79.52, H 6.96; found: C 79.51, H 6.97.

(S,S)-5,11,17,23-Tetra-*tert*-butyl-25,27-dibenzyloxy-26,28-bis(1,1′-binaphthyl-2,2′-dioxy-phosphanyloxy)calix[4]arene (8: cone): A suspension of calixarene **2** (2.000 g, 2.41 mmol) and NaH (60% dispersion in oil; 0.250 g, 6.25 mmol) in toluene (40 mL) was heated under reflux for 16 h. [(S)-(1,1′-Binaphthalene-2,2′-diyl)]chlorophosphite (1.750 g, 5.00 mmol) in toluene (20 mL) was added at 0°C and the reaction mixture was stirred for 2 h at room temperature. The crude reaction mixture was filtered through aluminium oxide. The aluminium oxide was then washed with toluene (2×30 mL). The filtered solution was concentrated to about 5 mL. Addition of hexane (30 mL) gave a precipitate containing **8** and its partial cone isomer (^{31}P{^{1}H} NMR (121 MHz, C$_6$D$_6$) of the partial cone isomer: $\delta = 133.5$ (s), 120.3 ppm (s)). Pure **8** was obtained by evaporation of the mother liquor (1.970 g, 56%); ^{1}H NMR (300 MHz, C$_6$D$_6$): $\delta = 7.69$–7.34 (m, 20 H; CH arom), 7.23–6.76 (m, 16 H; CH arom, m-ArH), 6.71 (d, $^4J = 2.4$ Hz, 4 H; m-ArH), 6.57 (d, $^4J = 2.4$ Hz, 2 H; m-ArH), 5.39 and 4.93 (AB system, $^2J = 11.8$ Hz, 4 H; CH$_2$Ph), 5.08 and 3.17 (AB system, $^2J = 11.8$ Hz, 4 H; ArCH$_2$Ar), 5.08 and 2.66 (AB system, $^2J = 11.8$ Hz, 4 H; ArCH$_2$Ar), 1.30 (s, 18 H; C(CH$_3$)$_3$), 1.01 ppm (s, 18 H; C(CH$_3$)$_3$); ^{13}C{^{1}H} NMR (75 MHz, C$_6$D$_6$): $\delta = 151.94$–121.43 (arom C's), 77.66 (s, OCH$_2$), 33.78 (s, C(CH$_3$)$_3$), 33.61 (s, C(CH$_3$)$_3$), 33.54 (s, ArCH$_2$Ar), 31.78 (s, ArCH$_2$Ar), 31.47 (s, C(CH$_3$)$_3$), 31.12 ppm (s, C(CH$_3$)$_3$); ^{31}P{^{1}H} NMR (121 MHz, C$_6$D$_6$): $\delta = 123.6$ ppm (s, OP(OAr)$_2$); elemental analysis calcd (%) for C$_{98}$H$_{90}$O$_8$P$_2$·toluene (1457.71+92.14): C 81.37, H 6.37; found: C 81.70, H 6.73.

(R,R)-5,11,17,23-Tetra-*tert*-butyl-25,27-dibenzyloxy-26,28-bis(1,1′-binaphthyl-2,2′-dioxyphosphanyloxy)calix[4]arene (9: cone): A suspension of calixarene **2** (2.000 g, 2.41 mmol) and NaH (60% dispersion in oil; 0.250 g, 6.25 mmol) in toluene (40 mL) was heated under reflux for 16 h at 110°C. [(R)-(1,1′-Binaphthalene-2,2′-diyl)]chlorophosphite (1.750 g, 5.00 mmol) in toluene (20 mL) was added at 0°C and the reaction mixture was stirred for 2 h at room temperature. The crude reaction mixture was filtered through aluminium oxide. The aluminium oxide was washed with toluene (2×30 mL). The filtered solution was concentrated to about 5 mL. Addition of hexane (30 mL) gave a precipitate containing **9** and its partial cone isomer (^{31}P{^{1}H} NMR (121 MHz, C$_6$D$_6$) of partial cone isomer: $\delta = 133.6$ (s), 120.0 ppm (s)). Pure **9** was obtained by evaporation of the mother liquor (2.636 g, 75%). ^{1}H NMR (300 MHz, C$_6$D$_6$): $\delta = 7.66$–7.39 (m, 20 H; CH arom), 7.17–6.77 (m, 14 H; CH arom), 6.79 (t, $^3J = 7.4$ Hz, 2 H; CH arom), 6.71 (d, $^4J = 2.0$ Hz, 4 H; m-ArH), 6.57 (d, $^4J = 2.2$ Hz, 2 H; m-ArH), 5.40 and 4.93 (AB system, $^2J = 11.8$ Hz, 4 H; CH$_2$Ph), 5.08 and 3.17 (AB system, $^2J = 13.0$ Hz, 4 H; ArCH$_2$Ar), 5.08 and 2.65 (AB system, $^2J = 13.0$ Hz, 4 H; ArCH$_2$Ar), 1.30 (s, 18 H; C(CH$_3$)$_3$), 1.01 ppm (s, 18 H; C(CH$_3$)$_3$); ^{13}C{^{1}H} NMR (75 MHz, C$_6$D$_6$): $\delta = 151.94$–121.43 (arom C's), 77.68 (s, OCH$_2$), 33.81 (s, C(CH$_3$)$_3$), 33.64 (s, C(CH$_3$)$_3$), 33.55 (s, ArCH$_2$Ar), 31.77 (s, ArCH$_2$Ar), 31.51 (s, C(CH$_3$)$_3$), 31.17 ppm (s, C(CH$_3$)$_3$); ^{31}P{^{1}H} NMR (121 MHz, C$_6$D$_6$): $\delta = 123.6$ ppm (s, OP(OAr)$_2$); elemental analysis calcd (%) for C$_{98}$H$_{90}$O$_8$P$_2$·2 C$_7$H$_8$ (1457.71+184.28): C 81.93, H 6.51; found: C 81.95, H 6.71.

(S,S)-5,11,17,23-Tetra-*tert*-butyl-25,27-di-2-methylnaphthalenyloxy-26,28-bis(1,1′-binaphthyl-2,2′-dioxyphosphanyloxy)calix[4]arene (10: cone): A suspension of calixarene **3** (0.847 g, 0.91 mmol) and NaH (60% dispersion in oil; 0.095 g, 2.37 mmol) in toluene (20 mL) was heated under reflux for 16 h. [(S)-(1,1′-Binaphthalene-2,2′-diyl)]chlorophosphite (0.670 g, 1.91 mmol) in toluene (10 mL) was added at 0°C and the reaction mixture was stirred for an additional 2 h at room temperature. The crude reaction mixture was filtered through aluminium oxide. The aluminium oxide was washed with toluene (2×15 mL). The filtered solution and washings were evaporated to dryness under reduced pressure. The resulting solid was then dissolved in hot hexane. The solution was cooled at −16°C, yielding microcrystals of **10** (0.652 g, 46% yield) as a white powder. The mother liquor contained **10** as well as its partial cone isomer (^{31}P{^{1}H} NMR (121 MHz, C$_6$D$_6$): $\delta = 133.7$ (s), 119.1 ppm (s)); Compound **10**: ^{1}H NMR (300 MHz, C$_6$D$_6$): $\delta = 8.06$ (s, 2 H; CH arom), 7.70 (dd, $^3J = 8.4$ Hz, $^4J = 1.3$ Hz, 2 H; CH arom), 7.55–7.32 (m, 16 H; CH arom), 7.23 (d, $^3J = 8.7$ Hz, 2 H; CH arom), 7.13–6.85 (m, 16 H; CH arom), 6.74 (t, $^3J = 7.8$ Hz, 2 H; CH arom), 6.70 (d, $^4J = 2.0$ Hz, 2 H; m-ArH), 6.65 (d, $^4J = 2.2$ Hz, 2 H; m-ArH), 6.55 (d, $^4J = 2.2$ Hz, 2 H; m-ArH), 5.42 and 5.00 (AB system, $^2J = 11.9$ Hz, 4 H; OCH$_2$), 5.21 and 3.12 (AB system, $^2J = 13.0$ Hz, 4 H; ArCH$_2$Ar), 5.13 and 2.71 (AB system, $^2J = 13.0$ Hz, 4 H; ArCH$_2$Ar), 1.25 (s, 18 H; C(CH$_3$)$_3$), 0.97 ppm (s, 18 H; C(CH$_3$)$_3$); ^{13}C{^{1}H} NMR (75 MHz, C$_6$D$_6$): $\delta = 152.22$–121.34 (arom C's), 77.96 (s, OCH$_2$), 33.76 (s, C(CH$_3$)$_3$), 33.61 (s, C(CH$_3$)$_3$), 33.49 (s, ArCH$_2$Ar), 31.75 (s, ArCH$_2$Ar), 31.44 (s, C(CH$_3$)$_3$), 31.09 ppm (s, C(CH$_3$)$_3$); ^{31}P{^{1}H} NMR (121 MHz, C$_6$D$_6$): $\delta = 122.0$ ppm (s, OP(OAr)$_2$); elemental analysis calcd (%) for C$_{106}$H$_{94}$O$_8$P$_2$ (1557.86): C 81.72, H 6.08; found: C 81.63, H 6.13.

(S,S)-5,11,17,23-Tetra-*tert*-butyl-25,27-di-9-fluorenyloxy-26,28-bis(1,1′-binaphthyl-2,2′-dioxyphosphanyloxy)calix[4]arene (11: cone and 14: partial cone): A suspension of calixarene **4** (2.350 g, 2.41 mmol) and NaH (60% dispersion in oil; 0.250 g, 6.25 mmol) in toluene (40 mL) was heated under reflux for 16 h. [(S)-(1,1′-Binaphthalene-2,2′-diyl)]chlorophosphite (1.750 g, 5.00 mmol) in toluene (20 mL) was added at 0°C and the reaction mixture was stirred for 2 h at room temperature. The crude reaction mixture was filtered through aluminium oxide and the aluminium layer was washed with toluene (2×30 mL). The filtered solution and washings were concentrated to about 5 mL. Addition of petroleum ether (50 mL) afforded crystals of **14** (partial cone) (0.350 g, 9%). The mother liquor was then evaporated to dryness. The residue was treated with hot hexane. The thus obtained suspension was filtered through a glass fritt, then evaporated to dryness, yielding pure **11** (cone) (0.530 g, 14%)

Cone calixarene 11: ^{1}H NMR (300 MHz, C$_6$D$_6$): $\delta = 8.76$ (d, $^3J = 7.5$ Hz, 2 H; CH arom), 7.65–7.60 (m, 4 H; CH arom), 7.55–7.46 (m, 10 H; CH arom), 7.24 (d, $^3J = 8.6$ Hz, 2 H; CH arom), 7.16–6.99 (m, 12 H; CH

arom), 6.87 (t, $^3J=7.5$ Hz, 2H; CH arom), 6.80–6.69 (m, 6H; CH arom), 6.61 (t, $^3J=7.7$ Hz, 2H; CH arom), 6.50 (d, $^3J=7.5$ Hz, 2H; CH arom), 6.41 (brs, 4H; CH arom), 6.17–6.14 (m, 4H; CH arom and OCH), 5.68 and 3.32 (AB system, $^2J=12.6$ Hz, 4H; ArCH_2Ar), 5.04 and 2.55 (AB system, $^2J=13.2$ Hz, 4H; ArCH_2Ar), 1.12 (s, 18H; C(CH_3)$_3$), 1.04 ppm (s, 18H; C(CH_3)$_3$); ^{13}C{^{1}H} NMR (75 MHz, C$_6$D$_6$): $\delta=151.51$–119.42 (arom C's), 84.20 (s, OCH), 33.76 (s, C(CH$_3$)$_3$), 33.61 (s, C(CH$_3$)$_3$), 33.37 (s, ArCH$_2$Ar), 32.92 (s, ArCH$_2$Ar), 31.24 (s, C(CH$_3$)$_3$), 31.19 ppm (s, C-(CH$_3$)$_3$); ^{31}P{^{1}H} NMR (121 MHz, C$_6$D$_6$): $\delta=118.7$ ppm (s, OP(OAr)$_2$); elemental analysis calcd (%) for C$_{110}$H$_{94}$O$_8$P$_2$ (1605.90): C 82.27, H 5.90; found: C 82.24, H 5.71.

Partial cone calixarene **14**: ^{1}H NMR (300 MHz, C$_6$D$_6$): $\delta=8.42$ (d, $^3J=7.4$ Hz, 1H; CH arom), 7.74–6.73 (m, 1H; CH arom), 6.63–6.58 (m, 2H; CH arom), 6.48 (brs, 2H; CH arom), 6.39 (d, $^3J=8.8$ Hz, 1H; CH arom), 6.30 (d, $^3J=7.5$ Hz, 1H; CH arom), 5.98 (s, 1H; OCH), 5.68 (s, 1H; OCH), 5.32 and 3.21 (AB system, $^2J=12.4$ Hz, 2H; ArCH_2Ar), 4.77 and 2.45 (AB system, $^2J=13.4$ Hz, 2H; ArCH_2Ar), 4.00 and 3.42 (AB system, $^2J=13.7$ Hz, 2H; ArCH_2Ar), 3.95 and 3.21 (AB system, $^2J=13.9$ Hz, 2H; ArCH_2Ar), 1.41 (s, 9H; C(CH_3)$_3$), 1.35 (s, 9H; C(CH_3)$_3$), 1.29 (s, 9H; C-(CH$_3$)$_3$), 1.14 ppm (s, 9H; C(CH_3)$_3$); ^{13}C{^{1}H} NMR (75 MHz, C$_6$D$_6$): $\delta=$152.16–119.37 (arom C's), 83.50 (s, OCH), 82.26 (s, OCH), 39.21 (s, ArCH$_2$Ar), 36.90 (s, ArCH$_2$Ar), 34.13 (s, C(CH$_3$)$_3$), 33.90 (s, C(CH$_3$)$_3$), 33.80 (s, C(CH$_3$)$_3$), 33.57 (s, C(CH$_3$)$_3$), 32.74 (s, ArCH$_2$Ar), 32.34 (s, ArCH$_2$Ar), 31.86 (s, C(CH$_3$)$_3$), 31.83 (s, C(CH$_3$)$_3$), 31.57 (s, C(CH$_3$)$_3$), 31.20 ppm (s, C(CH$_3$)$_3$); ^{31}P{^{1}H} NMR (121 MHz, C$_6$D$_6$): $\delta=133.4$ (s, OP-(OAr)$_2$), 119.46 ppm (s, OP(OAr)$_2$); elemental analysis calcd (%) for C$_{110}$H$_{94}$O$_8$P$_2$·toluene (1605.90+92.14): C 82.76, H 6.05; found: C 82.84, H 5.88. Crystals (colourless) of **14** suitable for X-ray diffraction were obtained by slow diffusion of petroleum ether into a solution of a mixture of **11** and **14** in toluene (see above, preparation of **14**).

(S,S)-25,27-Dipropyloxy-26,28-bis(1,1′-binaphthyl-2,2′-dioxyphosphany-loxy)calix[4]arene (12: cone): A suspension of calixarene **5** (1.220 g, 2.41 mmol) and NaH (60% dispersion in oil; 0.250 g, 6.25 mmol) in toluene (40 mL) was heated under reflux for 16 h. [(S)-(1,1′-Binaphthalene-2,2′-diyl)]chlorophosphite (1.750 g, 5.00 mmol) in toluene (20 mL) was added at 0°C and the reaction mixture was stirred for 2 h at room temperature. The crude reaction mixture was filtered through aluminium oxide. The aluminium layer was washed with toluene (2×30 mL). The filtered solution and the washings were concentrated to about 5 mL and petroleum ether was added (50 mL). After 3 days, colourless crystals of pure **12** were collected (0.580 g, 21%). As revealed by NMR spectroscopy, the mother liquor contained several other products which were not isolated. ^{1}H NMR (300 MHz, C$_6$D$_6$): $\delta=7.63$–7.37 (m, 18H; CH arom), 7.29 (d, $^3J=8.7$ Hz, 2H; CH arom), 6.89 (t, $^3J=7.6$ Hz, 2H; CH arom), 6.81 (d, $^3J=8.1$ Hz, 4H; CH arom), 6.37–6.61 (m, 8H; CH arom), 6.46 (d, $^3J=7.1$ Hz, 2H; CH arom), 5.03 and 3.44 (AB system, $^2J=13.6$ Hz, 4H; ArCH_2Ar), 4.91 and 2.97 (AB system, $^2J=13.6$ Hz, 4H; ArCH_2Ar), 3.83–3.67 (m, 4H; OCH_2), 1.84–1.64 (m, 4H; CH_2CH$_3$), 0.38 ppm (t, $^3J=7.3$ Hz, 6H; CH_2CH_3); ^{13}C{^{1}H} NMR (75 MHz, C$_6$D$_6$): $\delta=156.87$–121.92 (arom C's), 77.03 (s, OCH$_2$), 32.66 (s, ArCH$_2$Ar), 31.43 (s, ArCH$_2$Ar), 22.97 (s, CH$_2$CH$_3$), 9.57 ppm(s, CH$_2$CH$_3$); ^{31}P{^{1}H} NMR (121 MHz, C$_6$D$_6$): $\delta=134.4$ ppm (s, OP(OAr)$_2$); elemental analysis calcd (%) for C$_{74}$H$_{58}$O$_8$P$_2$·1.5 toluene (1137.22+138.20): C 79.57, H 5.53; found: C 79.65, H 5.62. Crystals of cone-**12** (colourless) suitable for X-ray diffraction were obtained by slow diffusion of petroleum ether into the reaction mixture after filtration over aluminium oxide.

(S,S)-Acetylacetato-{5,11,17,23-tetra-*tert*-butyl-25,27-dibenzyloxy-26,28-bis(1,1′-binaphthyl-2,2′-dioxyphosphanyloxy)calix[4]arene}rhodium(I) (15): A solution of [Rh(acac)(CO)$_2$] (0.088 g, 0.34 mmol) in CH$_2$Cl$_2$ (5 mL) was added to a solution of **8** (0.500 g, 0.34 mmol) in CH$_2$Cl$_2$ (250 mL). The resulting solution turned from green to yellow within a few minutes. After 16 h, the solvent was evaporated to dryness. The yellow solid which was washed with cold hexane (−78°C) to afford **15** (0.427 g, (75%). IR (KBr): $\tilde{\nu}=1518$, 1578 cm^{-1} (acac); ^{1}H NMR (300 MHz, CDCl$_3$): $\delta=7.95$ (d, $^3J=6.5$ Hz, 4H; CH arom), 7.72 (d, $^3J=8.1$ Hz, 2H; CH arom), 7.63 (d, $^3J=8.1$ Hz, 2H; CH arom), 7.57–7.49 (m, 4H; CH arom), 7.39 (d, $^3J=8.9$ Hz, 2H; CH arom), 7.33–6.99 (m, 20H; CH arom), 6.82 (d, $^4J=2.2$ Hz, 2H; m-ArH), 6.49 (d, $^4J=2.1$ Hz, 2H; m-

ArH), 6.29 (d, $^4J=2.0$ Hz, 2H; m-ArH), 6.23 (d, $^4J=2.0$ Hz, 2H; m-ArH), 5.69 and 5.02 (AB syste, $^2J=11.9$ Hzm, 4H; CH_2Ph), 5.22 and 3.00 (AB system, $^2J=13.0$ Hz, 4H; ArCH_2Ar), 5.22 and 2.81 (AB system, $^2J=13.0$ Hz, 4H; ArCH_2Ar), 4.56 (s, 1H; CH-acac), 1.03 (s, 18H; C(CH_3)$_3$), 0.76 (s, 18H; C(CH_3)$_3$), 0.30 ppm (s, 6H; CH_3-acaa); ^{13}C{^{1}H} NMR (75 MHz, CDCl$_3$): $\delta=183.16$ (s, CO-acac), 152.23–120.00 (arom C's), 97.99 (s, CH-acac), 77.79 (s, OCH$_2$), 33.60 (s, ArCH$_2$Ar), 33.59 (s, C-(CH$_3$)$_3$), 33.57 (s, C(CH$_3$)$_3$), 33.51 (s, ArCH$_2$Ar), 31.44 (s, C(CH$_3$)$_3$), 31.03 (s, C(CH$_3$)$_3$), 25.06 ppm (s, CH$_3$-acac); ^{31}P{^{1}H} NMR (121 MHz, CDCl$_3$): $\delta=126.4$ ppm (d, J(P,Rh)$=326.7$ Hz, OP(OAr)$_2$); MS (ESI TOF): m/z: 1682.57 [M+Na]$^+$, 1659.59 [M]$^+$, 1559.54 [M−C$_5$H$_7$O$_2$]$^+$ expected isotopic profiles; elemental analysis calcd (%) for C$_{103}$H$_{97}$O$_{10}$P$_2$Rh: C 74.54, H 5.89; found: C 74.61, H 5.88.

(S,S)-Acetylacetato-{5,11,17,23-tetra-*tert*-butyl-25,27-di-9-fluorenyloxy-26,28-bis(1,1′-binaphthyl-2,2′-dioxyphosphanyloxy)calix[4]arene}rhodi-um(I) (16): This complex was prepared according to the procedure described above for **15**, but starting from ligand **11**. Yield: 70%; IR (KBr): $\tilde{\nu}=1517$, 1579 cm^{-1} (acac); ^{1}H NMR (300 MHz, CDCl$_3$): $\delta=9.47$ (d $^3J=7.6$ Hz,, 2H; CH arom), 7.82 (d, $^3J=7.4$ Hz, 2H; CH arom), 7.66 (d, $^3J=7.5$ Hz, 4H; CH arom), 7.59–7.51 (m, 6H; CH arom), 7.44 (d, $^3J=8.9$ Hz, 2H; CH arom), 7.29–6.91 (m, 22H; CH arom), 6.53 (d, $^4J=2.1$ Hz, 2H; m-ArH), 6.45 (d, $^4J=2.1$ Hz, 2H; m-ArH), 6.24 (d, $^4J=2.2$ Hz, 2H; m-ArH), 6.21 (d, $^3J=7.6$ Hz, 2H; CH arom), 6.06 (s, 2H; OCH), 5.89 (d, $^3J=8.8$ Hz, 2H; CH arom), 5.86 and 3.75 (AB system, $^2J=12.3$ Hz, 4H; ArCH_2Ar), 4.97 and 2.46 (AB system, $^2J=13.4$ Hz, 4H; ArCH_2Ar), 4.47 (s, 1H; CH-acac), 0.91 (s, 18H; C(CH_3)$_3$), 0.20 ppm (s, 6H; CH_3-acac); ^{13}C{^{1}H} NMR (75 MHz, CDCl$_3$): $\delta=182.39$ (s, CO-acac), 152.00–119.16 (arom C's), 97.35 (s, CH-acac), 84.68 (s, OCH), 34.28 (s, ArCH$_2$Ar), 33.83 (s, C(CH$_3$)$_3$), 33.64 (s, ArCH$_2$Ar), 31.24 (s, C(CH$_3$)$_3$), 31.20 (s, C(CH$_3$)$_3$), 24.65 ppm (s, CH$_3$-acac); ^{31}P{^{1}H} NMR (121 MHz, CDCl$_3$): $\delta=126.1$ ppm (d, J(P,Rh)$=326.7$ Hz, OP(OAr)$_2$); MS (ESI TOF): m/z: 1806.59 [M]$^+$, 1707.55 [M−C$_5$H$_7$O$_2$]$^+$ expected isotopic profiles; elemental analysis calcd (%) for C$_{115}$H$_{101}$O$_{10}$P$_2$Rh: C 76.40, H 5.63; found: C 76.23, H 5.63.

Crystal structure of 12·toluene: $M_r=1229.28$, orthorhombic, $P2_1$, $a=11.857(2)$, $b=15.103(2)$, $c=34.846(4)$ Å, $V=6240.1(2)$ Å^3, $Z=4$, $\rho_{calcd}=1.308$ mg m^{-3}, $\mu=1.32$ cm^{-1}, $F(000)=1796$, $T=120(1)$ K. Data were collected on a Oxford Diffraction Xcalibur Saphir 3 diffractometer (graphite Mo$_{K\alpha}$ radiation, $\lambda=0.71073$ Å). The structure was solved with SIR-97,[47] which revealed the non-hydrogen atoms of the molecule. After anisotropic refinement, many hydrogen atoms were found with a Fourier difference analysis. The whole structure was refined with SHELX-97[48] and full-matrix least-square techniques (use of F^2; x, y, z, β_{ij} for P, C and O atoms, x, y, z in riding mode for H atoms); 820 variables and 5070 observations with $I>2.0\sigma(I)$; calcd $w=1/[\sigma^2(F_o^2)+(0.039\,P)^2]$ in which $P=(F_o^2+2F_c^2)/3$. R1$=0.070$, wR2$=0.0127$, $S_w=0.740$, $\Delta\rho<0.56$ e Å^{-3}, Flack parameter$=-0.02(2)$.

Crystal structure of 14·toluene: $M_r=1697.93$, monoclinic, space group $P2_1$, $a=11.9307(7)$, $b=14.7771(7)$, $c=26.7373(9)$ Å, $\beta=91.178(3)°$, $V=4712.8(4)$ Å^3, $Z=4$, $\rho_{calcd}=1.197$ mg m^{-3}, $\mu=1.06$ cm^{-1}, $F(000)=1796$, $T=110(1)$ K. Data were collected on a Oxford Diffraction Xcalibur Saphir 3 diffractometer (graphite Mo$_{K\alpha}$ radiation, $\lambda=0.71073$ Å). The structure was solved with SIR-97,[47] which revealed the non-hydrogen atoms of the molecule. After anisotropic refinement, many hydrogen atoms were found with a Fourier difference analysis. The whole structure was refined with SHELX-97[48] and full-matrix least-square techniques (use of F^2; x, y, z, β_{ij} for P, C and O atoms, x, y, z in riding mode for H atoms); 1144 variables and 10357 observations with $I>2.0\sigma(I)$; calcd $w=1/[\sigma^2(F_o^2)+(0.023\,P)^2]$ in which $P=(F_o^2+2F_c^2)/3$. R1$=0.041$, wR2$=0.063$, $S_w=0.731$, $\Delta\rho<0.25$ e Å^{-3}, Flack parameter$=0.00(6)$.

CCDC-622309 (**12**·toluene) and CCDC-609569 (**14**·toluene) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

General procedure for the hydroformylation experiments: The hydroformylation experiments were carried out in a glass-lined, 100 mL stainless steel autoclave containing a magnetic stirring bar. In a typical run, the autoclave was charged under nitrogen with of a solution of [Rh-

(acac)(CO)₂] (0.0005 g, 0.002 mmol) in toluene (1.0 mL), a solution of ligand in toluene (10 mL) and toluene (4.5 mL). Once closed, the autoclave was flushed twice with syngas (CO/H₂ 1:1 v/v), pressurised with a CO/H₂ mixture and heated. After 16 h, the autoclave was depressurised, olefin and, if necessary, internal standard (decane) were added to the reaction mixture. The autoclave was then heated and pressurised. The progress of the reaction was checked by monitoring the pressure decrease. During the experiments, several samples were taken and analysed by GC or ¹H NMR spectroscopy.

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