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FULL PAPER

Diphosphines based on an inherently chiral calix[4]arene scaffold: synthesis and use in enantioselective catalysis

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Received 12th February 2001, Accepted 12th June 2001
First published as an Advance Article on the web 8th August 2001

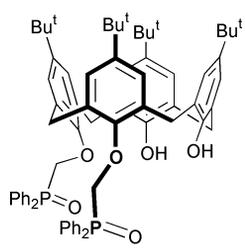
A series of calix[4]arenes bearing two phosphorus pendent groups *p*-Bu^t-calix[4]arene-25,26-[$CH_2P(O)Ph_2$]$_2$-27-(OR^1)-28-(OR^2) ($R^{1\text{ or }2}$ = CH_2CO_2Et, $R^{2\text{ or }1}$ = H, **2**; R^1 = R^2 = CH_2CO_2Et, **3**; $R^{1\text{ or }2}$ = C(O)Ocholesteryl, $R^{2\text{ or }1}$ = H, **4**; R^1 = R^2 = C(O)Ocholesteryl, **5**; $R^{1\text{ or }2}$ = (*R*)-$CH_2C(O)NHCMe(Ph)H$, $R^{2\text{ or }1}$ = H, **6**) and *p*-Bu^t-calix[4]arene-25,26-(CH_2PPh_2)$_2$-27-(OR^1)-28-(OR^2) (R^1 = (*R*)-$CH_2C(O)NHCMe(Ph)$ H, R^2 = H, **7**; R^1 = (*R*)-$CH_2C(O)NHCMe(Ph)H$, R^2 = $SiMe_3$, **8**; R^1 = (*R*)-$CH_2C(O)NHCMe(Ph)H$, R^2 = (*R*)-$CH_2C(O)NHCMe(Ph)H$, **10**) have been synthesised. The enantiomerically pure calixarenes **7**, **8** and **10** having an AABC substitution pattern are inherently chiral. Reaction of the latter three diphosphines with [Pd(2-Me-allyl)(THF)$_2$]BF_4 (THF = tetrahydrofuran) afforded the chelate complexes [Pd(2-Me-allyl)(diphosphine)]BF_4 **11**–**13**, respectively, while reaction with [Rh(NBD)(THF)$_2$]BF_4 (NBD = norbornadiene) resulted in quantitative formation of the complexes [Rh(NBD)(diphosphine)]BF_4 **14**–**16**, respectively. As a result of allyl rotation, the palladium complexes **11**–**13** exist in solution as two interconverting species. These complexes efficiently catalyse the alkylation of 1,3-diphenylprop-2-enyl acetate with dimethyl malonate, the turnovers being *ca.* 30 h^{-1}. Enantioselectivity was shown to depend on the size difference between the B and C substituents. Thus, while virtually no induction was observed with the chiral calixarene **10** bearing two identical substituents, ee's of 45% and 67% respectively were observed with **12** and **11**, which have a more marked dissymmetry. Similar trends were observed in the catalytic hydrogenation of dimethyl itaconate with the rhodium complexes **14**–**16**, leading to ee's of 48%, 25% and 0%, respectively. Related chiral calixarenes in which the two phosphine arms occupy proximal instead of distal phenolic positions were found to be considerably less effective in catalysis of both allylic alkylation and hydrogenation.

Introduction

Calix[4]arenes are remarkable building blocks which have become useful in many areas of synthetic chemistry.[1,2] This development mainly rests on the particular architecture of the calix[4]arene framework. The latter provides a circular platform which permits several functional groups to be oriented in the same direction and thus to generate sophisticated micro-environments organized around a central core.[3] Such polytopic ligands have found many practical applications, notably as selective cation binders,[4–6] molecular sensors,[7–10] and container molecules[11,12] as well as highly ordered materials.[13–15]

Our recent work in this field has been centred on the design and synthesis of P(III)-functionalised calix[4]arenes and their use in transition metal chemistry.[16–20] We have described some chiral phosphanes which were obtained from calix[4]arenes to which a chiral moiety had been attached on the lower rim prior to P(III)-functionalisation.[21] In terms of enantioselectivity the catalytic properties of these ligands were rather disappointing, presumably because the asymmetric carbon atoms were located too far from the catalytic centre and/or because the chiral dangling groups were not fixed in a rigid manner with respect to the calix scaffold. In the present work we report on the synthesis and catalytic properties of new optically active phosphines built on *inherently chiral*[22] calix[4]arene units possessing an AABC substitution pattern. We also describe the X-ray structure of an enantiomerically pure di(phosphine oxide) based on such a framework.

Although inherently chiral calixarenes have been known for some time[23–25] and have also been resolved in several instances,[26,27] catalytic properties of ligands derived from such structures remain unreported. The ligands described herein were all obtained by lower-rim functionalisation of the previously described di(phosphine oxide) **1**.[20] The conformational assignments were made using empirical NMR methods which are now well-established.[20,28] In the present paper, the phenolic substituents without a phosphorus atom will be termed auxiliary groups. It should be mentioned here that, to date, calixarene-derived phosphanes have only sparingly been used for catalytic purposes.[29–35]



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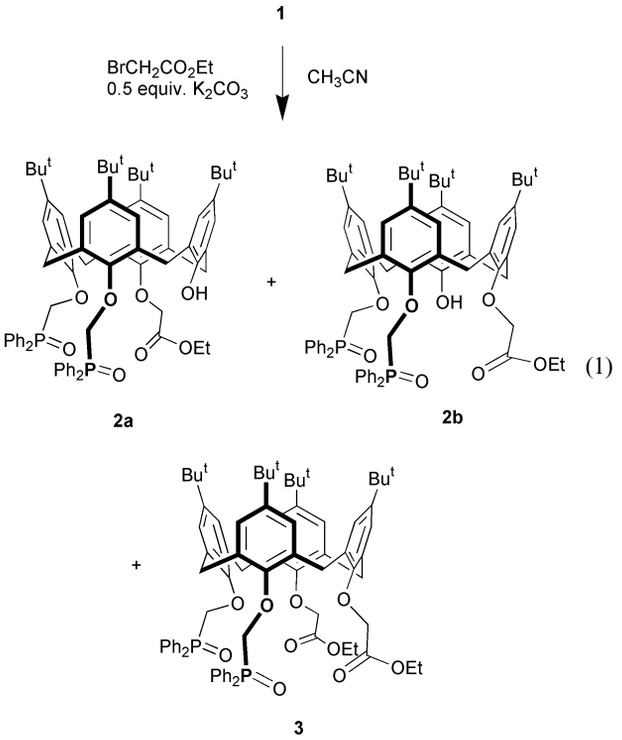
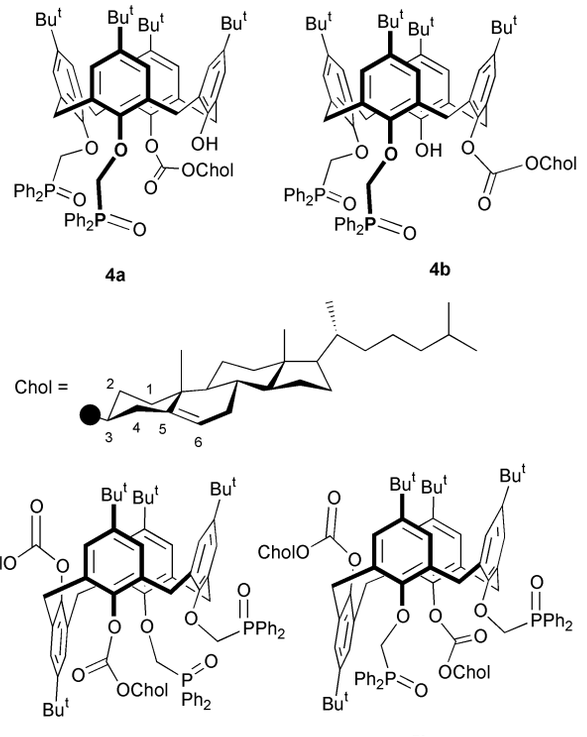
Results and discussion

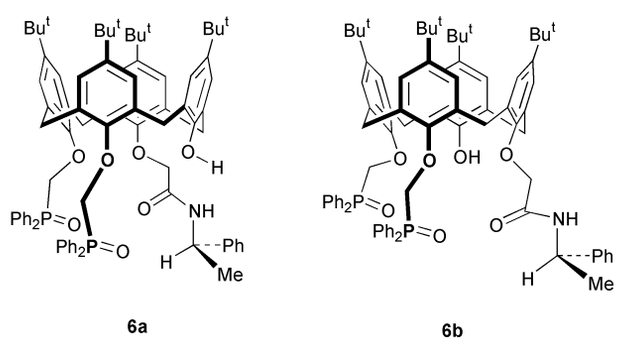
Synthesis of chiral ligands

Substitution of a single phenolic oxygen in **1** generates an inherently chiral calix[4]arene. The possibility of achieving monofunctionalisation was first assessed by carrying out the alkylation reaction shown in eqn. (1), using 1.0 equiv. of $BrCH_2CO_2Et$ and 0.5 equiv. of K_2CO_3. This reaction afforded the monoalkylated compounds **2a** and **2b** (racemic mixture) in 44% yield together with small amounts of the dialkylated derivative **3** (10%). The racemate **2** was separated from **3** by

 DOI: 10.1039/b101369f







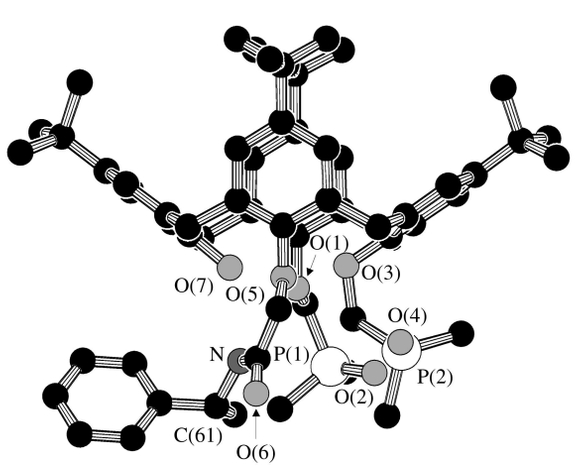


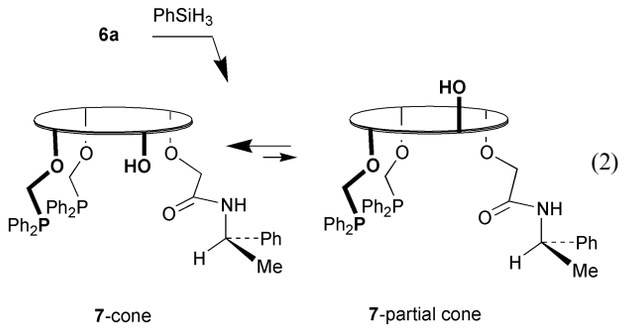
Fig. 1 Molecular structure of the chiral di(phoshine oxide) **6a** (for clarity only the *ipso* carbon atoms of the PPh_2 groups are shown).

column chromatography. As could be unambiguously deduced from the ^1H and ^{13}C NMR spectra, compounds **2** and **3** adopt a cone conformation (see Experimental section). Attempts to improve the yield of the monofunctionalised compound were unsuccessful.

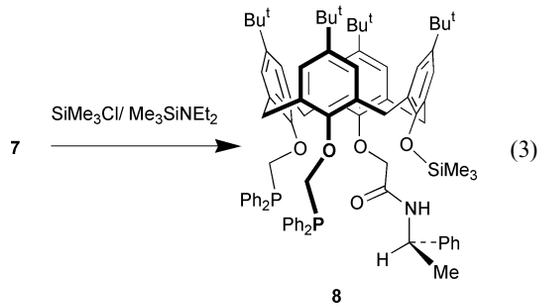
Higher yields were obtained in the monofunctionalisation of **1** using cholesteryl chloroformate–NEt_3. The carbonates thus formed, **4a** and **4b**, were obtained in *ca.* 70% yield. Both isomers contain a chiral cholesteryl fragment as part of an inherently chiral calix[4]arene and hence are diastereomers. As inferred from the ^{31}P NMR spectrum, the two diastereomers were formed in a *ca.* 1 : 1 ratio. The NMR data are again in keeping with cone conformations. Separation of these two isomers by column chromatography proved to be never better than partial, their R_f values being very close. Note, during the synthesis of **4a/4b** (**4**), small amounts of the dicholesteryl compounds **5a/5b** (diastereomeric mixture **5**) were also formed. They could be separated from **4** but again the two components **5a** and **5b** could not be separated from each other. The formation of both diastereomers (*ca.* 1 : 1 ratio) was deduced from the ^1H NMR spectrum which shows two distinct ABX systems for one CH_2 group. The assignment of a partial cone structure to **5** was made on the basis of the ^1H and ^{13}C spectra. The former shows four AB systems for the $ArCH_2$ groups, two of them displaying a large AB separation ($\Delta\delta$ = *ca.* 1.8 ppm), the other two a considerably smaller one ($\Delta\delta$ = 0.51 ppm and 0.27 ppm). Corroborating these observations, the ^{13}C NMR spectrum displays four $ArCH_2$ signals, two appearing at >37 ppm, the other two at <33 ppm. The latter values are in agreement with $ArCH_2Ar$ fragments containing aryl rings which are respectively *anti*- and *syn*-oriented.

Seeking reagents which allow both *mono*-functionalisation of **1** and convenient product separation, we reacted **1** with (+)-(*R*)-$BrCH_2C(O)NHCHMePh$ in the presence of 0.5 equiv. of K_2CO_3. The diastereomers formed, **6a** and **6b**, could readily be separated by column chromatography, the yields after work-up being respectively 29% and 26%. The absolute configuration of **6a** was determined by a single crystal X-ray diffraction study. This (Fig. 1[36]) also confirmed the cone conformation of the calixarene. The macrocyclic framework adopts the usual shape for a calix[4]arene in the cone conformation, with angles between the opposite phenoxy rings of 6° and 72°, respectively. A striking feature of the structure is the short N···O(17) separation (3.157(3) Å), which is consistent with the presence of a hydrogen-bonded NH group. As found in other compounds, the P=O bonds are oriented tangentially with respect to the cavity defined by the calix substituents.[16]

Reduction of compound **6a** with $PhSiH_3$ resulted in the formation of the optically active diphosphine **7**, eqn. (2). The ^1H and ^{31}P NMR spectra show that **7** exists in solution as a 10 : 1 mixture of two interconverting isomers. Owing to the

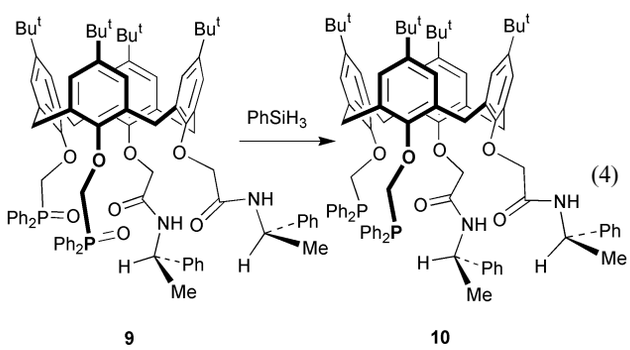


complexity of the ^{1}H NMR spectrum, only the conformation of the major isomer could unambiguously be established as a cone by ^{13}C NMR. We assign a partial cone conformation to the second isomer, considering the very facile through-the-annulus motion of phenoxy rings bearing small substituents.[37] It is well known that conformational inversion can be inhibited by incorporating sufficiently large substituents on the lower rim.[38] Thus, alkylation of the **7**-cone/**7**-partial cone mixture with Me_3SiCl–NEt_2SiMe_3 (eqn. (3)) afforded calixarene **8** which



proved to exist exclusively as a cone conformer. The formation of a single conformer is consistent with the fact that the precursors forming **7** are equilibrating species. As expected, the ^{31}P NMR spectrum of **8** shows two inequivalent P(III) atoms (−21.0 ppm and −21.4 ppm). The cone conformation of **8** was inferred from the ^{13}C NMR spectrum, in which all Ar*C*H_2Ar signals lie below 33 ppm.

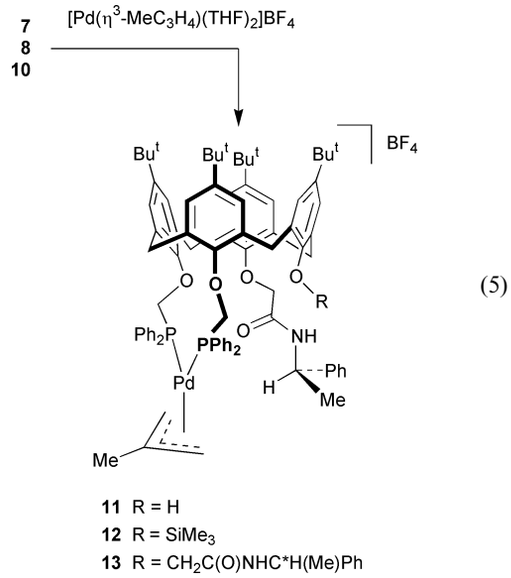
For the present study we also prepared the chiral di(phosphine oxide) **9**, bearing two identical, chiral substituents. This phosphine precursor was obtained in 75% yield by double alkylation with (*R*)-$BrCH_2C(O)NHCHMePh$. The NMR data of **9** are in full agreement with a cone conformation. As expected for a calixarene having no symmetry, the ^{1}H NMR spectrum of **9** shows four distinct ArC*H*$_2$Ar groups while its ^{31}P NMR spectrum displays two well-separated singlets (27.6 ppm and 24.8 ppm) in the phosphine oxide region. It is noteworthy that the two NH signals (at 8.93 ppm and 8.83 ppm) are considerably downfield-shifted with respect to those of $BrCH_2C(O)NHCHMePh$ (6.74 ppm), presumably because of hydrogen-bonding between the NH protons and the phosphoryl groups (in $CDCl_3$). Using $PhSiH_3$, compound **9** could be reduced quantitatively (eqn. (4)) to the corresponding



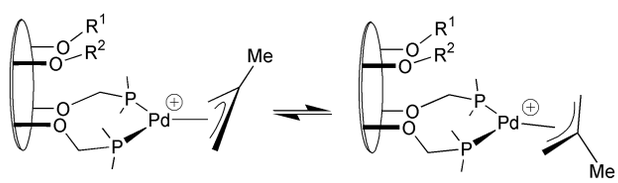
diphosphine **10** in which the cone conformation is retained. The two NH protons of **10** appear at 7.24 ppm and 6.91 ppm, suggesting that the NH groups are no longer involved in hydrogen bonding.

Synthesis of cationic palladium–(2-Me-allyl) and rhodium–(norbornadiene) complexes

The palladium complexes **11**–**13** were prepared in high yield by reaction of $[Pd(Me\text{-}allyl)(THF)_2]BF_4$ with the ligands **7**, **8** and **10**, respectively (eqn. (5)). These complexes were authenticated



by elemental analysis and FAB mass spectroscopy. As revealed by a variable temperature ^{31}P NMR study, each complex exists in solution as a mixture of two interconverting isomers (**11a/11b**; **12a/12b**; **13a/13b**). The NMR data indicate that these isomers must have a very similar structure. This observation may be interpreted in terms of allyl fluxionality giving two distinct isomers with different orientations of the C_{allyl}–Me bond (Scheme 1). Conformational change within the pallado-



Scheme 1

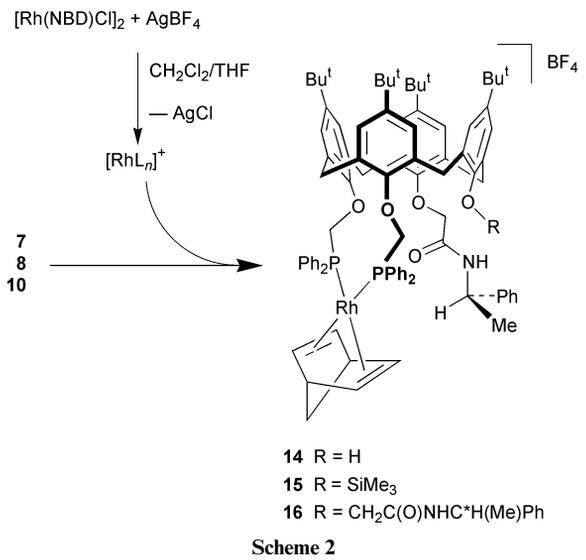
macrocycle could in principle also account for the observed equilibrium, but such a phenomenon is unlikely since in related, non-allylic $[PtCl_2(calix\text{-}diphos)]$ complexes,[20] no dynamics of the metallocyclic unit were observed. It should also be mentioned here that, as expected, all three ^{31}P NMR spectra display AB systems with coupling constants in accord with *cis*-arranged P atoms (35–40 Hz). While complexes **11** and **13** could unambiguously be identified as cone conformers, conformational assignment was not made for isomers **12a/12b** owing to the complexity of the NMR spectra.

For the preparation of the chelate complexes **14**–**16**, $[RhCl(NBD)]_2$ (NBD = norbornadiene) was used as precursor (Scheme 2). The latter was first treated with $AgBF_4$ in a CH_2Cl_2–THF mixture, resulting in formation of a cationic intermediate which was separated from silver chloride before being reacted with the particular disphosphine. For each complex, the ^{31}P NMR spectrum displays a single AB pattern with a coupling constant in agreement with *cis*-bonded phosphorus atoms (*ca.* 30 ppm). Significantly, the largest peak separation

Table 1 Palladium-catalysed alkylation of 1,3-diphenylprop-2-enyl acetate

Complex	Reaction time/h	Conversion (%)	ee's (%)	TOF[c]
11[a]	3.3	100	67	30
12[a]	3.3	100	45	30
13[a]	3.8	100	0	26
17[b]	4	100	8	25
18[b]	3	100	16	33
19[b]	5	100	6	20
20[b]	3	100	2	33

[a] Reaction conditions: 0.012 mmol catalyst, 1.2 mmol allylacetate, 2.4 mmol BSA, 2.4 mmol dimethyl malonate, 0.06 mmol KOAc; $T = 0$ °C; solvent: CH_2Cl_2. [b] Reaction conditions: 0.012 mmol catalyst, 1.2 mmol allylacetate, 2.4 mmol dimethyl malonate, 2.4 mmol NaH; $T = 67$ °C; solvent: THF. [c] Turnover frequency in h^{-1}. For the complexes **17**–**20** we observed an increase of the reaction rate when performing the catalytic runs with NaH in refluxing THF instead of BSA–KOAc–CH_2Cl_2, but the ee's remained unchanged.



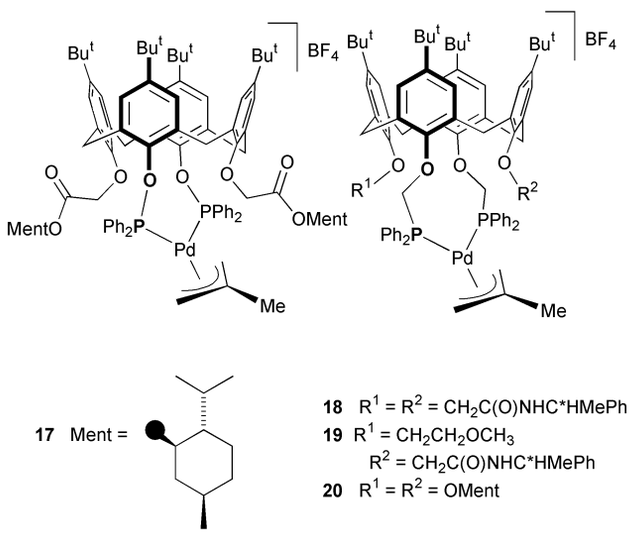
Scheme 2

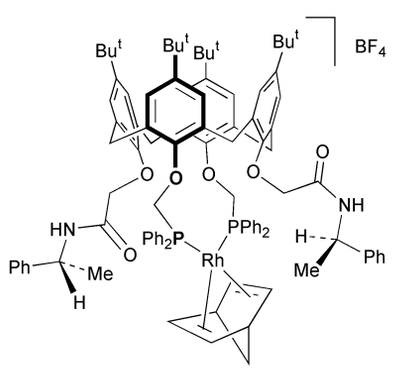
($\delta P_A - \delta P_B \approx 20$ ppm!) was observed for the calixarene bearing the sterically most disparate substituents (*i.e.* OH and OCH_2-C(O)NHCHMePh), namely complex **14**. For comparison, the signal separation is only 1 ppm in complex **16** having substituents equal in size, and 8 ppm in **15** containing the $SiMe_3$ and $CH_2C(O)NHCHMePh$ groups. Obviously the large peak separation observed in **14** reflects a strong "perturbation" of one of the two phosphino groups, possibly caused by a steric interaction with the adjacent amide group.

As inferred from the ^{13}C NMR spectra, the calixarene units in **14**–**16** are in a cone conformation. It should be emphasized that each rhodium complex exists as a single isomer. This finding further supports the interpretation given for the equilibrium observed in complexes **11**–**13**, involving allyl dynamics rather than structural changes within the metallocyclic unit.

Catalytic properties of 11–13 (allylic alkylation) and 14–16 (hydrogenation)

The catalytic activity of complexes **11**–**13** was assessed in the alkylation of 1,3-diphenylprop-2-enyl acetate with dimethyl malonate in the presence of BSA (BSA = $Me_3SiOC(NSiMe_3)$-CH_3). For this reaction a Pd : acetate ratio of 1 : 100 was used. Operating at 0 °C, complete substrate conversion occurred in less than 4 hours with all three complexes, corresponding to a turnover frequency of *ca.* 30 h^{-1} (Table 1). These activities compare well with that of other effective palladium-based alkylation catalysts.[39–41] Remarkably, while no asymmetric induction was observed with complex **13** bearing two *identical* chiral substituents, ee's of 45% and 67% were obtained with complexes **12** and **11**, respectively. These observations suggest that the presence of asymmetric carbon atoms as the only source of chirality has little influence on the selectivity. For comparison, we also evaluated the chiral complexes **17**–**20**[42] which are all based on non-inherently chiral calixarenes containing either one or two asymmetric carbon atoms integrated in the auxiliary groups. Note that in these calixarenes the two P atoms are tethered to *distal* positions. Complexes **17**–**20** gave poor enantioselectivities (Table 1), the best ee's being only 16%. It is also noteworthy that in the presence of BSA–KOAc–CH_2Cl_2 the activity of these complexes, *ca.* 6 h^{-1}, was lower than that reported above for **11**–**13**. However, we observed an increase of the reaction rate when performing the catalytic runs with NaH in refluxing THF instead of BSA–KOAc–CH_2Cl_2, the ee's remaining unchanged. The low ee's observed with **13** and **17**–**20** may be explained by the large separation between the stereogenic centre(s) and the metal unit, and the flexibility of the pendent amide, which both prevent effective induction. In contrast, an inherently chiral calix[4] backbone, as found in **11** and **12**, induces higher ee's.





The three diphosphines **14**–**16** were also used in catalytic olefin-hydrogenation. Thus, dimethyl itaconate is easily reduced with complex **16**, as expressed by a turnover frequency of 267 h^{-1} (Table 2). However, no asymmetric induction was observed, presumably again because of the long distance between the chiral carbons and the coordinated substrate. We note, however, that the catalytic activity of this complex is significantly higher than that observed for the related complex **21** (TOF: 10 h^{-1}).[21] It is plausible that, in the latter, the pocket-like metal environment hinders somewhat the access of the incoming olefin. The rate of hydrogenation significantly increases when using complexes **14** and **15**. The observed turnover frequencies are respectively 2000 and 1176 h^{-1}, while the corresponding

Table 2 Rhodium-catalysed hydrogenation of dimethyl itaconate[a]

Complex	Reaction time/h	Conversion (%)	ee's (%)	TOF[b]
14	0.10	100	48	2000
15	0.17	100	25	1176
16	0.75	100	0	267
21	20	100	0	10

[a] Reaction conditions: 0.02 mmol catalyst, 4.0 mmol dimethyl itaconate, P_{H_2} = 20 bar, T = 40 °C; solvent: MeOH. [b] Turnover frequency in h^{-1}.

enantioselectivities are 48% and 25%. We have no definitive explanation for the increased activity of these complexes with respect to that of **16**, but it is possible that the steric interaction between the metallocyclic unit and the auxiliary substituents decreases when the size of the latter become smaller. The net result is then that the steric interaction between the whole calixarene and the metal centre decreases, making the rhodium more accessible for an incoming olefin. On the other hand, the increased enantioselectivity observed with **14** and **15** suggests that the calix backbone effectively transfers to the metal centre the high steric anisotropy which characterises the domain comprising the two auxiliary groups. As in the allylic alkylation reactions described above, the more different the auxiliary groups are in size, the higher the chiral induction is. The better chirality transfer observed with calixarenes **7** and **8** may imply involvement of the phenyl substituents of the P atoms. Whether this occurs *via* direct steric interaction or *via* a backbone distortion is not clear at this stage.

In summary, we have described the first optically active diphosphines based on an inherently chiral calix[4]arene framework. For one of them, **6a**, the absolute configuration has been established by a single crystal X-ray diffraction study. Ligands **6a** and **7** display good activities when used as allylic alkylation and hydrogenation catalysts. The catalytic properties of the ligands have been compared to those of related diphosphines where the only sources of chirality are asymmetric carbon atoms belonging to the auxiliary groups. Our findings clearly indicate that in terms of activity, the calixarenes which possess two proximal $–CH_2PPh_2$ groups are superior to those having the phosphines appended to distal positions. Moreover, the inherently chiral calixarenes gave enantioselectivities significantly higher than those induced by the other ligands studied, suggesting that a chiral calix skeleton is able to effectively transfer the chiral information to the catalytic centre, while the presence alone of chiral C atoms located within the side chains has no significant influence on the selectivity. It appears likely that increasing the size difference between the two auxiliary groups should result in higher ee's.

Experimental

General procedures can be taken from ref. 20. Samples of 5,11,17,23-tetra-*tert*-butyl-25,26-dihydroxy-27,28-bis(diphenylphosphinoylmethoxy)calix[4]arene **1**,[16] (+)-(*R*)-$BrCH_2C(O)NHCH$-MePh,[21] (η^3-2-methylallyl)-(*P*,*P*′)-[5,11,17,23-tetra-*tert*-butyl-25,27-bis{(1*R*,2*S*,5*R*)-menthyloxycarbonylmethoxy}-26,28-bis-(diphenylphosphinooxy)calix[4]arene]palladium(II) tetrafluoroborate **17**,[42] (*R*,*R*)-(η^3-2-methylallyl)-(*P*,*P*′)-{5,11,17,23-tetra-*tert*-butyl-25,27-bis[(1-phenylethyl)carbamoylmethoxy]-26,28-bis(diphenylphosphinomethoxy)calix[4]arene}palladium(II) tetrafluoroborate **18**,[42] (*R*)-(η^3-2-methylallyl)-(*P*,*P*′)-{5,11,17,-23-tetra-*tert*-butyl-25-(3-oxabutyloxy)-27-[(1-phenylethyl)carbamoylmethoxy]-26,28-bis(diphenylphosphinomethoxy)calix[4]-arene}palladium(II) tetrafluoroborate **19**,[42] (η^3-2-methlylallyl)-(*P*,*P*′)-[5,11,17,23-tetra-*tert*-butyl-25,27-bis{(1*R*,2*S*,5*R*)-menthyloxycarbonylmethoxy}-26,28-bis(diphenylphosphinomethoxy)calix[4]arene]palladium(II) tetrafluoroborate **20**,[42] (norbornadiene){*cis*-(*P*,*P*′)-(*R*,*R*)-[5,11,17,23-tetra-*tert*-butyl-25,-27-bis[(1-phenylethyl)carbamoylmethoxy]-26,28-bis(diphenylphosphinomethoxy)calix[4]arene]}rhodium(I) tetrafluoroborate **21**,[21] [Pd(2-Me-allyl)Cl]$_2$,[43] [RhCl(NBD)]$_2$,[44] 1,3-diphenylpropenylacetate[45] and Me_3SiNEt_2,[46] were prepared by using literature procedures.

X-Ray crystallography

Crystals suitable for diffraction study were obtained by slow diffusion of tetrahydrofuran into a dichloromethane solution of the compound.

Crystal data for 6a·MeOH. $C_{81}H_{93}NO_8P_2$, M = 1270.59, triclinic, space group $P\bar{1}$, colourless prisms, a = 10.3100(3), b = 13.1130(6), c = 15.0380(6) Å, α = 109.403(2), β = 96.716(3), γ = 97.714(3)°, U = 1871.6(3) Å^3, Z = 1, D_c = 1.13 g cm^{-3}, μ = 0.112 mm^{-1}, $F(000)$ = 680. Data were collected on a Nonius KappaCCD diffractometer (graphite Mo-Kα radiation, 0.71073 Å) at −100 °C. 13115 Reflections collected with ($2.5 < \theta < 28.05°$), 5065 data with $I > 3\sigma(I)$. The structure was solved by direct methods and refined anisotropically on F^2 using the OpenMoleN package.[47] Absolute structure was determined refining Flack's x (0.02(7)) parameter. Hydrogen atoms were included using a riding model or rigid methyl groups. Two Bu^t groups (C(7) and C(55)) are disordered over two positions. Some disorder was also found in the methanol solvate. Final results: $R(F)$ = 0.041, $wR(F)$ = 0.056, goodness of fit = 1.061, 826 parameters, largest difference peak = 0.288 e Å^{-3}.

CCDC reference number 157446.

See http://www.rsc.org/suppdata/dt/b1/b101369f/ for crystallographic data in CIF or other electronic format.

Syntheses

5,11,17,23-Tetra-*tert*-butyl-25,26-bis(diphenylphosphinoylmethoxy)-27(or 28)-ethoxycarbonylmethoxy-28(or 27)-(hydroxy)calix[4]arene 2a and 2b (racemic mixture). A suspension of **1** (2.000 g, 1.86 mmol) and K_2CO_3 (0.140 g, 1.01 mmol) in acetonitrile (100 cm^3) was refluxed for 4 hours. Ethyl bromoacetate (0.310 g, 1.86 mmol) was added and the mixture refluxed for a further 4 days. The solvent was evaporated and the residue dissolved in CH_2Cl_2 (50 cm^3). The organic layer was washed with HCl 1 M (20 cm^3) and water (2 × 20 cm^3). The organic layer was dried over $MgSO_4$, then filtered and evaporated. The residue was purified by flash chromatography using AcOEt–hexane (50 : 50, v/v) as eluent. Compounds **2a** and **2b** (racemic mixture) were obtained as an analytically pure colourless powder (SiO_2, R_f = 0.37, AcOEt–hexane, 50 : 50, v/v). Yield: 0.941 g, 0.81 mmol, 44%; mp >220 °C; IR (KBr, cm^{-1}): ν(C=O) = 1736. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.91–7.79 and 7.52–7.21 (20H, P(O)Ph_2), 7.06 and 7.01 (AB spin system, 2H, *m*-ArH, ^4J = 2.3 Hz), 6.88 and 6.72 (AB spin system, 2H, *m*-ArH, ^4J = 2.4 Hz), 6.86 (s, 1H, OH exchanges with D_2O), 6.69 and 6.63 (AB spin system, 2H, *m*-ArH, ^4J = 2.4 Hz), 6.33 and 6.23 (AB spin system, 2H, *m*-ArH, ^4J = 2.3 Hz), 5.58 and 5.22 (ABX spin system with X = P, 2H, P(O)CH_2, ^2J(AB) = 14.9 Hz, ^2J(AX) = 4.1 Hz, ^2J(BX) = 4.0 Hz), 5.24 and 3.16 (AB spin system, 2H, $ArCH_2Ar$, ^2J = 12.9 Hz), 5.04 and 4.19 (AB spin system, 2H, OCH_2CO_2, ^2J = 15.7 Hz), 4.84 and 4.55 (ABX spin system with X = P, 2H, P(O)CH_2, ^2J(AB) = 13.5 Hz, ^2J(AX) = 0 Hz, ^2J(BX) = 8.6 Hz), 4.59 and 3.01 (AB spin system, 2H, $ArCH_2Ar$, ^2J = 13.5 Hz), 4.48 and 3.15 (AB spin system, 2H, $ArCH_2Ar$, ^2J = 12.7 Hz), 4.35 and 3.26 (AB spin system, 2H, $ArCH_2Ar$, ^2J = 13.6 Hz), 4.03 (q, 2H, CH_2CH_3, ^3J = 7.1 Hz), 1.31 (s, 9H, $C(CH_3)_3$), 1.22 (s, 9H, $C(CH_3)_3$), 1.15 (t, 2H, CH_2CH_3, ^3J = 7.1 Hz), 0.92 (s, 9H, $C(CH_3)_3$), 0.65 (s, 9H, $C(CH_3)_3$). ^{13}C{^{1}H} NMR (50 MHz, $CDCl_3$): δ 169.50 (s, CO_2), 153.29–124.77 (aryl C), 73.81 (d, P(O)CH_2, J(PC) = 82 Hz), 72.31 (s, CH_2CO_2), 70.71 (d, P(O)CH_2, J(PC) = 75 Hz), 60.51 (s, CH_2CH_3), 33.97 (s, $C(CH_3)_3$), 33.86 (2s, $C(CH_3)_3$), 33.56 (s, $C(CH_3)_3$), 31.84 (s,

ArCH$_2$Ar), 31.83, 31.60, 31.08 and 30.98 (4s, C(CH$_3$)$_3$), 14.21 (s, CH$_2$CH$_3$) (only a single ArCH$_2$Ar signal could be detected). ^{31}P{^{1}H} NMR (121 MHz, CDCl$_3$): δ 26.2 (s), 25.5 (s). Found: C, 72.16; H, 7.39. Calc. for $C_{74}H_{84}O_8P_2$ (M_r = 1163.40): C, 72.40; H, 7.28%. Small amounts of compound **3** were also formed. A rational, high yield synthesis of the latter is given below.

5,11,17,23-Tetra-*tert*-butyl-25,26-bis(diphenylphosphinoylmethoxy)-27,28-bis(ethoxycarbonylmethoxy)calix[4]arene 3. A suspension of **1** (0.500 g, 0.464 mmol) and K_2CO_3 (0.080 g, 0.579 mmol) in acetonitrile (30 cm^3) was refluxed for 2 hours. Ethyl bromoacetate (0.235 g, 1.41 mmol) was then added and the mixture refluxed for a further 72 hours. The solvent was evaporated and the residue dissolved in CH_2Cl_2 (50 cm^3). The organic layer was washed with HCl 1 M (20 cm^3) and water (2 × 20 cm^3). The organic layer was dried over $MgSO_4$, then filtered and evaporated. Drying the residue at 100 °C under vacuum for 24 hours afforded analytically pure **3**. Yield: 0.530 g, 0.424 mmol, 91%; mp >240 °C; IR (KBr, cm^{-1}): ν(C=O) = 1757. ^{1}H NMR (200 MHz, CDCl$_3$): δ 7.95–7.79 and 7.42–7.29 (20 H, P(O)Ph$_2$), 6.73 and 6.69 (AB spin system, 4H, *m*-ArH, ^4J = 2.3 Hz), 6.48 and 6.39 (AB spin system, 4H, *m*-ArH, ^4J = 2.2 Hz), 5.52 and 5.07 (ABX spin system with X = P, 4H, P(O)CH$_2$, ^2J(AB) = 14.8 Hz, ^2J(AX) = 0 Hz, ^2J(BX) = 0 Hz), 4.82 and 3.10 (AB spin system, 4H, ArCH$_2$Ar, ^2J = 12.7 Hz), 4.74 and 2.77 (AB spin system, 2H, ArCH$_2$Ar, ^2J = 13.0 Hz), 4.71 and 3.07 (AB spin system, 2H, ArCH$_2$Ar, ^2J = 13.1 Hz), 4.64 and 4.46 (AB spin system, 4H, CH$_2$CO$_2$, ^2J = 16.0 Hz), 4.09 (q, 4H, CH$_2$CH$_3$, ^3J = 7.1 Hz), 1.20 (t, 6H, CH$_2$CH$_3$), 1.04 (s, 18H, C(CH$_3$)$_3$), 0.97 (s, 18H, C(CH$_3$)$_3$). ^{13}C{^{1}H} NMR (50 MHz, CDCl$_3$): δ 170.68 (s, CO$_2$), 153.18–125.06 (aryl C), 71.73 (d, J(PC) = 77 Hz, P(O)CH$_2$), 71.25 (s, CH$_2$CO$_2$), 60.13 (s, CH$_2$CH$_3$), 33.82 (s, C(CH$_3$)$_3$), 33.73 (s, C(CH$_3$)$_3$), 32.18 (s, ArCH$_2$Ar), 31.38 (s, C(CH$_3$)$_3$), 14.26 (s, CH$_2$CH$_3$), (only a single ArCH$_2$Ar signal could be detected). ^{31}P{^{1}H} NMR (121 MHz, CDCl$_3$): δ 24.7 (s). FAB mass spectrum: *m*/*z* 1249.6 ([M + H]$^+$, 76%). Found: C, 74.97; H, 7.51. Calc. for $C_{78}H_{90}O_{10}P_2$ (M_r = 1249.49): C, 74.98; H, 7.26%.

5,11,17,23-Tetra-*tert*-butyl-25,26-bis(diphenylphosphinoylmethoxy)-27(or 28)-(cholesteryloxycarbonyloxy)-28(or 27)-(hydroxy)calix[4]arene 4a and 4b (mixture of diastereomers). A solution of **1** (5.000 g, 4.64 mmol), cholesteryl chloroformate (6.253 g, 13.92 mmol) and NEt$_3$ (15 cm^3) in CH$_2$Cl$_2$ (150 cm^3) was stirred at room temperature for 12 hours. The solution was then washed with 50 cm^3 HCl (1 M) and water (2 × 50 cm^3). The organic layer was dried over $MgSO_4$, filtered and evaporated. The residue was purified by flash chromatography using AcOEt–hexane (25 : 75, v/v) as eluent. Some cholesteryl derivatives eluted first followed by **5** (SiO_2, R_f = 0.31, AcOEt–hexane, 25 : 75, v/v, for spectroscopic data see below). Further elution gave **4a** and **4b** (diastereomeric mixture), (SiO_2, R_f = 0.19, AcOEt–hexane, 25 : 75, v/v). After evaporation, the residue was taken up in CH_2Cl_2. Addition of methanol and cooling at −78 °C afforded the product as a white microcrystalline powder. Yield: 4.770 g, 3.2 mmol, 69%; mp 178–181 °C; IR (KBr, cm^{-1}): ν(C=O) = 1755 (owing to the presence of two diastereomers, some signals are split). ^{1}H NMR (500 MHz, CDCl$_3$): δ 7.99–7.65 and 7.50–7.29 (20H, P(O)Ph$_2$), 7.01 and 6.89 (AB spin system, 2H, *m*-ArH, ^4J(AB) = 3.8 Hz), 6.89 and 6.67 (AB spin system, 2H, *m*-ArH, ^4J(AB) = 3.9 Hz), 6.62 and 6.58 (AB spin system, 2H, *m*-ArH, ^4J(AB) = 3.8 Hz), 6.46 and 6.38 (AB spin system, 2H, *m*-ArH, ^4J(AB) = 3.9 Hz and 4.6 Hz), 5.89 and 5.85 (2s (two diastereomers), 1H, OH, exchanges with D$_2$O), 5.73 and 4.72 (ABX spin system with X = P, 2H, P(O)CH$_2$, ^2J(AB) = 14.6 Hz, ^2J(AX) = 4.2 Hz, ^2J(BX) = 6.1 Hz), 5.40 and 5.29 (2d (two diastereomers), 1H, H-6, ^3J = 5.2 Hz), 5.00 and 4.84 (ABX spin system with X = P, 2H, P(O)CH$_2$, ^2J(AB) = 14.2 Hz, ^2J(AX) = 4.4 Hz, ^2J(BX) = 0 Hz), 4.90 and 2.93 (AB spin system, 2H, ArCH$_2$Ar, ^2J(AB) = 12.9 Hz), 4.54 (m, 1H, H-3), 4.48 and 3.24 (AB spin system, 2H, ArCH$_2$Ar, ^2J(AB) = 13.4 Hz), 4.44 and 3.00 (AB spin system, 2H, ArCH$_2$Ar, ^2J(AB) = 12.9 Hz), 4.05 and 3.25 (AB spin system, 2H, ArCH$_2$Ar, ^2J(AB) = 13.1 Hz), 2.57–0.69 (43H, cholesteryl), 1.25 and 1.24 (2s (two diastereomers), 9H, C(CH$_3$)$_3$), 1.20 and 1.18 (2s (two diastereomers), 9H, C(CH$_3$)$_3$), 0.85 and 0.82 (2s (two diastereomers), 9H, C(CH$_3$)$_3$), 0.83 (s, 9H, C(CH$_3$)$_3$). ^{13}C{^{1}H} NMR (50 MHz, CDCl$_3$): δ 153.97–131.95 (quaternary aryl C), 131.57–124.89 (aryl C), 122.86 (s, C-6), 78.35 (s, C-3), 73.25 (d, J(PC) = 78.0 Hz, P(O)CH$_2$), 71.46 (d, J(PC) = 74.9 Hz, P(O)CH$_2$), 56.79 (s, C-14), 56.24 (s, C-17), 50.04 (s, C-9), 42.41 (s, C-13), 39.83 (s, C-12 tentative assignment), 39.60 (s, C-1 tentative assignment), 38.10 (s, CH$_2$), 36.95 (s, CH$_2$), 36.62 (s, C-10), 36.28 (s, CH$_2$), 35.87 (s, CH), 34.00 (s, C(CH$_3$)$_3$), 33.84 (2s, C(CH$_3$)$_3$), 33.73 (s, C(CH$_3$)$_3$), 32.65 (s, ArCH$_2$Ar), 32.43 (s, ArCH$_2$Ar), 31.97 (s, C-7 tentative assignment), 31.75 (s, C(CH$_3$)$_3$), 31.57 (s, C(CH$_3$)$_3$), 31.05 (2s, C(CH$_3$)$_3$), 28.32 (s, C-16), 28.09 (s, CH), 27.78 (s, CH$_2$), 24.38 (s, CH$_2$), 23.91 (s, CH$_2$), 22.91 (s, CH$_3$), 22.66 (s, CH$_3$), 21.15 (s, C-11), 19.52 (s, CH$_3$), 18.82 (s, CH$_3$), 11.97 (s, CH$_3$). ^{31}P{^{1}H} NMR (121 MHz, CDCl$_3$): δ 25.37 (2s), 25.25 and 25.00 (2s, two diastereomers). FAB mass spectrum: *m*/*z* 1490.0 ([M + H]$^+$, 51%). Found: C, 79.13; H, 8.32. Calc. for $C_{98}H_{122}O_8P_2$ (M_r = 1489.96): C, 79.00; H, 8.25%. The numbering used for the cholesteryl atoms is as in ref. 48.

5,11,17,23-Tetra-*tert*-butyl-25,26-bis(diphenylphosphinoylmethoxy)-27,28-bis(cholesteryloxycarbonyloxy)calix[4]arene (partial cone) 5a and 5b (mixture of diastereomers). Trace amounts of this compound were obtained in the synthesis of **4a/4b**, after chromatography. Recrystallisation from CH_2Cl_2–MeOH afforded a white microcrystalline powder. Yield: 0.232 g, 0.122 mmol, 3%; mp 189–199 °C; IR (KBr, cm^{-1}): ν(C=O) = 1749.7. ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.98–7.05 (20H, P(O)Ph$_2$), 7.47 and 6.98 (AB spin system, 2H, *m*-ArH, ^4J = 2.1 Hz), 6.79 and 6.24 (AB spin system, 2H, *m*-ArH, ^4J = 2.4 Hz), 6.77 and 6.52 (AB spin system, 2H, *m*-ArH, ^4J = 2.4 Hz), 6.72 and 6.32 (AB spin system, 2H, *m*-ArH, ^4J = 1.5 Hz), 5.41 (broad signal, 2H, H-6), 5.34 and 4.01 (ABX spin system with X = P, 2H, P(O)CH$_2$, ^2J(AB) = 15.3 Hz, ^2J(AX) = 7.0 Hz, ^2J(BX) = 7.2 Hz), 4.86 and 4.41 (ABX spin system with X = P, 2H, P(O)CH$_2$, ^2J(AB) = 14.2 Hz, ^2J(AX) = 4.4 Hz, ^2J(BX) = 4.6 (av.) Hz), 4.75 and 2.97 (AB spin system, 2H, ArCH$_2$Ar, ^2J = 14 Hz), 4.56 and 2.72 (AB spin system, 2H, ArCH$_2$Ar, ^2J = 14.2 Hz), 4.41 (m, 2H, H-3), 3.87 and 3.36 (AB spin system, 2H, ArCH$_2$Ar, ^2J = 13.8 Hz), 3.76 and 3.49 (AB spin system, 2H, ArCH$_2$Ar, ^2J = 13.8 Hz), 2.60–0.68 (86H, 2 × cholesteryl), 1.20 (s, 9H, C(CH$_3$)$_3$), 1.05 (s, 9H, C(CH$_3$)$_3$), 0.88 (s, 9H, C(CH$_3$)$_3$), 0.86 (s, 9H, C(CH$_3$)$_3$). Owing to the presence of two diastereomers, the ^{1}H NMR spectrum shows two ABX spin systems for one PCH$_2$ group. ^{13}C{^{1}H} NMR (50 MHz, CDCl$_3$): δ 168.78 (CO), 154.85–132.53 (quaternary aryl C), 132.43–124.43 (aryl C), 122.99 (s, C-6), 122.83 (s, C-6), 77.98 (s, C-3), 72.12 (d, P(O)CH$_2$, J(PC) = 80.3 Hz), 68.99 (d, P(O)CH$_2$, J(PC) = 75.4 Hz), 56.71 (s, C-14), 56.15 (s, C-17), 49.99 (s, C-9), 42.32 (s, C-13), 39.73 (s, C-12 tentative assignment), 39.53 (s, C-1 tentative assignment), 37.96 (s, CH$_2$), 37.83 (s, ArCH$_2$Ar), 37.01 (s, ArCH$_2$Ar), 36.91 (s, CH$_2$), 36.61 (s, C-10), 36.19 (s, CH$_2$), 35.80 (s, CH), 33.83, 33.70, 33.40 (3s, C(CH$_3$)$_3$), 32.61 (s, ArCH$_2$Ar), 31.96 (s, C-7 tentative assignment), 31.60, 31.47 (2s, C(CH$_3$)$_3$), 28.36 (s, C-16), 28.03 (s, CH), 27.63 (s, CH$_2$), 24.29 (s, CH$_2$), 23.83 (s, CH$_2$), 22.81 (s, CH$_3$), 22.55 (s, CH$_3$), 21.04 (s, C-11), 19.18 (s, CH$_3$), 18.72 (s, CH$_3$), 11.87 (s, CH$_3$). ^{31}P{^{1}H} NMR (121 MHz, CDCl$_3$): δ 26.21 (s), 25.21 (s). Found: C, 79.46; H, 8.58. Calc. for $C_{126}H_{166}O_{10}P_2$ (M_r = 1902.61): C, 79.54; H, 8.25%. Compound **5** was also formed by alkylation of a **4a/4b** mixture.

(*R*)-5,11,17,23-Tetra-*tert*-butyl-25,26-bis(diphenylphosphinoylmethoxy)-27(or 28)-[(1-phenylethyl)carbamoylmethoxy]-28-

(or 27)-(hydroxy)calix[4]arene 6a and 6b (mixture of diastereomers). A suspension of K_2CO_3 (0.115 g, 0.83 mmol) and **1** (1.500 g, 1.39 mmol) in MeCN (250 cm^3) was refluxed for 3 h. (*R*)-(+)-2-Bromo-*N*-(1-phenylethyl)acetamide (0.371 g, 1.53 mmol) was added and the suspension was further refluxed for 48 h. After evaporation of the solvent, the residue was taken up in CH_2Cl_2 (150 cm^3). The solution was washed with 1 M HCl (80 cm^3), then with water (2 × 80 cm^3). The organic layer was dried with $MgSO_4$, filtered and evaporated to dryness. The solid residue was subjected to flash chromatography using the following procedure: an AcOEt–hexane (1 : 1, v/v) mixture was used first as eluent to remove a mixture of **1** (19%), **9** (29%) and **6b** (SiO_2, R_f = 0.55, AcOEt–hexane, 1 : 1, v/v). Further elution gave pure stereoisomer **6a** (SiO_2, R_f = 0.51, AcOEt–hexane, 1 : 1, v/v) obtained as a colourless solid. A second chromatography was then performed on the **1/9/6b** mixture using CH_2Cl_2–MeOH (98 : 2, v/v) as eluent to remove unreacted **1** (SiO_2, R_f = 0.53, CH_2Cl_2–MeOH, 98 : 2, v/v). However separation of the stereoisomer **6b** was not achieved and a mixture of **6b** and **9** was recovered (SiO_2, R_f = 0.52, CH_2Cl_2–MeOH, 98 : 2, v/v). Spectroscopic characterization of **6b**: $^{31}P\{^1H\}$ NMR (202 MHz, 293 K, $CDCl_3$): δ 25.9 (s) and 25.3 (s). Spectroscopic data for **6a**: Yield: 0.448 g, 26%; mp 190–191 °C; IR (KBr, cm^{-1}): ν(OH) = 3423br, ν(NH) = 3292br, ν(C=O) = 1669s, ν(P=O, tentative assignment) = 1192s. ^1H NMR (500 MHz, 293 K, $CDCl_3$): δ 9.17 (d, ^3J = 7 Hz, 1H, NH), 7.96–7.91, 7.84–7.70 and 7.52–7.11 (m, 20H, PPh_2), 7.02 and 6.98 (AB spin system, 2H, *m*-ArH, ^4J = 3 Hz), 6.92 and 6.83 (AB spin system, 2H, *m*-ArH, ^4J = 3 Hz), 6.57 and 6.51 (AB spin system, 2H, *m*-ArH, ^4J = 3 Hz), 6.44 and 6.42 (AB spin system, 2H, *m*-ArH, ^4J = 3 Hz), 5.89 and 4.94 (ABX spin system with X = P, 2H, PCH_2O, ^2J(AB) = 14 Hz, ^2J(AX) = 0 Hz, ^2J(BX) = 3 Hz), 5.26 and 3.03 (AB spin system, 2H, $ArCH_2Ar$, ^2J = 13 Hz), 5.16 (AMX_3 spin system, 1H, NHC*H*Me(Ph), $^3J_{AM} = {}^3J_{AX}$ = 7 Hz), 5.15 (s, 1H, OH), 4.83 and 4.65 (ABX system with X = P, 2H, PCH_2O, ^2J(AB) = 14 Hz, ^2J(AX) = 2 Hz, ^2J(BX) = 7 Hz), 4.65 and 3.02 (AB spin system, 2H, $ArCH_2Ar$, ^2J = 13 Hz), 4.28 and 3.10 (AB spin system, 2H, $ArCH_2Ar$, ^2J = 13 Hz), 4.23 and 3.56 (AB spin system, 2H, $OCH_2C(O)N$, ^2J = 14 Hz), 3.70 and 3.07 (AB spin system, 2H, $ArCH_2$, ^2J = 13 Hz), 1.51 (d, 3H, NHCH(C*H*$_3$)Ph, ^3J = 7 Hz), 1.30, 1.23, 0.85 and 0.78 (4s, 36H, C(C*H*$_3$)$_3$). $^{13}C\{^1H\}$ NMR (100 MHz, 293 K, $CDCl_3$): δ 168.69 (s, C=O), 154.34–129.35 (quaternary aryl C), 132.12–124.92 (aryl CH), 75.72 (s, O*C*H_2C(O)N), 72.53 (d, PCH_2O, J(PC) = 81 Hz), 72.05 (d, PCH_2O, J(PC) = 77 Hz), 48.28 (s, NH*C*H(Me)Ph), 33.94, 33.86, 33.65 and 33.62 (4s, *C*$(CH_3)_3$), 31.98, 31.85 and 31.21 (3s, $ArCH_2$), 31.66, 31.50 and 30.94 (3s, C(*C*H_3)$_3$), 21.20 (s, NHCH(*C*H_3)Ph) (one $ArCH_2$ signal is probably overlapping with a C(*C*H_3)$_3$ signal). $^{31}P\{^1H\}$ NMR (202 MHz, 293 K, $CDCl_3$): δ 27.7 and 26.3 (2s). Found: C, 77.80; H, 7.33; N, 1.18. Calc. for $C_{80}H_{89}NO_7P_2$ (M_r = 1238.51): C, 77.58; H, 7.24; N, 1.13%.

(*R*)-5,11,17,23-Tetra-*tert*-butyl-25,26-bis(diphenylphosphinomethoxy)-27-[(1-phenylethyl)carbamoylmethoxy]-28-(hydroxy)-calix[4]arene 7. A suspension of **6a** (2.500 g, 2.02 mmol) in phenylsilane (15 cm^3, 121.56 mmol) was refluxed for 2 days. After evaporation of the solvent *in vacuo*, the residue was subjected to flash chromatography using CH_2Cl_2 as eluent. The fraction obtained with R_f = 0.45 (SiO_2, CH_2Cl_2) was evaporated to dryness yielding **7** as a colourless powder. The NMR spectra of the compound showed evidence for the presence of two conformers (10 : 1 ratio) in solution. Owing to the complexity of the NMR spectrum showing two equilibrating species, only a selection of spectroscopic data are given for the major conformer, **7**-cone. Yield: 2.000 g, 82%; mp 175–177 °C; IR (KBr, cm^{-1}): ν(OH) = 3447br, ν(NH) = 3349br, ν(C=O) = 1677s. ^1H NMR (400 MHz, 293 K, $CDCl_3$): δ 8.79 (d, 1H, NH, ^3J = 8 Hz), 1.34, 1.31, 0.84 and 0.79 (4s, 36H, $C(CH_3)_3$). $^{13}C\{^1H\}$ NMR (100 MHz, 293 K, $CDCl_3$): δ 168.93 (s, C=O), 79.00 (d, J(PC) = 6 Hz, PCH_2O), 75.93 (d, PCH_2O, J(PC) = 11 Hz), 74.04 (s, O*C*H_2C(O)N), 48.75 (s, NH*C*H(Me)Ph), 32.78, 32.70 and 32.34 (3s, $ArCH_2$), 31.79, 31.71, 31.03 and 30.94 (4s, C(*C*H_3)$_3$), 22.52 (s, NHCH(*C*H_3)Ph) (one $ArCH_2$ signal is probably overlapping with a *tert*-butyl signal). $^{31}P\{^1H\}$ NMR (121 MHz, 293 K, $CDCl_3$): δ −20.4 and −20.7 (2s). Found: C, 79.50; H, 7.38; N, 1.23. Calc. for $C_{80}H_{89}NO_5P_2$ (M_r = 1206.51): C, 79.64; H, 7.43; N, 1.16%.

(*R*)-5,11,17,23-Tetra-*tert*-butyl-25,26-bis(diphenylphosphinomethoxy)-27-[(1-phenylethyl)carbamoylmethoxy]-28-(trimethylsilyloxy)calix[4]arene 8. To a solution of **7** (1.000 g, 0.83 mmol) in toluene (35 cm^3) were added Me_3SiNEt_2 (0.240 cm^3, 1.24 mmol) and small amounts of Me_3SiCl. The solution was heated to 60 °C for 2 h. The solvent was evaporated to dryness under vacuum yielding a white solid which was subjected to flash chromatography (pre-treated SiO_2 with 5% NEt_3 in CH_2Cl_2) using AcOEt–hexane (8 : 92, v/v) as eluent. The fraction obtained with R_f = 0.31 (SiO_2–NEt_3, AcOEt–hexane, 8 : 92, v/v) was evaporated to dryness yielding **8** as a colourless powder. Yield: 0.448 g, 90%; mp 201–203 °C; IR (KBr, cm^{-1}): ν(NH) = 3415br, ν(NH) = 3338br sh, ν(C=O) = 1677s. ^1H NMR (400 MHz, 293 K, $CDCl_3$): δ 7.36–7.16 (m, 20H, PPh_2), 7.09 (d, 1H, NH, ^3J = 7 Hz), 6.85–6.53 (m, 8H, *m*-ArH), 5.27 (AMX_3 system, 1H, NHC*H*Me(Ph), ^3J(AM) = ^3J(AX) = 7 Hz), 5.16 and 4.94 (ABX system with X = P, 2H, PCH_2O, ^2J(AB) = 14 Hz, ^2J(AX) = 2 Hz, ^2J(BX) = 4 Hz), 4.96 and 4.75 (AB spin system, 2H, PCH_2O, ^2J = 13 Hz), 4.84 and 4.66 (AB spin system, 2H, $OCH_2C(O)N$, ^2J = 14 Hz), 4.52 and 2.98 (AB spin system, 2H, $ArCH_2$, ^2J(AB) = 14 Hz), 4.50 and 3.03 (AB spin system, 2H, $ArCH_2$, ^2J = 13 Hz), 4.49 and 3.12 (AB spin system, 2H, $ArCH_2$, ^2J = 13 Hz), 4.28 and 2.82 (AB spin system, 2H, $ArCH_2$, ^2J = 13 Hz), 1.50 (d, 3H, NHCH(C*H*$_3$)Ph, ^3J = 7 Hz), 1.16, 1.13, 1.06 and 1.04 (4s, 36H, *tert*-butyl), 0.29 (s, 9H, $SiMe_3$). $^{13}C\{^1H\}$ NMR (100 MHz, 293 K, $CDCl_3$): δ 169.35 (s, C=O), 153.41–131.06 (quaternary aryl C), 133.67–124.62 (aryl CH), 76.93 and 76.18 (2d, PCH_2O, J(PC) = 8 Hz), 73.51 (s, O*C*H_2C(O)N), 48.57 (s, NH*C*H(Me)Ph), 33.92, 33.87 and 33.79 (3s, *C*$(CH_3)_3$), 32.27, 32.26 and 31.56 (3s, $ArCH_2$), 31.48, 31.39 and 31.27 (3s, C(*C*H_3)$_3$), 21.41 (s, NHCH(*C*H_3)Ph) (one $ArCH_2$ signal is probably overlapping with a *tert*-butyl signal), 1.00 (s, $SiMe_3$). $^{31}P\{^1H\}$ NMR (121 MHz, 293 K, $CDCl_3$): δ −21.0 and −21.4 (2s). Found: C, 77.79; H, 7.51; N, 1.16. Calc. for $C_{83}H_{98}NO_5P_2Si$ (M_r = 1279.70): C, 77.90; H, 7.72; N, 1.09%.

(*R,R*)-5,11,17,23-Tetra-*tert*-butyl-25,26-bis(diphenylphosphinoylmethoxy)-27,28-bis[(1-phenylethyl)carbamoylmethoxy]-calix[4]arene 9. A suspension of K_2CO_3 (5.130 g, 37.11 mmol) and **1** (4.000 g, 3.71 mmol) in MeCN (350 cm^3) was refluxed for 3 h. Then (*R*)-(+)-2-bromo-*N*-(1-phenylethyl)acetamide (5.394 g, 1.53 mmol) was added and the suspension was refluxed for 7 d. After evaporation of the solvent, the residue was taken up in CH_2Cl_2 (250 cm^3), washed with 1 M HCl (120 cm^3), then with water (2 × 90 cm^3). The organic layer was dried with $MgSO_4$, filtered and evaporated to dryness. The solid residue was subjected to flash chromatography using AcOEt–hexane (2 : 3, v/v) as eluent. Compound **9** was obtained as an analytically pure colourless solid (SiO_2, R_f = 0.42, AcOEt–hexane, 2 : 3, v/v). Yield: 3.895 g, 75%; mp 165–166 °C; IR (KBr, cm^{-1}): ν(NH) = 3430br sh, ν(NH) = 3300br, ν(C=O) = 1654s, ν(P=O, tentative assignment) = 1200s. ^1H NMR (400 MHz, 293 K, $CDCl_3$): δ 8.93 and 8.83 (2d, 2H, NH, ^3J = 8 Hz), 7.93–7.88, 7.76–7.71 and 7.53–7.12 (m, 20H, PPh_2), 6.68 and 6.66 (AB spin system, 2H, *m*-ArH, $^4J \approx 1$ Hz), 6.66 and 6.54 (AB spin system, 2H, *m*-ArH, ^4J = 2 Hz), 6.50 and 6.41 (AB spin system, 2H, *m*-ArH, $^4J \approx 1$ Hz), 6.43 and 6.42 (AB spin system, 2H, *m*-ArH, ^4J = 2 Hz), 6.01 and 4.92 (AB spin system, 2H, PCH_2O, ^2J(AB) = 14 Hz), 5.20 and 5.12 (2 AMX_3 spin systems, 2H, NHC*H*Me(Ph), ^3J(AM) = ^3J(AX) = 7 Hz), 5.12 and 5.05 (ABX spin system with X = P, 2H, PCH_2O, ^2J(AB) = 12 Hz,

^2J(AX) = 3 Hz, ^2J(BX) = 5 Hz), 4.96 and 2.77 (AB spin system, 2H, $ArCH_2$, ^2J = 13 Hz), 4.88 and 4.58 (AB spin system, 2H, $OCH_2C(O)N$, ^2J = 15 Hz), 4.65 and 3.06 (AB spin system, 2H, $ArCH_2$, ^2J = 13 Hz), 4.49 and 3.03 (AB spin system, 2H, $ArCH_2$, ^2J = 13 Hz), 4.42 and 3.92 (AB spin system, 2H, $OCH_2C(O)N$, ^2J = 13 Hz), 3.98 and 2.35 (AB spin system, 2H, $ArCH_2$, ^2J = 13 Hz), 1.34 and 1.32 (2d, 2 × 3H, NHCH-(CH_3)Ph, ^3J = 7 Hz), 1.05, 1.03 and 0.90 (3s, 9H + 18H + 9H, $C(CH_3)_3$). $^{13}C\{^1H\}$ NMR (100 MHz, 293 K, $CDCl_3$): δ 170.20 and 168.93 (2s, C=O), 154.72–130.56 (quaternary aryl C), 131.96–124.56 (aryl CH), 74.01 and 73.10 (2s, $OCH_2C(O)N$), 72.05 (d, PCH_2O, J(PC) = 80 Hz), 71.50 (d, PCH_2O, J(PC) = 78 Hz), 48.47 and 48.04 (2s, NHCH(Me)Ph), 33.75 and 33.63 (2s, $C(CH_3)_3$), 32.52, 31.59 and 30.57 (3s, $ArCH_2$), 31.37, 31.30 and 31.26 (3s, $C(CH_3)_3$), 21.50 and 21.36 (2s, $NHCH(CH_3)Ph$) (one $ArCH_2$ signal is probably overlapping with a *tert*-butyl signal). $^{31}P\{^1H\}$ NMR (121 MHz, 293 K, $CDCl_3$): δ 27.6 and 24.8 (2s). Found: C, 77.07; H, 7.02; N, 2.20. Calc. for $C_{90}H_{100}N_2O_8P_2$ (M_r = 1399.74): C, 77.23; H, 7.20; N, 2.00%.

(*R*,*R*)-5,11,17,23-Tetra-*tert*-butyl-25,26-bis(diphenylphosphinomethoxy)-27,28-bis[(1-phenylethyl)carbamoylmethoxy]-calix[4]arene 10. A suspension of **9** (2.280 g, 1.63 mmol) in phenylsilane (1.5 cm^3, 8.15 mmol) was refluxed for 21 days. After evaporation of the solvent *in vacuo*, the residue was subjected to flash chromatography using CH_2Cl_2 as eluent. The fraction obtained with R_f = 0.13 (SiO_2, CH_2Cl_2) was evaporated to dryness yielding **10** as a colourless powder. Yield: 1.695 g, 76%; mp 171–173 °C; IR (KBr, cm^{-1}): ν(NH) = 3446br sh, ν(NH) = 3284br, ν(C=O) = 1669s. ^1H NMR (400 MHz, 293 K, $CDCl_3$): δ 7.24 and 6.91 (2d, 2H, NH, ^3J = 8 Hz), 7.44–7.16 (m, 20H, PPh_2), 6.76–6.60 (m, 8H, *m*-ArH), 5.12 (2AMX$_3$ systems, 2H, NHC*H*Me(Ph), ^3J(AM) = ^3J(AX) = 7 Hz), 5.09 and 5.03 (AB spin system, 2H, PCH_2O, ^2J(AB) = 14Hz), 5.03 and 4.81 (ABX system with X = P, 2H, PCH_2O, ^2J(AB) = 12 Hz, ^2J(AX) = 0 Hz, ^2J(BX) = 5 Hz), 4.71 and 2.90 (AB spin system, 2H, $ArCH_2$, ^2J = 13 Hz), 4.62 and 4.25 (AB spin system, 2H, $OCH_2C(O)N$, ^2J = 15 Hz), 4.56 and 4.25 (AB spin system, 2H, $OCH_2C(O)N$, ^2J = 13 Hz), 4.46 and 3.09 (AB spin system, 2H, $ArCH_2$, ^2J = 13 Hz), 4.25 and 3.04 (AB spin system, 4H, $ArCH_2$, ^2J = 13 Hz), 1.49 and 1.36 (2d, 2 × 3H, NHCH-(CH_3)Ph, ^3J = 7 Hz), 1.13, 1.12, 1.05 and 1.01 (4s, 36H, $C(CH_3)_3$). $^{13}C\{^1H\}$ NMR (100 MHz, 293 K, $CDCl_3$): δ 169.09 and 168.96 (2s, C=O), 153.74–132.30 (quaternary aryl C), 133.49–124.79 (aryl CH), 76.60 and 76.16 (2d, PCH_2O, J(PC) = 9 Hz), 74.22 and 73.96 (2s, $OCH_2C(O)N$), 48.78 and 48.42 (2s, NHCH(Me)Ph), 33.92, 33.89, 33.85 and 33.79 (4s, $C(CH_3)_3$), 32.56, 32.43, 32.39 and 31.93 (4s, $ArCH_2$), 31.48 and 31.36 (2s, $C(CH_3)_3$), 21.47 and 21.26 (2s, $NHCH(CH_3)Ph$). $^{31}P\{^1H\}$ NMR (121 MHz, 293 K, $CDCl_3$): δ −21.4 and −21.4 (2s) (the signals are resolved). Found: C, 79.14; H, 7.56; N, 2.02. Calc. for $C_{90}H_{100}N_2O_6P_2$ (M_r = 1367.71): C, 79.03; H, 7.37; N, 2.05%.

General procedure for the syntheses of the Pd(II) complexes 11–13

Typically, a solution of $AgBF_4$ (0.08 mmol) in THF (1 cm^3) was added to a solution of $[Pd(\eta^3\text{-}C_4H_7)Cl]_2$ (0.04 mmol) in CH_2Cl_2 (4 cm^3). After 5 min, the solution was decanted to eliminate AgCl. The supernatant was filtered through Celite and added to a solution of the appropriate ligand (0.08 mmol) in CH_2Cl_2 (300 cm^3). After 1 h the solution was concentrated to *ca.* 5 cm^3 and addition of pentane afforded a colourless precipitate.

(η^3-2-Methylallyl)-(*P*,*P*′)-(*R*)-{5,11,17,23-tetra-*tert*-butyl-25,26-bis(diphenylphosphinomethoxy)-27-[(1-phenylethyl)carbamoylmethoxy]-28-(hydroxy)calix[4]arene}palladium(II) tetrafluoroborate 11. Yield: 80%; mp 185 °C (dec.); IR (KBr, cm^{-1}): ν(OH) = 3500br, ν(NH) = 3417br, ν(C=O) = 1685s. $^{31}P\{^1H\}$ NMR (121 MHz, 293 K, $CDCl_3$): δ 17.9 and 13.4 (2 AB systems, ^2J(AB) = 40 Hz). FAB mass spectrum: *m*/*z* 1366 ([M − BF_4]$^+$, 20%). Found: C, 69.59; H, 6.60; N, 0.99. Calc. for $C_{84}H_{96}NO_5P_2PdBF_4$ (M_r = 1454.83): C, 69.35; H, 6.65; N, 0.96%.

(η^3-2-Methylallyl)-(*P*,*P*′)-(*R*)-{5,11,17,23-tetra-*tert*-butyl-25,26-bis(diphenylphosphinomethoxy)-27-[(1-phenylethyl)carbamoylmethoxy]-28-(trimethylsilyloxy)calix[4]arene}palladium(II) tetrafluoroborate 12. Yield: 82%; mp 211 °C (dec.); IR (KBr, cm^{-1}): ν(NH) = 3372br, ν(C=O) = 1677s. $^{31}P\{^1H\}$ NMR (121 MHz, 293 K, CD_2Cl_2): δ 15.2 and 13.5 (2 AB systems, ^2J(AB) = 35 Hz). FAB mass spectrum: *m*/*z* 1439 ([M − BF_4]$^+$, 100%). Found: C, 66.64; H, 6.78; N, 0.93. Calc. for $C_{87}H_{105}NO_5P_2SiPdBF_4{\cdot}0.5CH_2Cl_2$ (M_r = 1528.02 + 42.46): C, 66.92; H, 6.80; N, 0.89%.

(η^3-2-Methylallyl)-(*P*,*P*′)-(*R*,*R*)-{5,11,17,23-tetra-*tert*-butyl-25,26-bis(diphenylphosphinomethoxy)-27,28-bis[(1-phenylethyl)-carbamoylmethoxy]calix[4]arene}palladium(II) tetrafluoroborate 13. Yield: 77%; mp 220 °C (dec.); IR (KBr, cm^{-1}): ν(NH) = 3366br, ν(C=O) = 1672s. $^{31}P\{^1H\}$ NMR (121 MHz, 293 K, $CDCl_3$): δ 12.5 and 10.4 (2AB systems, ^2J(AB) = 35 Hz). FAB mass spectrum: *m*/*z* 1527 ([M − BF_4]$^+$, 100%). Found: C, 69.90; H, 6.70; N, 1.75. Calc. for $C_{94}H_{107}N_2O_6P_2PdBF_4$ (M_r = 1616.06): C, 69.86; H, 6.67; N, 1.73%.

General procedure for the syntheses of the Rh(I) complexes 14–16

Typically, a solution of $AgBF_4$ (0.08 mmol) in THF (1 cm^3) was added to a solution of $[Rh(NBD)Cl]_2$ (0.04 mmol) in CH_2Cl_2 (4 cm^3). After 5 min, the solution was decanted to eliminate AgCl. The supernatant was filtered through Celite and added to a solution of the ligand (0.08 mmol) in CH_2Cl_2 (300 cm^3). After 1 h the solution was concentrated to *ca.* 5 cm^3 and addition of pentane afforded an orange precipitate.

(Norbornadiene){*cis*-(*P*,*P*′)-(*R*)-[5,11,17,23-tetra-*tert*-butyl-25,26-bis(diphenylphosphinomethoxy)-27-[(1-phenylethyl)carbamoylmethoxy]-28-(hydroxy)calix[4]arene]}rhodium(I) tetrafluoroborate 14. Yield: 82%; mp 220 °C (dec.); IR (KBr, cm^{-1}): ν(C=O) = 1678s. ^1H NMR (500 MHz, 293 K, CD_2Cl_2): δ 8.05 (d, 1H, NH, ^3J = 8 Hz), 7.79–6.53 (m, 33H, PPh_2 + *m*-ArH), 6.54 and 3.49 (AB spin system, 2H, $ArCH_2$, ^2J(AB) = 14 Hz), 4.96 and 3.48 (AB spin system, 2H, $ArCH_2$, ^2J(AB) = 14 Hz), 4.78 (br s, 4H, HC=CH of NBD), 4.68 (AMX$_3$ spin system, 1H, NHC*H*Me(Ph), ^3J(AM) = ^3J(AX) = 7 Hz), 4.58 and 4.43 (AB spin system, 2H, $OCH_2C(O)N$, ^2J(AB) = 14 Hz), 4.58 and 3.86 (AB spin system, 2H, PCH_2O, ^2J(AB) = 13 Hz), 4.48 and 3.38 (AB spin system, 2H, $ArCH_2$, ^2J(AB) = 14 Hz), 4.46 and 3.96 (AB spin system, 2H, PCH_2O, ^2J(AB) = 13 Hz), 4.49 and 3.88 (AB spin system, 2H, $ArCH_2$, ^2J(AB) = 13 Hz), 4.44 and 3.82 (AB spin system, 2H, $ArCH_2$, ^2J(AB) = 14 Hz), 4.07 (br s, 2H, CH of NBD), 1.58 (s, 2H, CH_2 of NBD), 1.40, 1.36, 1.13 and 0.97 (4s, 36H, *tert*-butyl), 0.81 (d, 3H, $NHCH(CH_3)Ph$, ^3J = 7 Hz). $^{13}C\{^1H\}$ NMR (125 MHz, 293 K, $CDCl_3$): δ 167.83 (s, C=O), 156.80–128.21 (quaternary aryl C), 135.02–125.54 (aryl CH), 82.23 and 78.00 (2s, HC=CH of NBD), 76.04 (s, $OCH_2C(O)N$), 75.91 and 71.81 (2d, PCH_2O, J(PC) = 31 Hz), 69.12 (br s, CH_2 of NBD), 53.83 (s, CH of NBD), 49.17 (s, NHCH(Me)Ph), 36.48 (s, $ArCH_2$), 34.93, 34.81, 34.62 and 34.58 (4s, $C(CH_3)_3$), 32.77, 32.68 and 31.98 (3s, $ArCH_2$), 32.36, 32.22 and 31.63 (3s, $C(CH_3)_3$), 21.72 (s, $NHCH(CH_3)Ph$). $^{31}P\{^1H\}$ NMR (121 MHz, 293 K, $CDCl_3$): δ 33.6 and 12.9 (2 ABX systems with X = Rh, ^2J(AB) = 30 Hz, J(P–Rh) = 157 Hz). FAB mass spectrum: *m*/*z* 1400 ([M − BF_4]$^+$, 100%). Found: C, 70.50; H, 6.38; N, 1.23. Calc. for $C_{87}H_{97}NO_5P_2RhBF_4$ (M_r = 1488.40): C, 70.21; H, 6.57; N, 0.94%.

(Norbornadiene){*cis*-(*P*,*P*′)-(*R*)-[5,11,17,23-tetra-*tert*-butyl-25,26-bis(diphenylphosphinomethoxy)-27-[(1-phenylethyl)carb-

amoylmethoxy]-28-(trimethylsilyloxy)calix[4]arene]}rhodium(I) tetrafluoroborate 15. Yield: 86%; mp 163 °C (dec.); IR (KBr, cm^{-1}): ν(NH) = 3392br, ν(C=O) = 1677s. ^{1}H NMR (400 MHz, 293 K, $CDCl_3$): δ 7.96 (d, ^{1}H, NH, ^3J = 7 Hz), 7.75–6.09 (m, 33H, PPh_2 + *m*-ArH), 5.62 and 5.33 (AB spin system, 2H, PCH_2O, ^2J (AB) = 13 Hz), 5.60 and 5.28 (AB spin system, 2H, PCH_2O, ^2J (AB) = 13 Hz), 4.97 (AMX_3 spin system, ^{1}H, NHC*H*Me(Ph), ^3J(AM) = ^3J(AX) = 7 Hz), 4.66 and 4.01 (AB spin system, 2H, $OCH_2C(O)N$, ^2J (AB) = 14 Hz), 4.49 and 3.42 (AB spin system, 2H, $ArCH_2$, ^2J (AB) = 14 Hz), 4.45 and 3.12 (AB spin system, 2H, $ArCH_2$, ^2J (AB) = 13 Hz), 4.36 (br s, 4H, HC=CH of NBD), 3.85 (br s, 2H, CH of NBD), 4.27 and 3.12 (AB spin system, 2H, $ArCH_2$, ^2J(AB) = 13 Hz), 3.96 and 3.00 (AB spin system, 2H, $ArCH_2$, ^2J(AB) = 13 Hz), 1.43 (s, 2H, CH_2 of NBD), 1.28 (d, 3H, NHCH(CH_3)Ph, ^3J = 7 Hz), 1.39, 1.36, 0.98 and 0.66 (4s, 36H, *tert*-butyl), 0.14 (s, 9H, $SiMe_3$). ^{13}C{^{1}H} NMR (100 MHz, 293 K, $CDCl_3$): δ 167.69 (s, C=O), 153.64–125.11 (quaternary aryl C), 134.31–124.32 (aryl CH), 81.80 and 77.66 (2s, HC=CH of NBD), 73.56 (s, OCH_2C(O)N), 73.12 (m, PCH_2O), 68.50 (br s, CH_2 of NBD), 51.98 (s, CH of NBD), 48.58 (s, NH*C*H(Me)Ph), 35.77 (s, $ArCH_2$), 34.27, 34.17, 33.90 and 33.34 (4s, *C*(CH_3)$_3$), 32.40 (s, $ArCH_2$), 31.70 and 31.07 (2s, C(*C*H_3)$_3$), 21.56 (s, NHCH(*C*H_3)Ph), 0.42 (s, $SiMe_3$) (two $ArCH_2$ signals are probably overlapping with a *tert*-butyl signal). ^{31}P{^{1}H} NMR (121 MHz, 293 K, $CDCl_3$): δ 21.3 and 13.4 (2 ABX systems with X = Rh, ^2J(AB) = 28 Hz, J(P–Rh) = 148 Hz). FAB mass spectrum: *m*/*z* 1473 ([M − BF_4]$^+$, 100%). Found: C, 69.20; H, 7.13; N, 0.84. Calc. for $C_{90}H_{106}NO_5P_2SiRhBF_4$ (*M*r = 1561.55): C, 69.22; H, 6.84; N, 0.90%.

(Norbornadiene){*cis*-(*P*,*P*′)-(*R*,*R*)-[5,11,17,23-tetra-*tert*-butyl-25,26-bis(diphenylphosphinomethoxy)-27,28-bis[(1-phenylethyl)carbamoylmethoxy]calix[4]arene]}rhodium(I) tetrafluoroborate 16. Yield: 86%; mp 191 °C (dec.); IR (KBr, cm^{-1}): ν(NH) = 3364br, ν(C=O) = 1670s. ^{1}H NMR (400 MHz, 293 K, $CDCl_3$): δ 7.79 and 7.75 (2d, 2H, NH, ^3J = 8 Hz), 7.54–7.01 (m, 20H, PPh_2), 6.93–6.69 (m, 8H, *m*-ArH), 5.70 and 5.41 (ABX spin system with X = P, 2H, PCH_2O, ^2J(AB) = 12 Hz, ^2J(AX) = 2 Hz, ^2J(BX) = 5 Hz), 5.67 and 5.32 (ABX spin system with X = P, 2H, PCH_2O, ^2J(AB) = 12 Hz, ^2J(AX) = 3 Hz, ^2J(BX) = 5 Hz), 4.97 (2AMX_3 spin systems, 2H, NHC*H*-Me(Ph), ^3J(AM) = ^3J(AX) = 7 Hz), 4.93 and 4.65 (AB spin system, 2H, $OCH_2C(O)N$, ^2J(AB) = 15 Hz), 4.93 and 3.03 (AB spin system, 2H, $ArCH_2$, ^2J(AB) = 13 Hz), 4.85 and 3.38 (AB spin system, 2H, $ArCH_2$, ^2J(AB) = 13 Hz), 4.84 and 3.29 (AB spin system, 2H, $ArCH_2$, ^2J(AB) = 13 Hz), 4.83 and 4.79 (AB spin system, 2H, $OCH_2C(O)N$, ^2J(AB) = 13 Hz), 4.57 and 3.09 (AB spin system, 2H, $ArCH_2$, ^2J(AB) = 13 Hz), 4.35 (br s, 4H, HC=CH of NBD), 3.82 (br s, 2H, CH of NBD), 1.44 and 1.36 (2d, 2 × 3H, NHCH(CH_3)Ph, ^3J = 7 Hz), 1.38 (s, 2H, CH_2 of NBD), 1.17, 1.11, 1.09 and 1.04 (4s, 36H, *tert*-butyl). ^{13}C{^{1}H} NMR (100 MHz, 293 K, $CDCl_3$): δ 168.59 and 168.52 (2s, C=O), 153.24–125.70 (quaternary aryl C), 133.04–124.65 (aryl CH), 79.49 and 79.10 (2s, HC=CH of NBD), 74.02 (m, PCH_2O), 73.85 and 73.48 (2s, OCH_2C(O)N), 67.58 (br s, CH_2 of NBD), 52.19 (s, CH of NBD), 48.93 and 48.84 (2s, NH*C*H(Me)Ph), 34.02, 33.96 and 33.90 (3s, *C*(CH_3)$_3$), 33.78, 32.00, 31.91 and 31.81 (4s, $ArCH_2$), 31.44 and 31.35 (2s, C(*C*H_3)$_3$), 22.21 and 21.93 (2s, NHCH(*C*H_3)Ph). ^{31}P{^{1}H} NMR (121 MHz, 293 K, $CDCl_3$): δ 17.5 and 16.4 (2ABX systems with X = Rh, ^2J(AB) = 35 Hz, J(P–Rh) = 150 Hz). FAB mass spectrum: *m*/*z* 1525 ([M − BF_4]$^+$, 45%). Found: C, 69.98; H, 6.75; N, 1.68. Calc. for $C_{94}H_{107}N_2O_6P_2RhBF_4$ (M_r = 1612.52): C, 70.10; H, 6.69; N, 1.74%.

Allylic alkylation experiments

Method a (see Table 1). To a solution of the catalyst (0.012 mmol) in CH_2Cl_2 (8 cm^3) were successively added a solution of 1,3-diphenylprop-2-enyl acetate (300 mg, 1.2 mmol) in CH_2Cl_2 (1 cm^3), BSA (0.58 cm^3, 2.38 mmol), dimethyl malonate (0.27 cm^3, 2.38 mmol) and KOAc (0.006 g, 0.06 mmol). The mixture was then stirred at 0 °C.

Method b. Sodium malonate (2.5 mmol) was prepared from NaH (0.100 g, 60% dispersion in mineral oil, 2.5 mmol) and dimethyl malonate (0.29 cm^3, 2.5 mmol) in THF (5 cm^3). To this suspension was then added a solution of 1,3-diphenylprop-2-enyl acetate (0.300 g, 1.2 mmol) in THF (1 cm^3) and a solution of the catalyst (0.012 mmol) in THF (3 cm^3). The mixture was refluxed until the reaction was completed. The reaction was monitored by TLC (SiO_2, R_f = 0.5 for starting compound, R_f = 0.2 for alkylated product, AcOEt–hexane, 5 : 1, v/v). After completion a few drops of acetic acid were added to quench the reaction. The oily residue, obtained after work-up, was subjected to flash chromatography using AcOEt–hexane (5 : 1, v/v) as eluent. After evaporation of the fraction with R_f = 0.2, the purity of the methyl-2-carbomethoxy-3,5-diphenylpent-4-enoate sample was checked by ^{1}H NMR. The enantiomeric excess was determined by ^{1}H NMR with an optically active shift reagent, (+)-Eu(hfc)$_3$. A dilute $CDCl_3$ solution of the organic substrate was prepared in a NMR tube and small quantities of the shift reagent were progressively added until a clean splitting of the peaks was achieved.

Hydrogenation experiments

The catalytic runs were performed in a 100 cm^3 glass-lined steel autoclave containing a magnetic stirring bar. In a typical experiment, the autoclave was charged with a MeOH solution of the catalyst precursor (15 cm^3, 0.02 mmol) under nitrogen. The autoclave was flushed twice with H_2 and then pressurised to 20 bar at 40 °C for 1 h to preform the active catalyst. After cooling and depressurisation, dimethyl itaconate (200 equiv.) was introduced. The autoclave was then pressurised again with H_2 at 20 bar and 40 °C. At pre-set times, samples were taken to follow the progress of the reaction and analysed by Gas Chromatography (WCOT fused silica; stationary phase CP-Sil 5 CB). The enantiomeric excess was determined by ^{1}H NMR with an optically active shift reagent, (+)-Eu(hfc)$_3$. A dilute $CDCl_3$ solution of the organic substrate was prepared in a NMR tube and small quantities of the shift reagent were progressively added until a clean splitting of the peaks was achieved.

Acknowledgements

We thank Prof. J. Harrowfield (University of Perth, WA) for his interest in this work. We are grateful to Genzyme Pharmaceuticals (Switzerland) for a gift of rhodium trichloride.

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