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Cavity-shaped phosphane ligands. Phosphane-amide hybrids based on a calix[4]arene matrix and their chelating behavior towards platinum and rhodium[†]

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Summary – The di(amide)-diphosphane hybrids 5,11,17,23-tetra-*tert*-butyl-25,27-bis(diethylcarbamoylmethoxy)-26,28-bis(diphenylphosphinomethoxy)calix[4]arene (cone) **7** and (*R*,*R*)-(+)-5,11,17,23-tetra-*tert*-butyl-25,27-bis[(1-phenylethyl) carbamoylmethoxy]-26,28-bis(diphenylphosphinomethoxy)calix[4]arene (cone) **8** were prepared in three steps from *p*-*tert*-butylcalix[4]arene **1**. Reaction of **1** with 1.1 equiv K_2CO_3 and 2 equiv $BrCH_2C(O)NR^1R^2$ ($R^1 = R^2 =$ Et and $R^1 =$ (*R*)-CHMePh, $R^2 =$ H) proceeds via the selective alkylation of two diametrically located phenol rings and gave the di(amide)-di(hydroxy) compounds **2** and **3**, respectively, both in a cone conformation. Deprotonation of **2** and **3** with 2 equiv ^{t}BuONa followed by alkylation with 2 equiv $Ph_2P(O)CH_2OTs$ yielded the phosphane oxides **4** and **5** respectively (cone conformers). The structure of **4** was confirmed by an X-ray diffraction study. Crystal data for **4** : triclinic, space group $P\bar{1}$, with $a = 14.316$ (4) Å, $b = 15.272$ (4) Å, $c = 18.100$ (5) Å, $\alpha = 86.98(2)°$, $\beta = 74.93$ (2)°, $\gamma = 87.61$ (2)°, and $Z = 2$. The structure was solved by direct methods and refined to $R = 0.060$. Functionalization of **2** with ^{t}BuKO instead of ^{t}BuNaO led to the partial cone isomer **6** in which one phosphoryl group is positioned **anti** with respect to the three other pendant groups. The quantitative reduction of **4** and **5**, leads to the diphosphanes **7** and **8**, respectively, and was performed in refluxing $PhSiH_3$. The sequential reaction of $[RhCl(norbornadiene)]_2$ with 2 equiv $AgBF_4$ and 2 equiv **8** gave the cationic complex *cis*-[RhCl(norbornadiene)·**8**](BF_4) **9**. Complex **9** catalyzes the hydroformylation of styrene at 40°C, under a CO/H_2-pressure of 40 bar, leading to 2-phenylpropanal and 3-phenylpropanal in a ratio 95:5. Reaction of **7** with $[PtCl_2$(cycloocta-1,5-diene)] gave the chelate complex **10**. The structure of **10** has been determined from three-dimensional X-ray data. Crystal data for **10** $\cdot CH_2Cl_2$: triclinic, space group $P\bar{1}$, with $a = 12.481$ (9) Å, $b = 17.558$ (5) Å, $c = 20.43$ (1) Å, $\alpha = 95.20$ (4)°, $\beta = 103.68$ (8)°, $\gamma = 92.79$ (4)°, and $Z = 2$. The structure was refined to $R = 0.096$. The phosphorus atoms are *cis*-bonded to the metal center and the platinum atom lies above the cavity defined by the four substituents of the calixarene. All compounds have been characterized by elemental analyses, IR and ^1H, $^{13}C\{^1H\}$ and $^{31}P\{^1H\}$ NMR spectroscopy.

phosphane / macrocycle / chirality / calixarene / rhodium / platinum / hydroformylation

Introduction

The synthesis and use of functional phosphane ligands is a continuing central theme in molecular chemistry with important implications in homogeneous catalysis, in particular for the finding of highly selective catalytic reactions [1]. It is well known that in complexes with such ligands a functional group can provide a weakly bonded donor atom which can liberate a vacant site or promote a key step in a catalytic cycle by transient binding to the metal center [2]. More commonly, phosphanes with functional groups may allow the formation of dissymetric chelate complexes in which the differing *trans* influences of the binding atoms are determining for high selectivities [3, 4]. Surprisingly, little effort has been devoted to the use of ligands mixing macrocyclic receptor moieties with exocyclic P(III) centers [5]. One potential advantage of such systems is to combine molecular recognition with transition metal catalysis. The capture of a substrate and its controlled orientation by a cavity-shaped fragment may result in a regio and/or stereoselective transformation of the substrate by the neighboring metal center. This could notably facilitate selective reactions with substrates with few functional groups and therefore not well suited for metal binding. As a part of a programme aiming at the preparation of phosphino-macrocyclic ligands [6, 7], we present here the synthesis and properties of mixed

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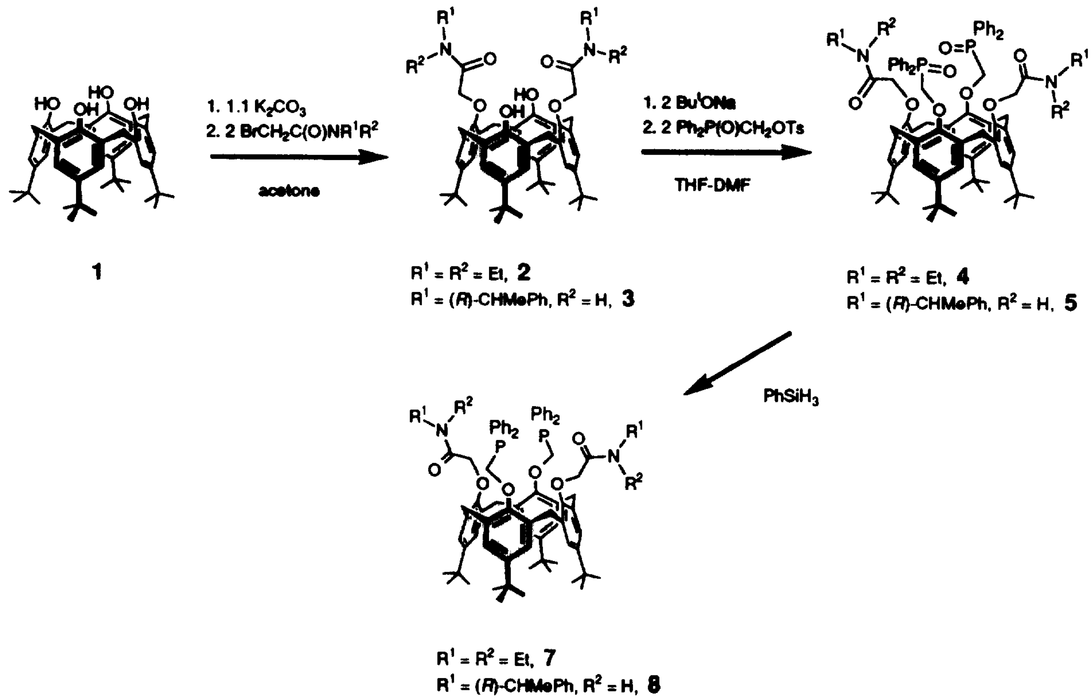
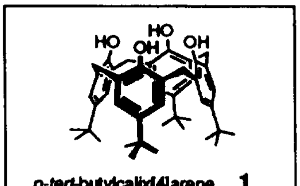
* Correspondence and reprints



Scheme 1

diphosphane-di(amide) compounds derived from *p-tert*-butylcalix[4]arene **1**, a matrix allowing the straightforward anchoring of four donor functionalities.



p-tert-butylcalix[4]arene **1**

In the present work we also describe the first X-ray structure of a platinum complex derived from a calix[4]arene ligand as well as that of a calix[4]arene substituted by two phosphane oxide groups and two amide functionalities.

Results and discussion

The preparation of the new phosphane-amide hybrids is represented in scheme 1. The introduction of two carbamoyl functionalities into precursor **1** was achieved by treating an acetone suspension of **1** with 1.1 equiv of K_2CO_3 and by refluxing the resulting mixture with 2 equiv of the appropriate bromoacetamide. This strategy leads selectively to distally dialkylated calix[4]arenes [8]. Thus, the use of $BrCH_2C(O)NEt_2$ or (+)-(*R*)-$BrCH_2C(O)NHCHMePh$ resulted respectively in the formation of compounds **2** [9] and **3**, obtained each in *ca* 75% yield.

Both compounds are in a cone conformation as may be deduced unambiguously from the chemical shift values of the $ArCH_2Ar$ carbon atoms (31.93 for **2**, 32.32 and 32.10 for **3**), which lie in the critical range 29-33 ppm, typical for methylene groups bridging *syn* oriented aryl rings [10, 11]. It is noteworthy that the ^1H NMR spectrum of the chiral compound **3** (fig 1) shows two distinct $ArCH_AH_BAr$ patterns due to the absence of any symmetry plane in this molecule. Interestingly, the inequivalence of the $ArCH_AH_BAr$ protons is more pronounced in **2** than in **3** ($\delta_A - \delta_B = 1.21$ for **2** and 0.61 and 0.79 for **3**), indicating a lower degree of cone flattening in **2** [12]. Furthermore, whereas the IR spectrum of **3** (in toluene) displays the expected

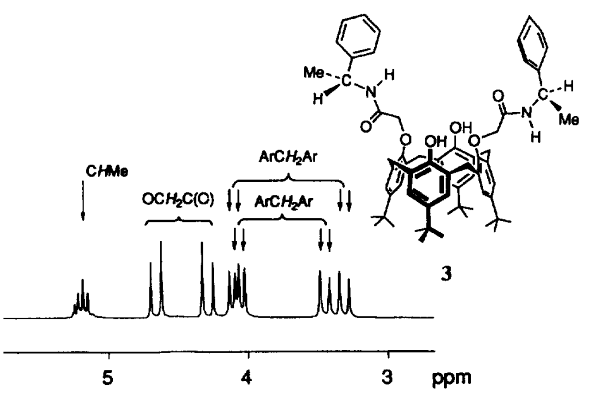
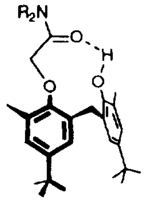
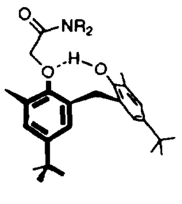


Fig 1. ^1H NMR ($CDCl_3$) spectrum of **3**.

single ν(OH) band (3 336 cm^{-1}) and a single ν(CO) band (1 685 cm^{-1}), that of **2** shows two ν(OH) bands (3 386 and 3 290 cm^{-1}) and two ν(CO) bands (1 667 and 1 648 cm^{-1}). The somewhat "anomalous" spectroscopic data observed for **2** could be related to a fast exchange between different cone conformers in solution involving hydrogen bonds of type A and B (see below), *ie* in which the OH groups are either bonded to the carbonyl group of an amide or to the neighboring phenolic oxygen atom. Note that hydrogen bonds of type B are not unusual for dihydroxy-difunctionalized calix[4]arenes [9].



A



B

Obviously, in an A-type structure the two amide groups come closer together than in a B-type structure. Since the amide groups of **3** are bulkier than those of **2**, the possibility of forming hydrogen bonds of type A becomes unlikely for **3**. This could then explain why **3** appears to be more flattened than **2**.

Reaction of **2** and **3** with ^{t}BuONa and subsequent treatment with $Ph_2P(O)CH_2OTs$ yielded the corresponding phosphane oxides **4** and **5**, in 74 and 95% yield respectively. During this second alkylation step, the cone conformation is maintained, as evidenced by the spectroscopic data of **4** and **5** and by the crystal structure determination of **4**. An ORTEP representation of this molecule is shown in figure 2. Selected bond lengths and angles are given in table I. The cavity created by the four phenolic rings resembles that of other tetrafunctionalized calix[4]arenes with a cone conformation [13, 14]. Two of the phenolic aryl rings are almost cofacial (the dihedral angle between the two aryl rings substituted by the amide groups is 5°), whereas the other two opposite rings are almost perpendicular (95.5°) (fig 3). The inclinations of the four macrocyclic phenyl rings with respect to the reference plane [15] are 139.0, 88.5, 136.4 and 93.9°. There are some conformational differences between the chains bearing the functional groups. In each "amide" chain, the Ph-O and the corresponding CH_2-C(O) bonds are in a *trans* conformation with respect to the O-CH_2 bond. This contrasts with the "phosphoryl" chains, in which the Ph-O and the corresponding P-CH_2 bonds are almost in an *cis* conformation. Each carbonyl group points towards a PPh_2 group so that these groups can be regarded as directed towards the interior of the pocket defined by the calixarene substituents. Unlike the CO groups, the P=O groups point towards the exterior of the cavity, both P=O bonds being roughly parallel to the O(3)-O(7) segment (the O(2)-P(1)-O(3)-O(7) and O(6)-P(2)-O(7)-O(3) dihedral angles are both close to 160°). The phosphorus atoms have the expected tetrahedral geometry, but for each of these atoms, one C-P-C angle is significantly smaller than the other two (see table I). As can be deduced from the rather short O(2)-C(6) (3.442 Å) and O(6)-C(42) (3.414 Å) distances, these C-P-C contractions are likely to reflect a strong repulsion between an oxygen lone pair of each phosphoryl group and the phenolic ring to which the P=O group is linked. A certain degree of stacking between the C(55)...C(60) and C(14)...C(19) aryl rings may also amplify this effect (the distance between the two centroids is 5.13 Å).

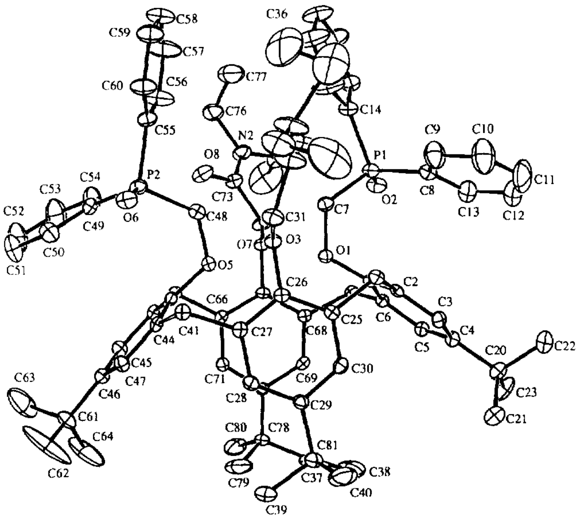


Fig 2. Ortep drawing and numbering scheme for **4**. Thermal ellipsoids are represented at the 30% probability level.

Table I. Important interatomic distances and angles in **4**.

	Distances		
P(1)-C(8)	1.802(6)	P(2)-C(48)	1.810(4)
P(1)-C(14)	1.812(5)	P(2)-C(55)	1.806(5)
P(1)-C(7)	1.817(4)	P(2)-C(49)	1.806(5)
P(1)-O(2)	1.478(3)	P(2)-O(6)	1.479(3)
N(1)-C(32)	1.338(7)	N(2)-C(73)	1.340(6)
O(1)-C(7)	1.422(5)	O(5)-C(48)	1.429(5)
O(8)...O(4)	6.460(5)	O(3)...O(7)	5.248(5)
O(1)...O(5)	3.277(5)		
	Angles		
C(7)-P(1)-O(2)	116.1(2)	C(48)-P(2)-O(6)	115.2(2)
C(7)-P(1)-C(8)	108.4(2)	C(48)-P(2)-C(49)	108.3(2)
O(2)-P(1)-C(8)	111.5(2)	O(6)-P(2)-C(49)	111.8(2)
O(2)-P(1)-C(14)	112.0(2)	O(6)-P(2)-C(55)	111.4(2)
C(8)-P(1)-C(14)	106.8(2)	C(49)-P(2)-C(55)	107.6(2)
O(1)-C(7)-P(1)	119.4(3)	O(5)-C(48)-P(2)	119.2(3)

As found earlier [7], the use of ^{t}BuONa as a base is a crucial point for the selective formation of a mixed tetra-alkylated cone conformer starting from a distally dialkylated cone precursor. When ^{t}BuOK was used instead of ^{t}BuONa, compound **6** was formed selectively (eq 1).

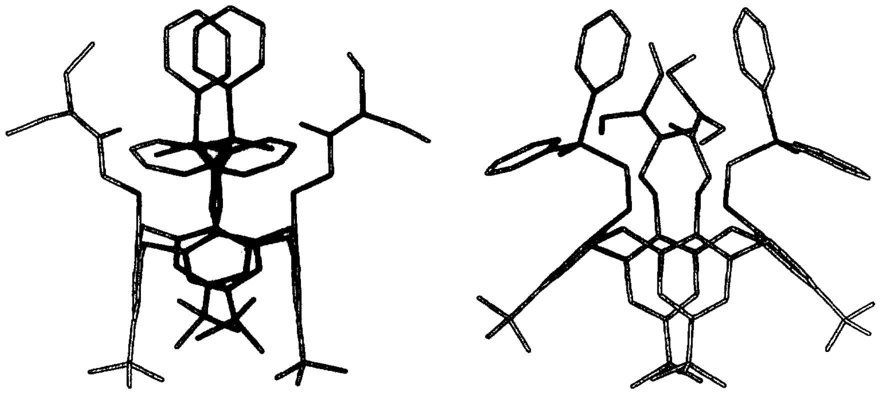
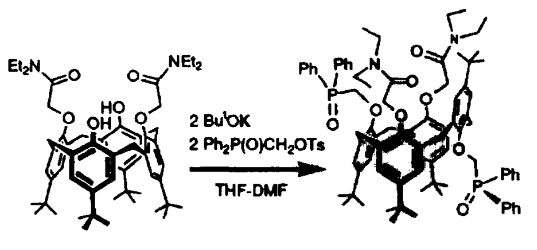


Fig 3. Two views (MolView [30]) of **4** showing the relative inclination of the opposite aryl rings of the calixarene part.

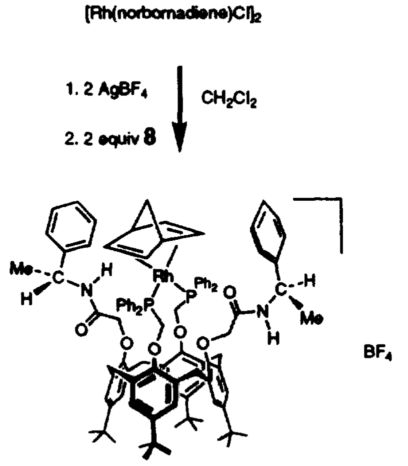


2 **6** [1]

The assignment of the exact conformation of **6** was made on the basis of the ^1H and ^{31}P NMR spectra. The ^1H NMR spectrum of **6** shows three ^tBu signals with respective intensities 9:18:9, indicating a partial cone conformer. The presence of two distinct singlets (25.2 and 21.9 ppm) in the ^{31}P NMR spectrum establishes that the phenoxy rings bearing the phosphane oxide groups are positioned *anti*. Two distinct signals are also observed in the ^{13}C NMR spectrum for the $ArCH_2Ar$ carbon atoms, one at 32.30 ppm, typical for methylene groups bridging *syn*-aryl rings, another one at 36.38, lying in the expected range for *anti* oriented aryl rings (*ie ca* 35-39 ppm) [10]. It is likely that the selective formation of cone-diamides by using Na-salts is template-controlled.

The final step for the preparation of the hybrid phosphanes **7** and **8** may be achieved by refluxing (110°C) a toluene solution of the corresponding phosphane oxides in the presence of a 20-fold excess of phenylsilane. This reaction is selective and quantitative, but requires long reaction times (10 d for the reduction of compound **4**, and 35 d for the reduction of **5**). The reaction time for a full conversion can however be significantly reduced by performing the reduction in boiling $PhSiH_3$ (120°C). Under these conditions, the reactions were found to be complete after *ca* 60 h. The use of $HSiCl_3$ as reducing agent led to the formation of a number of reaction products. This may be assigned to side reactions of the chlorosilane with the amide functions. Physical data characterizing **7** and **8** are given in the *Experimental section*. To the best of our knowledge **7** and **8** are the first calix[4]arenes combining phosphane and amide functionalities. In both phosphanes, the two phosphorus atoms are separated by 14-membered skeletons.

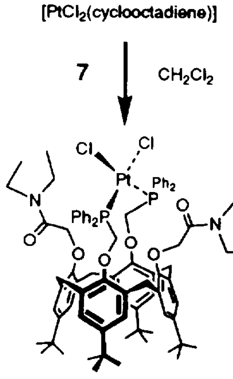
Reaction of $[RhCl(norbornadiene)]_2$ with 2 equiv of $AgBF_4$ and the di(phosphane) **8** gave complex **9** in 80% yield (eq 2). The ^{31}P NMR spectrum of **9** displays a doublet at 23.1 ppm (J_{Rh-P} = 151 Hz), indicating the coordination of both phosphorus atoms. The FAB mass spectrum of **9** shows an intense peak at m/z = 1 562 corresponding to a $[(diphosphane)Rh(norbornadiene)]^+$ cation. A molecular weight determination by osmometry ($CHCl_3$) unambiguously confirmed the monomeric nature of complex **9** and hence established the chelating behavior of the phosphane.



9 [2]

Complex **9** catalyzes the hydroformylation of styrene. Operating at 40°C, under a pressure of 40 atm (CO/H_2 = 1:1) and at a styrene-to-metal ratio of 350:1 (solvent CH_2Cl_2/benzene), full conversion of styrene was achieved after 48 h. Reaction analysis revealed the formation of 2-phenylpropanal and 3-phenylpropanal in a 95:5 ratio. Such a high regioselectivity is not unusual for rhodium-phosphane catalysts [16, 17]. The rather low reaction rate observed (*ca* 7.5 turnovers per Rh per hour) is possibly due to a partial encapsulation (see below) of the metal center preventing somewhat the approach of the substrate.

An illustration of the chelating behavior of **7** was found by reacting this diphosphane with 1 equiv of $[PtCl_2(cycloocta\text{-}1,5\text{-}diene)_2]$ (eq 3). This reaction yielded quantitatively complex **10**, the molecular weight of which was determined osmometrically (CH_2Cl_2). The *cis* arrangement of the phosphorus atoms may be deduced from the J_{PPt} coupling constant (3 555 Hz). The ^1H NMR spectrum displays a single AB pattern for the $ArCH_2Ar$ hydrogens, showing that the cone conformation is maintained upon complexation.



10 [3]

The solid state structure of **10** · CH_2Cl_2 was elucidated by an X-ray diffraction study. Its crystal structure is shown in figure 4. Important bond lengths and angles are given in Table II. This study confirms that the ligand behaves as a *cis*-chelater and the platinum atom lies above a hemispherical cavity made of a set of four functional groups. In the same way as in compound **4**, the aryl rings with the amide groups are almost parallel (dihedral angle = 3(1)°); the angle between those bearing the phosphino groups is 99°(1). In contrast to the solid state structure of **4**, the amide groups are folded back from the substituent cavity. This situation minimizes the steric repulsion between the P-aryl rings and the amide groups. Indeed, as a result of metal complexation in **10**, the phosphino groups are much closer to the center of the cavity created by the four calixarene substituents than in **4**. The platinum atom is in an almost planar ligand environment, the maximum deviation out of the plane being 0.136 (9) Å for Cl(1). The P-Pt bond lengths (2.236 (9) and 2.238 (9) Å) are close to those found for other complexes of the type [*cis*-$PtCl_2(P{\cap}P)$] with chelating diphosphanes (*eg*, [*cis*-$PtCl_2\{Ph_2P(CH_2)_5PPh_2\}$] (2.237 (3) and 2.256 (3) Å) [18], [*cis*-$PtCl_2\{Ph_2P(CH_2)_2PPh_2\}$] (2.215 (2) and 2.221 (2) Å) [19]. As a general rule, the Pt-P bonds in such complexes increase with the chelate size [20]. In view of the high standard deviations obtained for **10**, this trend cannot be confirmed in the present case. The Pt-Cl bonds also lie in the normal range [20, 21]. The rather large P(1)-Pt-P(2) angle (103.6 (3)°) reflects the large size of the matrix bearing the pendant phosphane arms and possibly also its limited flexibility. The two CH_2PPh_2 groups are unsymmetrically attached to the calixarene macrocycle. In one of them, the methylene hydrogens are pointing toward the inside of the cavity generated by the calixarene substituents whereas in the other they are directed toward the exterior of this cavity. The metal plane is somewhat inclined with respect to the "calixarene axis" (the dihedral angle between this plane and the reference plane is 112.4 (4)°). This leads to a larger folding back of one of the two amide groups. Interestingly, the room temperature NMR spectra indicate a C_2 symmetrical structure for this complex, suggesting a fan-like motion of the metal plane in solution (figure 5). Molecular models show that, from a steric point of view, in complexes **10** and **9** the functional side chains may occupy

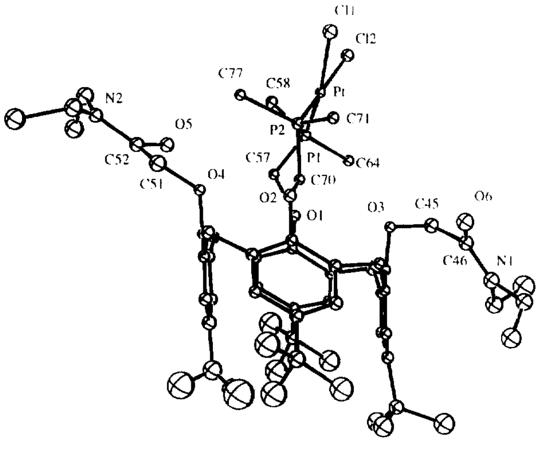


Fig 4. Ortep drawing for **10** · CH_2Cl_2 using equivalent isotropic temperature factors. For clarity only the ipso atoms of the *P*-phenyl groups have been represented.

Table II. Important interatomic distances and angles in **10**·CH_2Cl_2.

	Distances		
Pt-P(1)	2.236(9)	Pt-P(2)	2.238(9)
Pt-Cl(1)	2.308(9)	Pt-Cl(2)	2.318(9)
P(1)-C(57)	1.79(3)	P(2)-C(70)	1.67(3)
P(1)-C(58)	1.80(3)	P(2)-C(71)	1.82(3)
P(1)-C(64)	1.79(3)	P(2)-C(77)	1.85(2)
N(1)-C(46)	1.28(4)	N(2)-C(52)	1.41(1)
O(1)-C(57)	1.41(3)	O(2)-C(70)	1.43(3)
O(1)...O(2)	4.23(3)	O(3)...O(4)	5.84(3)
	Angles		
C(57)-P(1)-C(58)	98(1)	C(70)-P(2)-C(71)	100(1)
C(57)-P(1)-C(64)	106(1)	C(70)-P(2)-C(77)	107(1)
C(58)-P(1)-C(64)	106(1)	C(71)-P(2)-C(77)	105(1)
P(1)-C(57)-O(1)	116(2)	P(2)-C(70)-O(2)	111(2)
P(1)-Pt-Cl(2)	85.0(3)	P(2)-Pt-Cl(1)	86.4(3)
Cl(1)-Pt-Cl(2)	85.4(3)		

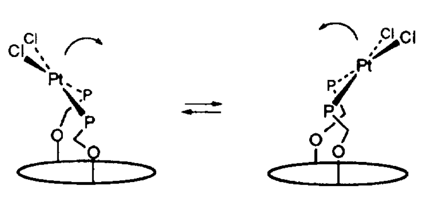


Fig 5. Possible dynamics for **10**.

a space located above the metal plane. This property could be highly relevant to a good control of selectivity in a catalytic process involving these metal centers, notably when the functional group contains chiral information. However, we must be aware that because of the rather semi-encapsulated character of the metal atom in such complexes the approach of substrates to the metal center could be somewhat hindered. This possible limitation could, at least in part, explain why the reaction rate for styrene hydroformylation with complex **9** is lower than usually observed with rhodium-diphosphane complexes.

In conclusion, this work has described the synthesis of new multifunctional diphosphanes based on a calix[4]arene. These ligands were suitable for the formation of transition metal chelate complexes in which the metal centers may be viewed as located in a hemispherical ligand environment. Further work will concentrate on the catalytic properties of the complexes obtained from such ligands. The complexing properties of the (phosphane oxide)-amide hybrids also remain to be explored.

Experimental section

Reagents and physical measurements

All manipulations involving phosphanes were performed in Schlenk-type flasks under argon. Solvents were dried by conventional methods and distilled immediately prior to use. IR spectra were recorded on a IFS 25 Bruker spectrometer (4 000-400 cm^{-1}). The ^{1}H and ^{31}P{^{1}H} and ^{13}C{^{1}H} NMR spectra were recorded by using a FT Bruker WP-200 SY instrument. The ^{1}H NMR data were referenced to residual protonated solvents; ^{13}C chemicals shifts are reported relative to deuterated solvents; the ^{31}P NMR data are given relative to external H_3PO_4. A positive sign denotes a value downfield from the reference. The mass spectra of (+)-(*R*)-$BrCH_2C(O)NHCHMePh$ and compounds **2-8** were recorded on a TSQ-70 Finnigan-Mat spectrometer and those of compounds **9** and **10** on a ZAB HF VG Analytical using tetraglyme as a matrix. The compounds *p-tert*-butylcalix[4]arene **1** [22], $Ph_2P(O)CH_2OTs$ [23], [RhCl(norbornadiene)]$_2$ [24], and [$PtCl_2$(cyclooctadiene)] [25] were prepared by using literature procedures. ^{t}BuOK and ^{t}BuONa were dissolved prior to use in THF and the resulting suspension filtered through a glass fritt to remove insoluble impurities. After removal of the solvent, these salts were stored under argon. Phenylsilane was purchased from Aldrich.

Syntheses of the bromoacetamide reagents

- *2-Bromo-*N,N*-diethylacetamide* $BrCH_2C(O)NEt_2$

Another preparation of this compound has been described previously, using $BrCH_2C(O)Cl$ groups as a starting material [26]. The following procedure avoids the use of this sensitive reagent. To a stirred cold (0°C) solution of bromoacetic acid (50.00 g, 0.36 mol) in CH_2Cl_2 (700 mL) was slowly added dicyclohexylcarbodiimide (74.25 g, 0.36 mol). After stirring for 0.5 h, the mixture was cooled to −10°C and diethylamine (26.3 g, 0.37 mol) in CH_2Cl_2 (50 mL) was added dropwise. Stirring was continued for 2 h, and the suspension was allowed to warm to room temperature. It was then filtered into a flask containing 500 mL cold water. The organic layer was washed successively with 1 N HCl and saturated sodium bicarbonate solution and then dried with $MgSO_4$. Removal of the solvent and distillation of the residue under reduced pressure (93°C, 0.1 mm Hg) afforded the product as a colorless liquid.

Yield 45.0 g, 64.4%.

IR (KBr) : $\nu_{C=O}$ 1 645 s cm^{-1}.

^{1}H NMR ($CDCl_3$) : δ 3.84 (s, 2H, $BrCH_2$), 3.39 and 3.38 (2q, 4H, CH_2CH_3, J = 7.1 Hz), 1.25 and 1.13 (2t, 6H, CH_2CH_3, J = 7.1 Hz).

- *(+)-(*R*)-2-Bromo-*N*-(1-phenylethyl)acetamide (+)-(*R*)-*$BrCH_2C(O)NHCHMePh$

To a stirred cold (0°C) solution of bromoacetic acid (27.200 g, 0.196 mol) in CH_2Cl_2 (500 mL) and 4-(dimethylamino)pyridine (2.000 g, 16.37 mmol) was slowly added dicyclohexylcarbodiimide (40.441 g, 0.196 mol). After stirring for 0.5 h, the mixture was cooled to −10°C and (*R*)-(+)-1-phenylethylamine (23.752 g, 0.196 mol) in CH_2Cl_2 (50 mL) was added dropwise. Stirring was continued for 2 h, and the suspension was allowed to warm to room temperature. It was then filtered into a flask containing 300 mL cold water. The organic layer was washed successively with 1 N HCl and saturated sodium bicarbonate solutions and then dried with $MgSO_4$. Removal of the solvent and precipitation from ethanol/hexane under cooling and stirring afforded the product as a white solid (R_f = 0.62 with CH_2Cl_2/MeOH 99:1, v/v).

Yield 28.0 g, 60.8%, mp 107-109°C.

$[\alpha]_D^{20}$ +58.4° (c = 2 g/100 mL, toluene).

Found : C, 49.73; H, 4.80; N, 5.71. Anal calc for $C_{10}H_{12}BrNO$ (M_r = 242.12) : C, 49.61; H, 5.00; N, 5.79.

MS (CI), m/z (%) : 242 (8) (M^+).

IR (KBr) : ν_{NH} = 3 266 s, $\nu_{C=O}$ = 1 648 s cm^{-1}.

^{1}H NMR ($CDCl_3$) : δ 7.34 (m, 10H, ArH), 6.74 (brd s, 1H, NH), 5.11 (AMX_3 spin system, 1H, CHMePh, $^3J_{AX} \approx {}^3J_{AM}$ = 7.2 Hz), 3.92 and 3.84 (AB spin system, 2H, $BrCH_2$, J = 13.8 Hz), 1.53 (d, 3H, CH_3, ^3J = 6.9 Hz).

^{13}C{^{1}H} NMR ($CDCl_3$) : δ 164.79 (s, C=O), 142.37 (s, aromatic C_{quat}), 128.69, 127.51 and 126.03 (3s, aromatic CH), 49.51 (s, *C*HMePh), 29.15 (s, $BrCH_2$), 21.59 (s, Me).

Syntheses of the hybrid macrocyclic ligands

- *5,11,17,23-Tetra-*tert*-butyl-25,27-bis(diethylcarbamoylmethoxy)-26,28-dihydroxycalix[4]arene* **2**

A suspension of *p-tert*-butylcalix[4]arene (15.000 g, 23.11 mmol) and K_2CO_3 (3.514 g, 25.43 mmol) in acetone (600 mL) was stirred at room temperature overnight. 2-Bromo-*N,N*-diethylacetamide (9.870 g, 50.86 mmol) was then added and the mixture was refluxed for 15 h. After cooling and filtration, the solvent was evaporated to dryness. The residue was dissolved in CH_2Cl_2 (300 mL) and the thus obtained solution washed with a saturated NH_4Cl solution (200 mL) and then with water (200 mL). The organic layer was dried over $MgSO_4$ and, after filtration, precipitation with EtOH yielded **2** as a pure white solid (R_f = 0.69 CH_2Cl_2/MeOH 94:6, v/v).

Yield 15.0 g, 74%, mp 235°C, decomp.

Found : C, 76.89; H, 9.19; N, 3.21. Anal calc for $C_{56}H_{78}N_2O_6$ (M_r = 875.26) : C, 76.85; H, 8.98; N, 3.20.

MS (CI), m/z (%) : 874 (79) (M^+).

IR (toluene) : ν_{OH} = 3 386 ms and 3 290 m, $\nu_{C=O}$ = 1 667 s and 1 648 s cm^{-1}.

IR (KBr) : ν_{OH} = 3 403 ms and 3 300 m, $\nu_{C=O}$ = 1 651 s br cm^{-1}.

^{1}H NMR ($CDCl_3$) : δ 7.82 (s, 2H, ArOH), 6.88 (s, 8H, *m*-ArH), 4.83 (s, 4H, OCH_2CONEt_2), 4.48 and 3.27 (AB spin system, 8H, $ArCH_2Ar$, J = 13.1 Hz), 3.47

(q, 8H, $\mathrm{C}H_2\mathrm{CH_3}$, ^3J = 7.1 Hz), 1.27 (t, 6H, $\mathrm{CH_2C}H_3$, ^3J = 7.1 Hz), 1.17 (t, 6H, $\mathrm{CH_2C}H_3$, ^3J = 7.1 Hz), 1.16 (s, 18H, ^{t}Bu), 1.06 (s, 18H, ^{t}Bu).

$^{13}\mathrm{C}\{^1\mathrm{H}\}$ NMR ($\mathrm{CDCl_3}$) : δ 167.88 (s, C=O), 152.20, 150.03, 146.62, 140.96, 133.37 and 127.68 (6s, aromatic $\mathrm{C_{quat}}$), 125.55 and 124.77 (2s, aromatic CH), 73.50 (s, $\mathrm{O}C\mathrm{H_2CONEt_2}$), 41.11 and 40.11 (2s, $C\mathrm{H_2CH_3}$), 33.91 and 33.65 (2s, $C\mathrm{(CH_3)_3}$), 31.93 (s, $\mathrm{Ar}C\mathrm{H_2Ar}$), 31.54 and 31.19 (2s, $\mathrm{C(}C\mathrm{H_3)_3}$), 14.28 and 12.97 (2s, $\mathrm{CH_2}C\mathrm{H_3}$).

• *(*R,R*)-(−)-5,11,17,23-Tetra-*tert*-butyl-25,27-dihydroxy-26,28-bis[(1-phenylethyl)carbamoylmethoxy]calix[4]arene* **3**

A mixture of *p-tert*-butylcalix[4]arene (13.000 g, 20.03 mmol) and $\mathrm{K_2CO_3}$ (3.040 g, 22.00 mmol) in dry acetone (500 mL) was stirred at room temperature overnight. (+)-(*R*)-2-Bromo-*N*-(1-phenylethyl)acetamide (10.427 g, 43.065 mmol) was then added and the mixture was refluxed for 24 h. After cooling and filtration, the solvent was evaporated to dryness. The residue was dissolved in $\mathrm{CH_2Cl_2}$ (300 mL) and the resulting solution was washed with a saturated $\mathrm{NH_4Cl}$ solution (200 mL) and then with water (200 mL). The organic layer was dried over $\mathrm{MgSO_4}$. After filtration, precipitation from $\mathrm{CH_2Cl_2/EtOH}$ yielded **3** as a pure white solid (R_f = 0.63 $\mathrm{CH_2Cl_2/MeOH}$ 98:2, v/v).

Yield 14.8 g, 76%, mp > 280°C.

$[\alpha]_\mathrm{D}^{20} = -44.8°$ (c = 2 g/100 mL, toluene).

Found : C, 79.00; H, 8.34; N, 2.85. Anal calc for $\mathrm{C_{64}H_{78}N_2O_6}$ (M_r = 971.35) : C, 79.14; H, 8.09; N, 2.88.

MS (CI), m/z (%) : 970 (97) ($\mathrm{M^+}$).

IR (toluene) : ν_OH and ν_NH = 3 336 ms, $\nu_\mathrm{C=O}$ = 1 685 s $\mathrm{cm^{-1}}$.

^{1}H NMR ($\mathrm{CDCl_3}$) : δ 9.26 (d, 2H, NH, ^3J = 7.5 Hz), 7.53 (s, 2H, ArOH), 7.31-7.19 (m, 10H, $\mathrm{NHCHMeC_6}H_5$), 7.09 and 7.07 (AB spin system, 4H, *m*-ArH, ^4J = 2.4 Hz), 6.90 and 6.88 (AB spin system, 4H, *m*-ArH, ^4J = 2.4 Hz), 5.18 (dq, $\mathrm{AMX_3}$ spin system, 2H, $\mathrm{NHC}H\mathrm{MePh}$, $^3J_\mathrm{AM} \approx {}^3J_\mathrm{AX}$ = 7.6 Hz), 4.65 and 4.28 (AB spin system, 4H, $\mathrm{OC}H_2\mathrm{CONHR}$, J = 15.3 Hz), 4.10 and 3.31 (AB spin system, 4H, $\mathrm{ArCH_2Ar}$, J = 13.2 Hz), 4.06 and 3.45 (AB spin system, 4H, $\mathrm{ArCH_2Ar}$, J = 13.5 Hz), 1.65 (d, 6H, $\mathrm{NHCHC}H_3\mathrm{Ph}$, ^3J = 7.0 Hz), 1.30 (s, 18H, ^{t}Bu), 1.03 (s, 18H, ^{t}Bu).

$^{13}\mathrm{C}\{^1\mathrm{H}\}$ NMR ($\mathrm{CDCl_3}$) : δ 167.39 (s, C=O), 149.46, 149.16, 148.30, 143.13, 142.84, 132.21, 132.10, 126.75 and 126.52 (9s, aromatic $\mathrm{C_{quat}}$), 128.43, 127.30, 126.60, 125.88, 125.74 and 125.40 (6s, aromatic CH), 74.87 (s, $\mathrm{O}C\mathrm{H_2CONHR}$), 49.42 (s, $\mathrm{NH}C\mathrm{HMePh}$), 34.03 and 33.90 (2s, $C\mathrm{(CH_3)_3}$), 32.32 and 32.10 (2s, $\mathrm{Ar}C\mathrm{H_2Ar}$), 31.60 and 30.90 (2s, $\mathrm{C(}C\mathrm{H_3)_3}$), 21.20 (s, $\mathrm{NHCH}C\mathrm{H_3Ph}$).

• *5,11,17,23-Tetra-*tert*-butyl-25,27-bis(diethylcarbamoylmethoxy)-26,28-bis(diphenylphosphinoylmethoxy)calix[4]arene (cone)* **4**

A solution of **2** (5.00 g, 5.71 mmol) in a THF/DMF (9:1, v/v) mixture (170 mL) was refluxed with ^{t}BuONa (1.237 g, 12.87 mmol) for 1 h. $\mathrm{Ph_2P(O)CH_2OTs}$ (4.856 g, 12.56 mmol) was then added and the solution refluxed for 48 h. After filtration, the solvents were removed under reduced pressure using a vacuum pump coupled to the evaporating apparatus. The residue was taken up in $\mathrm{CH_2Cl_2}$ (150 mL) and washed with a saturated $\mathrm{NH_4Cl}$ solution (150 mL) and then with water (100 mL). The organic layer was dried over $\mathrm{MgSO_4}$ and concentrated to *ca* 20 mL. Addition of acetone under stirring and cooling gave a white microcrystalline powder of the product (R_f = 0.26 $\mathrm{CH_2Cl_2/MeOH}$ 74:26, v/v).

Yield 5.50 g, 74%, mp > 277°C.

Found : C, 75.73; H, 7.81; N, 2.05. Anal calc for $\mathrm{C_{82}H_{100}N_2O_8P_2}$ (M_r = 1 303.66) : C, 75.55; H, 7.73; N, 2.15.

MS (CI), m/z (%) : 1 302 (10) ($\mathrm{M^+}$).

IR (KBr) : $\nu_\mathrm{C=O}$ = 1 658 s $\mathrm{cm^{-1}}$; $\nu_\mathrm{P=O}$ not assigned because of bands of the calixarene part near 1 204 $\mathrm{cm^{-1}}$.

^{1}H NMR ($\mathrm{CDCl_3}$) : δ 8.33-8.22 and 7.80-7.58 (m, 20H, $\mathrm{P(O)Ph_2}$), 6.91 (s, 4H, *m*-ArH), 6.64 (s, 4H, *m*-ArH), 6.13 (s, 4H, $\mathrm{OCH_2P(O)Ph_2}$), 4.81 and 2.64 (AB spin system, 8H, $\mathrm{ArCH_2Ar}$, J = 14.7 Hz), 4.64 (s, 4H, $\mathrm{OCH_2CONEt_2}$), 3.21 (q, 4H, $\mathrm{C}H_2\mathrm{CH_3}$, ^3J = 7.9 Hz), 3.05 (q, 4H, $\mathrm{C}H_2\mathrm{CH_3}$, ^3J = 8.0 Hz), 0.75 (s, 18H, ^{t}Bu), 0.72 (t, 6H, $\mathrm{CH_2C}H_3$, ^3J = 8.2 Hz), 0.41 (t, 6H, $\mathrm{CH_2C}H_3$, ^3J = 8.0 Hz), 0.30 (s, 18H, ^{t}Bu).

$^{13}\mathrm{C}\{^1\mathrm{H}\}$ NMR ($\mathrm{CDCl_3}$) : δ 167.94 (s, C=O), 153.03-132.30 (aromatic $\mathrm{C_{quat}}$), 131.07, 130.89, 130.47, 127.97, 127.74, 124.63 and 124.48 (aromatic CH), 72.10 (s, $\mathrm{O}C\mathrm{H_2CONEt_2}$), 69.14 (d, $\mathrm{OCH_2P(O)Ph_2}$, J_PC = 69.3 Hz), 41.65 and 40.21 (2s, $C\mathrm{H_2CH_3}$), 33.83 and 33.43 (2s, $C\mathrm{(CH_3)_3}$), 32.27 (s, $\mathrm{Ar}C\mathrm{H_2Ar}$), 31.55 and 31.00 (2s, $\mathrm{C(}C\mathrm{H_3)_3}$), 14.65 and 12.90 (2s, $\mathrm{CH_2}C\mathrm{H_3}$).

$^{31}\mathrm{P}\{^1\mathrm{H}\}$ NMR ($\mathrm{CH_2Cl_2/C_6D_6}$) : δ +23.7 (s, $\mathrm{P(O)Ph_2}$).

• *(*R,R*)-(+)-5,11,17,23-Tetra-*tert*-butyl-25,27-bis[(1-phenylethyl)carbamoylmethoxy]-26,28-bis(diphenylphosphinoylmethoxy)calix[4]arene* **5**

Compound **3** (8.000 g, 8.24 mmol) was added to a solution of ^{t}BuONa (1.97 g, 20.50 mmol) in a dry THF/DMF (9:1, v/v) mixture (250 mL). After the solution was stirred under reflux for 1 h, $\mathrm{Ph_2P(O)CH_2OTs}$ (7.300 g, 18.89 mmol) was added and the mixture was refluxed for 60 h. After cooling and filtration, the solvents were removed under reduced pressure using a vacuum pump coupled to the evaporating apparatus. The residue was taken up in $\mathrm{CH_2Cl_2}$ (200 mL) and washed with a saturated $\mathrm{NH_4Cl}$ solution (100 mL) and then with water (100 mL). The organic layer was dried over $\mathrm{MgSO_4}$, filtered and concentrated to *ca* 20 mL. Addition of acetone under stirring and cooling gave a white precipitate of the product (R_f = 0.45 $\mathrm{CH_2Cl_2/MeOH}$ 92:8, v/v).

Yield 10.8 g, 95%, mp > 280°C.

$[\alpha]_\mathrm{D}^{20} = +48.0°$ (c = 2 g/100 mL, toluene).

Found : C, 77.39; H, 7.37; N, 1.99. Anal calc for $\mathrm{C_{90}H_{100}N_2P_2O_8}$ (M_r = 1 399.76) : C, 77.23; H, 7.20; N, 2.00.

MS (CI), m/z (%) : 1 398 (5) ($\mathrm{M^+}$).

IR (KBr) : ν_NH = 3 259 s, $\nu_\mathrm{C=O}$ = 1 676 s $\mathrm{cm^{-1}}$.

^{1}H NMR ($\mathrm{CDCl_3}$) : δ 9.30 (d, 2H, NH, ^3J = 8.4 Hz), 7.80-7.68 and 7.56-6.96 (m, 30H, aromatic H), 6.92 (s, 4H, *m*-ArH), 6.45 and 6.39 (AB spin system, 4H, *m*-ArH, ^4J = 2.4 Hz), 4.98 (dq, $\mathrm{AMX_3}$ spin system, 2H, $\mathrm{NHC}H\mathrm{MePh}$, $^3J_\mathrm{AM} \approx {}^3J_\mathrm{AX}$ = 7.5 Hz), 4.82 and 4.57 (ABX spin system, 4H, $\mathrm{OCH_AH_BP(O)Ph_2}$, J_AB = 13.9 Hz, J_AX = 7.6 Hz, J_BX = 6.5 Hz), 4.78 and 3.19 (AB spin system, 4H, $\mathrm{ArCH_2Ar}$, J = 12.9 Hz), 4.76 and 4.11 (AB spin system, 4H, $\mathrm{OC}H_2\mathrm{CONHR}$, J = 12.3 Hz), 4.68 and 3.03 (AB spin system, 4H, $\mathrm{ArCH_2Ar}$, J = 12.8 Hz), 1.44 (d, 6H, $\mathrm{NHCHC}H_3\mathrm{Ph}$, ^3J = 7.0 Hz), 1.25 (s, 18H, ^{t}Bu), 0.82 (s, 18H, ^{t}Bu).

$^{13}\mathrm{C}\{^1\mathrm{H}\}$ NMR ($\mathrm{CDCl_3}$) : δ 167.06 (s, C=O), 154.29-124.96 (aromatic $\mathrm{C_{quat}}$), 132.05-124.89 (aromatic CH), 72.91 (d, $\mathrm{OCH_2P(O)Ph_2}$, J_PC = 83.0 Hz), 70.90 (s, $\mathrm{O}C\mathrm{H_2CONHR}$), 48.15 (s, $\mathrm{NH}C\mathrm{HMePh}$), 33.91 and 33.54 (2s, $C\mathrm{(CH_3)_3}$), 32.16 and 31.99 (2s, $\mathrm{Ar}C\mathrm{H_2Ar}$), 31.63 and 31.02 (2s, $\mathrm{C(}C\mathrm{H_3)_3}$), 22.09 (s, $\mathrm{NHCH}C\mathrm{H_3Ph}$.

$^{31}\mathrm{P}\{^1\mathrm{H}\}$ NMR ($\mathrm{CH_2Cl_2/C_6D_6}$) : δ +27.1 (s, $\mathrm{P(O)Ph_2}$).

• 25,27-syn-26,28-anti-5,11,17,23-Tetra-tert-butyl-25,27-bis(diethylcarbamoylmethoxy)-26,28-bis(diphenylphosphinoylmethoxy)calix[4]arene (partial cone) 6

A solution of **2** (5.000 g, 5.71 mmol) in a THF/DMF (9:1, v/v) mixture (170 mL) was refluxed with ^{t}BuOK (1.444 g, 12.87 mmol) for 1 h. $Ph_2P(O)CH_2OTs$ (4.856 g, 12.56 mmol) was then added and the solution refluxed for 36 h. After filtration, the solvents were removed under reduced pressure. The residue was taken up in CH_2Cl_2 (150 mL) and washed with a saturated NH_4Cl solution (150 mL) and then with water (100 mL). The organic layer was dried over $MgSO_4$ and concentrated to *ca* 20 mL. Addition of acetone under stirring and cooling gave the product as a white microcrystalline powder (R_f = 0.26 CH_2Cl_2/MeOH 93:7, v/v).

Yield 5.66 g, 76%, mp > 280°C.

Found : C, 75.67; H, 7.80; N, 2.06. Anal calc for $C_{82}H_{100}N_2O_8P_2$ (M_r = 1 303.66) : C, 75.55; H, 7.73; N, 2.15.

MS (CI), m/z (%) : 1 303 (7) ($M + H^+$).

IR (KBr) : $\nu_{C=O}$ = 1 663 s cm^{-1}; $\nu_{P=O}$ not assigned due to bands of the calixarene part near 1 206 cm^{-1}.

^{1}H NMR ($CDCl_3$) : δ 7.92-7.82, 7.72-7.65 and 7.47-7.25 (20H, $P(O)Ph_2$), 7.22 (s, 2H, *m*-ArH), 6.98 and 6.33 (AB spin system, 4H, *m*-ArH of $ArOCH_2CONEt_2$, ^4J = 2.4 Hz), 6.61 (s, 2H, *m*-ArH), 5.14 and 4.71 (2s, 4H, $OCH_2P(O)Ph_2$), 4.64 and 4.48 (AB spin system, 4H, OCH_2CONEt_2, J = 13.2 Hz), 4.48 and 2.79 (AB spin system, 4H, $ArCH_2Ar$, J = 13.2 Hz), 3.91 and 3.80 (AB spin system, 4H, $ArCH_2Ar$, J = 13.4 Hz), 3.46 and 3.39 (2q, 8H, CH_2CH_3, ^3J = 7.1 Hz), 1.24 (s, 9H, ^{t}Bu), 1.19 (t, 6H, CH_2CH_3, ^3J = 6.9 Hz), 1.16 (t, 6H, CH_2CH_3, ^3J = 7.0 Hz), 1.08 (s, 9H, ^{t}Bu), 0.91 (s, 18H, ^{t}Bu).

$^{13}C\{^1H\}$ NMR ($CDCl_3$) : δ 167.85 (s, C=O), 155.26-124.67 (aromatic C), 71.40 (s, OCH_2CONEt_2), 70.63 (d, $OCH_2P(O)Ph_2$, J_{PC} = 77.6 Hz), 68.44 (d, $OCH_2P(O)Ph_2$, J_{PC} = 68 Hz), 41.75 and 40.60 (2s, CH_2CH_3), 36.38 (s, *anti*-$ArCH_2Ar$), 33.80 and 33.54 (2s, $C(CH_3)_3$), 32.30 (s, *syn*-$ArCH_2Ar$), 31.54, 31.40 and 31.27 (3s, $C(CH_3)_3$), 14.64 and 13.20 (2s, CH_2CH_3).

$^{31}P\{^1H\}$ NMR ($CDCl_3$) : δ +25.2 and 21.9 (2s, $P(O)Ph_2$).

• 5,11,17,23-Tetra-tert-butyl-25,27-bis(diethylcarbamoylmethoxy)-26,28-bis(diphenylphosphinomethoxy)calix[4]arene (cone) 7

A suspension of compound **4** (3.00 g, 2.30 mmol) in phenylsilane (40 mL) was refluxed for 48 h. After cooling, the solution was filtered and phenylsilane was removed under reduce pressure. The trapped phenylsilane was recovered. The residue was dissolved in CH_2Cl_2 (*ca* 10 mL) and addition of EtOH (40 mL) under stirring and cooling afforded the product as a white precipitate (R_f = 0.49 CH_2Cl_2/MeOH 9:1, v/v).

Yield 2.7 g, 92%, mp 275-278°C.

Found : C, 77.40; H, 8.11; N, 2.15. Anal calc for $C_{82}H_{100}N_2O_6P_2$ (M_r = 1 271.67) : C, 77.45; H, 7.93; N, 2.20.

MS (CI), m/z (%) : 1 270 (17) (M^+), 1 333 (6) ($MO_2 + H^+$).

IR (KBr) : $\nu_{C=O}$ = 1 652 s cm^{-1}.

^{1}H NMR ($CDCl_3$) : δ 7.49-7.41 and 7.23-7.17 (m, 20H, PPh_2), 6.76 (s, 4H, *m*-ArH), 6.42 (s, 4H, *m*-ArH), 5.68 (d, 4H, OCH_2PPh_2, $^2J_{PH}$ = 2.5 Hz), 4.46 (s, 4H, OCH_2CONEt_2), 4.43 and 2.91 (AB spin system, 8H, $ArCH_2Ar$, J = 12.9 Hz), 3.29 (q, 4H, CH_2CH_3, ^3J = 7.1 Hz), 3.22 (q, 4H, CH_2CH_3, ^3J = 7.1 Hz), 1.23 (s, 18H, ^{t}Bu), 1.04 (t, 6H, CH_2CH_3, ^3J = 7.1 Hz), 0.99 (t, 6H, CH_2CH_3, ^3J = 7.1 Hz), 0.83 (s, 18H, ^{t}Bu).

$^{13}C\{^1H\}$ NMR ($CDCl_3$) : δ 167.56 (s, C=O), 153.15-132.01 (aromatic C_{quat}), 133.69, 133.31, 127.99, 127.95, 127.82, 124.78 and 124.67 (aromatic CH), 73.85 (d, OCH_2PPh_2, J_{PC} = 8.71 Hz), 72.96 (s, OCH_2CONEt_2), 41.34 and 40.02 (2s, CH_2CH_3), 33.90 and 33.51 (2s, $C(CH_3)_3$), 32.23 (d, $ArCH_2Ar$, $^5J_{PH}$ = 4.61 Hz), 31.58 and 31.08 (2s, $C(CH_3)_3$), 14.43 and 13.07 (2s, CH_2CH_3).

$^{31}P\{^1H\}$ NMR (CH_2Cl_2/C_6D_6) : δ −22.4 (s, PPh_2).

• (R,R)-(+)-5,11,17,23-Tetra-tert-butyl-25,27-bis[(1-phenylethyl)carbamoylmethoxy]-26,28-bis(diphenylphosphinomethoxy)calix[4]arene 8

A suspension of compound **5** (6.000 g, 4.28 mmol) in phenylsilane (80 mL) was refluxed for 60 h. After cooling, the solution was filtered and phenylsilane was removed under reduce pressure. The trapped phenylsilane was recovered. The residue was dissolved in a small amount of CH_2Cl_2 and the addition of ethanol (50 mL) under cooling and stirring afforded a white precipitate of the product.

Yield 5.4 g, 92%, mp 235-240°C.

$[\alpha]_D^{20}$ = +34.6° (c = 2 g/100 mL, toluene).

Found : C, 79.28; H, 7.65; N, 2.05. Anal calc for $C_{90}H_{100}N_2P_2O_6$ (M_r = 1 367.76) : C, 79.03; H, 7.37; N, 2.05.

MS (CI), m/z (%) : 1 367 (6) (M^+).

IR (KBr) : ν_{NH} = 3 329 s, $\nu_{C=O}$ = 1 676 s, 1 659 s, 1 645 s cm^{-1}.

^{1}H NMR ($CDCl_3$) : δ 7.32 (d, 2H, NH, ^3J = 7.7 Hz), 7.29-7.17 (m, 30H, aromatic H), 6.66 (s, 4H, *m*-ArH), 6.59 and 6.56 (AB spin system, 4H, *m*-ArH, ^4J = 2.5 Hz), 5.20 (dq, AMX_3 spin system, 2H, NHC*H*MePh, $^3J_{AM} \approx {}^3J_{AX}$ = 7.5 Hz), 5.04 and 4.93 (ABX spin system, 4H, $OCH_AH_BPPh_2$, J_{AB} = 12.5 Hz, J_{AX} = 3.5 Hz, J_{BX} = 2.7 Hz), 4.52 (s, 4H, OCH_2CONHR), 4.42 and 3.04 (AB spin system, 4H, $ArCH_2Ar$, J = 13.06vHz), 4.39 and 2.97 (AB spin system, 4H, $ArCH_2Ar$, J = 12.9 Hz), 1.38 (d, 6H, $NHCHCH_3Ph$, ^3J = 7.0 Hz), 1.04 (s, 36H, ^{t}Bu).

$^{13}C\{^1H\}$ NMR ($CDCl_3$) : δ 169.17 (s, C=O), 153.41-125.04 (aromatic C_{quat}), 133.22, 133.00, 132.85, 132.64, 128.65, 128.58, 128.43, 128.31, 127.04, 126.36, 125.53, 125.46 and 125.11 (aromatic CH), 76.31 (d, OCH_2PPh_2, J_{PC} = 8.8 Hz), 74.33 (s, OCH_2CONHR), 48.50 (s, NH*C*HMePh), 33.75 (s, $C(CH_3)_3$), 32.04 (br s, $ArCH_2Ar$), 31.30 (s, $C(CH_3)_3$), 21.46 (s, $NHCHCH_3Ph$).

$^{31}P\{^1H\}$ NMR (CH_2Cl_2/C_6D_6) : δ −20.9 (s, PPh_2).

• 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 norbornadiene rhodium (I) tetrafluoroborate 9

A solution of $AgBF_4$ (0.100 g, 0.514 mmol) in THF (1 mL) was added to a solution of $[RhCl(norbornadiene)]_2$ (0.118 g, 0.256 mmol) in dichloromethane (3 mL). Stirring was stopped after 5 min. The supernatant solution and dichloromethane washings of the AgCl precipitate were then filtered through Celite into a solution of **8** (0.700 g, 0.512 mmol) in CH_2Cl_2 (25 mL). After 1 h stirring, the solution was concentrated to *ca* 5 mL and addition of diethylether (30 mL) afforded a golden precipitate which was filtered and dried *in vacuo*.

Yield 0.643 g, 76%, mp 208°C (decomp).

Found : C, 68.90; H, 6.69; N, 1.64. Anal calc for $C_{97}H_{108}BF_4N_2O_6P_2Rh \cdot 0.5CH_2Cl_2$ (M_r = 1 649.61 + 42.46) : C, 69.21; H, 6.49; N, 1.66.

MS (FAB), m/z (%) : 1 562 (100) $[(M - BF_4)]^+$, 1 470 (60) $[(M - BF_4 - \text{norbornadiene})]^+$.

Table III. Crystallographic data for **4** and **10**·CH_2Cl_2.

Chemical formula	$C_{82}H_{100}N_2O_8P_2$	$C_{82}H_{100}N_2O_6Cl_2P_2Pt{\cdot}CH_2Cl_2$
Formula weight	1 303.7	1 622.6
a (Å)	14.316 (4)	12.481(9)
b (Å)	15.272 (4)	17.558(5)
c (Å)	18.100 (5)	20.43(1)
α (°)	86.98 (2)	95.20(4)
β (°)	74.93 (2)	103.68(8)
γ (°)	87.61 (2)	92.79(4)
V (Å^3)	3 814.2 (3)	4 330 (4)
Z	2	2
Space group	$P\,\bar{1}$ (No 2)	$P\,\bar{1}$ (No 2)
T (°C)	20	20
λ (Å)	0.7107	0.7107
D_{calc} (g cm^{-3})	1.135	1.244
F (000)	1 400	1 676
μ (cm^{-1})	1.063	18.43
Min and max transmission coefficients	0.91, 1.00	0.42, 1.55
Range of collected data (°)	$2 < \theta < 24$	$2 < \theta < 20$
Scan type	$\omega - 2\theta$	$\omega - 2\theta$
No of unique reflections	6 273	4 723
$n(I) < n\sigma(I)$	3	4
No of parameters refined	847	686
$R = \Sigma\|\|F_o\| - \|F_c\|\|/\Sigma\|F_o\|$	0.060	0.096
$R_\omega = [\Sigma\omega(F_o - F_c)^2/\Sigma\omega(F_o)^2]^{1/2}$	0.082	0.107
Weighting scheme	$\omega = 4I/\sigma^2(I) + (0.08I)^2$	$[\sigma^2(I) + (0.04F_0^2)^2]^{-1/2}$

IR (KBr) : $\nu_{NH} = 3\,371$ s, $\nu_{C=O} = 1\,686$ s and $1\,675$ s cm^{-1}.

^{1}H NMR ($CDCl_3$) : δ 8.09-8.01, 7.77-7.71 and 7.62-7.27 (30H, aromatic H), 6.90 and 6.88 (AB spin system, 4H, m-ArH, $^4J = 2.4$ Hz), 6.61 (d, 2H, NH, $^3J = 7.9$ Hz), 6.41 (s, 4H, m-ArH), 5.77 and 5.47 (br AB spin system, 4H, $OCH_AH_BPPh_2$, $J_{AB} = 12.6$ Hz), 5.14 (dq, AMX_3 spin system, 2H, NHCHMePh, $^3J_{AM} \approx {}^3J_{AX} = 7.3$ Hz), 4.26 and 2.94 (AB spin system, 4H, $ArCH_2Ar$, $J = 13.4$ Hz), 4.19 and 4.00 (2 br signals, 4H, HC=CH of norbornadiene), 3.91 (s, 4H, OCH_2CONHR), 3.82 and 2.79 (AB spin system, 4H, $ArCH_2Ar$, $J = 13.2$ Hz), 3.83 (br signal, 2H, CH of norbornadiene), 1.55 (d, 6H, NHCHCH_3Ph, $^3J = 7.0$ Hz), 1.46 (br s, 2H, CH_2 of norbornadiene), 1.27 (s, 18H, ^{t}Bu), 0.78 (s, 18H, ^{t}Bu).

$^{13}C\{^1H\}$ NMR ($CDCl_3$) : δ 168.05 (s, C=O), 152.37-124.84 (aromatic C), 81.95 (br s, HC=CH of norbornadiene), 73.80 (s, OCH$_2$CONHR), 72.09 (t, AA′XX′M system with A=C, X=P, M=Rh), 68.29 (br s, CH_2 of norbornadiene), 51.85 (s, CH of norbornadiene), 49.08 (s, NHCHMePh), 33.82 and 33.63 (2s, C(CH_3)$_3$), 31.50 and 31.00 (s, C(CH$_3$)$_3$), 29.57 (s, ArCH$_2$Ar), 22.00 (s, NHCHCH$_3$Ph).

$^{31}P\{^1H\}$ NMR ($CDCl_3$) : δ 23.1 (d, PPh_2, $J_{PRh} = 151$ Hz).

• Cis-*dichloro-5,11,17,23-tetra*-tert-*butyl-25,27-bis (diethylcarbamoylmethoxy)-26,28-bis(diphenylphosphinomethoxy)calix[4]arene platinum (II)* **10**

To a solution of [$PtCl_2$(cycloocta-1,5-diene)] (0.050 g, 0.134 mmol) in CH_2Cl_2 (15 mL) was dropwise added within 15 min a solution of **7** (0.170 g, 0.134 mmol) in CH_2Cl_2 (35 mL). After stirring for 1 h the solution was concentrated to 5 mL and pentane was added to yield **10** as an analytically pure white powder.

Yield 0.192 g, 93%, mp > 280°C.

Found : C, 64.02; H, 6.44; N, 1.57. Anal calc for $C_{82}H_{100}Cl_2N_2O_6P_2Pt$ (M_r = 1 537.66) : C, 64.05; H, 6.56; N, 1.82.

MS (FAB), m/z (%) : 1 501 (100) ((M − Cl)$^+$).

IR (KBr) : $\nu_{C=O} = 1\,663$ s cm^{-1}.

^{1}H NMR ($CDCl_3$) : δ 8.23-8.14 and 7.50-7.7.35 (20H, PPh_2), 6.95 (s, 4H, m-ArH), 6.43 (s, 4H, m-ArH), 5.91 (s with br Pt satellites, 4H, OCH_2PPh_2, $^3J_{PtH} \approx 23$ Hz), 4.35 (s, 4H, OCH_2CONEt_2), 4.12 and 2.92 (AB spin system, 8H, $ArCH_2Ar$, $J = 13.6$ Hz), 3.36 (q, 4H, CH_2CH$_3$, $^3J = 7.0$ Hz), 3.11 (q, 4H, CH_2CH$_3$, $^3J = 7.0$ Hz), 1.29 (s, 18H, ^{t}Bu), 1.17 (t, 6H, CH$_2$CH_3, $^3J = 7.0$ Hz), 1.14 (t, 6H, CH$_2$CH_3, $^3J = 7.0$ Hz), 0.78 (s, 18H, ^{t}Bu).

$^{13}C\{^1H\}$ NMR ($CDCl_3$) : δ 166.54 (s, C=O), 152.39-124.63 (aromatic C), 71.92 (s, OCH$_2$CONEt$_2$), 71.74 (3 lines, OCH_2PPh_2, $J_{PC} + J_{P'C} = 41.8$ Hz), 40.73 and 39.99 (2s, CH$_2$CH$_3$), 33.80 and 33.60 (2s, C(CH$_3$)$_3$), 31.50 and 30.99 (2s, C(CH$_3$)$_3$), 30.50 (s, ArCH$_2$Ar), 14.35 and 13.05 (2s, CH$_2$$CH_3$).

$^{31}P\{^1H\}$ NMR ($CDCl_3$) : δ 7.4 (s with Pt satellites, PPh_2, $J_{PPt} = 3\,555$ Hz).

X-ray data collection and processing for **4**

This X-ray structure determination was done by JF and A De C. Colorless crystals of **4** were isolated from a methanol-d_4 solution. Crystal data and details of data collection are given in table III. The unit cell was obtained from the angular settings of 25 reflections (10° $\leqslant \theta \leqslant$ 11°); 13 851 reflections were collected on a Enraf-Nonius CAD4F diffractometer (4° $\leqslant 2\theta \leqslant$ 48°); 6 273 with $I > 3\sigma(I)$ were used for determination and refinement of the structure. No decay was observed during the data collection period. For all subsequent computations the Enraf-Nonius Molen package was used [27]. Intensities were corrected for Lorentz, polarization and absorption factors, the latter using the gaussian method. The structure was solved using Multan and refined by full matrix least-squares with anisotropic thermal parameters for all non-hydrogen atoms. The function minimized was $\Sigma\omega(|Fo| - |Fc|)^2$, where $\omega = 4I/\sigma^2(I) + (0.08I)^2$. Hydrogen atoms were introduced at their computed coordinates (C-H = 0.95 Å) in structure factor calculations and were assigned isotropic thermal parameters of $B = 1.3\ B_{equiv}$(C) Å^2. The final difference map showed no significant residual peaks (0.05 eÅ^3). The neutral-atom scattering factors used for all atoms and anomalous scattering factors for all non-hydrogen atoms were obtained from standard sources [28]. Atomic coordinates with estimated standard deviations corresponding to the final least-squares refinement cycles are given in Table IV, selected bond lengths and angles in table I. The following tables are available as supplementary material : hydrogen and non hydrogen atoms positional parameters (table S1), a complete set of bond distances (table S2), a complete set of bond angles (table S3), observed structure factors and amplitudes for all observed reflections (table S4), thermal parameters (table S5).

Table IV. Atom coordinates and equivalent isotropic thermal factors for **4**^{a}.

	x	y	z	B (Å^2)
C1	0.7479(3)	0.3532(3)	0.6039(2)	2.59(9)
C2	0.6553(3)	0.3759(3)	0.5971(2)	2.45(9)
C3	0.6471(3)	0.4350(3)	0.5389(2)	3.2(1)
C4	0.7257(3)	0.4751(3)	0.4892(2)	3.1(1)
C5	0.8170(3)	0.4532(3)	0.5004(2)	2.9(1)
C6	0.8305(3)	0.3923(3)	0.5568(2)	2.61(9)
O1	0.7624(2)	0.2990(2)	0.6643(2)	2.93(6)
C7	0.7536(3)	0.2068(3)	0.6624(3)	3.3(1)
P1	0.80015(9)	0.15279(8)	0.57258(7)	3.56(3)
O2	0.8992(2)	0.1754(2)	0.5287(2)	4.64(8)
C8	0.7146(4)	0.1717(3)	0.5155(3)	4.6(1)
C9	0.6193(4)	0.1491(5)	0.5414(4)	7.6(2)
C10	0.5558(5)	0.1640(7)	0.4948(5)	11.2(3)
C11	0.5924(5)	0.2021(7)	0.4223(4)	11.7(3)
C12	0.6831(5)	0.2256(5)	0.3983(4)	9.5(2)
C13	0.7450(5)	0.2111(4)	0.4437(3)	6.8(2)
C14	0.7927(3)	0.0384(3)	0.6050(3)	4.0(1)
C15	0.8694(3)	−0.0160(3)	0.5710(3)	4.5(1)
C16	0.8698(4)	−0.1044(4)	0.5887(4)	6.3(2)
C17	0.7947(5)	−0.1395(4)	0.6426(5)	8.0(2)
C18	0.7191(5)	−0.0864(4)	0.6792(5)	9.8(2)
C19	0.7180(4)	0.0027(4)	0.6593(4)	7.9(2)
C20	0.7091(3)	0.5425(3)	0.4275(3)	3.9(1)
C21	0.6409(4)	0.6167(4)	0.4659(3)	5.7(1)
C22	0.6605(4)	0.4986(4)	0.3734(3)	5.9(1)
C23	0.8028(4)	0.5829(4)	0.3799(3)	6.6(2)
C24	0.5669(3)	0.3473(3)	0.6585(2)	2.85(9)
C25	0.5563(3)	0.3987(3)	0.7296(2)	2.51(9)
C26	0.5585(3)	0.3595(3)	0.7996(2)	2.59(9)
C27	0.5623(3)	0.4090(3)	0.8609(2)	2.58(9)
C28	0.5589(3)	0.5000(3)	0.8509(2)	3.0(1)
C29	0.5511(3)	0.5420(3)	0.7838(2)	3.0(1)
C30	0.5503(3)	0.4901(3)	0.7239(2)	3.1(1)
O3	0.5604(2)	0.2676(2)	0.8066(2)	3.04(6)
C31	0.4675(3)	0.2319(3)	0.8329(3)	4.2(1)
C32	0.4691(4)	0.1437(3)	0.8035(4)	6.3(2)
O4	0.5404(3)	0.1155(3)	0.7600(4)	15.8(2)
N1	0.3886(3)	0.0972(3)	0.8254(3)	7.4(1)
C33	0.2974(4)	0.1294(4)	0.8731(4)	8.2(2)
C34	0.2286(6)	0.1643(8)	0.8313(7)	16.0(4)
C35	0.3893(6)	0.0039(7)	0.7662(6)	17.0(4)
C36	0.4207(8)	−0.0339(7)	0.8173(7)	19.0(4)
C37	0.5412(4)	0.6422(3)	0.7739(3)	4.4(1)
C38	0.4361(5)	0.6656(4)	0.7693(4)	8.7(2)
C39	0.5563(6)	0.6891(4)	0.8408(4)	8.7(2)
C40	0.6095(6)	0.6750(4)	0.6993(4)	9.6(2)
C41	0.5730(3)	0.3678(3)	0.9368(2)	2.9(1)
C42	0.6709(3)	0.3841(3)	0.9497(2)	2.66(9)
C43	0.7539(3)	0.3428(3)	0.9049(2)	2.55(9)
C44	0.8458(3)	0.3634(3)	0.9096(2)	2.62(9)
C45	0.8527(3)	0.4220(3)	0.9637(2)	3.1(1)
C46	0.7729(3)	0.4645(3)	1.0106(2)	3.0(1)
C47	0.6821(3)	0.4442(3)	1.0018(2)	3.1(1)
O5	0.7406(2)	0.2893(2)	0.8493(2)	3.01(6)
C48	0.7509(3)	0.1962(3)	0.8588(3)	3.3(1)
P2	0.70952(9)	0.14453(8)	0.95341(7)	3.52(3)
O6	0.6104(2)	0.1706(2)	0.9962(2)	4.54(8)
C49	0.7972(3)	0.1632(3)	1.0064(3)	3.9(1)
C50	0.7649(4)	0.2027(4)	1.0754(3)	6.0(2)
C51	0.8290(5)	0.2205(5)	1.1177(3)	8.4(2)
C52	0.9239(5)	0.1986(6)	1.0919(4)	9.4(2)
C53	0.9582(5)	0.1606(5)	1.0237(4)	8.7(2)
C54	0.8951(4)	0.1438(4)	0.9800(3)	5.9(2)
C55	0.7182(3)	0.0298(3)	0.9324(3)	4.0(1)
C56	0.8001(4)	−0.0138(4)	0.8918(4)	7.7(2)
C57	0.7971(5)	−0.1012(4)	0.8793(5)	9.4(2)
C58	0.7138(4)	−0.1465(3)	0.9039(4)	7.2(2)
C59	0.6327(4)	−0.1049(4)	0.9415(4)	6.6(2)
C60	0.6351(4)	−0.0165(3)	0.9557(4)	5.7(2)
C61	0.7847(3)	0.5336(3)	1.0645(3)	4.2(1)
C62	0.6984(5)	0.5677(5)	1.1133(5)	19.2(2)
C63	0.8460(6)	0.4959(6)	1.1162(4)	13.0(3)
C64	0.8538(7)	0.6005(5)	1.0238(5)	15.1(3)
C65	0.9351(3)	0.3326(3)	0.8507(2)	2.81(9)
C66	0.9461(3)	0.3878(3)	0.7771(2)	2.36(9)
C67	0.9430(3)	0.3523(2)	0.7089(2)	2.40(9)
C68	0.9395(3)	0.4055(3)	0.6444(2)	2.49(9)
C69	0.9454(3)	0.4955(3)	0.6502(2)	2.68(9)
C70	0.9549(3)	0.5337(3)	0.7150(2)	2.83(9)
C71	0.9538(3)	0.4779(3)	0.7777(2)	2.9(1)
O7	0.9391(2)	0.2610(2)	0.7075(2)	2.84(6)
C72	1.0274(4)	0.2181(3)	0.6759(3)	5.1(1)
C73	1.0345(3)	0.1310(3)	0.7168(3)	3.7(1)
O8	0.9839(2)	0.1150(2)	0.7813(2)	5.7(1)
N2	1.1025(3)	0.0736(3)	0.6811(2)	5.2(1)
C74	1.1601(5)	0.0845(4)	0.6022(4)	9.0(2)
C75	1.2570(7)	0.1169(8)	0.5948(7)	17.1(4)
C76	1.1134(4)	−0.0119(4)	0.7215(4)	6.5(2)
C77	1.0479(6)	−0.0767(5)	0.7065(5)	10.6(3)
C78	0.9683(3)	0.6321(3)	0.7181(3)	3.8(1)
C79	0.8883(6)	0.6698(4)	0.7806(4)	9.7(2)
C80	1.0661(5)	0.6471(4)	0.7337(4)	8.4(2)
C81	0.9690(4)	0.6823(3)	0.6433(3)	5.9(2)
C82	0.9287(3)	0.3710(3)	0.5703(2)	2.65(9)

[a] Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as : $(4/3)[a^2\beta(1,1) + b^2\beta(2,2) + c^2\beta(3,3) + ab(\cos\gamma)\beta(1,2) + ac(\cos\beta)\beta(1,3) + bc(\cos\alpha)\beta(2,3)]$.

X-ray data collection and processing for $\mathbf{10}\cdot CH_2Cl_2$

This study was performed by LT. Colorless crystals of **10**·CH_2Cl_2 were obtained from a dichloromethane solution of **10**. Crystal data and details of data collection are given in Table III. The sample (0.30 × 0.40 × 0.40) was studied on a CAD4 ENRAF NONIUS diffractometer using the same radiation as for **4**. The cell parameters were obtained by fitting a set of 25 high θ reflections. The data collection (intensity control variations : 3.5%) gave 7 673 reflections from which 4 723 independent ($R_{\text{int}} = 0.028$) with $I > 4\sigma(I)$. After Lorentz and polarization corrections, the structure was solved by direct methods which revealed most of the non-hydrogen atoms. The remaining ones, in particular those of the dichloromethane molecule, were found by successive scale factor and Fourier difference calculations. An absorption correction was applied with the DIFABS program [29]. The hydrogen atoms were set in theoretical position (0.95 Å) and the whole structure was refined by full-matrix least-squares techniques (use of F magnitude). Atomic scattering factors as above. All the calculations were performed on a Digital MicroVAX 3100 computer with the Molen package [27]. Atomic coordinates and equivalent isotropic thermal factors are given in table V, important interatomic distances and angles in table II. The following tables are available as supplementary material : hydrogen and non hydrogen atoms positional parameters (table S6), a complete set of bond distances (table S7), a complete set of bond angles (table S8), observed structure factors and amplitudes for all observed reflections (table S9), thermal parameters (table S10).

Table V. Atom coordinates and equivalent isotropic thermal factors for **10**·CH_2Cl_2[a].

	x	y	z	B (Å^2)
Pt	0.7759(1)	0.30793(7)	0.52090(6)	2.91(2)
Cl1	0.8571(8)	0.2965(5)	0.4226(4)	6.2(3)
Cl2	0.6371(7)	0.3410(4)	0.4580(4)	4.8(2)
Cl3	0.226(3)	0.456(2)	0.014(2)	13.1(9)*
Cl4	0.128(2)	0.542(2)	−0.070(1)	11.7(8)*
P1	0.6912(7)	0.3456(4)	0.6066(4)	3.9(2)
P2	0.9164(8)	0.2678(4)	0.5674(4)	4.0(2)
O1	0.731(2)	0.2866(9)	0.7235(9)	3.5(5)
O2	0.993(2)	0.196(1)	0.6574(9)	4.5(5)
O3	0.674(1)	0.105(1)	0.6387(9)	3.3(5)
O4	1.009(2)	0.3809(9)	0.7488(9)	3.6(5)
O5	0.960	0.514	0.736	6.2*
O6	0.669(2)	−0.035(1)	0.552(1)	8.2(7)*
N1	0.543(3)	−0.087(2)	0.618(2)	7.4(8)*
N2	1.152	0.592	0.743	5.7*
C1	1.138(3)	0.268(2)	0.768(2)	4.8(9)
C2	0.848(2)	0.032(1)	0.671(1)	3.4(7)
C3	0.543(3)	0.157(2)	0.736(1)	7(1)
C4	0.834(2)	0.399(2)	0.832(2)	3.9(8)
C5	1.105(2)	0.179(2)	0.753(1)	4.0(8)
C6	1.148(2)	0.127(2)	0.788(1)	3.8(7)
C7	1.104(3)	0.049(1)	0.781(1)	4.5(8)
C8	1.011(3)	0.022(2)	0.740(2)	4.9(9)
C9	0.962(2)	0.070(1)	0.703(1)	4.4(7)
C10	1.019(2)	0.149(1)	0.707(1)	3.6(7)
C11	0.756(2)	0.036(2)	0.716(1)	3.3(7)
C12	0.754(2)	0.002(2)	0.773(1)	3.9(8)
C13	0.676(3)	0.008(2)	0.818(1)	4.5(8)
C14	0.611(2)	0.063(2)	0.804(1)	3.9(8)
C15	0.615(2)	0.094(1)	0.749(1)	3.0(7)
C16	0.679(2)	0.079(1)	0.701(1)	3.2(7)
C17	0.582(2)	0.227(1)	0.788(1)	3.9(7)
C18	0.529(3)	0.229(2)	0.841(1)	4.6(9)
C19	0.559(2)	0.289(2)	0.891(1)	4.4(8)
C20	0.661(2)	0.343(2)	0.885(1)	3.9(8)
C21	0.718(2)	0.343(2)	0.832(1)	3.3(7)
C22	0.681(2)	0.288(2)	0.782(1)	3.3(7)
C23	0.922(3)	0.352(2)	0.846(1)	4.0(8)
C24	0.913(2)	0.318(2)	0.904(1)	4.1(8)
C25	0.988(3)	0.270(2)	0.921(1)	6(1)
C26	1.062(3)	0.261(2)	0.876(1)	4.8(9)
C27	1.070(3)	0.292(2)	0.819(1)	3.8(8)
C28	1.000(2)	0.346(2)	0.806(1)	3.0(7)
C29	1.164(3)	−0.006(2)	0.821(2)	7(1)
C30	1.277(5)	0.011(4)	0.810(3)	15(2)*
C31	1.101(5)	−0.084(4)	0.822(3)	14(2)*
C32	1.173(6)	0.008(4)	0.889(3)	17(2)*
C33	0.655(3)	−0.041(2)	0.880(2)	6.6(9)*
C34	0.562(5)	−0.116(3)	0.864(3)	13(2)*
C35	0.757(4)	−0.066(3)	0.900(3)	12(2)*
C36	0.619(4)	−0.003(3)	0.933(3)	12(2)*
C37	0.500(3)	0.291(2)	0.948(2)	6.7(9)*
C38	0.389(6)	0.233(4)	0.958(4)	16(2)*
C39	0.554(6)	0.277(4)	1.008(4)	17(2)*
C40	0.478(7)	0.362(5)	0.963(4)	19(3)*
C41	0.979(4)	0.231(3)	0.984(3)	11(1)*
C42	0.990(9)	0.153(7)	0.980(6)	27(4)*
C43	1.066(8)	0.246(5)	1.022(5)	22(3)*
C44	0.869(6)	0.219(4)	1.013(4)	18(3)*
C45	0.584(3)	0.057(2)	0.604(2)	6.2(9)*
C46	0.597(3)	−0.028(2)	0.588(2)	6.2(9)*
C47	0.456(4)	−0.084(3)	0.660(2)	9(1)*
C48	0.348(5)	−0.093(4)	0.617(3)	15(2)*
C49	0.558(4)	−0.168(2)	0.609(2)	8(1)*
C50	0.622(4)	−0.191(3)	0.661(3)	11(1)*
C51	1.093(3)	0.449(2)	0.746(2)	8(1)*
C52	1.069	0.523	0.750	6.0*
C53	1.095	0.666	0.741	9.0*
C54	1.066	0.685	0.806	11.0*
C55	1.258	0.586	0.737	9.0*
C56	1.364	0.648	0.798	12.0*
C57	0.752(2)	0.355(1)	0.688(1)	3.3(7)
C58	0.689(2)	0.447(2)	0.599(2)	4.2(7)
C59	0.795(2)	0.506(2)	0.603(2)	5.2(9)
C60	0.786(4)	0.587(1)	0.594(2)	8(1)
C61	0.695(4)	0.607(2)	0.578(3)	12(1)
C62	0.603(3)	0.547(2)	0.575(2)	7(1)
C63	0.600(3)	0.470(2)	0.583(2)	5.0(9)
C64	0.549(2)	0.293(1)	0.613(1)	3.7(7)
C65	0.484(2)	0.310(2)	0.663(1)	5.0(8)
C66	0.374(2)	0.262(2)	0.668(2)	8(1)
C67	0.339(3)	0.196(2)	0.616(3)	13(2)
C68	0.408(2)	0.187(2)	0.578(2)	9(1)
C69	0.513(2)	0.227(2)	0.571(2)	6(1)
C70	0.902(2)	0.229(1)	0.641(1)	3.1(6)
C71	0.947(2)	0.187(2)	0.519(1)	3.7(7)
C72	0.856(3)	0.117(2)	0.510(1)	4.7(8)
C73	0.870(2)	0.054(2)	0.473(1)	4.9(9)
C74	0.962(4)	0.057(2)	0.443(2)	10(2)
C75	1.051(3)	0.122(2)	0.447(2)	10(1)
C76	1.042(3)	0.196(2)	0.485(2)	7(1)
C77	1.047(2)	0.346(2)	0.573(1)	3.2(7)
C78	1.033(2)	0.421(2)	0.558(2)	4.7(8)
C79	1.128(3)	0.484(2)	0.562(2)	7(1)
C80	1.227(4)	0.469(2)	0.581(2)	10(1)
C81	1.240(2)	0.399(2)	0.596(2)	7(1)
C82	1.149(2)	0.331(2)	0.589(2)	5.5(9)
C83	0.246(7)	0.475(5)	−0.069(4)	8(2)*

[a] Starred atoms were refined isotropically. Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as : (4/3) $[a^2\beta(1,1) + b^2\beta(2,2) + c^2\beta(3,3) + ab(\cos\gamma)\beta(1,2) + ac(\cos\beta)\beta(1,3) + bc(\cos\alpha)\beta(2,3)]$.

Hydroformylation experiment

The catalytic run was performed in a glass-lined stainless-steel autoclave (100 mL) containing a magnetic stirring bar. After two argon-vacuum cycles, a solution of complex **8** (0.040 g, 0.024 mmol) in CH_2Cl_2 (3 mL)/C_6H_6 (14 mL) was transferred to the autoclave. The reactor was pressurized to 2 bar by a mixture of $CO/H_2 = 1{:}1$ and the autoclave was heated to 40°C for 20 min. The autoclave was cooled to room temperature, slowly vented and styrene (0.909 g, *ca* 1.0 mL, 8.67 mmol) was added using a syringe. The reactor was then pressurized to 40 bar by a mixture of $CO/H_2 = 1{:}1$ and heated to 40°C for 48 h. After cooling and venting the yellow solution was quickly analysed by GC.

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Supplementary Material Available

The following tables are available as supplementary material from the British Library Document Supply Center, Boston Spa, Wetherby, West Yorkshire, LS23 7BQ, UK, for **4** and **10**·CH_2Cl_2, respectively : hydrogen and non-hydrogen atoms positional parameters (table S1 and S6), a complete set of bond distances (table S2 and S7), a complete set of bond angles (table S3 and S8), observed structure factors and amplitudes for all observed reflections (table S4 and S9), and thermal parameters (table S5 and S10).

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