DALTON
FULL PAPER

Calix[4]arene derived phosphites: their hydrolytic stability and complexes with gold(I), platinum(II,0), palladium(II) and iridium(I)

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Received 11th November 1999, Accepted 1st February 2000

Improved syntheses of the monophosphites $\mathbf{L_a}$ and $\mathbf{L_b}$ derived from calix[4]arene and *p-tert*-butylcalix[4]arene respectively are reported. Both $\mathbf{L_a}$ and $\mathbf{L_b}$ are thermally stable and air stable even in refluxing toluene; moreover they are not hydrolysed by aqueous HCl or NaOH. The two-coordinate gold(I) complexes [AuCl($\mathbf{L_a}$)] and [AuCl($\mathbf{L_b}$)] are readily made from [AuCl(tht)] (tht = tetrahydrothiophene). Treatment of K[$PtCl_3(C_2H_4)$] with $\mathbf{L_a}$ gives the mononuclear *cis*-[$PtCl_2(\mathbf{L_a})_2$] whereas $\mathbf{L_b}$ gives the binuclear *trans*-[$Pt_2Cl_2(\mu\text{-}Cl)_2(\mathbf{L_b})_2$]. The platinum(0) complexes [Pt(**L**)(nor)$_2$] and [Pt(**L**)$_2$(nor)] (**L** = $\mathbf{L_a}$ or $\mathbf{L_b}$, nor = norbornene) have been characterised in solution by ^{31}P and ^{195}Pt NMR spectroscopy. Treatment of [$PdCl_2(NCPh)_2$] with $\mathbf{L_a}$ gives a poorly soluble complex assigned the structure [$PdCl_2(\mathbf{L_a})_2$]. Treatment of [$PdCl_2(NCPh)_2$] with $\mathbf{L_b}$ gives the binuclear [$Pd_2Cl_2(\mu\text{-}Cl)_2(\mathbf{L_b})_2$] which reacts with Y to give bridge-cleaved products [$PdCl_2(Y)(\mathbf{L_b})$] (Y = CO, CNBu^t or CNMe). The iridium complexes [IrCl($\mathbf{L_a}$)(cod)] and [IrCl($\mathbf{L_b}$)(cod)] are made by the additions of $\mathbf{L_a}$ or $\mathbf{L_b}$ to [$Ir_2(\mu\text{-}Cl)_2(cod)_2$]. The crystal structures of [$Pt_2Cl_2(\mu\text{-}Cl)_2(\mathbf{L_b})_2$], [$Pd_2Cl_2(\mu\text{-}Cl)_2(\mathbf{L_b})_2$], [$PdCl_2(CNBu^t)(\mathbf{L_b})$] and [IrCl($\mathbf{L_a}$)(cod)] have been determined. The calixarene conformation in all cases has arenes in {down, out, up, up} orientations with one aryl blocking an axial site at the square planar metal. The cone angles are 160° for $\mathbf{L_a}$ and 176° for $\mathbf{L_b}$. The bulkiness of the ligand is such as to preclude octahedral geometry at the metal. The *trans* influence of the ligands $\mathbf{L_a}$ and $\mathbf{L_b}$ appear to be greater than either chloride or isocyanide. The P–O distances and the O–P–O angles imply that $\mathbf{L_a}$ and $\mathbf{L_b}$ are less π-acidic than most triarylphosphite ligands.

Introduction

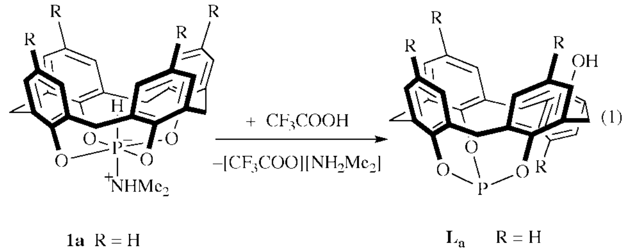
The susceptibility of phosphites to hydrolysis[1] limits their application as ligands for homogeneous catalysis.[2,3] Cyclic phosphites, particularly those derived from biphenols or binaphthols, are kinetically relatively stable to hydrolysis[3] and are important ligands for hydroformylation,[4,5] hydrocyanation,[3,6] and other catalyses.[7]

The fused tricyclic monophosphites $\mathbf{L_a}$ and $\mathbf{L_b}$ derived from calix[4]arenes were reported by Lattman *et al.*[8] and attracted our attention because they should be highly kinetically stabilised to hydrolysis and therefore potentially useful for catalysis. Lattman *et al.*[9] also reported the iron(0) complex [$Fe(CO)_4\mathbf{L_b}$].

In this paper we describe our studies on the hydrolytic stability of $\mathbf{L_a}$ and $\mathbf{L_b}$ and their coordination chemistry with gold, platinum, palladium and iridium. We and others have found that the rhodium complexes of $\mathbf{L_a}$, $\mathbf{L_b}$ and related phosphites are hydroformylation catalysts as discussed in the following papers.[10]

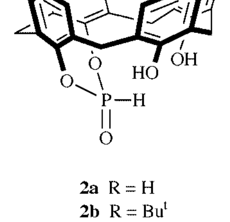
Results and discussion

The phosphites $\mathbf{L_a}$ and $\mathbf{L_b}$ were made in multigram quantities by a scale-up of Lattman's method (eqn. 1).[8] For example,



1a R = H **L$_a$** R = H
1b R = Bu^t **L$_b$** R = Bu^t

the slow addition of CF_3CO_2H to a stirred solution of the six-coordinate phosphorus(V) precursor **1b** gave $\mathbf{L_b}$ along with *ca.* 10% of an impurity identified as a phosphonate from its characteristic doublet in the ^{31}P NMR spectrum at δ +2.1 with ^1J(PH) 806 Hz and assigned structure **2b**; this assignment is further supported by the observation of three AB patterns in the ^{1}H NMR spectrum (δ 3.5–4.5) in the intensity ratio 1 : 2 : 1 for the benzylic CH_2 which is consistent with 1,2-isomer **2b**. Subsequent purification gave pure $\mathbf{L_b}$ in multigram quantities. The partial cone conformation of the calixarene phosphites is deduced from ^{1}H and ^{13}C NMR in solution[11] and X-ray crystallography (see below).



2a R = H
2b R = Bu^t

The stability of $\mathbf{L_a}$ and $\mathbf{L_b}$ is remarkable: no decomposition was observed by ^{31}P NMR after solid samples of $\mathbf{L_a}$ and $\mathbf{L_b}$ had been heated in air at 300 °C for 1 h nor when toluene solutions of $\mathbf{L_a}$ and $\mathbf{L_b}$ were refluxed in air for 24 h. When triphenylphosphite is refluxed in aqueous acetone it decomposes fully within 3 h but under similar conditions (see Experimental section) both $\mathbf{L_a}$ and $\mathbf{L_b}$ showed no decomposition after 24 h. Solutions of $\mathbf{L_a}$ and $\mathbf{L_b}$ in $CDCl_3$ were shaken with 1 M aqueous HCl or 1 M aqueous NaOH and after 30 min, no decomposition was detected by ^{31}P NMR spectroscopy.

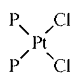
Gold(I) chemistry

Complexes **3a** and **3b** were prepared by the addition of [AuCl(tht)] (tht = tetrahydrothiophene) to one equivalent of the appropriate phosphite $\mathbf{L_a}$ or $\mathbf{L_b}$ in CH_2Cl_2. The *p-tert*-butylcalix[4]arene phosphite complex **3b** was soluble in common organic solvents while the unsubstituted analogue **3a** was insoluble in CH_2Cl_2 and only sparingly soluble in dmso. The complex [AuCl{P(OPh)$_3$}] has been reported[12] but not its ^{31}P chemical shift and so we determined it to be δ 110 which means it has a coordination chemical shift $\Delta\delta$ (−18) similar to the new complexes **3a** (−12) and **3b** (−14).

3a P = $\mathbf{L_a}$
3b P = $\mathbf{L_b}$

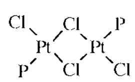
Platinum(II) chemistry

Addition of the unsubstituted calix[4]arene phosphite $\mathbf{L_a}$ to K[PtCl$_3$(C$_2$H$_4$)] produced a white solid that was insoluble in most common solvents and was sparingly soluble only in dmso; this made purification difficult and we were unable to obtain satisfactory elemental analyses. The product was assigned the mononuclear structure **4a** on the basis of the triplet ^{195}Pt NMR signal and absorptions at 307 and 325 cm^{-1} in the IR spectrum typical of ν(PtCl) bands for a *cis*-PtCl$_2$ group. The value of ^1J(PtP) in **4a** of 6629 Hz is significantly larger than the value of 5793 Hz reported[13] for *cis*-[PtCl$_2${P(OPh)$_3$}$_2$].



4a P = $\mathbf{L_a}$
4b P = $\mathbf{L_b}$

Treatment of K[PtCl$_3$(η^2-C$_2$H$_4$)] with $\mathbf{L_b}$ did not give the corresponding mononuclear **4b** even in the presence of an excess of $\mathbf{L_b}$. Instead the binuclear platinum(II) complex **5b** is formed which has been fully characterised (see Experimental section). The binuclear structure of **5b** is supported by the doublet resonance in the ^{195}Pt NMR spectrum, the very large ^1J(PtP) of 7348) consistent with the phosphite being *trans* to a bridging chloro ligand, and absorptions at 350 and 270 cm^{-1} in the IR spectrum as expected for terminal and bridging ν(PtCl) bands.



5a P = $\mathbf{L_a}$
5b P = $\mathbf{L_b}$

Single crystals of **5b** as a solvate were grown from CH_2Cl_2/hexane. The crystal structure (see Fig. 1) shows molecules of **5b** lying at sites of crystallographic inversion symmetry and containing a typical planar Pt$_2$(μ-Cl)$_2$Cl$_2$P$_2$ core based on square planar coordination geometry (mean deviation from plane 0.047 Å) at the Pt(II) centres. The Pt–P and Pt–Cl distances (see Table 1) are of normal dimensions (and similar to the Pd–L distances in **8b**, see below) although the Pt–(μ-Cl) distance *trans* to the phosphite is substantially longer than that *trans* to the terminal chloride ligand (by *ca.* 0.12 Å) indicating that the phosphite $\mathbf{L_b}$ has a much stronger *trans* influence than the chloride ligand. Both of the P–Pt–Cl angles are greater than the ideal 90° (P(1)–Pt(1)–Cl(1) 93.98(6)°, P(1)–Pt(1)–Cl(2A) 92.92(6)°).[18b]

The observation that $\mathbf{L_b}$ forms the binuclear **5b** rather than **4b** while $\mathbf{L_a}$ forms the mononuclear **4a** rather than **5a** is consistent with the greater bulk of $\mathbf{L_b}$.

Table 1 Selected interatomic bond lengths (Å) and bond angles (°) for **5b**·4CH$_2$Cl$_2$·C$_6$H$_6$

Pt(1)–P(1)	2.169(2)
Pt(1)–Cl(2)	2.326(2)
Pt(1)–Cl(1)	2.275(2)
Pt(1)–Cl(2A)	2.396(2)
P(1)–O(2)	1.593(4)
P(1)–O(3)	1.584(4)
P(1)–O(4)	1.569(4)
P(1)–Pt(1)–Cl(1)	93.98(6)
Cl(1)–Pt(1)–Cl(2A)	89.00(6)
P(1)–Pt(1)–Cl(2)	92.92(6)
Cl(2)–Pt(1)–Cl(2A)	83.99(6)
O(2)–P(1)–O(3)	104.0(2)
O(4)–P(1)–O(3)	106.6(2)
O(2)–P(1)–O(4)	104.5(2)

Symmetry operation for suffix A: $-x, -y, -z$.

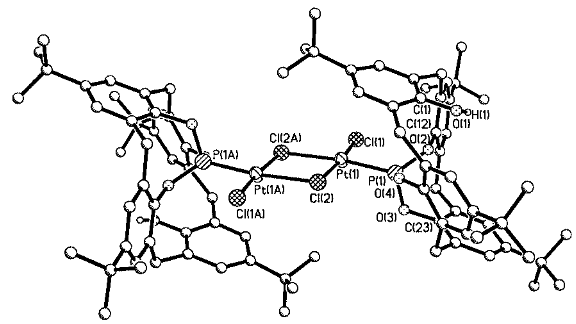
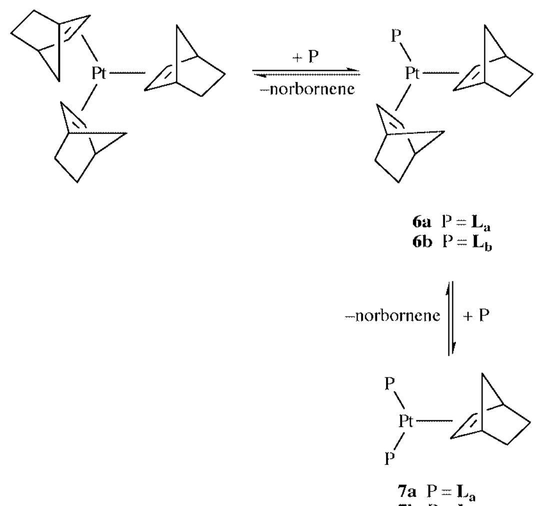


Fig. 1 Molecular structure of binuclear platinum(II) complex **5b**. Selected atoms are labelled and all hydrogens are omitted for clarity.

Platinum(0) chemistry

Addition of [Pt(nor)$_3$] (nor = η-norbornene) to a CH_2Cl_2 solution containing either phosphite $\mathbf{L_a}$ or $\mathbf{L_b}$ gave mixtures of complexes which were unambiguously characterised in solution as PtL and PtL$_2$ (L = $\mathbf{L_a}$ or $\mathbf{L_b}$) species from the doublet and triplet ^{195}Pt NMR signals respectively. The products are assigned the structures **6a,b** and **7a,b** on the basis of the ^{31}P NMR data which are similar to those for [Pt{P(OPh)$_3$}(nor)$_2$] and [Pt{P(OPh)$_3$}$_2$(nor)].[13] Mixtures were obtained regardless of the quantity of ligand added showing that the equilibria in eqn. (2) are established in solution. Attempts to isolate single



6a P = $\mathbf{L_a}$
6b P = $\mathbf{L_b}$

7a P = $\mathbf{L_a}$
7b P = $\mathbf{L_b}$

(2)

species were unsuccessful since the components had very similar solubilities. There was no evidence for the formation of [PtL$_3$] or [PtL$_4$] species when a large excess of calix[4]arene phosphites $\mathbf{L_a}$ or $\mathbf{L_b}$ was added which is consistent with the large bulk of these ligands.

Table 2 Selected bond lengths (Å) and bond angles (°) for **8b**·6.67$CHCl_3$

Pd(1)–P(1)	2.1874(14)
Pd(1)–Cl(2)	2.261(2)
Pd(1)–Cl(1)	2.307(2)
Pd(1)–Cl(1A)	2.392(2)
P(1)–O(2)	1.574(3)
P(1)–O(3)	1.583(3)
P(1)–O(4)	1.573(3)
P(1)–Pd(1)–Cl(1)	94.54(5)
Cl(2)–Pd(1)–P(1)	88.73(6)
Cl(1A)–Pd(1)–Cl(2)	90.54(6)
Cl(1)–Pd(1)–Cl(1A)	86.03(5)
O(2)–P(1)–O(3)	104.8(2)
O(4)–P(1)–O(3)	107.5(2)
O(2)–P(1)–O(4)	104.9(2)

Symmetry operation for suffix A: $-x, -y, -z$.

Table 3 Selected bond lengths (Å) and bond angles (°) for **10**·C_6H_6-C_5H_{12}

Pd(1)–P(1)	2.214(2)
Pd(1)–Cl(2)	2.291(2)
Pd(1)–Cl(1)	2.353(2)
Pd(1)–C(50)	1.927(6)
P(1)–O(2)	1.562(4)
P(1)–O(3)	1.573(4)
P(1)–O(4)	1.595(4)
P(1)–Pd(1)–C(50)	90.9(2)
Cl(1)–Pd(1)–P(1)	88.33(6)
Cl(2)–Pd(1)–C(50)	89.5(2)
Cl(1)–Pd(1)–Cl(2)	90.94(7)
O(2)–P(1)–O(3)	105.7(2)
O(4)–P(1)–O(3)	105.8(2)
O(2)–P(1)–O(4)	104.3(2)

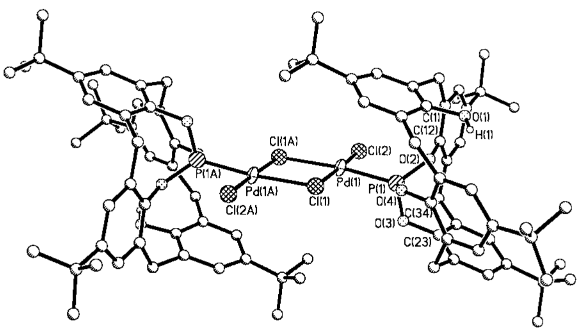


Fig. 2 Molecular structure of binuclear palladium(II) complex **8b**. Selected atoms are labelled and all hydrogens are omitted for clarity.

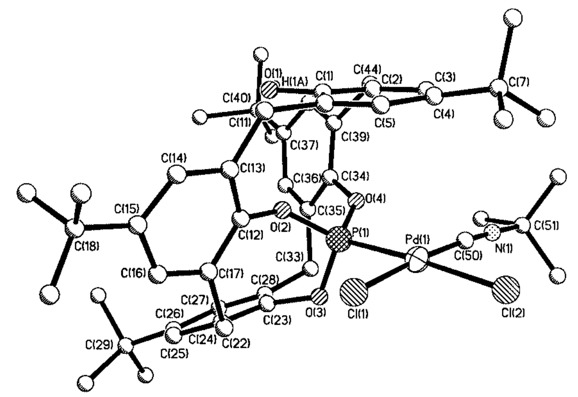
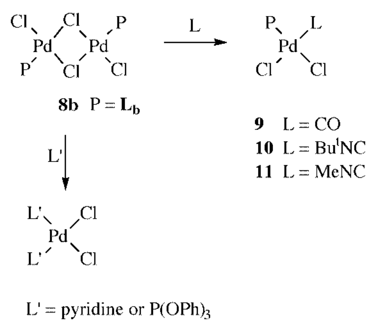


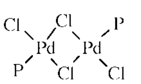
Fig. 3 Molecular structure of mononuclear palladium(II) complex **10**. Selected atoms are labelled and all hydrogens are omitted for clarity.



Scheme 1

Palladium(II) chemistry

Treatment of [$PdCl_2(NCPh)_2$] with $\mathbf{L_b}$ gave the binuclear palladium(II) species **8b** as the only phosphorus-containing product, even when an excess of ligand was used. The complex was fully characterised (see Experimental section) and the binuclear structure confirmed by X-ray crystallography. Single crystals of solvated **8b** were grown from $CDCl_3$. The molecular structure of **8b** in the crystal (Fig. 2, Table 2) is very similar to that of the analogous platinum(II) species **5b** reported above, and again shows exact inversion symmetry with a planar Pd_2-(μ-$Cl)_2Cl_2P_2$ core and planar coordination geometry (rms deviation 0.045 Å) at palladium. The dimensions of the molecule are all very close to those in the platinum case and in respect of the Pd(μ-$Cl)_2Cl_2P_2$ core they are similar to those of [$Pd_2(\mu$-$Cl)_2$-Cl_2{P(OPh)$_3$}$_2$].[14]



8b P = $\mathbf{L_b}$

A series of reactions was carried out between **8b** and CO, MeNC, Bu^{t}NC, pyridine, and P(OPh)$_3$, the progress of which was monitored by $^{31}P\{^1H\}$ NMR spectroscopy (Scheme 1). Simple bridge-cleavage occurred only with the smallest ligands. For example when CO was bubbled slowly through a solution of **8b**, the mononuclear species **9** was formed with ν(CO) 2141 cm^{-1}. However if the CO was added too rapidly or an excess of CO was present, displaced calix[4]arene phosphite $\mathbf{L_b}$ was detected by ^{31}P NMR spectroscopy. Mononuclear complexes **10** and **11** were formed with the rod-like ligands Bu^{t}NC and MeNC but when **8b** was treated with the larger ligands, L′ = pyridine and P(OPh)$_3$, the calix[4]arene phosphite $\mathbf{L_b}$ was completely displaced and presumably [$PdCl_2L'_2$] were produced. These results are again consistent with the phosphite ligand $\mathbf{L_b}$ being very bulky.

Single crystals of **10** were grown from C_6H_6/pentane and its structure as a solvate was confirmed by X-ray crystallography (Fig. 3, Table 3). The conformation of ligand $\mathbf{L_b}$ is essentially the same as for **5b** and **8b** as are its internal dimensions. The complex shows square planar coordination geometry (rms deviation 0.025 Å) at palladium as expected with only small deviation of *cis* coordination angles from 90°. The two better π-acceptor ligands, the phosphite and the isocyanide, are mutually *cis*; similar behaviour in *cis*-bis-phosphite complexes of Pt(II) has been noted by us previously.[15] The Pd–Cl distance *trans* to $\mathbf{L_b}$ is *ca.* 0.05 Å longer than that *trans* to C(50), implying that $\mathbf{L_b}$ exerts a stronger *trans* influence than *tert*-butyl isocyanide. The isocyanide ligand is nearly eclipsed with the P(1)–O(4) bond (torsion angle C(50)–Pd(1)–P(1)–O(4) = −20.4°), which allows the *tert*-butyl group and the aryl group on O(4) to be far apart. In contrast the oxygen with the *gauche* conformation, O(2), whose aryl substituent would not be compatible with a *cis* ligand carrying such a bulky substituent, lies close to Cl(1) (torsion angle Cl(1)–Pd(1)–P(1)–O(2) = 41.0°).

Table 4 Selected bond lengths (Å) and angles (°) for **13a**·$0.5C_6H_6$ [a]

Ir(1)–P(1)	2.2644(11)
Ir(1)–Cl(1)	2.3605(11)
Ir(1)–X1A	2.115(4)
Ir(1)–X1B	2.000(4)
P(1)–O(2)	1.608(3)
P(1)–O(3)	1.604(3)
P(1)–O(4)	1.596(3)
Cl(1)–Ir(1)–P(1)	94.51(14)
Cl(1)–Ir(1)–X1A	88.6(1)
X1B–Ir(1)–X1A	86.2(1)
P(1)–Ir(1)–X1B	91.1(1)
O(2)–P(1)–O(3)	101.9(1)
O(4)–P(1)–O(3)	103.9(2)
O(2)–P(1)–O(4)	103.0(1)

[a] X1A, X1B are the centroids of the C=C bonds in the cod ligand.

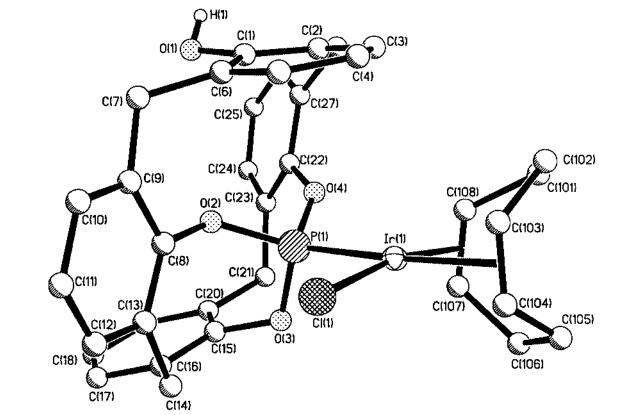
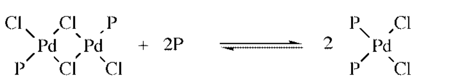


Fig. 4 Molecular structure of mononuclear iridium(I) complex **13a**. Selected atoms are labelled and all hydrogens are omitted for clarity.

Addition of $[PdCl_2(NCPh)_2]$ to two equivalents of $\mathbf{L_a}$ gave an orange precipitate which was insoluble in most common solvents but sparingly soluble in warm dmso. The ^{31}P NMR spectrum showed a mixture of products present. Three singlets in the intensity ratio of *ca.* 1 : 2 : 1 were tentatively associated with the components of the equilibrium shown in eqn. (3). One



(3)

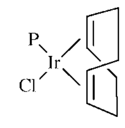
8a P = $\mathbf{L_a}$ **12a** P = $\mathbf{L_a}$

of the singlets at δ 116 was free phosphite, a second δ 47.6 was assigned to the binuclear species **8a**, the analogue of **8b**, on the basis of the similarity of their δ(P) values; the third singlet at δ 64.1 is tentatively assigned to the mononuclear complex **12a**, the analogue of the platinum(II) species **4a**.

Iridium(I) chemistry

Addition of $[Ir_2Cl_2(cod)_2]$ to a CH_2Cl_2 solution containing two equivalents of $\mathbf{L_a}$ or $\mathbf{L_b}$ gave the mononuclear complexes **13a** and **13b**, which have been fully characterised (see Experimental section). Single crystals of **13a** as a benzene solvate were grown from CH_2Cl_2/benzene and the structure determined by X-ray crystallography (see Fig. 4, Table 4). The complex has square-planar geometry at Ir distorted such that the Ir–Cl bond lies out of the plane formed by Ir(1), P(1) and the centroids of the C=C double bonds (rms deviation from that plane = 0.019 Å, Cl(1) deviation 0.46 Å). The Ir–C distances show the phosphite ligand to be exerting a stronger *trans* influence than the chloride ligand (Ir–C *trans* to P being longer by *ca.* 0.11 Å).

In all the structures reported here, as is often the case with calixarenes, the crystals are solvated, particularly heavily so in



13a P = $\mathbf{L_a}$
13b P = $\mathbf{L_b}$

the case of complexes of $\mathbf{L_b}$. It is apparent from the coordination chemistry described above that the phosphites $\mathbf{L_a}$ and $\mathbf{L_b}$ are both very bulky. The cone angles [16] are calculated from the crystal structures to be 160° for $\mathbf{L_a}$ and average 176° for $\mathbf{L_b}$. These values lie between those for $P(OC_6H_4Me\text{-}2)_3$ (θ = 141°) and $P(OC_6H_3Me_2\text{-}2,6)_3$ (θ = 190°). The greater bulk of $\mathbf{L_b}$ and $\mathbf{L_a}$ is manifest from the fact that at no time are two *cis* $\mathbf{L_b}$ ligands on platinum(II) or palladium(II) observed. The calixarene conformation in all cases reported here is of type ***e***,[10b] with arenes in sequence *douu* {down, out, up, up} for oxygens O(1, 2, 3 and 4) respectively. This leads to a very asymmetric ligand profile in which one aryl (that at O(1)) occupies a position near a vacant axial site of the square planar metal and lies nearly parallel to the coordination plane. This arrangement implies rotation about the M–P bond will be a high energy process. In each case the most bulky substituent at phosphorus, the "down" aryl at O(1), is eclipsed with the least bulky aspect of the square planar centre, its empty axial site. This implies that the O(3) site at phosphorus is also *cis* to an axial site (that *trans* to the site blocked by the aryl at O(1)) while O(2) and O(4) are both close to the (filled) equatorial sites *cis* to the phosphite. The bulkiness of the ligand is such as to preclude octahedral geometry at the metal (and also *TBPY* geometry probably), at least in this conformation.

The ligand symmetry is clearly C_1, but dynamic interconversion of conformations *douu* and *duuo* [10b] would interconvert the environments of O(2) and O(4) and hence give time-averaged C_s symmetry to the NMR spectra and the chemistry of $\mathbf{L_a}$ and $\mathbf{L_b}$. This is not however compatible with the asymmetry of the *cis* ligands in species such as **10**. Therefore complexes such as **10** are chiral and seem likely to retain chirality in the absence of ligand dissociation.

The observed calixarene conformation is associated with a conformation at phosphorus [17] in which the M–P–O–C torsion at O(2) is *gauche* (M–P–O–C torsion angle *ca.* −40°) and *anti* at O(3), O(4) (Pt–P–O–C torsion angles *ca.* 160 and 180°). This is unusual compared with most $P(OR)_3$ species [18] and is doubtless required by the constraints of the calixarene. The distortions that are associated in the M–P–O angles and P–O–C angles presumably arise from the same source. Thus the M–P–O(2) angle is close to 120° while the other Pt–P–O angles are *ca.* 109° and conversely the P–O–C angle at O(3) is relatively small, *ca.* 120°, while those at O(2) and O(4) are larger (*ca.* 130 and 140° respectively). The P–O distances and the O–P–O angles show less variation and are somewhat shorter and somewhat larger respectively than is the norm for triarylphosphite species (average values *ca.* 1.58 Å and 105°).[15] This may therefore imply that $\mathbf{L_b}$ and $\mathbf{L_a}$ will be less π-acidic than most triarylphosphite ligands without such constrained bond angles. The *trans* influence of the ligands $\mathbf{L_a}$ and $\mathbf{L_b}$ appear to be greater than either chloride or isocyanide (at least as measured by *trans* M–Cl or M–alkene bond lengths).

The kinetic inertness and large bulk of $\mathbf{L_a}$ and $\mathbf{L_b}$ make them of interest as ligands for hydroformylation catalysis.[10]

Experimental

Unless otherwise stated, all reactions were carried out under a dry nitrogen atmosphere using standard Schlenk line techniques. With the exception of the Pt(0) species, all the metal complexes were air stable in the solid state, so once prepared were stored in air. Solvents were dried and nitrogen-saturated by refluxing them under a nitrogen atmosphere over appropriate drying agents: calcium hydride (for dichloromethane, chloroform and acetonitrile), sodium/benzophenone (for diethyl ether and tetrahydrofuran), sodium (for pentane, toluene, benzene and hexane) and anhydrous magnesium sulfate (for acetone). Commercial reagents were used as supplied unless otherwise stated and other starting materials prepared by literature methods: $K[PtCl_3(\eta^2\text{-}C_2H_4)]$,[19] $[Pt(nor)_3]$,[20] $[PdCl_2(cod)]$,[21] $[PdCl_2(NCPh)_2]$,[22] [AuCl(tht)][23] and $[Ir_2Cl_2(cod)_2]$.[24] Unsubstituted H-calix[4]arene was prepared by the reverse Friedel–Crafts method of Gutsche.[25] Infrared spectra were recorded on either a Nicolet 5ZDX or a Perkin-Elmer 1600. NMR spectra were recorded on a JEOL GX400 at *ca.* 23 °C: ^{31}P (162 MHz, δ to high frequency of 85% H_3PO_4), ^{13}C (100 MHz, δ to high frequency of $SiMe_4$), ^{195}Pt (81 MHz, δ to high frequency Ξ(Pt) of 21.4 MHz) and ^1H (400 MHz, δ to high frequency of $SiMe_4$), *J* in Hz.

Preparation of precursor 1b

To a stirred suspension of *p-tert*-butylcalix[4]arene (20.0 g, 30.9 mmol) in benzene (350 cm^3), $P(NMe_2)_3$ (6.16 cm^3, 34.0 mmol) was added dropwise over 30 min. After stirring the mixture for 24 h at room temperature, the resulting white precipitate was filtered off, washed with benzene (50 cm^3) and dried *in vacuo* for 24 h to yield the white solid **1b** (19.13 g, 86%). Elemental analysis, found (calc): C, 76.7 (76.5); H, 8.4 (8.4); N, 1.9 (1.9); P, 4.3 (4.3)%. ^{31}P NMR ($CDCl_3$): δ −117.5 [^1J(PH) 729]. ^1H NMR ($CDCl_3$): δ 1.21 [s, 36H, C(CH_3)$_3$], 3.13 [dd, 4H, Ar-CH*H*-Ar, ^2J(HH) 11.2, ^5J(PH) 1.8], 3.51 [dd, 6H, N(CH_3)$_2$, ^3J(PH) 9.7, ^3J(PH) 5.6], 4.63 [d, 1H, P*H*, ^1J(PH) 729], 4.67 [dd, 4H, Ar-C*H*H-Ar, ^2J(HH) 11.2, ^5J(PH) 6.7], 6.25 (br s, 1H, N*H*), 7.25 (s, 8H, Ph). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 31.7 [s, C(CH_3)$_3$], 34.4 [s, *C*(CH_3)$_3$], 36.1 (s, *C*H_2), 44.8 [d, N(*C*H_3)$_2$, ^2J(PC) 4], 124.8 (s,*C*H), 137.7 [d, *C*(CH_2), ^3J(PC) 9], 145.8 [d, *C*C(CH_3)$_3$, ^5J(PC) 5], 148.0 [d, *C*O, ^2J(PC) 7]. Using a similar procedure the analogue **1a** was synthesised from H-calix[4]arene. Elemental analysis, found (calc): C, 71.9 (72.3); H, 5.7 (5.7); N, 2.4 (2.4); P, 5.6 (6.2)%. ^{31}P NMR ($CDCl_3$): δ −119.5 [^1J(PH) 729]. ^1H NMR ($CDCl_3$): δ 3.20 [dd, 4H, Ar-CH*H*-Ar, ^2J(HH) 11.7, ^5J(PH) 2.1], 3.54 [dd, 6H, N(CH_3)$_2$, ^3J(HH) 9.4, ^3J(PH) 5.9], 4.69 [d, 1H, P*H*, ^1J(PH) 729], 4.70 [dd, 4H, Ar-C*H*H-Ar, ^2J(HH) 11.7, ^5J(PH) 6.7], 6.30 (br s, 1H, N*H*), 6.73 [dt, 4H, Ph, ^3J(HH) 7.4, ^5J(PH) 2.8], 7.02 [d, 8H, Ph, ^3J(HH) 7.3]. ^{13}C NMR ($CDCl_3$): δ 35.0 (s, *C*H_2), 44.5 [d, N(*C*H_3)$_2$, ^2J(PC) 4], 123.3 (s, *C*H), 127.6 [d, *C*(CH_2), ^3J(PC) 9], 138.2 [d, *C*H, ^5J(PC) 6], 150.0 [d, *C*O, ^2J(PC) 7].

p-tert-Butylcalix[4]arene phosphite L_b

To a CH_2Cl_2 (350 cm^3) solution of **1b** (20.0 g, 27.7 mmol), CF_3CO_2H (2.44 cm^3, 30.5 mmol) was added dropwise over 30 min. The clear solution was left stirring for 4 h at room temperature, after which time the solvent was removed *in vacuo* to yield a white solid. ^{31}P NMR spectroscopy revealed this solid product to be a mixture of phosphite L_b and phosphonate **2b**. By passing a CH_2Cl_2 (100 cm^3) solution of this white solid through a 15 cm^3 Al_2O_3 (grade III) column (ϕ 3.5 cm) using further CH_2Cl_2 (100 cm^3) as eluent, pure L_b was obtained as the only fraction (13.67 g, 73%). Elemental analysis, found (calc.): C, 77.9 (78.1); H, 8.0 (7.9); P, 4.3 (4.6)%. ^{31}P NMR ($CDCl_3$) δ 112.9. ^1H NMR ($CDCl_3$): δ 1.21 [s, 9H, C(CH_3)$_3$], 1.31 [s, 9H, C(CH_3)$_3$], 1.39 [s, 18H, C(CH_3)$_3$], 3.62 [d, 2H, Ar-CH*H*-Ar, ^2J(HH) 15.4], 3.71 [d, 2H, Ar-CH*H*-Ar, ^2J(HH) 17.0], 4.29 [d, 2H, Ar-C*H*H-Ar, ^2J(HH) 17.0], 4.49 [d, 2H, Ar-C*H*H-Ar, ^2J(HH) 15.4], 4.74 (br s, 1H, OH), 7.11 (s, 2H, Ph), 7.17 [d, 2H, Ph, ^4J(HH) 2.1], 7.22 (s, 2H, Ph), 7.25 [d, 2H, Ph, ^4J(HH) 2.4]. ^{13}C NMR ($CDCl_3$): δ 31.5 [m, C(*C*H_3)$_3$], 34.1 [m, *C*(CH_3)$_3$], 37.0 (m, *C*H_2), 125.7 (s, *C*H), 125.9 (s, *C*H), 126.4 (s, *C*H), 126.6 (s, *C*H), 129.9 [s, *C*(CH_2)], 131.3 [s, *C*(CH_2)], 133.1 [s, *C*(CH_2)], 134.6 [s, *C*(CH_2)], 144.1–149.7 (m, Ph). H-Calix[4]arene phosphite L_a was synthesised and purified using the above procedure (69%). Elemental analysis, found (calc.); C, 73.7 (74.3); H, 4.8 (4.7); P, 6.1 (6.9)%. ^{31}P NMR ($CDCl_3$): δ 112.9. ^1H NMR ($CDCl_3$): δ 3.57 [d, 2H, Ar-CH*H*-Ar, ^2J(HH) 15.1], 3.67 [d, 2H, Ar-CH*H*-Ar, ^2J(HH) 16.8], 4.28 [d, 2H, Ar-C*H*H-Ar, ^2J(HH) 16.8], 4.54 [d, 2H, Ar-C*H*H-Ar, ^2J(HH) 15.1], 4.66 (br s, 1H, OH), 6.66–7.21 (m, 12H, Ph). ^{13}C NMR ($CDCl_3$): δ 33.1 (s, *C*H_2), 36.3 (s, *C*H_2), 122.2–135.3 (m, Ph), 146.2–152.1 (m, Ph).

Thermal and hydrolytic stability tests for calixarene phosphites L_a and L_b

(a) In air, L_b (150 mg, 0.22 mmol) was placed in a round-bottom flask and heated in an oven at 300 °C for 1 h and then allowed to cool to ambient temperature. Then the ^{31}P NMR spectrum was measured and no decomposition was detected. In a separate experiment L_a was subjected to the same conditions again with no decomposition detected. (b) In air, a toluene (5 cm^3) solution of L_b (150 mg, 0.22 mmol) was refluxed for 24 h. After this time the ^{31}P NMR spectrum was measured and no decomposition was detected. In a separate experiment L_a was subjected to the same conditions again with no decomposition detected. (c) To a solution of L_b (1.0 g, 1.48 mmol) in CH_2Cl_2 (10 cm^3) and acetone (10 cm^3), distilled water (1.67 cm^3, 93.1 mmol) was added and the solution appeared homogeneous. This mixture was heated under reflux, with stirring, and the ^{31}P NMR spectrum of a sample was recorded after 30 min, 1 h, 3 h and 24 h and showed no decomposition had taken place. In a separate experiment L_a was subjected to the same conditions again with no decomposition detected. (d) To a solution of L_b (30 mg) in $CDCl_3$ (0.6 cm^3) in an NMR tube was added 1 M aqueous HCl (0.4 cm^3) and the biphasic system shaken for 30 min. The ^{31}P NMR spectrum was then recorded which showed no decomposition had taken place. In a separate experiment L_a was subjected to the same conditions again with no decomposition detected. (e) To a solution of L_b (30 mg) in $CDCl_3$ (0.6 cm^3) in an NMR tube was added 1 M aqueous NaOH (0.4 cm^3) and the biphasic system shaken for 30 min and then the ^{31}P NMR spectrum was recorded which showed no decomposition had taken place. In a separate experiment L_a was subjected to the same conditions again with no decomposition detected.

Preparation of [AuCl(L_b)] 3b

To a CH_2Cl_2 (10 cm^3) solution of [AuCl(tht)] (71.1 mg, 0.22 mmol), L_b (150 mg, 0.22 mmol) was added. The solution was stirred for 2 h at room temperature. All volatiles were then removed *in vacuo* to yield white solid **3b** (183 mg, 91%). Elemental analysis found (calc.): C, 58.9 (58.1); H, 6.1 (5.8); P, 3.4 (3.4)%. ^{31}P NMR ($CDCl_3$): δ 99.1.^1H NMR ($CDCl_3$): δ 1.22 [s, 9H, C(CH_3)$_3$], 1.29 [s, 18H, C(CH_3)$_3$], 1.33 [s, 9H, C(CH_3)$_3$], 3.48 [d, 2H, Ar-CH*H*-Ar, ^2J(HH) 14.7], 3.76 [d, 2H, Ar-C*H*H-Ar, ^2J(HH) 16.5], 4.22 [d, 2H, Ar-C*H*H-Ar, ^2J(HH) 16.5], 4.30 [d, 2H, Ar-C*H*H-Ar, ^2J(HH) 14.7], 7.05–7.20 (m, 8H, Ph). ^{13}C NMR ($CDCl_3$): δ 29.6–36.6 [m, *tert*-butyls, Ar*C*H_2Ar from calix[4]arene ligand], 125.5–132.4 (m, *C*H), 144.2–150.3. The analogue **3a** was made similarly in 73% yield. Elemental analysis, found (calc. for **3a**·CH_2Cl_2): C, 44.8 (45.3); H, 3.0 (3.0); P, 3.5 (4.0)%]. ^{31}P NMR (d^6-dmso): δ 99.1. ^1H NMR ($CDCl_3$): δ 3.76 [d, 2H, Ar-CH*H*-Ar, ^2J(HH) 14.7], 3.80 [d, 2H, Ar-CH*H*-Ar, ^2J(HH) 16.1], 4.24 [d, 2H, Ar-C*H*H-Ar, ^2J(HH) 16.1], 4.30 [d, 2H, Ar-C*H*H-Ar, ^2J(HH) 14.7], 6.67–7.39 (m, 12H, Ph). ^{13}C NMR ($CDCl_3$): δ 33.9 (s, Ar*C*H_2Ar,), 34.9 (s, Ar*C*H_2Ar), 122.3 (s, Ph), 126.1 (m, Ph), 148.5 (s, Ph), 152.8 (s, Ph).

Preparation of *cis*-[$PtCl_2(L_a)_2$] 4a

To a pale yellow solution of $K[PtCl_3(\eta^2\text{-}C_2H_4)]$ (61.5 mg, 0.17 mmol) in CH_2Cl_2 (10 cm^3) and acetone (10 cm^3), L_a (150 mg, 0.33 mmol) was added. The solution was stirred for 2 h at room temperature during which time an off-white precipitate was produced. This was filtered off to yield pale yellow solid **4a** (122 mg, 63%). IR (Nujol mull, cm^{-1}), 307, 325 ($\nu_{Pt–Cl}$). ^{31}P NMR (d^6-dmso): δ 37.9 [^1J(PtP) 6629]. ^{195}Pt NMR (d^6-dmso): δ 458 [t, ^1J(PtP) 6629].

Preparation of *trans*-[Pt_2Cl_2(μ-Cl)$_2$(L_b)$_2$] 5b

To a pale yellow solution of K[$PtCl_3$(η^2-C_2H_4)] (81.8 mg, 0.22 mmol) in CH_2Cl_2 (10 cm^3) and acetone (10 cm^3), L_b (150 mg, 0.22 mmol) was added. The solution was stirred for 2 h at room temperature during which time an off-white precipitate was produced. This was filtered off to yield pale yellow solid **5b** (154.7 mg, 74%). Single crystals of **5b** were grown by slow diffusion of hexane into a CH_2Cl_2 solution layered in an NMR tube. Elemental analysis, found (calc. for **5b**·3CH_2Cl_2): C, 51.5 (51.1); H, 5.6 (5.3)%]. IR (Nujol mull, cm^{-1}), 350w ($\nu_{Pt–Cl}$), 270w ($\nu_{Pt–\mu–Cl}$). ^{31}P NMR ($CDCl_3$): δ 2.2 [^1J(PtP) 7348]. ^{195}Pt NMR ($CDCl_3$): δ −650 [d, ^1J(PtP) 7348].

Reaction of [Pt(nor)$_3$] with L_b

To a colourless solution of [Pt(nor)$_3$] (52.8 mg, 0.11 mmol) in CH_2Cl_2 (10 cm^3), L_b (150 mg, 0.22) was added. The solution was stirred for 2 h at room temperature and then all volatiles were removed *in vacuo* to yield an off-white solid. ^{31}P and ^{195}Pt NMR spectroscopy showed this to be a mixture of **6b** [δ(P) 130.3, ^1J(PtP) 6084, δ(Pt) −1361 (d)] and **7b** [δ(P) 137.5, ^1J(PtP) 5991, δ(Pt) −820 (t)]. Using a similar procedure a mixture of **6a** [δ(P) 131.0, ^1J(PtP) 6199, δ(Pt) −1349 (d)] and **7a** [δ(P) 137.0, ^1J(PtP) 6060, δ(Pt) −834 (t)] were prepared from L_a.

Preparation of *trans*-[Pd_2Cl_2(μ-Cl)$_2$(L_b)$_2$] 8b

To an orange solution of [$PdCl_2$(NCPh)$_2$] (170 mg, 0.44 mmol) in CH_2Cl_2 (10 cm^3), L_b (150 mg, 0.22 mmol) was added. The solution was stirred for 2 h at room temperature and then all volatiles were removed *in vacuo*. The resulting solid was recrystallised from CH_2Cl_2 (8 cm^3) and pentane (20 cm^3) to give the orange powder **8b** (293 mg, 78%). Single crystals of **8b** were grown by slow evaporation of a $CDCl_3$ solution in an NMR tube. Elemental analysis, found (calc.); C, 61.5 (61.9); H, 6.4 (6.3)%]. ^{31}P NMR ($CDCl_3$) δ 38.1. ^{1}H NMR ($CDCl_3$): δ 1.26 [s, 9H, C(CH_3)$_3$], 1.30 [s, 9H, C(CH_3)$_3$], 1.66 [s, 18H, C(CH_3)$_3$], 3.50 [d, 2H, Ar-CH*H*-Ar, ^2J(HH) 14.3], 3.88 [d, 2H, Ar-CH*H*-Ar, ^2J(HH) 16.7], 4.26 [d, 2H, Ar-C*H*H-Ar, ^2J(HH) 16.7], 4.53 [d, 2H, Ar-C*H*H-Ar, ^2J(HH) 14.3], 4.37 (br s, 1H, OH), 7.09 (br s, 2H, Ph), 7.11 (br s, 2H, Ph), 7.18 (s, 2H, Ph), 7.37 (s, 2H, Ph). ^{13}C NMR ($CDCl_3$): δ 31.3 [m, C(CH$_3$)$_3$], 32.4 [m, C(CH$_3$)$_3$], 34.2–35.6 (m, CH$_2$), 124.0–132.8 (m, CH), 143.8–144.5 (m, CH), 148.8–150.0 (m, CH).

Bridge-cleavage reactions of *trans*-[Pd_2Cl_2(μ-Cl)$_2$(L_b)$_2$]

(a) With CO. Binuclear complex **8b** (150 mg, 0.09 mmol) was dissolved in CH_2Cl_2 (10 cm^3) and CO was bubbled through the orange solution at the rate of one bubble per second for 30 min at room temperature. Then all volatiles were removed *in vacuo* to give an orange powder. Satisfactory elemental analyses were not obtained but the main product was assigned the structure *trans*-[$PdCl_2$(CO)(L_b)] **9** on the basis of IR (CH_2Cl_2, cm^{-1}), 2141m (ν_{CO}) and ^{31}P NMR (d^6-dmso) δ 71.6. Satisfactory elemental analyses were not obtained for this product.

(b) With Bu^{t}NC. To an orange solution of **8b** (100 mg, 0.06 mmol) in CH_2Cl_2 (5 cm^3), Bu^{t}NC (13.2 μl, 0.12 mmol) was slowly added over 5 min and the solution stirred for 30 min at room temperature. All volatiles were then removed *in vacuo* to give a pale orange solid. ^{31}P NMR (d^6-dmso) δ 63.6. Single crystals of [$PdCl_2$(NCBu^t)(L_b)] **10** were grown by slow diffusion of pentane into a benzene solution of **10** by layering in an NMR tube.

(c) With MeNC. To a dark orange solution of **8b** (100 mg, 0.06 mmol) in CH_2Cl_2 (5 cm^3), MeNC (*ca.* 4.8 mg, 0.14 mmol) was slowly added using a calibrated high vacuum Schlenk line. The solution was stirred for 5 min during which time the colour changed to pale yellow. All volatiles were then removed *in vacuo* to yield a pale yellow solid whose ^{31}P{^{1}H} NMR spectrum (d^6-dmso), δ 66.6 was very similar to **10** and was therefore assigned the structure [$PdCl_2$(NCMe)(L_b)] **11**. Satisfactory elemental analyses were not obtained for this product.

(d) With pyridine or P(OPh)$_3$. Treatment of $CDCl_3$ solutions of **8b** with these ligands under similar conditions to those above were shown by ^{31}P NMR to contain only displaced L_b.

Reaction of [$PdCl_2$(NCPh)$_2$] with L_a

To a solution of [$PdCl_2$(NCPh)$_2$] (84.7 mg, 0.22 mmol) in CH_2Cl_2 (15 cm^3), L_a (200 mg, 0.44 mmol) was added and the orange solution stirred for 1 h at room temperature. Then the resulting orange precipitate was filtered off and a ^{31}P NMR spectrum measured in warm dmso. This showed a mixture of free L_a and palladium(II) complexes to have been produced, which were assigned structures [Pd_2Cl_4(L_a)$_2$] **8a** and [$PdCl_2$(L_a)$_2$] **12**, see Results and discussion.

Preparation of [IrCl(L_b)(cod)] 13b

To an orange solution of [Ir_2Cl_2(cod)$_2$] (74.4 mg, 0.11 mmol) in CH_2Cl_2 (15 cm^3), L_b (150 mg, 0.22 mmol) was added. The solution was stirred for 2 h at room temperature and then all volatiles were removed *in vacuo* to yield pale orange solid **13b** (206 mg, 92%). Elemental analysis, found (calc.): C, 56.4 (56.4); H, 6.4 (6.0); P, 3.0 (2.7)%. ^{31}P NMR (C_6D_6) δ 77.9. ^{1}H NMR ($CDCl_3$): δ 1.17 [s, 9H, C(CH_3)$_3$], 1.20 [s, 9H, C(CH_3)$_3$], 1.23 [s, 18H, C(CH_3)$_3$], 1.48 [m, 4H, CH_2 of cod], 2.28 [m, 4H, CH_2 of cod], 3.38 (m, 2H, C*H* of cod), 5.02 (m, 2H, C*H* of cod), 3.50 [d, 2H, Ar-CH*H*-Ar, ^2J(HH) 14.2], 3.78 [d, 2H, Ar-CH*H*-Ar, ^2J(HH) 16.6], 4.26 [d, 2H, Ar-C*H*H-Ar, ^2J(HH) 16.6], 4.42 [d, 2H, Ar-C*H*H-Ar, ^2J(HH) 14.2], 4.34 (br s, 1H, OH), 7.08 (s, 2H, Ph), 7.10 (s, 2H, Ph), 7.13 (s, 2H, Ph), 7.15 (s, 2H, Ph). ^{13}C NMR ($CDCl_3$): δ 27.3–51.9 (m, cod, *tert*-butyls, ArCH$_2$Ar from calix[4]arene ligand), 120.4–134.2 and 147.2–153.0 (m, CH). The analogue **13a** was made by a similar procedure from L_a in 97% yield. Single crystals of **13a** were grown by slow diffusion of benzene into a CH_2Cl_2 solution of **13a** layered in a NMR tube. Elemental analysis found (calc. for **13a**·1.5CH_2Cl_2): C, 48.8 (49.2); H, 3.8 (4.0); P, 2.7 (3.4)%. ^{31}P NMR ($CDCl_3$) δ 74.8. ^{1}H NMR ($CDCl_3$): δ 1.51 (m, 4H, CH_2 of cod), 2.28 (m, 4H, CH_2 of cod), 3.32 (m, 2H, C*H* of cod), 5.13 (m, 2H, C*H* of cod), 3.46 [d, 2H, Ar-CH*H*-Ar, ^2J(HH) 14.0], 3.79 [d, 2H, Ar-CH*H*-Ar, ^2J(HH) 16.5], 4.24 [d, 2H, Ar-C*H*H-Ar, ^2J(HH) 16.5], 4.47 [d, 2H, Ar-C*H*H-Ar, ^2J(HH) 14.0], 4.36 (br s, 1H, OH), 6.67 [t, 1H, Ph, ^3J(HH) 8.9], 6.95–7.14 (m, 11H, Ph). ^{13}C NMR ($CDCl_3$): δ 28.6 [d, ArCH$_2$Ar, ^4J(PH) 4.0], 33.6 [d, ArCH$_2$Ar, ^4J(PH) 4.6], 31.7, 35.5, 35.8, 53.4 (s, cod signals), 121.2–132.7 (m, CH), 148.8, 151.9 (m, CH).

X-Ray crystal structure determinations

Details of the structure determinations of crystals of **5b**·4CH_2Cl_2·C_6H_6, **10**·C_6H_6·C_5H_{12}, **8b**·6.67$CHCl_3$ and **13a**·0.5C_6H_6 are given in Table 5. All non-hydrogen atoms were assigned anisotropic displacement parameters and refined without positional constraints, except for some disordered atoms. All solvent molecules except for the benzene in **13a**·0.5C_6H_6 were disordered and their *Uij* and geometries were restrained and constrained as necessary. In **8b**·6.67$CHCl_3$ the *tert*-butyl group at C(19) was disordered across two sites with occupancies of 0.848(8) and 0.154(8).

CCDC reference number 186/1836.

See http://www.rsc.org/suppdata/dt/a9/a908960h/ for crystallographic files in .cif format.

Table 5 Selected crystallographic details for the crystal structure determinations of **5b**·$4CH_2Cl_2$·C_6H_6, **8b**·6.67$CHCl_3$, **10**·C_6H_6·C_5H_{12} and **13a**·0.05C_6H_6

	5b·$4CH_2Cl_2$·C_6H_6	**8b**·6.67$CHCl_3$	**10**·C_6H_6·C_5H_{12}	**13a**·0.5C_6H_6
Empirical formula	$C_{98}H_{120}Cl_{12}O_8P_2Pt_2$	$C_{94}H_{112}Cl_{24}O_8P_2Pd_2$	$C_{60}H_{80}Cl_2NO_4PPd$	$C_{39}H_{36}ClO_4PIr$
Formula weight	2303.46	2495.38	1087.52	827.30
Crystal system	Triclinic	Triclinic	Monoclinic	Triclinic
a/Å	13.6605(14)	13.312(3)	22.871(4)	8.914(2)
b/Å	13.821(2)	13.923(3)	13.852(3)	10.115(2)
c/Å	14.660(2)	16.352(3)	18.117(3)	18.556(3)
α/°	104.270(11)	106.68(3)		82.27(2)
β/°	101.943(12)	95.68(3)	93.104(12)	84.47(2)
γ/°	104.796(8)	107.47(3)		71.912(14)
V/Å^3	2483.4(5)	2711.8(9)	5731(2)	1573.3(5)
T/K	173(2)	173(2)	153(2)	173(2)
Space group	$P\bar{1}$ (no. 2)	$P\bar{1}$ (no. 2)	Cc (no. 9)	$P\bar{1}$ (no. 2)
Z	1	1	4	2
μ/mm^{-1}	3.222	1.004	0.490	4.422
Total reflns	15724	10006	11314	10208
Independent reflns	10877	9545	7145	6989
R_{int}	0.0576	0.0269	0.0312	0.0257
R_1 [$I > 2\sigma(I)$ data]	0.0476	0.0507	0.0447	0.0288

Acknowledgements

We thank Rhône-Poulenc (Lyon) for a studentship (to C. J. C.), EPSRC for financial support and Johnson-Matthey for a generous loan of platinum compounds.

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Paper a908960h