The Construction of P−O/P−N Ligands on Platinum and Palladium[‡]

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A variety of diphenyldiphosphinites have been prepared in a very stable form as Pt^{II} or Pd^{II} complexes by adding diols to a solution containing *cis*-[$MCl_2(PPh_2Cl)_2$] (M = Pt or Pd) preformed in situ from *cis*-[MCl_2(1,5-COD)] (M = Pt; M = Pd) and PPh_2Cl. This synthetic pathway can be used for diphosphinites derived from aliphatic 1,2 and 1,3 diols and also from the aromatic catechol. Besides the P–O bond, it is also shown here that the P–N bond can also be formed via nucleophilic attack of an amine group on coordinated PPh_2Cl in the presence of a base resulting in some AMPP and BAMP complexes of Pt^{II} and Pd^{II}. The X-ray crystal structures of the [*cis*-1,2-cyclohexanediyl bis(diphenylphosphinite)]platinum dichloride, of the AMPP palladium complex from (1*R*,2*S*)-(−)-norephedrine and of the BAMP palladium complex [*P*,*P*′-diphenyl-1,2-cyclohexanediylbis(imino)bisphosphane]-palladium dichloride have been determined. The chemical and optical stabilities of many complexes in solution have been monitored by ^{31}P NMR spectroscopy.

Introduction

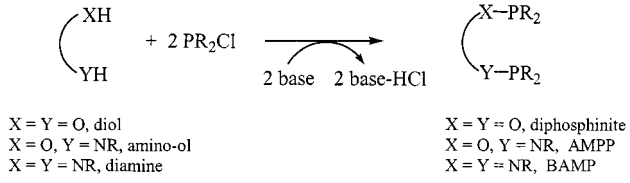
P-donor chiral ligands are widely used in metal-based asymmetric catalysis, because of the intrinsic ability of phosphorus to favour the substrate coordination, to stabilise intermediates of various processes and to provide selectivity through steric effects.[2] So far the most significant success is still represented by the asymmetric hydrogenation of prochiral olefins using Rh^{I} complexes of chiral diphosphanes.[3]

Research in this field has been developed since the early seventies and a large variety of chiral diphosphanes have been prepared and tested. Although great success has been achieved in the enantioselective conversion of some substrates, a few problems still remain unsolved:

i) Rh or Ru/chiral diphosphane catalysts are very efficient but their activity is restricted to a narrow group of transformations because only highly functionalised substrates (e.g. amino acids precursors) undergo coordination, the primary step of the process.

ii) The synthesis of chiral diphosphanes is often expensive and time consuming and requires delicate and awkward reactants.[4]

For these reasons the design and preparation of new ligands for chiral catalysts is still a lively topic and groups of phosphorated compounds other than diphosphanes have been taken into consideration. In particular chiral diphosphinites,[5] AMPP ("aminophosphanes-phosphinites") and BAMP ["bis(amino)phosphanes"][6] have been recently considered particularly for their synthetic accessibility based on the reaction of chlorophosphanes with diols, amino-ols and diamines (Scheme 1).



Scheme 1

The wide variety of asymmetric precursors belonging to these groups, especially from the natural chiral pool, enormously extends the number of easily accessible structural variations on the basic structure of these ligands.

Although the classical preparation of 1,2-(diphenyl)diphosphinites from diols and chlorodiphenylphosphane has been described in some papers as an easy clean process,[7] some problems have been raised[8] and in our hands this reaction gave poor and variable results because of the tendency of both the reagent chlorodiphenylphosphane and of the reaction products to undergo oxidative processes giving a variety of P^{V} species. On the other hand we noticed that 1,2-diphenylphosphinites are greatly stabilised by coordination to metal ions and therefore we have recently proposed an alternative synthetic pathway where a few examples of diphosphinite ligands were built up in the coordination sphere of Pt^{II} or Pd^{II} acting as templates.[1]

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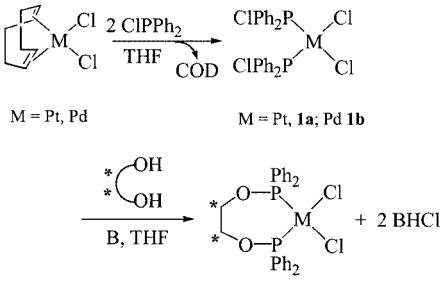
With the aim to demonstrate the generality of the above metal template method, in this paper we extend its application to the preparation of different kinds of coordinated diphosphinites, and also show that the P−N bond can be formed by nucleophilic substitution on coordinated chlorophosphane by an amine group leading to aminophosphane-phosphinites (AMPP) or bis(amino)phosphanes (BAMP).

Results and Discussion

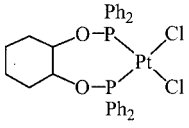
i) Preparation of Coordinated Diphosphinites

In our previous paper we showed that 1,2- and 2,3-bis(diphenylphosphinito)butanediols and isopropyl bis(diphenylphosphinito)tartrate can be prepared as coordinated ligands on Pt and Pd by a two-step process, starting from $[MCl_2(1,5\text{-COD})]$ (M = Pt, Pd), whose reaction with chlorodiphenylphosphane gave the intermediate complexes *cis*-$[MCl_2(PPh_2Cl)_2]$ (**1a**, M = Pt; **1b,** M = Pd), characterised in situ by ^{31}P NMR spectroscopy and converted into the relative diphenylphosphinite complex by addition of the corresponding diols in the presence of a base (Scheme 2).[1]



Scheme 2

In this paper we show that this template synthesis can be extended to other ligands: in particular we prepared the diphenylphosphinite from *cis*-1,2-cyclohexanediol in the platinum-coordinated form. This ligand is the optically inactive form derived from (1*R*,2*S*)-cyclohexanediol, and is the diastereomeric form of the optically active (1*R*,2*R*) or (1*S*,2*S*)-cyclohexane-1,2-diyl bis(diphenylphosphinite), which have already been tested in asymmetric catalysis.[9]



2a

Complex **2a** co-precipitated with py·HCl from the reaction mixture in THF and was purified by extraction with water and dichloromethane.

Due to the equivalence of the two phosphorus atoms, the ^{31}P NMR of **2a** shows a broad single signal at δ = 87.9 ppm, with satellites and $^1J_{Pt,P}$ = 3995 Hz, a typical value for a phosphorus atom *trans* to a chloride atom. The broadness of the signal is due to the fast equilibrium between two conformational forms where one P atom occupies the equatorial position while the other one is axial and vice versa.

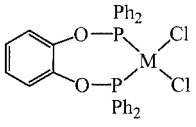
A variable-temperature experiment showed, at low temperature (− 55 °C), two distinct signals with satellites (δ_{P_A} = 74.8 ppm, $^1J_{Pt,P_A}$ = 3834 Hz, δ_{P_B} = 98.7 ppm $^1J_{Pt,P_B}$ = 4149 Hz), which coalesce at 25 °C into the above described broad singlet, which becomes sharper at +55 °C.

Solutions of **2a** in pure chloroform or in a $CHCl_3$/acetone mixture, examined by ^{31}P NMR, did not show any sign of decomposition even in the presence of oxygen and/or water after five days.

A recrystallisation of **2a** at room temperature from dichloromethane and diethyl ether gave crystals for X-ray crystal structure determination.

In order to demonstrate also that aromatic bis(diphenylphosphinites) can be formed on Pt, complex **3a** derived from catechol was prepared. The functionalisation of catechol can be proposed as a simple model for more complicated and more relevant aromatic systems like calixarenes.[10]

The ^{31}P spectrum of **3a** in $CHCl_3$ is a sharp singlet with satellites at δ = 93.4 ppm ($^1J_{Pt,P}$ = 4043 Hz); when the solution was treated with an excess of soluble CN^-, the spectrum changed into a singlet at δ = 114.1 ppm, due to the free ligand **3**. The following addition of $[PdCl_2(1,5\text{-COD})]$ to this solution gave the Pd analogue **3b** in situ, showing a singlet shifted to δ = 122 ppm. This chemical shift trend, with the Pd complex downfield and the Pt complex upfield, relative to the free ligand, has been found in general for the diphosphinites we have considered here and for the previously reported analogues.[1]



M = Pt, **3a**
M = Pd, **3b**

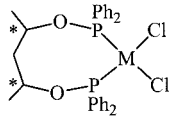
Using the optically active (*R*,*R*)-(−)-2,4-pentanediol, which gave the optically active Pt and Pd complexes **4a** and **4b**, we succeeded in demonstrating that it is possible to obtain eight-membered rings by this route.

The platinum complex **4a** has been obtained from $[PtMe_2(1,5\text{-COD}]$ by treatment with PPh_2Cl to give the dimethyl intermediate, which is then treated with (*R*,*R*)-(−)-2,4-pentanediol, giving the immediate precipitation of **4a**.

The reaction occurs via nucleophilic attack of both the OH groups on the phosphorus atoms. The outgoing HCl causes the protonolysis of the two Pt−Me groups giving rise to the final dichloro complex. The use of the dimethyl intermediate is very convenient because it avoids the use of the base and produces volatile CH_4 as the only side product.

Because of the instability of the corresponding precursor [$PdMe_2$(1,5-COD)], the corresponding palladium complex **4b** was obtained from [$PdCl_2$(1,5-COD)].

The complete characterisation of **4a** and **4b** is reported in the Exp. Sect. It is worth noting that for **4a** the value of $^1J_{Pt,P}$ = 4176 Hz, is more than 100 Hz larger than the corresponding coupling constant in seven-membered ring complexes.



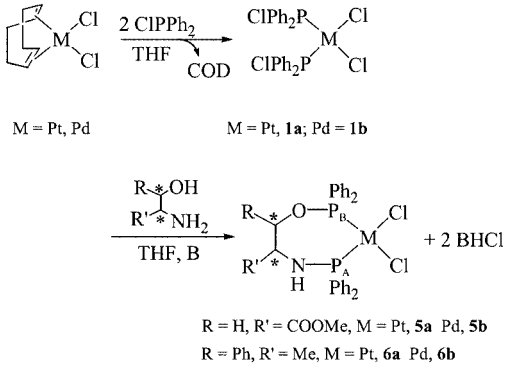
M = Pt, **4a**
M = Pd, **4b**

ii) Preparation of Coordinated AMPP

After the preparation of a series of bis(diphenylphosphinites) we reasoned that X−P bonds other than O−P could be conveniently built by nucleophilic substitution of chloride on the coordinated phosphorus centre.

Due to the interest in the catalysis of both aminophosphane-phosphinites (AMPP) and bis(amino)phosphanes (BAMP),[6] we tried to use amino groups (NH_2 or NHR) as nucleophiles in order to form N−P bonds.

By adding 1,2-amino-ols to a solution containing the preformed intermediates **1a** or **1b**, we succeeded in obtaining some examples of coordinated AMPP (Scheme 3).



M = Pt, Pd M = Pt, **1a**; Pd = **1b**

R = H, R' = COOMe, M = Pt, **5a** Pd, **5b**
R = Ph, R' = Me, M = Pt, **6a** Pd, **6b**

Scheme 3

By following the reactions using ^{31}P NMR spectroscopy, we noticed that the formation of the O−P bond is the first step occurring in a few minutes, followed by the slow making of N−P, with ring closure.

In this case it is necessary to assist the reaction using NEt_3, which is a stronger base than the $-NH_2$ group, in order to avoid the protonation of the amine group, which will make it unreactive.

We chose the methyl ester of the natural occurring amino acid L-serine, bearing an OH group in the β position, for this reaction and we obtained the Pt complex **5a** and the Pd analogue **5b**.

The ^{31}P NMR spectrum of **5a** shows two doublets of doublets with satellites at δ = 43.5 ppm (P_A, $^1J_{Pt,P_A}$ = 3887 Hz; $^2J_{P_BP_A}$ = 12 Hz) and 94.7 ppm (P_B, $^1J_{Pt,P_B}$ = 4075 Hz; $^2J_{P_AP_B}$ = 12 Hz) in the ranges expected for aminophosphane and phosphinites respectively.

The palladium complex **5b** presents two doublets at δ = 67.8 ppm (P_A, $^2J_{P_BP_A}$ = 32 Hz) and 124.9 ppm (P_B, $^2J_{P_AP_B}$ = 32 Hz) both at lower fields with respect to the corresponding peaks in **5a**.

Another example of optically active AMPP complexes, **6a** and **6b**, have been obtained via template synthesis using the optically active amino alcohol (1*R*,2*S*)-(−)-norephedrine.

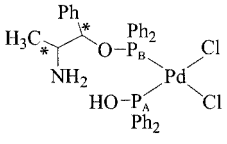
In ^{31}P NMR, **6a** is characterised by two doublets with satellites, due to the aminophosphinic moiety 45.9 ppm (P_A, $^1J_{Pt,P_A}$ = 3917 Hz and $^2J_{P_BP_A}$ = 11 Hz) and the phosphinitic group at 93.8 (P_B, $^1J_{Pt,P_B}$ = 4104 Hz and $^2J_{P_AP_B}$ = 11 Hz) ppm. ^{1}H NMR spectroscopy is very useful for checking the identity of the product and its purity (see Exp. Sect. for complete assignments): in particular at δ = 2.0 ppm a singlet is visible with satellites ($^3J_{PtH}$ = 55 Hz) belonging to the nitrogen bonded proton.

The palladium complex **6b**, obtained by treatment of **1b** with (1*R*,2*S*)-(−)-norephedrine and NEt_3 in benzene, shows two doublets at δ = 70.5 ppm (P_A, $^2J_{P_BP_A}$ = 35 Hz) and 123.6 ppm (P_B, $^2J_{P_AP_B}$ = 35 Hz). Its X-ray crystal structure has been determined (see further).

In these reactions the use of NEt_3 as a base affects the purity of the products, always contaminated by NEt_3HCl, which therefore require purification procedures.

In order to avoid salt contamination we reasoned that the use of a heterogeneous base could be convenient. With this aim, we tried to add solid $NaHCO_3$ to the reaction mixture in THF, together with a water sequestrating agent (e.g. anhydrous Na_2SO_4). Under these conditions, the reaction between **1b** and (1*R*,2*S*)-(−)-norephedrine gave complex **7b**, where the O−P bond is formed while the second-coordinated PPh_2Cl has been hydrolysed to PPh_2OH by the equivalent of water resulting from the reaction of $NaHCO_3$ with HCl. This indicates that the dehydrating agents (Na_2SO_4 or molecular sieves) that we tried, in order to avoid this hydrolytic process, are not efficient in comparison with the competing hydrolysis of the homogeneous coordinated PPh_2Cl.

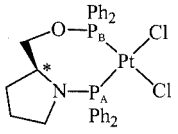
Complex **7b** contains a coordinated monodentate aminophosphinite (AMP), a type of ligand mentioned previously for its ability to give P/N six-membered chelate rings of interest in catalysis.[6]



7b

The reaction of preformed **1a** with the aminoalcohol L-prolinol bearing a secondary amino group gave complex **8a**.

The NMR spectroscopic data of **8a** are consistent with the data previously reported for the same complex obtained by the classical synthetic procedure from the preformed ligand.[11]



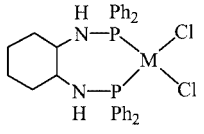
8a

iii) Preparation of Coordinated BAMP

Finally we have considered the possibility of extending the metal template method to the preparation of BAMP ligands.

The most interesting member of this group is the *N*,*N*′-bis(diphenylphosphanyl)-1,2-diaminocyclohexane ($DACHP_2$), whose palladium complex has recently been described as an efficient tool for the resolution of racemic amino acids.[12]

The platinum complex has been obtained from [$PtMe_2$(1,5-COD] by treatment with PPh_2Cl to give the dimethyl intermediate, which is then treated with (1*R*,2*R*)-*trans*-diaminocyclohexane, resulting in the immediate precipitation of **9a**. The corresponding palladium complex **9b** was obtained starting from [$PdCl_2$(1,5-COD)] (see Exp. Sect.). We determined the X-ray crystal structure of **9b**, recrystallised from dichloromethane and diethyl ether.



M = Pt, **9a**
M = Pd, **9b**

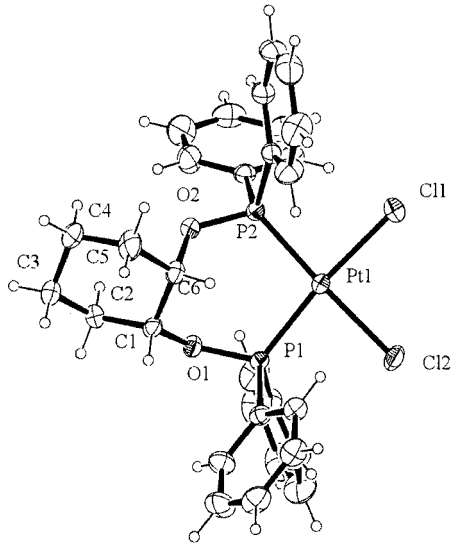


Figure 1. ORTEP view of compound **2a** showing the thermal ellipsoids at 30% level of probability

iv) X-ray Crystal Structures of 2a, 6b and 9b

By the slow diffusion of Et_2O into CH_2Cl_2 solutions, crystals suitable for structure diffractometric analysis were obtained for one member of each group: diphosphinites (**2a**), AMPP (**6b**) and BAMP (**9b**).

An ORTEP[13] view of each structure (**2a**, **6b** and **9b**) is given in Figure 1−3 and a selection of bond lengths and angles is reported in Table 1. All the complexes present a slightly distorted square-planar geometry with the metal centre bonded to two chloride and two phosphorus atoms belonging to the ligand. The seven-membered chelate rings resemble twisted half-chair conformations.

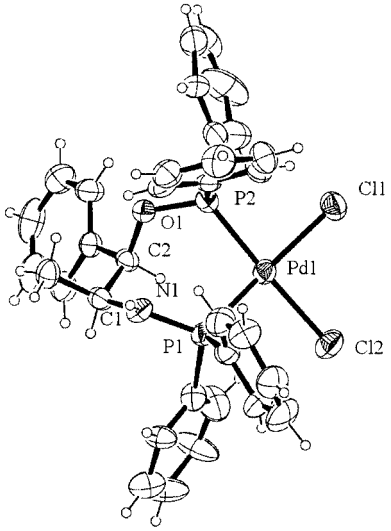


Figure 2. ORTEP view of compound **6b** showing the thermal ellipsoids at 30% level of probability

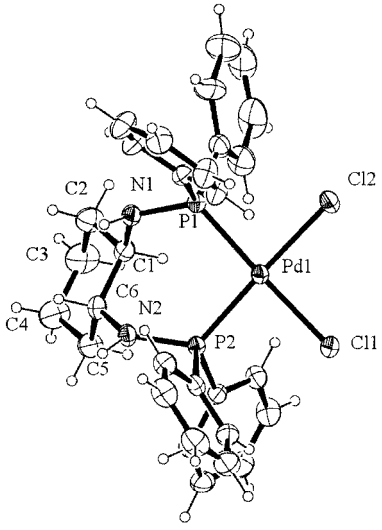


Figure 3. ORTEP view of compound **9b** showing the thermal ellipsoids at 30% level of probability

The molecules of complex **2a**, in the crystals, display C1 and C6 atoms in configurations (*R*) and (*S*), respectively. Since the solution does not show optical activity, it is evident that this compound crystallizes with separation of the

Table 1. Selected bond lengths (Å) and angles (°) (* values of the four independent molecules of the asymmetric unit)

Compound	**2a**	**6b***	**9b**
Pt1/Pd1−Cl1	2.364(2)	2.358(3), 2.359(3), 2.358(3), 2.358(3)	2.383(1)
Pt1/Pd1−Cl2	2.359(1)	2.359(3), 2.345(2), 2.345(3), 2.357(3)	2.367(1)
Pt1/Pd1−P1	2.223(1)	2.286(2), 2.261(2), 2.248(5), 2.239(2)	2.238(1)
Pt1/Pd1−P2	2.218(1)	2.230(2), 2.252(2), 2.244(2), 2.222(2)	2.263(1)
P1−O1	1.605(3)		
P2−O2	1.597(4)		
P2−O1		1.609(6), 1.598(6), 1.595(7), 1.614(7)	
P1−N1		1.694(8), 1.663(8), 1.675(8), 1.670(8)	1.663(3)
P2−N2			1.656(3)
O1−C1	1.452(4)		
O1−C2		1.442(9), 1.463(9), 1.422(12), 1.440(10)	
O2−C6	1.456(5)		
N1−C1		1.463(12), 1.485(12), 1.499(13), 1.450(12)	1.462(6)
N2−C6			1.462(5)
C1−C2		1.521(12), 1.546(13), 1.531(17), 1.536(12)	
C1−C6	1.511(7)		1.521(6)
Cl1−Pt1/Pd1−Cl2	88.19(4)	91.0(1), 91.0(1), 91.4(1), 89.6(1)	91.13(3)
Cl1−Pt1/Pd1−P1	171.67(4)	169.6(1), 169.6(1), 169.6(1), 163.5(1)	174.34(3)
Cl1−Pt1/Pd1−P2	88.82(4)	86.9(1), 88.5(1), 89.1(1), 88.5(1)	86.24(3)
Cl2−Pt1/Pd1−P1	85.59(4)	88.1(1), 86.1(1), 85.2(1), 90.1(1)	86.35(4)
Cl2−Pt1/Pd1−P2	177.01(3)	176.4(1), 176.4(1), 175.2(1), 173.6(1)	176.87(3)
P1−Pt1/Pd1−P2	97.41(4)	93.5(1), 95.0(1), 95.1(1), 93.5(1)	96.12(3)
Pt1/Pd1−P1−O1	118.5(1)		
Pt1/Pd1−P2−O1		116.9(2), 114.6(2), 115.3(3), 119.5(3)	
Pt1/Pd1−P2−O2	118.1(1)		
Pt1/Pd1−P1−N1		116.9(3), 116.1(3), 115.7(3), 118.1(3)	120.0(1)
Pt1/Pd1−P2−N2			123.2(1)

enantiomers. The C1 and C2 atoms in complex **6b** are in configurations (*S*) and (*R*), respectively. In complex **9b** both C1 and C6 atoms display the (*R*) configuration. The molecules in the crystals are coupled by means of two N2−H···Cl1 and N1−H···Cl2 hydrogen bonds: N2···Cl1(x + 1, y, z) = 3.236(3) Å and N1···Cl2(x+ 1, y, z) = 3.348(3) Å.

Conclusions

The preparation of a variety of Pt^{II} and Pd^{II} complexes through the metal template procedure proves that this new method can be proposed as an easy and accessible general synthetic pathway to P−O and P−N containing ligands, which are obtained in a convenient metal-stabilized form.

Experimental Section

All reactions and manipulations were routinely performed under dry nitrogen by using standard Schlenk-tube techniques. Tetrahydrofuran was bi-distilled over $LiAlH_4$, while diethyl ether and benzene were purified by distillation over sodium/benzophenone. Pyridine and triethylamine were distilled and stored over KOH. $CDCl_3$, used as solvent for NMR spectra, was dried with molecular sieves (4 Å).

PPh_2Cl (d = 1.23 g·mL^{-1}) was purified by distillation under nitrogen, stored at −15 °C and checked by ^{31}P NMR spectroscopy before use. All the other solvents and chemicals were reagent grade and, unless otherwise stated, were used as received from commercial suppliers. ^1H and ^{31}P NMR spectra (always ^1H decoupled) were recorded with a Bruker AC200 spectrometer operating at 200.13 MHz (^1H) and 81.01 MHz (^{31}P). Peak positions are given in ppm relative to tetramethylsilane (^1H) and to external 85% H_3PO_4 (^{31}P). Elemental analyses (C,H,N) were performed using a Carlo Erba model 1106 elemental analyser. Optical rotations were obtained with a Perkin−Elmer 241 at 25 °C.

Literature methods were used for the preparation of [$PtCl_2$(1,5-COD)],[14] [$PtMe_2$(1,5-COD)][15] and [$PdCl_2$(1,5-COD)].[16]

Synthesis of 2a: PPh_2Cl (144 μL, 0.802 mmol) was added dropwise, whilst stirring at room temperature, to a suspension of [$PtCl_2$(1,5-COD)] (0.150 g, 0.401 mmol) in THF (25 mL) placed in a Schlenk flask. The immediate formation of the dichloro diphosphane complex **1a** was unambiguously confirmed by ^{31}P NMR spectroscopy (δ =73.4 ppm, $^1J_{Pt,P}$ = 4069 Hz [1]).
The addition of pyridine (65 μL, 0.802 mmol) and *cis*-1,2-cyclohexanediol (0.047 g, 0.401 mmol) gave a cloudy mixture, which persisted whilst stirring at room temperature for 18 h. The white precipitate, composed of **2a** and pyridinium chloride, was then filtered, re-dissolved in CH_2Cl_2 and the solution was washed with 10 mL of water three times, dried with Na_2SO_4 and then taken to dryness under vacuum to give pure **2a** as a white solid. Yield 0.170 g (56%). $C_{30}H_{30}Cl_2O_2P_2Pt$ (750.5): calcd. C 48.01, H 4.03; found C 47.95, H 4.31. ^1H NMR (200 MHz, $CDCl_3$, 25 °C): δ = 1.2−1.5 (m, 4 H, CH), 1.6−1.9 (m, 4 H, CH), 4.5 (m, 2 H, CH−O), 7.3−7.9 (m, 20 H, Ph) ppm. ^{31}P NMR (81.01 MHz, $CDCl_3$, 25 °C): δ = 87.9 ppm (br. s, $^1J_{Pt,P}$ = 3995 Hz). Recrystallisation of crude **2a** from dichloromethane/ethanol gave crystals suitable for diffractometric study.

Synthesis of 3a: Complex **3a** was prepared in the same way as above using catechol (0.044 g, 0.401 mmol). After 18 h a small amount of

pyridinium chloride was filtered off, while the product remained in solution. The product was confirmed by ^{31}P NMR spectroscopic inspection. The solution was taken to dryness under vacuum and the oily residue was redissolved in CH_2Cl_2 (1 mL). Pure **3a**, as a white solid, was precipitated by addition of Et_2O (15 mL) and separated by filtration; yield 0.270 g (90%). $C_{30}H_{24}Cl_2O_2P_2Pt$ (744.4): calcd. C 48.40, H 3.25; found C 47.91, H 3.35. ^1H NMR (200 MHz, $CDCl_3$, 25 °C): δ = 6.1 (m, 2 H, CH), 6.85 (m, 2 H, CH), 7.4−8.1 (m, 20 H, Ph) ppm. ^{31}P NMR (81.01 MHz, $CDCl_3$, 25 °C): δ = 93.7 (s, $^1J_{Pt,P}$ = 4043 Hz) ppm.

Synthesis of 4a: [$PtMe_2$(1,5-COD)] (0.100 g, 0.300 mmol) was dissolved in bi-distilled THF (20 mL) and PPh_2Cl (108 μL, 0.600 mmol) was added. After checking the complete formation of the Pt containing intermediate [$PtMe_2(PPh_2Cl)_2$] by ^{31}P NMR spectroscopy (δ =100.3 ppm, $^1J_{Pt,P}$ = 1915 Hz), the solution was treated with (2*R*,4*R*)-(−)-pentanediol (0.031 g, 0.300 mmol). The initially clear solution was kept at room temperature for three days and during this time the progressive precipitation of a white solid was observed. Later the pure solid product was filtered away and dried under vacuum over P_2O_5. Yield 0.140 g (63%). $C_{29}H_{30}Cl_2O_2P_2Pt$ (738.5): calcd. C 47.17, H 4.09; found C 46.88, H 4.24. ^1H NMR (200 MHz, $CDCl_3$, 25 °C): δ = 0.8 (d, $^3J_{H,H}$ = 7.3 Hz, 6 H, CH_3), 1.8 (t, $^3J_{H,H}$ = 7.3 Hz, 2 H, CH_2), 4.35 (m, 2 H, CH), 7.3−8.1 (m, 20 H, Ph) ppm. ^{31}P NMR (81.01 MHz, $CDCl_3$, 25 °C): δ = 91.8 ppm (s, $^1J_{Pt,P}$ = 4176 Hz). $[\alpha]_D^{25}$ = −42.6 (*c* = 0.55, CH_2Cl_2).

Synthesis of 4b: PPh_2Cl (126 μL, 0.700 mmol) was added to [$PdCl_2$(1,5-COD)] (0.100 g, 0.350 mmol) suspended in 25 mL of dry THF: the solution turned yellow and the presence of **1b** was checked by ^{31}P NMR spectroscopy (δ =96 ppm, broad singlet) .[1] At this point pyridine (57 μL) and (2*R*,4*R*)-(−)-2,4-pentanediol (0.036 g, 0.350 mmol) were added to the solution which became cloudy. After stirring for 24 h the solid (**4b** and pyHCl) was filtered, redissolved in 1 mL of CH_2Cl_2 and extracted three times with water (10 mL). The organic phase was taken to dryness, resulting in **4b** as a yellow powder. Yield 0.100 g (44%). $C_{29}H_{30}Cl_2O_2P_2Pd$ (649.8): calcd. C 53.60, H 4.65; found C 53.80, H 4.73. ^1H NMR (200 MHz, $CDCl_3$, 25 °C): δ = 0.75 (d, $^3J_{H,H}$ = 7.3 Hz, 6 H, CH_3), 1.8 (t, $^3J_{H,H}$ = 7.3 Hz, 2 H, CH_2), 4.35 (m, 2 H, CH), 7.5−8.2 (m, 20 H, Ph) ppm. ^{31}P NMR (81.01 MHz, $CDCl_3$, 25 °C): δ = 121.8 (s) ppm. $[\alpha]_D^{25}$ = −61.4 (*c* = 0.5, CH_2Cl_2).

Synthesis of 5a: PPh_2Cl (96 μL, 0.535 mmol) was added dropwise whilst stirring at room temperature to a suspension of [$PtCl_2$(1,5-COD)] (0.100 g, 0.267 mmol) in THF (25 mL), resulting in **1a**. The addition of triethylamine (0.802 mmol) and L-serin methyl ester hydrochloride (0.042 g, 0.267 mmol) gave a cloudy mixture due to the formation of partially insoluble NEt_3 hydrochloride.
After 2 hours, another 50 mL of THF was added and the solution was stirred for a further two hours. The white precipitate was then filtered away and the solution, containing the impure product was taken to dryness. The residue was dissolved in CH_2Cl_2 and water was added in order to eliminate NEt_3HCl. The organic layer was finally dried with Na_2SO_4 and then taken to dryness under vacuum to give pure **5a** as a white solid. Yield 0.090 g (45%) $C_{28}H_{27}Cl_2NO_3P_2Pt$ (753.5): calcd. C 44.64, H 3.61, N 1.86; found C 44.60, H 3.80, N 1.89. ^1H NMR (200 MHz, $CDCl_3$, 25 °C): δ = 3.4 (br. s, $^3J_{PtH}$ = 45 Hz, 1 H, NH), 3.75 (s, 3 H, CH_3O), 4.0 (m, 1 H, CH−N), 4.4 (m, 2 H, C-CH_2O), 7.3−8.0 (m, 20 H, Ph) ppm. ^{31}P NMR (81.01 MHz, $CDCl_3$, 25 °C): δ = 43.6 (d, P_A, $^1J_{Pt,P_A}$ = 3885, $^2J_{P_BP_A}$ = 12 Hz), 94.9 (d, P_B, $^1J_{Pt,P_B}$ = 4074, $^2J_{P_AP_B}$ = 12 Hz) ppm. $[\alpha]_D^{25}$ = −20.8 (*c* = 0.58, CH_2Cl_2).

Synthesis of 6a: This complex was prepared in the same manner as **5a**, but by replacing L-serin methyl ester hydrochloride with (1*R*,2*S*)-(−)-di(norephedrine) (0.041 g, 0.267 mmol). The reaction gave **6a** as a white solid. Yield 0.096 g (46%). $C_{33}H_{31}Cl_2NOP_2Pt$ (785.5): calcd. C 50.46, H 3.98, N 1.78; found C 49.96, H 4.03, N 1.98. ^1H NMR (200 MHz, $CDCl_3$, 25 °C): δ = 0.95 (d, $^3J_{H,H}$ = 7.3 Hz, 3 H, CH_3), 2.0 (br. s, $^3J_{PtH}$ = 55 Hz, 1 H, NH), 4.0 (br. s, 1 H, CH−N), 5.35 (m, 1 H, CH−O), 6.8−8.2 (m, 25 H, CH arom.) ppm. ^{31}P NMR (81.01 MHz, $CDCl_3$, 25 °C): δ = 45.9 (d, P_A, $^1J_{Pt,P_A}$ = 3917, $^2J_{P_BP_A}$ = 11.3 Hz), 93.8 (d, P_B, $^1J_{Pt,P_B}$ = 4104, $^2J_{P_AP_B}$ = 11.5 Hz) ppm. $[\alpha]_D^{25}$ = −42.8 (*c* = 0.54, CH_2Cl_2).

Synthesis of 6b: [$PdCl_2$(1,5-COD)] (0.150 g, 0.525 mmol) was suspended in distilled benzene (25 mL) and PPh_2Cl (189 μL, 1.050 mmol) was added to give the immediate formation of the yellow soluble intermediate **1b**. Triethylamine (147 μL, 1.050 mmol) and (1*R*,2*S*)-(−)-norephedrine (0.080 g, 0.525 mmol) were added in sequence, followed by the precipitation of NEt_3HCl. After 18 hours of stirring, the solution containing **6b** was separated by filtration, and taken to dryness. The yellow-orange solid product was purified by recrystallisation from CH_2Cl_2 and diethyl ether Yield 0.215 g (59%). $C_{33}H_{31}Cl_2NOP_2Pd$ (696.9): calcd. C 56.88, H 4.48, N 2.01; found C 56.54, H 4.48, N 1.91. ^1H NMR (200 MHz, $CDCl_3$, 25 °C): δ = 0.95 (d, $^3J_{H,H}$ = 7.3 Hz, 3 H, CH_3), 2.0 (br. s, 1 H, NH), 3.9 (br. s, 1 H, CH−N), 5.2 (m, 1 H, CH−O), 6.8−8.2 (m, 25 H, Ph) ppm. ^{31}P NMR (81.01 MHz, $CDCl_3$, 25 °C): δ = 70.5 (d, P_A, $^2J_{P_BP_A}$ = 35 Hz), 123.6 (d, P_B, $^2J_{P_AP_B}$ = 35 Hz) ppm. $[\alpha]_D^{25}$ = −13.2 (*c* = 0.53, CH_2Cl_2). Recrystallisation of crude **6b** from dichloromethane/diethyl ether gave crystals suitable for a diffractometric study.

Synthesis of 7b: PPh_2Cl (189 μL, 1.050 mmol) was added to a suspension containing [$PdCl_2$(1,5-COD)] (0.150 g, 0.525 mmol) in 25 mL of bi-distilled THF: the mixture became clear and yellow and the complete formation of **1b** was checked by ^{31}P NMR spectroscopy. A large excess (0.500 g each) of $NaHCO_3$ and Na_2SO_4, previously dried at 120 °C for 10 h, was suspended in this solution, followed by the addition of (1*R*,2*S*)-(−)-norephedrine (0.079 g, 0.525 mmol). After stirring vigorously for 24 h, the salts were eliminated by filtration and the solution was taken to dryness, giving a solid residue of **7b**; yield 0.220 g (59%), which was recrystallised with CH_2Cl_2 and diethyl ether. $C_{33}H_{33}Cl_2NO_2P_2Pd$ (714.9): calcd. C 55.44, H 4.65, N 1.96; found C 55.72, H 4.90, N 2.01. ^1H NMR (200 MHz, $CDCl_3$, 25 °C): δ = 1.1 (d, $^3J_{H,H}$ = 7.3 Hz, 3 H, CH_3), 3.0 (m, 2 H, NH_2), 3.2 (br. s, 1 H, CH−N), 4.6 (m, $^3J_{H,H}$ = 8.2 Hz, 1 H, CH−O), 7.0−8.0 (m, 25 H, Ph) ppm. ^{31}P NMR (81.01 MHz, $CDCl_3$, 25 °C): δ = 63.2 (d, P_A, $^2J_{P_BP_A}$ = 15 Hz), 115.4 (d, P_B, $^2J_{P_AP_B}$ = 15 Hz) ppm.

Synthesis of 8a: PPh_2Cl (144 μL, 0.802 mmol) was added dropwise, whilst stirring at room temperature, to a suspension of [$PtCl_2$(1,5-COD)] (0.150 g, 0.401 mmol) in THF (25 mL), resulting in **1a**. The addition of triethylamine (112 μL, 0.802 mmol) and 40 μL of L-prolinol (0.401 mmol, *d* = 1.025 g·mL^{-1}) gave a cloudy mixture due to the formation of partially insoluble triethylamine hydrochloride. After stirring for 24 h at room temperature the salt was filtered away and the solution treated as above (see preparation of **5a**) to obtain **8a** as a white solid; yield 0.153 g (52%). $C_{29}H_{29}Cl_2NOP_2Pt$ (735.5): calcd. C 47.36, H 3.97, N 1.90; found C 46.96, H 4.12, N 1.89. ^1H NMR (200 MHz, $CDCl_3$, 25 °C): δ = 1.5−4.0 (m, 6 H, CH_2), 3.3−3.8 (m, 2 H, CH_2−O), 4.9 (br. s, 1 H, CH−N), 7.0−8.0 (m, 25 H, Ph) ppm. ^{31}P NMR (81.01 MHz, $CDCl_3$, 25 °C): δ = 51.3 (d, P_A, $^1J_{Pt,P_A}$ = 4030, $^2J_{P_BP_A}$ = 14 Hz), 80.7 (d, P_B, $^1J_{Pt,P_B}$ = 3941, $^2J_{P_AP_B}$ = 14 Hz) ppm. $[\alpha]_D^{25}$ = +17.8 (*c* = 0.53, CH_2Cl_2).

Synthesis of 9a: The complex was prepared from [$PtMe_2$(1,5-COD)] (0.100 g, 0.300 mmol), following the same procedure described above for **4a**, replacing the diol with (1*R*,2*R*)-*trans*-diaminocyclohexane (0.034 g, 0.300 mmol). The precipitation of **9a** occurred within five minutes as a white solid, which was filtered and dried with P_2O_5; yield 0.170 g (77%). $C_{30}H_{32}Cl_2N_2P_2Pt$ (748.5): calcd. C 48.14, H 4.31, N 3.74; found C 47.88, H 4.38, N 3.67. ^{1}H NMR (200 MHz, CD_2Cl_2, 25 °C): δ = 0.6−1.0 (m, 4 H, CH), 1.5 (m, 2 H, CH), 1.7 (d, 2 H, CH), 2.4 (s, $^3J_{PtH}$ = 32 Hz, 2 H, NH), 3.3 (br. s, 2 H, CH−N), 7.3−8.0 (m, 20 H, Ph) ppm. ^{31}P NMR (81.01 MHz, CD_2Cl_2, 25 °C): δ = 40.6 (s, $^1J_{Pt,P}$ = 4003 Hz) ppm.

Synthesis of 9b: This palladium complex was prepared as described above for **6b**, using THF as solvent and replacing the amino-ol with (1*R*,2*R*)-*trans*-diaminocyclohexane (0.060 g, 0.525 mmol). The product co-precipitated with NEt_3HCl in two hours and after filtration was re-dissolved in CH_2Cl_2 and extracted three times with water. The organic phase, taken to dryness, gave pure **9b** as a yellow solid; yield 0.160 g (46%). $C_{30}H_{32}Cl_2N_2P_2Pd$ (659.9): calcd. C 54.61, H 4.89, N 4.25; found C 54.68, H 4.70, N 4.55. ^{1}H NMR (200 MHz, CD_2Cl_2, 25 °C): δ = 0.6−1.0 (m, 4 H, CH), 1.5 (m, 2 H, CH), 1.7 (d, 2 H, CH), 2.3 (s, 2 H, NH), 3.3 (br. s, 2 H, CH−N), 7.3−8.0 (m, 20 H, Ph) ppm. ^{31}P NMR (81.01 MHz, CD_2Cl_2, 25 °C): δ = 65.9 ppm (s). $[\alpha]_D^{25}$ = +32.8 (*c* = 0.54, CH_2Cl_2). Recrystallisation of crude **9b** from dichloromethane/diethyl ether gave crystals suitable for a diffractometric study.

Removal of Coordinated Ligands from Platinum and Their Transfer to Palladium: This experiment was performed with the platinum complexes **4a**, **5a**, **6a** and **8a**. In a typical experiment, an excess of tetrabutylammonium cyanide (5 equiv.) was added to a solution containing the Pt complex (0.010 g) in $CDCl_3$ (0.8 mL). The progress of the reaction was monitored by ^{31}P NMR spectroscopy. After 15 min the spectrum showed the signals of the free ligand:

4: δ = 105.8 ppm (s)

5: δ = 116.9 ppm (s)

6: δ = 112.8 ppm (s) (PO), 38.8 ppm (s) (PN)

8: δ = 114.1 ppm (s) (PO), 46.4 ppm (s) (PN).

At this point an excess (2 equiv.) of [$PdCl_2$(1,5-COD)] was added to the solution and after ten minutes the signals of the corresponding palladium dichloride complex were visible in the ^{31}P NMR spectrum.

In an analogous manner the treatment of the palladium complex **9b** with tetrabutylammonium cyanide in $CDCl_3$, followed by the addition of [$PtCl_2$(1,5-COD)], allowed the observation of the spectrum of ligand **9** (δ = 33.6 ppm, s) and then of **9a**, assigned by comparison with a genuine sample.

The palladium complex **7b**, containing the monodentate aminophosphinite ligand **7**, after addition of CN^-, also gave the free ligand [δ = 111.5 ppm (s), PO] together with another unidentified phosphorus containing product [δ = 62.7 ppm (s)].

Chemical Stability Tests: In a typical experiment, 10^{-2} M solutions of the complex in $CDCl_3$, CH_2Cl_2, THF and benzene were prepared without exclusion of air and the ^{31}P NMR spectrum monitored after 30 min, 5 h and after 3 days. No changes were observed. A few drops of water were then added to each solution and the spectrum checked after 3 min and then after 24 h. Under these conditions all of the spectra were also found to be unchanged.

Optical Stability Tests: The values of $[\alpha]_D^{25}$ were determined for solutions of complexes **4a**, **4b**, **5a**, **6a**, **6b**, **8a** and **9b** as reported above. The optical rotations were redetermined for the same solutions after 3 days and each value was found unchanged.

X-ray Crystal Structure Determinations: X-ray diffraction data for compounds **2a**, **6b** and **9b** were collected on a Nonius Kappa CCD diffractometer, at room temperature (*T* = 295 K), with graphite monochromated Mo-K_α radiation (λ = 0.7107 Å) and corrected for Lorentz polarization and absorption (SORTAV)[17] effects. The structures were solved by direct methods (SIR97)[18] and refined (SHELXL-97)[19] by full-matrix least-squares with anisotropic non-hydrogen and hydrogen atoms on calculated positions, riding on their carrier atoms.

Crystal Data. 2a: $C_{30}H_{30}Cl_2O_2P_2Pt{\cdot}CH_2Cl_2$; trigonal, space group $P3_2$, *a* = 9.8264(1), *c* = 29.2991(2) Å, *V* = 2450.04(4) Å^3, *Z* = 3, $D_{calcd.}$ = 1.699 g·cm^{-3}. Intensity data collected with θ ≤ 30°; 9447 independent reflections measured; 8644 reflections observed [$I > 2\sigma(I)$]. Final *R* (observed reflections) = 0.028 and *Rw* (all reflections) = 0.063, *S* = 1.026, Flack parameter [20] = −0.012(3).

6b: $C_{33}H_{31}Cl_2NOP_2Pd{\cdot}1/2CH_2Cl_2$; triclinic, space group *P*1, *a* = 11.6343(2), *b* = 14.3753(3), *c* = 20.3486(4) Å, α = 93.0527(7), β = 92.4847(7), γ = 91.6164(9)°, *V* = 3393.6(1) Å^3, *Z* = 4, $D_{calcd.}$ = 1.447 g·cm^{-3}. Intensity data collected with θ ≤ 27°; 26342 independent reflections measured; 20677 reflections observed [$I > 2\sigma(I)$]. Final *R* = 0.098 (observed reflections) and *Rw* = 0.281 (all reflections), *S* = 1.029, Flack parameter = 0.03(4). The asymmetric unit contains four independent molecules of the complex and two molecules of dichloromethane.

9b: $C_{30}H_{32}Cl_2N_2P_2Pd$; monoclinic, space group $P2_1$, *a* = 7.5164(1), *b* = 16.2585(3), *c* = 12.4538(2) Å, β = 96.4409(7)°, *V* = 1512.32(4) Å^3, *Z* = 2, $D_{calcd.}$ = 1.449 g·cm^{-3}. Intensity data collected with θ ≤ 30°, 7940 independent reflections measured; 7416 reflections observed [$I > 2\sigma(I)$]. Final *R* = 0.039 (observed reflections), *Rw* = 0.101 (all reflections), *S* = 1.043, Flack parameter = 0.00(2).

CCDC-219076, 219077 and CCDC-219078 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: (internat.) +44-1223-336-033; E-mail: deposit@ccdc.cam.ac.uk].

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