

Template Synthesis of Chiral Vicinal Diphosphinites as Their Pt^{II} and Pd^{II} Complexes

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Keywords: Template synthesis / Ligand design / P ligands / Platinum / Palladium

The metal-templated synthesis of a few examples of vicinal diphenylphosphinites is accomplished when the corresponding vicinal diols react with the diphenylchlorophosphane complexes *cis*-[MCl₂(PPh₂Cl)₂] (M = Pt, Pd) in anhydrous THF. This process is proposed as a new synthetic route for Pt^{II} and Pd^{II} complexes of the new ligands 1,2-bis(diphenylphosphinito)butane, 2,3-bis(diphenylphosphinito)butane, and 2,3-bis(diphenylphosphinito)diisopropyl-L-tartrate, containing seven-membered chelate rings including stereogenic

carbons. The new chiral phosphane-phosphinite (*R*)-3-(diphenylphosphanyl)-2-(diphenylphosphinito)propanol has also been obtained as a Pt^{II} six-membered chelate. The X-ray crystal structure of some of the described complexes and NMR evidence of the possibility of removing the ligands from the metal are reported.

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Introduction

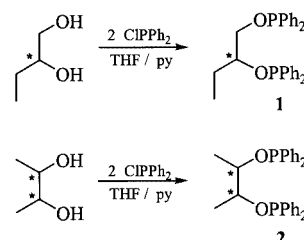
Chiral diphosphinites are a well-documented alternative to chiral diphosphanes as ligands for metal ions to give metal complexes that can be exploited in various processes with the double function of catalysts and asymmetry inductors.^[1] Particular attention has been given to vicinal diphosphinites whose coordination gives a seven-membered chelate ring similar in size to the successful DIOP-Rh system.^[2]

Several examples of chiral diphosphinites obtained by the functionalization of diols belonging to the natural chiral pool have been reported.^[3] In particular Rajan-Babu et al. have described asymmetric diphosphinites obtained by the functionalization of sugars and have shown that it is possible to drive some enantioselective hydrogenations to one product or to the other depending on the hydroxy groups selected for the transformation into phosphinites.^[4]

Despite the interest of diphosphinites for catalysis, the synthesis of those deriving from low-weight vicinal diols has not been described, with the sole exception of bis(diphenylphosphinite)ethane,^[5] observed in 1999 in solution but not isolated.

The apparent lack of attention paid to the simplest vicinal diphosphinites could be due to the known moisture and oxygen sensitivity^[6] reported for some members of this group of ligands, which makes their use in catalysis not very convenient and their synthesis quite puzzling.

In fact our attempts to prepare 1,2- and 2,3-bis(diphenylphosphinite)butane by the classical route (Scheme 1) – reaction of the corresponding diols with PPh₂Cl – gave **1** and **2** as impure products in low yield.



Scheme 1

Nevertheless, when we succeeded in obtaining a few square-planar Pt^{II} and Pd^{II} complexes from crude **1** and **2**, we noticed that the stability of such molecules is greatly enhanced by the coordination. We therefore reasoned that it should be possible to design a general alternative synthetic route for diphenylphosphinites where they could be built inside the coordination sphere of metal ions (metal template synthesis).

In this paper we compare two synthetic pathways to platinum and palladium dichloride complexes of **1** and **2**: in the first one **1** and **2** are prepared in solution as free ligands and then coordinated to the metal by substitution of COD in [MCl₂(1,5-COD)] (M = Pt, Pd); in the second, the reaction of the diphenylchlorophosphane complexes *cis*-[MCl₂(PPh₂Cl)₂] (**3a**, M = Pt; **3b**, M = Pd) with 1,2- or 2,3-butanediol leads to the same complexes in a shorter time and with higher yield and purity.

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This “metal-template” synthesis can be extended to more functionalised ligands, and we also report NMR evidence of the possibility of removing these ligands from the metal exploiting the sequestering action of CN^- on Pt and Pd.

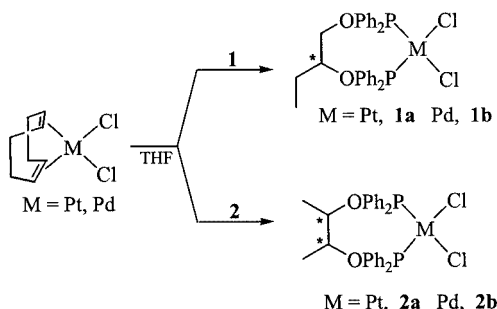
Results and Discussion

Generation of the Diphosphinites **1** and **2** in Solution and Their Coordination to Pt and Pd

The diphosphinites **1** and **2** can be obtained from the reaction of 1,2- and 2,3-butanediol^[7] respectively with two equivalents of PPh_2Cl in THF or pyridine (see Exp. Sect.). The reactions were followed by ^{31}P NMR spectroscopy and it was observed that, in both cases, PPh_2Cl ($\delta = 82.5$ ppm) is completely consumed in about 60 min to give the required product (two singlets at $\delta = 115.7$ and 111.5 ppm for **1** and one singlet at $\delta = 112.2$ ppm for **2**) together with a few phosphorus-containing side products.

The major drawback of this direct preparation of **1** and **2** is that impure products were obtained even under carefully controlled conditions. The ^{31}P NMR spectrum of the reaction mixture showed the presence of side products generated both by phosphorus oxidation and by PPh_2Cl decomposition due probably to traces of water contained in the reacting liquid diols.

All attempts to improve the purity of **1** and **2** obtained by this route using chromatographic techniques led to further decomposition. The instability of free phosphinites has been observed before.^[6] Nevertheless, the addition of $[\text{MCl}_2(1,5\text{-COD})]$ ($\text{M} = \text{Pt}, \text{Pd}$) to a THF solution containing crude **1** or **2** leads to the precipitation of their platinum (**1a** and **2a**) and palladium (**1b** and **2b**) dichloride complexes in pure form (Scheme 2).



Scheme 2

The ^{31}P NMR spectrum of **1a** shows two doublets with satellites at $\delta = 90.2$ and 89.3 ppm indicating that each phosphorus is coupled to platinum ($^1J_{\text{P,Pt}} = 4045$ and 3994 Hz, typical values for phosphorus *trans* to chloride^[8]) and to the other phosphorus ($^2J_{\text{P,P}} = 12$ Hz). The corresponding palladium complex **1b** also shows a doublet of doublets at $\delta = 119.1$ and 118.4 ppm ($^2J_{\text{P,P}} = 35.7$ Hz).

Both **2a** and **2b** show a singlet (with satellites for **2a**, $^1J_{\text{P,Pt}} = 4021$ Hz) in the ^{31}P NMR spectrum due to the equivalence of the two phosphorus atoms in these complexes.

While **1** and **2** undergo rapid decomposition in solution in the presence of traces of oxygen and/or water, solutions of **1a**, **1b**, **2a**, or **2b** in pure chloroform or in $\text{CHCl}_3/\text{acetone}$ do not show any sign of decomposition (by ^{31}P NMR spectroscopy) even in the presence of oxygen and/or water after five days: these observations indicate that coordination to Pt^{II} or Pd^{II} dramatically reduces the susceptibility of phosphinites to oxidation and hydrolysis.

Template Synthesis of **1** and **2**

In an attempt to design a more convenient route to diphosphinites we considered that, because the major reason for the interest in these compounds is the use of their complexes with metal ions in catalysis, it should be advantageous to produce them inside the coordination sphere of metal ions of catalytic value, thus obtaining the metal complexes directly. Pt^{II} and Pd^{II} complexes appeared to be convenient models for this synthetic approach. The metal-templated synthesis we carried out is described in Scheme 3.

Treatment of $[\text{MCl}_2(1,5\text{-COD})]$ ($\text{M} = \text{Pt}, \text{Pd}$) with two equivalents of PPh_2Cl in carefully dried THF gives *cis*- $[\text{MCl}_2(\text{PPh}_2\text{Cl})_2]$ **3a** ($\text{M} = \text{Pt}$) and **3b** ($\text{M} = \text{Pd}$), which have been described before.^[9]

We found that the coordinated chlorophosphane in **3a** and **3b** is still able to react with hydroxy groups. In fact, the reaction of **3a** or **3b** with 1,2- or 2,3-butanediol gave **1a**, **1b**, **2a**, and **2b** which precipitated as pure products in high yields, with elimination of HCl in solution.

Complexes **1a** and **2b** gave crystals suitable for an X-ray crystal-structure determination.

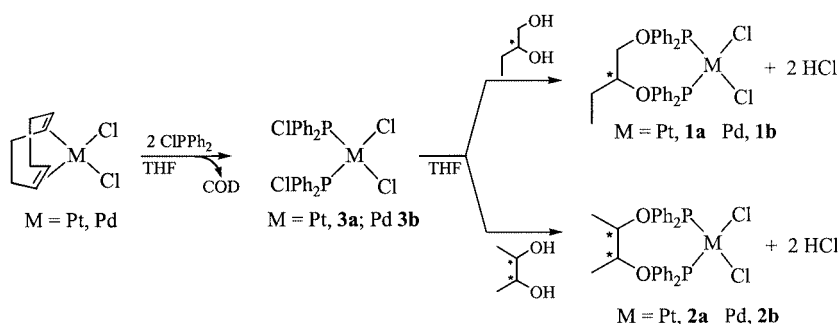
X-ray Crystal Structures of **1a** and **2b**

ORTEP^[10] views of the structure of **1a** and **2b** are shown in Figures 1 and 2, respectively. Selected bond lengths and angles are reported in Table 1. Both complexes present a slightly distorted square-planar geometry, with the metal centre bonded to two chlorides and to two phosphorus atoms belonging to the diphosphinite ligand. The coordination of **1** or **2** to the metal leads to the formation of a seven-membered ring with a boat conformation. The nature of the metallic centre does not significantly affect the bond angles and lengths in the coordination sphere.

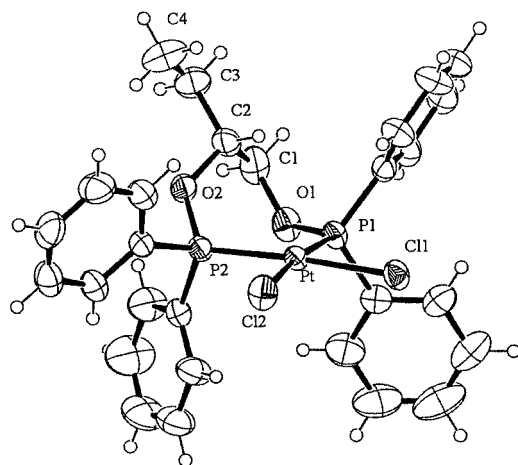
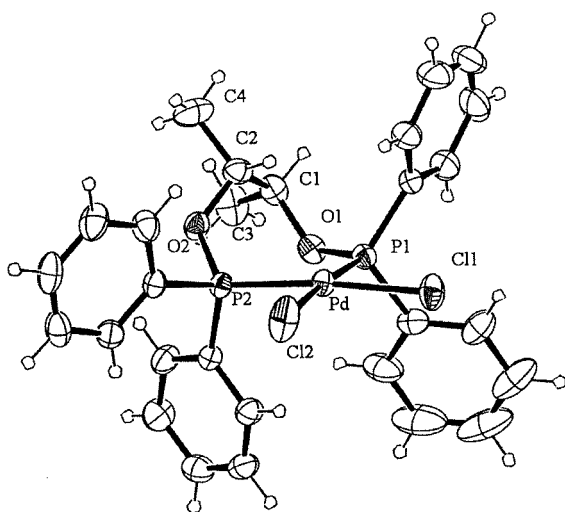
A few examples of X-ray crystal structures of diphosphinito complexes have been reported before. For example, both *fac*- $[\text{ReBr}(\text{CO})_3(\text{L}-\text{L})]$ and *fac*- $[\text{ReH}(\text{CO})_3(\text{L}-\text{L})]$ [$\text{L}-\text{L} = 1,2\text{-bis}(\text{diphenylphosphinito})\text{ethane}$] contain seven-membered $\text{ReP}_2\text{O}_2\text{C}_2$ rings with a twisted chair conformation.^[5]

Removal of **1** from Its Pt and Pd Complexes

The sequestering action of cyanide for platinum(II) is well-known.^[11] When **1a** was dissolved in CDCl_3 and treated with 4.5 equiv. of soluble $(\text{Bu}_4\text{N})\text{CN}$, the ^{31}P NMR spectrum showed that, in the first step, both the platinum-coordinated chlorides are replaced by cyanide within 5–10 minutes. Further observations show that the diphosphinite **1** is progressively replaced by cyanide and after 30–40 mi-



Scheme 3

Figure 1. ORTEP^[10] view of complex **1a** showing the thermal ellipsoids at the 40% probability levelFigure 2. ORTEP^[10] view of complex **2b** showing the thermal ellipsoids at the 40% probability levelTable 1. Selected bond lengths [Å] and angles [°] for compounds **1a** and **2b**

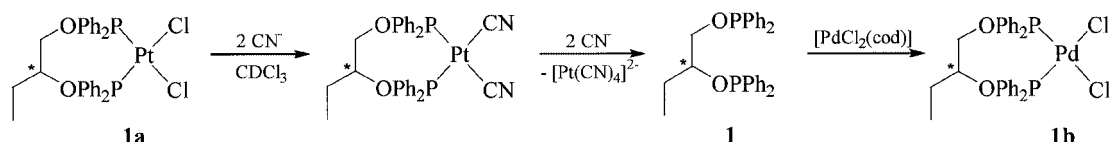
1a		2b	
Pt–Cl1	2.354(1)	Pd–Cl1	2.352(1)
Pt–Cl2	2.354(1)	Pd–Cl2	2.334(1)
Pt–P1	2.221(1)	Pd–P1	2.235(1)
Pt–P2	2.224(1)	Pd–P2	2.237(1)
P1–O1	1.604(3)	P1–O1	1.608(2)
P2–O2	1.601(2)	P2–O2	1.611(2)
O1–C1	1.463(5)	O1–C1	1.451(3)
O2–C2	1.446(4)	O2–C2	1.442(3)
C1–C2	1.503(6)	C1–C2	1.520(3)
Cl1–Pt–Cl2	88.33(3)	Cl1–Pd–Cl2	92.23(2)
Cl1–Pt–P1	86.64(3)	Cl1–Pd–P1	85.74(2)
Cl1–Pt–P2	176.09(3)	Cl1–Pd–P2	173.74(2)
Cl2–Pt–P1	172.94(4)	Cl2–Pd–P1	175.27(3)
Cl2–Pt–P2	91.47(3)	Cl2–Pd–P2	88.64(2)
P1–Pt–P2	93.22(3)	P1–Pd–P2	92.92(2)

notes the free ligand **1** is the only phosphorus-containing product.

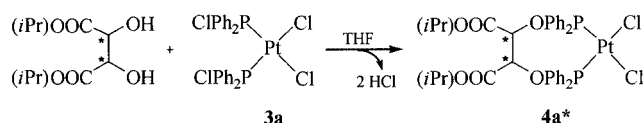
The addition of a small quantity of [PdCl₂(1,5-COD)] to this solution gives the immediate formation of **1b** (Scheme 4), indicating that the shift of **1** from platinum to palladium can be obtained by the addition of cyanide. An analogous experiment showed that the reverse process of ligand transfer from palladium (**1b**) to platinum is also easily achievable.

Template Synthesis of the New Diphosphinite **4** on Platinum

In an attempt to extend the applicability of our template synthesis of phosphinites to more functionalised ligands, we tried the addition of (+)-diisopropyl L-tartrate to the intermediate [Pt(PPh₂Cl)₂Cl₂] (**3a**) preformed in situ in THF. After 18 hours the formation of the optically active complex **4a*** was complete (Scheme 5).



Scheme 4



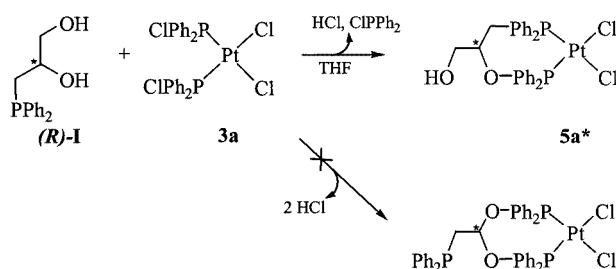
Scheme 5

This complex was isolated and fully characterised (see Exp. Sect.). The ^{31}P NMR spectrum shows a singlet for the two equivalent phosphorus atoms at $\delta = 94.7$ ppm, in the typical downfield range of diphenylphosphinites, with satellites due to the Pt coupling ($^1J_{\text{P,Pt}} = 4003$ Hz).

The optical rotation of **4a*** was measured in CHCl_3 ($[\alpha]_{\text{D}}^{25} = -10.6$ ($c = 0.5$, CHCl_3)). This result confirms the expectation that optically active complexes are obtained when a diol bearing a stereogenic carbon is used in an optically active form, due to the fact that the diol reaction with **3a** or **3b** does not involve the chiral carbon.

Template Synthesis of the New Phosphane-phosphinite-ol **5** on Platinum

The optically active phosphane-diol (**R**)-**I** (Scheme 6) can be obtained in two steps from the commercial precursor (*R*)-2,2-dimethyl-1,3-dioxolane-4-methanol *p*-toluenesulfonate through a known procedure.^[12]



Scheme 6

When (**R**)-**I** is added to a solution of $[\text{Pt}(\text{PPh}_2\text{Cl})_2\text{Cl}_2]$ (**3a**) its phosphinic group replaces the less nucleophilic PPh_2Cl and the *C*(2)hydroxy group reacts with the remaining coordinated PPh_2Cl (Scheme 6). The driving force of this process is probably the formation of a thermodynamically stable six-membered chelate ring. Complex **5a*** is recovered as the only platinum-containing species.

The identity of **5a***, determined by elemental and spectroscopic analysis, was confirmed by X-ray crystal structure (see below) and its optical rotation was measured (see Exp. Sect.). The ^{31}P NMR spectrum of **5a*** shows two doublets with satellites, one at $\delta = 84.7$ ppm, typical of a coordinate phosphinite, while the coordinated phosphinic P resonates at $\delta = -0.4$ ppm: each phosphorus is coupled to platinum ($^1J_{\text{P,Pt}} = 3858$ and 3482 Hz, respectively) and to the other phosphorus ($^2J_{\text{P,P}} = 17.7$ Hz).

It is noteworthy that **5a*** contains the new ligand (*R*)-3-(diphenylphosphanyl)-2-(diphenylphosphinito)propanol

(**5**), whose direct synthesis would not be possible without protection of the *C*(3)-hydroxy group. Not many examples of phosphane-phosphinites have been reported,^[13] and **5** is a rare example of this class of ligand with *C*-chirality.

It should also be noted that the reaction of **3a** with both the OH groups of (**R**)-**I** would give a potentially tridentate phosphane-diphosphinite ligand acting in only a bidentate manner; no evidence of this process was observed.

The deplatination of **5a*** with CN^- in solution (CDCl_3) allowed the observation of a ^{31}P NMR spectrum consistent with that expected for the free ligand **5** – a doublet at $\delta = 111$ ppm, typical for a ROPPH_2 group, and a second doublet in the phosphinic range ($\delta = -23$ ppm), each coupled to the other with a $^4J_{\text{P,P}}$ coupling constant of 7 Hz.

X-ray Crystal Structure of **5a***

The recrystallisation of **5a*** from CH_2Cl_2 and diethyl ether gave crystals whose X-ray structure is shown in Figure 3. Selected bond lengths and angles are given in Table 2.

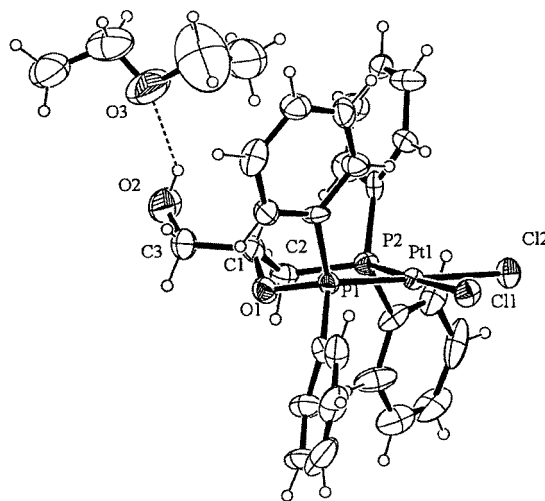


Figure 3. ORTEP^[10] view of complex **5a*** linked by hydrogen bonds to a solvent molecule of diethyl ether showing the thermal ellipsoids at the 40% probability level.

Table 2. Selected bond lengths [Å] and angles [°] for compound **5a***

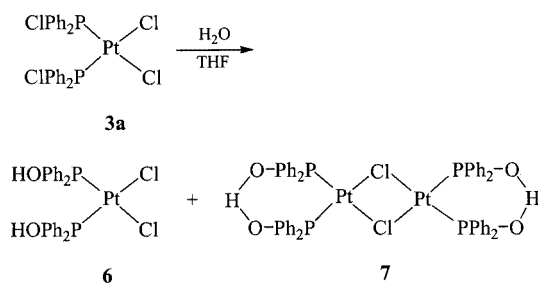
5a*			
Pt1–Cl1	2.352(4)	Cl1–Pt1–Cl2	89.3(1)
Pt1–Cl2	2.364(5)	Cl1–Pt1–P1	87.4(2)
Pt1–P1	2.209(5)	Cl1–Pt1–P2	177.1(2)
Pt1–P2	2.239(5)	Cl2–Pt1–P1	176.6(2)
P1–O1	1.60(1)	Cl2–Pt1–P2	88.0(2)
P2–C2	1.81(2)	P1–Pt1–P2	95.2(1)
C1–O1	1.44(2)		
C1–C2	1.49(2)		
C1–C3	1.52(2)		
C3–O2	1.38(2)		
Hydrogen bond			
O2–H2	0.82		
O3...H2	2.10		
O2...O3	2.78(2)		
O2–H2...O3	140		

The complex displays a slightly distorted square-planar geometry. The Pt1–P1–P2–C1–C2–O1 six-membered ring assumes a half-chair conformation with the C1 atom in the *R* configuration, as determined by the Flack parameter $[-0.02(4)]$ calculated after the least-square refinement. The molecular packing forms channels which include molecules of diethyl ether linked by means of an O2–H···O3 hydrogen bond $[O2\cdots O3 = 2.78(2) \text{ \AA}]$ to the hydroxyl group of the complex.

Hydrolysis of 3a and 3b

The above-described synthesis of diphenylphosphinites on Pt or Pd must be carried out in water-free conditions as we observed that, in the presence of even small quantities of water, competitive hydrolysis of the intermediate complexes **3a** and **3b** prevents the formation of the diphosphinite complexes.

We found that the addition of water to a THF solution of **3a** (Scheme 7) produces a mixture of complex $[\text{PtCl}_2(\text{PPh}_2\text{OH})_2]$ (**6**; $\delta = 71.1 \text{ ppm}$, $^1J_{\text{P,Pt}} = 4065 \text{ Hz}$) and of another species, **7**, whose ^{31}P NMR spectrum shows a singlet with satellites at $\delta = 50.5 \text{ ppm}$ ($^1J_{\text{P,Pt}} = 4090 \text{ Hz}$).



Scheme 7

Recrystallisation of the mixture from THF and diethyl ether gave crystals of **7**, which has been identified before^[9] on the basis of its NMR spectroscopic data. The X-ray crystal structure (Figure 4) showed that **7** is the dimeric neutral species $[\text{Pt}(\mu\text{-Cl})(\text{Ph}_2\text{POHOPPh}_2)]_2$ with bridging chloride ligands and terminal PPh_2OH and PPh_2O moieties connected by hydrogen bonds. Although the hydrolysis of **3a** has been studied in detail in the past,^[9] the structure of **7** has not been reported before.

In a similar way, the presence of water converts the palladium species **3b** into another species whose ^{31}P NMR spectrum is a singlet at $\delta = 78.1 \text{ ppm}$, coincident with the signal reported for the palladium analogue of **7** $[\text{Pd}(\mu\text{-Cl})(\text{Ph}_2\text{POHOPPh}_2)]_2$.^[9c]

X-ray Crystal Structure of 7

Crystals of **7** were obtained from THF and diethyl ether and its X-ray structure is shown in Figure 4. Selected bond lengths and angles are given in Table 3.

The complex is essentially planar and displays a C_s symmetry. The molecule is characterized by two strong hydrogen bonds $\text{O1-H}\cdots\text{O2}$ and $\text{O4-H}\cdots\text{O3}$ with very short

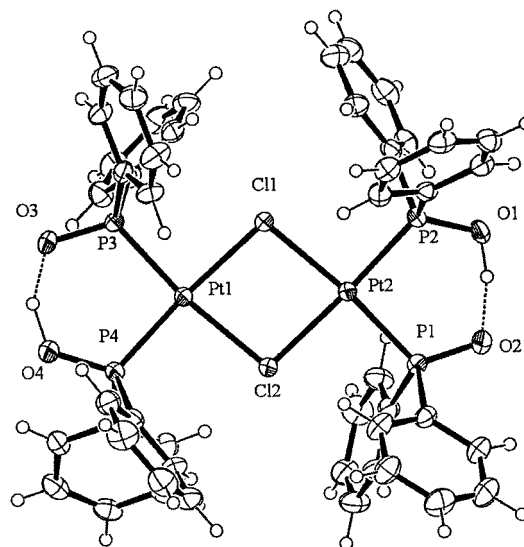


Figure 4. ORTEP^[10] view of complex **7** showing the thermal ellipsoids at the 40% probability level

Table 3. Selected bond lengths [$\text{\AA}$] and angles [$^\circ$] for compound **7**

7			
Pt1–Cl1	2.430(1)	Cl1–Pt1–Cl2	81.76(4)
Pt1–Cl2	2.420(1)	Cl1–Pt1–P3	91.17(4)
Pt1–P3	2.237(1)	Cl1–Pt1–P4	172.25(5)
Pt1–P4	2.229(1)	Cl2–Pt1–P3	172.27(4)
Pt2–Cl1	2.413(1)	Cl2–Pt1–P4	93.89(4)
Pt2–Cl2	2.415(1)	P3–Pt1–P4	93.49(5)
Pt2–P1	2.227(1)	Cl1–Pt2–Cl2	82.21(4)
Pt2–P2	2.227(1)	Cl1–Pt2–P1	172.84(4)
P1–O2	1.550(4)	Cl1–Pt2–P2	93.71(4)
P2–O1	1.544(4)	Cl2–Pt2–P1	91.54(5)
P3–O3	1.544(4)	Cl2–Pt2–P2	175.28(5)
P4–O4	1.540(4)	P1–Pt2–P2	92.67(5)
		Pt1–Cl1–Pt2	97.63(4)
		Pt1–Cl2–Pt2	97.84(4)
Hydrogen bonds			
O1–H	0.99(6)	O4–H	1.10(6)
O2···H	1.44(6)	O3···H	1.39(6)
O1···O2	2.415(6)	O3···O4	2.404(5)
O1–H···O2	165(5)	O4–H···O3	149(5)

$\text{O}\cdots\text{O}$ distances $[\text{O1}\cdots\text{O2} = 2.415(6) \text{ \AA}$ and $\text{O4}\cdots\text{O3} = 2.404(5) \text{ \AA}]$. They belong to the $(\text{O}-\text{H}\cdots\text{O})^-$ class of negative-charge-assisted H-bonds $[(-)\text{CAHB}]^{[14]}$ where the negative charge is shared between two oxygens. Accordingly, all the P–O bonds are of similar lengths [in the range $1.540(4)–1.550(4) \text{ \AA}$], and are significantly longer than the P=O distances $[1.48–1.50 \text{ \AA}]^{[15]}$ between phosphorus and neutral oxygen.

Conclusions

The experiments described in this paper show that vicinal diphosphinites can be obtained in the metal-chelate sta-

bilised form, starting from the corresponding 1,2-diols, whose stereochemistry is retained in the process.

We are now investigating the possibility to extend this preparative method to asymmetric complexes of other metals (e.g. Rh or Ru) and of other groups of ligands (e.g. amidophosphane-phosphinites and aminophosphane-phosphinites^[16]) relevant to asymmetric catalysis.

Experimental Section

All reactions and manipulations were routinely performed under a dry nitrogen atmosphere by using standard Schlenk-tube techniques. Tetrahydrofuran was doubly distilled from over LiAlH₄, while diethyl ether was purified by distillation from over sodium/benzophenone. Dichloromethane and methanol were purified by distillation from calcium hydride. Pyridine was distilled and stored over KOH. CDCl₃, used as solvent for the NMR spectra, was dried over molecular sieves (4 Å). PPh₂Cl (d = 1.23 g·mL⁻¹) was purified just prior to use by distillation under nitrogen. All the other solvents and chemicals were reagent grade and, unless otherwise stated, were used as received from commercial suppliers. Infrared spectra were obtained in CsI, using a Nicolet 510 P FT-IR (4000–200 cm⁻¹) spectrometer. ¹H and ³¹P NMR spectra (always ¹H decoupled) were recorded on Bruker AC200 spectrometers operating at 200.13 MHz (¹H) and 81.01 MHz (³¹P). Peak positions are given in ppm relative to tetramethylsilane (¹H) and to external 85% H₃PO₄ (³¹P). Elemental analyses (C, H, N) were performed using a Carlo Erba model 1106 elemental analyser. Optical rotations were obtained on a Perkin–Elmer 241 at 25 °C.

Literature methods were used for the preparation of [PtCl₂(1,5-COD)]^[17] and [PdCl₂(1,5-COD)]^[18].

The diol **R-I** was prepared in two steps from commercial *p*-toluenesulfonate of (*R*)-2,2-dimethyl-1,3-dioxolane-4-methanol by the reported procedure.^[12]

Synthesis of Pt and Pd Complexes of Ligands 1 and 2

Synthesis of 1a. Method a: A THF (5 mL) solution of 1,2-butanediol (117 mg, 1.3 mmol) was prepared in a Schlenk flask equipped with a dropping funnel and cooled to 0 °C (ice bath). The dropping funnel was charged with THF (5 mL), PPh₂Cl (0.57 mL, 3.2 mmol), pyridine (3 mL), and the mixture was added dropwise to the diol solution whilst stirring. After the addition of a few drops, white pyridinium chloride started to precipitate. After the end of the addition, the reaction mixture was kept stirring at 0 °C for an hour, then the white solid was filtered off under nitrogen on celite, giving a colourless solution whose ³¹P NMR analysis showed the presence of a main species consistent with **1** [³¹P NMR (81.01 MHz, CDCl₃, 25 °C): P_a 115.7(s), P_b 111.5 (s) ppm] together with small amount of other unidentified species.

The volume of this solution was reduced to 20 mL by addition of THF and solid [PtCl₂(1,5-COD)] (500 mg, 1.3 mmol) was added at room temperature. The reaction mixture was stirred for 1 h at room temperature; during this period the product precipitated as a white solid, which was then filtered and washed with diethyl ether (390 mg, 41%).

Method b: A solution of PPh₂Cl (100 µL, 0.56 mmol) in 5 mL of THF was added dropwise whilst stirring to a solution of [PtCl₂(1,5-COD)] (100 mg, 0.27 mmol) in THF (10 mL) placed in a Schlenk flask at room temperature. The immediate formation of the dichlorophosphane complex **3a** was unambiguously confirmed by ³¹P

NMR spectroscopy (δ = 73.4 ppm, ¹J_{Pt} = 4069 Hz^[9]). The addition of 1,2-butanediol (24 µL, 0.27 mmol) gave a colourless mixture, and within 10 minutes **1a** began to separate as a white microcrystalline precipitate. Slow addition of diethyl ether completed the precipitation. The solid product was filtered off, washed with diethyl ether, and dried under vacuum (130 mg, 67%). C₂₈H₂₈Cl₂O₂P₂Pt: calcd. C 46.4, H 3.9%; found C 46.6, H 4.0%. IR: ν_a(Pt–Cl) 317; ν_s(Pt–Cl) 293 cm⁻¹. ¹H NMR (200 MHz, CDCl₃, 25 °C): δ = 0.7 (t, ³J_{H,H} = 7 Hz, 3 H, -CH₃), 1.7–1.4 (m, 2 H, -CH₂Me), 3.8–4.2 (m, 2 H, -CH₂OP), 4.4 (m, 1 H, -CHOP), 7.0–8.0 (m, 20 H, Ph) ppm. ³¹P NMR (81.01 MHz, CDCl₃, 25 °C): δ = P_a 90.2 (d, ¹J_{PtP} = 4045 Hz), P_b 89.3 (d, ¹J_{PtP} = 3994 Hz) ppm, ²J_{PaPb} = 12 Hz.

Recrystallization of the crude product from dichloromethane/ethanol gave crystals suitable for an X-ray diffraction study.

Synthesis of 2a. Method a: A solution of ligand **2** was prepared from 2,3-butanediol (117 mg, 1.3 mmol), following the method described above for **1**. The ³¹P NMR analysis showed the presence of a signal consistent with **2** [³¹P NMR (81.01 MHz, CDCl₃, 25 °C): δ = 112.2 (s) ppm].

[PtCl₂(1,5-COD)] (500 mg, 1.3 mmol) was added to this solution and the procedure described above for **1a** (method a) was followed. The workup gave **2a** as white crystals. (352 mg, 38%).

Method b: Complex **2a** was obtained as a white solid (137 mg, 70%) following the procedure described above for **1a** (method b), based on 100 mg of [PtCl₂(1,5-COD)] (0.27 mmol) and replacing 1,2-butanediol with 2,3-butanediol. C₂₈H₂₈Cl₂O₂P₂Pt: calcd. C 46.38, H 3.89%; found C 46.43, H 3.90%. IR: ν_a(Pt–Cl) 321; ν_s(Pt–Cl) 295 cm⁻¹. ¹H NMR (200 MHz, CDCl₃, 25 °C): δ = 1.2 (d, ³J_{H,H} = 6.1 Hz, 6 H, -CH₃), 4.6 (m, 2 H, -CHOP), δ = 7.0–8.0 (m, 20 H, Ph) ppm. ³¹P NMR (81.01 MHz, CDCl₃, 25 °C): δ = 90.4 ppm (s, ¹J_{PtP} = 4021 Hz).

Synthesis of 1b. Method a: The diphosphinite **1** was generated in THF (20 mL) from 1,2-butanediol (153 mg, 1.7 mmol), PPh₂Cl (0.64 mL, 3.5 mmol), and pyridine (3 mL) as described above for **1a**. Solid [PdCl₂(1,5-COD)] (495 mg, 1.7 mmol) was then added at room temperature with vigorous stirring. Within a few minutes, **1b** precipitated as a yellow solid. The crude product was filtered and washed with diethyl ether (572 mg, 53%). Recrystallization from dichloromethane/ethanol gave yellow crystals.

Method b: The intermediate complex **3b** was prepared in situ by adding a solution of PPh₂Cl (314 µL, 1.75 mmol) in 5 mL of THF dropwise to a second solution of [PdCl₂(1,5-COD)] (250 mg, 0.87 mmol) in THF (20 mL). When the complete formation of **3b** was confirmed by ³¹P NMR spectroscopy (δ = 96 ppm), 1,2-butanediol (81 mg, 0.9 mmol) was added to give a pale yellow mixture. Within a few minutes **1b** began to precipitate as a yellow solid. Slow addition of diethyl ether completed the precipitation. The solid product was filtered off, washed with diethyl ether, and dried under vacuum. (409 mg, 74%). C₂₈H₂₈Cl₂O₂P₂Pd: calcd. C 52.85, H 4.44%; found C 53.02, H 4.58%. IR: ν_a(Pd–Cl) 315; ν_s(Pd–Cl) 290 cm⁻¹. ¹H NMR (200 MHz, CDCl₃, 25 °C): δ = 0.7 (t, ³J_{H,H} = 6.1 Hz, 3 H, -CH₃), 1.7 (m, 2 H, -CH₂Me), 4.1 (m, 2 H, -CH₂OP); 4.4 (m, 1 H, -CHOP), 7.0–8.0 (m, 20 H, Ph) ppm. ³¹P NMR (81.01 MHz, CDCl₃, 25 °C): δ = P_a 119.1 (d), P_b 118.4 (d) ppm, ²J_{PaPb} = 35.7 Hz.

Synthesis of 2b. Method a: Complex **2b** was prepared as a yellow crystalline solid (227 mg, 51%) from [PdCl₂(1,5-COD)] (200 mg, 0.7 mmol) and a solution where ligand **2** was generated from 2,3-butanediol (72 mg, 0.8 mmol) following the procedure described above for **1b**.

Method b: Complex **2b** was obtained also following the procedure described above for **1b** (method b), using 2,3-butanediol. Yield 74%. $C_{28}H_{28}Cl_2O_2P_2Pd$: calcd. C 52.85, H 4.44%; found C 52.31, H 4.57%. IR: $\nu_a(Pd-Cl)$ 311; $\nu_s(Pd-Cl)$ 299 cm^{-1} . 1H NMR (200 MHz, $CDCl_3$, 25 $^{\circ}C$): δ = 1.2 (d, $^3J_{H,H}$ = 6.1 Hz, 6 H, $-CH_3$), 4.5 (m, 2 H, $-CHOP$), 7.3–8.0 (m, 20 H, Ph) ppm. ^{31}P NMR (81.01 MHz, $CDCl_3$, 25 $^{\circ}C$): δ = 118.5 (s) ppm.

Template Synthesis of Other Diphosphinites on Pt^{II}

Synthesis of $4a^*$: The intermediate complex $[PtCl_2(PPh_2Cl)_2]$ (**3a**; 1.1 mmol) was formed in THF and checked by NMR spectroscopy as described for the previous reactions.

(+)-Diisopropyl L-tartrate (232 μL , 1.1 mmol) dissolved in THF (5 mL) was then added to the reaction mixture. After 18 h the complete formation of $4a^*$ was detected by ^{31}P NMR spectroscopy. This solution was reduced to a volume of 5 mL and the product was precipitated with *n*-pentane, washed with the same solvent and dried under vacuum (716 mg, 75%). $C_{34}H_{36}Cl_2O_6P_2Pt$: calcd. C 47.00, H 4.15%; found C 47.30, H 4.10%. IR: $\nu(CO)$ 1745; $\nu_a(Pt-Cl)$ 302; $\nu_s(Pt-Cl)$ 292 cm^{-1} . 1H NMR (200 MHz, $CDCl_3$, 25 $^{\circ}C$): δ = 1.1 (dd, $^3J_{H,H}$ = 6 Hz, 12 H, $-OCH(CH_3)_2$), 4.7 (septet, $^3J_{H,H}$ = 6 Hz, 2H, $-OCH(CH_3)_2$), 5.2 (m, 2 H, $-CHOP$), 7.2–8.0 (m, 20 H, Ph) ppm. ^{31}P NMR (81.01 MHz, $CDCl_3$, 25 $^{\circ}C$): δ = 94.7 (s, $^1J_{PtP}$ = 4003 Hz) ppm. $[\alpha]_D^{25}$ = -10.6 (c = 0.5, $CHCl_3$).

Synthesis of Complex $5a^*$: The intermediate complex $[PtCl_2(PPh_2Cl)_2]$ (**3a**; 0.77 mmol) was formed in THF and checked by NMR spectroscopy as described for the previous reactions. A solution of the phosphane-diol *R*-**1** (200 mg 0.77 mmol) in 5 mL of THF was then added to the reaction mixture and within 10 minutes a white solid began to precipitate. The addition of diethyl ether completed the precipitation of $5a^*$, which was filtered off, washed with diethyl ether and dried under vacuum. (404 mg, 74%). $C_{27}H_{26}Cl_2O_2P_2Pt \cdot C_2H_{10}O$: calcd. C 47.48, H 4.59%; found C 47.55, H 4.68%. IR: $\nu(OH)$ 3450; $\nu_a(Pt-Cl)$ 306; $\nu_s(Pt-Cl)$ 291 cm^{-1} . 1H NMR (200 MHz, $CDCl_3$, 25 $^{\circ}C$): δ = 1.2 (t, 6 H, $-CH_2P$), 3.5 (m, 7 H, OH + Et_2O + CH_2OH), 3.9 (m, 1 H, $-CHOP$), 7.5 (m, 20 H, Ph) ppm. ^{31}P NMR (81.01 MHz, $CDCl_3$, 25 $^{\circ}C$): δ = P_a 84.7 (d, $^1J_{PtP}$ = 3858 Hz), P_b -0.4 (d, $^1J_{PtP}$ = 3482 Hz) ppm, $^2J_{PaPb}$ = 17.7 Hz. $[\alpha]_D^{25}$ = $+40.0$ (c = 0.25, $CHCl_3$).

NMR Experiments

Hydrolysis of **3a and **3b**:** A solution of PPh_2Cl (300 μL , 1.67 mmol) in dry THF (20 mL) was added dropwise in 15 min to a second solution of $[PtCl_2(1,5-COD)]$ (308 mg, 0.82 mmol) in 30 mL of THF containing 30 μL of water. The mixture was stirred at room temperature. The ^{31}P NMR analysis of an aliquot after two hours showed the formation of **3a** and **6** [δ = 71.1 ppm (s, $^1J_{PtP}$ = 4065 Hz)] in an approximate 1:1 ratio, which increased with time. After 18 h, the signal of **3a** had disappeared and **6** and **7** [δ = 50.5 ppm/s, $^1J_{PtP}$ = 4090 Hz)] were observed in a 2:1 ratio. At this point, a reduction of the solution volume and the slow addition of diethyl ether induced the separation of a small amount of white crystals whose X-ray structure was determined.

In a similar way, when water (2 equiv.) was added to the palladium complex **3b**, generated in THF from PPh_2Cl (150 μL , 0.83 mmol) and $[PdCl_2(1,5-COD)]$ (117 mg, 0.41 mmol), the ^{31}P NMR showed a mixture of species, the most abundant of which was represented by a singlet at δ = 78.1 ppm $\{[Pt(Pd-Cl)(Ph_2POHOPPh_2)]_2\}^{[9c]}$.

Removal and Transfer of Ligand **1**

$(Bu_4N)CN$ (4.5 equiv.; 33 mg, 0.121 mmol) was added to a $CDCl_3$ solution (0.8 mL) of **1a** (15 mg, 0.027 mmol) in a 5-mm screw-cap

NMR tube. The progress of the reaction was monitored by ^{31}P NMR spectroscopy: within the time necessary for NMR acquisition the substitution of both the chlorides in **1a** with two cyanides was completed (P_a δ = 100.9 ppm, d, $^1J_{PtP}$ = 2815 Hz and P_b δ = 99.5 ppm, d, $^1J_{PtP}$ = 2834, $^2J_{PP}$ 19.6 Hz). The following decomposition of this dicyanide derivative into $[Pt(CN)_4]^{2-}$ and free ligand **1** occurred in about 30 minutes as denoted by the observation of the signals of **1** [δ = P_a 115.7 (s), P_b 111.5 (s) ppm] exclusively. At this point, the addition of $[PdCl_2(COD)]$ (8.5 mg, 0.03 mmol) to the same NMR tube showed the immediate appearance of the signals of **1b**.

An analogous multi-step transmetallation process was performed by addition of an excess of solid $(Bu_4N)CN$ to a solution of the palladium complex **1b** (15 mg, 0.02 mmol) in 0.8 mL of $CDCl_3$, followed by $[PtCl_2(1,5-COD)]$ (11 mg, 0.03 mmol). The final ^{31}P NMR spectrum showed the phosphinito-platinum complex **1a** to be the only phosphorus-containing species.

Removal of Ligand **5** from Platinum Complex $5a^*$

A sample of complex $5a^*$ (10 mg, 0.014 mmol) was dissolved in $CDCl_3$ and a ^{31}P NMR spectrum recorded. Solid $(Bu_4N)CN$ was progressively added to this solution. After the first addition of two equivalents (7.5 mg), a ^{31}P NMR spectrum consistent with the cyanide analogue of complex $5a^*$ was detected (dd, δ = 92 and -4.4 ppm, $^1J_{PtP}$ = 2716 and $^1J_{PtP}$ = 2398 Hz respectively, $^2J_{PP}$ = 25.6 Hz). Further addition of a large excess of $(Bu_4N)CN$ (5 equiv., 20 mg) produced the appearance of a new pattern showing two coupled doublets (δ = 111 and -23 ppm, $^4J_{PP}$ = 7 Hz), as expected for the phosphane-phosphinite-ol **5**.

X-ray Crystal Structure of **1a, **2b**, $5a^*$, and **7**:** The crystal data were collected using a Nonius Kappa CCD diffractometer with graphite monochromatized Mo- K_α radiation and corrected for Lorentz, polarization and absorption (SORTAV)^[19] effects. The structures were solved by direct and Fourier methods (SIR92)^[20] and refined on F^2 (SHELXL-97)^[21] using full-matrix least-squares with all non-H atoms anisotropic and hydrogen atoms at calculated positions, riding on their carrier atoms.

1a: $C_{28}H_{28}Cl_2O_2P_2Pt$, M = 724.43, T = 295 K, monoclinic, space group $P2_1/n$, a = 8.9098(2), b = 17.8502(4), c = 18.1605(4) Å, β = 103.749(1) $^{\circ}$, U = 2805.5(1) Å³, Z = 4, D_c = 1.715 g·cm⁻³, μ = 53.269 cm⁻¹. Collected reflections = 18446 ($\theta \leq 30^{\circ}$), unique reflections = 8130, R_{int} = 0.031, observed reflections = 6311 [$I \geq 2\sigma(I)$]. Final R (observed reflections) = 0.0335, R_w (all reflections) = 0.0659.

2b: $C_{28}H_{28}Cl_2O_2P_2Pd$, M = 635.74, T = 295 K, monoclinic, space group $P2_1/n$, a = 9.2571(2), b = 15.4091(3), c = 19.7280(4) Å, β = 90.248(1) $^{\circ}$, U = 2814.0(1) Å³, Z = 4, D_c = 1.501 g·cm⁻³, μ = 9.865 cm⁻¹. Collected reflections = 18078 ($\theta \leq 30^{\circ}$), unique reflections = 8135, R_{int} = 0.036, observed reflections = 6188 [$I \geq 2\sigma(I)$]. Final R (observed reflections) = 0.0347, R_w (all reflections) = 0.0845.

$5a^*$: $C_{27}H_{26}Cl_2O_2P_2Pt \cdot C_4H_{10}O$, M = 784.53, T = 295 K, orthorhombic, space group $P2_12_12_1$, a = 8.0995(1), b = 18.0184(3), c = 21.9803(4) Å, U = 3207.8(1) Å³, Z = 4, D_c = 1.624 g·cm⁻³, μ = 46.702 cm⁻¹. Collected reflections = 16288 ($\theta \leq 27^{\circ}$), unique reflections = 4850, R_{int} = 0.049, observed reflections = 4057 [$I \geq 2\sigma(I)$]. Flack parameter^[22] = $-0.02(4)$. Final R (observed reflections) = 0.0428, R_w (all reflections) = 0.1102.

7: $C_{48}H_{42}Cl_2O_4P_4Pt_2$, M = 1267.78, T = 150 K, triclinic, space group $P\bar{1}$, a = 11.9217(2), b = 13.3152(2), c = 16.1860(4) Å, α = 94.6411(7), β = 99.4177(7), γ = 115.3400(7) $^{\circ}$, U = 2257.78(8) Å³,

$Z = 2$, $D_c = 1.865 \text{ g}\cdot\text{cm}^{-3}$, $\mu = 64.935 \text{ cm}^{-1}$. Collected reflections = 28569 ($\theta \leq 28^\circ$), unique reflections = 10307, $R_{\text{int}} = 0.056$, observed reflections = 8727 [$I \geq 2\sigma(I)$]. Both the hydrogens forming intramolecular hydrogen bonds O1–H $\cdots$ O2 and O4–H $\cdots$ O3 were refined isotropically. Final R (observed reflections) = 0.0362, R_w (all reflections) = 0.0928.

CCDC-189474, 189475, 189476, 189477 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at <http://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; Email:deposit@ccdc.cam.ac.uk].

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Received July 30, 2002
[I02340]