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X-ray crystal structures of novel platinum(II) and palladium(II) complexes of dialkyl phosphonated phosphines

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Abstract

Two diethyl phosphonated phosphine ligands of formula $Ph_2P(CH_2)_3PO_3Et_2$ (ligand **L**) and $Ph_2P(4\text{-}C_6H_4PO_3Et_2)$ (ligand **L′**) were used to prepare different complexes of platinum(II) (**1**, *cis*-$PtCl_2L_2$; **2**, *trans*-$PtCl_2L_2{\cdot}H_2O$; **3A** and **3B**, *cis*- and *trans*-$PtCl_2L'_2$) and palladium(II) (**4**, $[PdCl_2L]_2$; **5**, *trans*-$PdCl_2L_2{\cdot}H_2O$; **6**, *trans*-$PdCl_2L'_2{\cdot}CH_2Cl_2$). The single-crystal X-ray structure analyses of complexes **1**, **2**, **4**–**6** indicate that complexation involved only the phosphine end, whereas the strong polarization of the P=O bond was highlighted by the formation of hydrogen bonds with a water molecule in **2** and **5**, and with a dichloromethane molecule in **6**, with an exceptionally short C–H···O hydrogen bond length (C···O separation 3.094(3) Å). © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Platinum(II) complexes; Palladium(II) complexes; Dialkyl phosphonated phosphines; Hydrogen bonding

1. Introduction

Platinum(II) and palladium(II) complexes are well known not only for their great importance as catalysts in organic synthesis [1], but also for their biological and pharmacological interest [2]. Ligands containing both a strongly electron-donating phosphine group and a co-ordinatively labile phosphonate group are prone to form hemilabile transition metal complexes, which are of interest in catalytic applications [3,4]. Moreover phosphonated phosphines provide a route to water-soluble complexes [5–13] alternative to sulfonated phosphines. An important feature of phosphine-phosphonate complexes is the possibility to immobilize them between the layers of zirconium phosphates [12,14] or double hydroxides [15]. The phosphonate group may also be used to anchor these complexes on supports such as metal oxides or bone tissues, thus opening a wide field of applications in supported catalysis and chemotherapy [3,16,17]. However, despite the interest raised by phosphine-phosphonate ligands very few X-ray structures have been reported for platinum(II) [4] or palladium(II) [10] complexes with such ligands.

We recently reported that not only phosphonic acids but also phosphonic esters (ethyl or trimethylsilyl) could be used as coupling agents to modify titania or alumina surfaces [18,19]; alternatively, the phosphonate groups can be dispersed within a matrix of metal oxide by sol–gel processing [19,20]. Our purpose in studying complexes with phosphine-phosphonate ligands is to prepare heterogeneous catalysts by these two routes. Here we report the preparation and characterization of platinum(II) and palladium(II) complexes derived from the ligands $Ph_2P(CH_2)_3PO_3Et_2$ (ligand **L**) and $Ph_2P(4\text{-}C_6H_4PO_3Et_2)$ (ligand **L′**) (Table 1). The single-crystal X-ray structure analysis of five of these compounds indicates that the complexation of the metal involves

Table 1
Platinum(II) and palladium(II) complexes prepared

	$L = Ph_2P(CH_2)_3PO_3Et_2$	$L' = Ph_2P(4\text{-}C_6H_4PO_3Et_2)$
Platinum	*cis*-$PtCl_2L_2$ [a], **1** *trans*-$PtCl_2L_2{\cdot}H_2O$ [a], **2**	*cis*-$PtCl_2L'_2$, **3A** *trans*-$PtCl_2L'_2$, **3B**
Palladium	$[PdCl_2L]_2$ [a], **4** *trans*-$PdCl_2L_2{\cdot}H_2O$ [a], **5**	*trans*-$PdCl_2L'_2{\cdot}CH_2Cl_2$ [a], **6**

[a] Structure determined by single-crystal X-ray diffraction.

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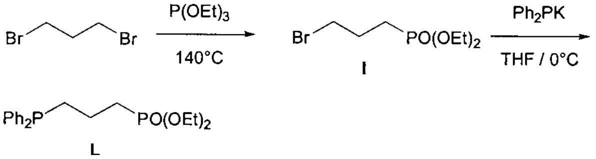
only the phosphine end, whereas the strongly polarized phosphoryl oxygen forms hydrogen bonds with a water molecule in **2** and **5**, and with a dichloromethane molecule in **6**.

2. Results and discussion

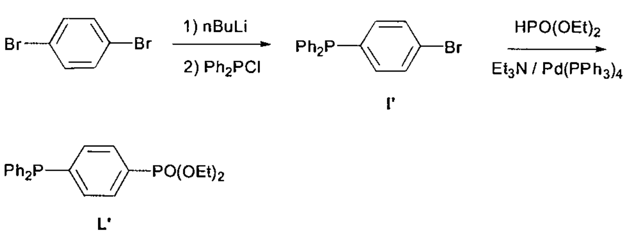
2.1. Synthesis of the ligands

Ligand **L** was synthesized in two steps according to Eq. (1). $Br(CH_2)_3PO_3Et_2$ (I) was obtained by an Arbuzov reaction [21]. Then the nucleophilic phosphination with Ph_2PK [22] afforded **L** in high yield (86%) as a colourless oil which presented ^{31}P-NMR chemical shifts at -17.5 ppm (Ph_2P) and at 30.9 ppm ($PO(OEt)_2$) in CH_2Cl_2–acetone-d_6 mixture.



(1)

Ligand **L′** was synthesized in two steps according to Eq. (2). The intermediate $Br(4\text{-}C_6H_4PPh_2)$ (I′) was prepared by the method reported by McEwen et al. [23], then it was subjected to a Pd catalyzed coupling reaction [24] to give **L′** as a yellow oil in 52% yield (^{31}P-NMR chemical shifts at -4.6 ppm (Ph_2P) and 18.3 ppm (PO_3Et_2) in acetone-d_6).



(2)

2.2. Complexes of platinum(II)

2.2.1. Ligand **L**

Usually, the reaction of $PtCl_2(PhCN)_2$ with phosphine ligands leads to mixtures of *cis* and *trans* isomers [25–29]. Actually the reaction of ($PtCl_2(PhCN)_2$) with two equivalents of ligand **L** in dichloromethane led to a mixture of white (complex **1**) and yellow crystals (complex **2**). Complexes **1** and **2** were separated by crystallization from a CH_2Cl_2–pentane mixture and single crystals suitable for X-ray diffraction study were obtained.

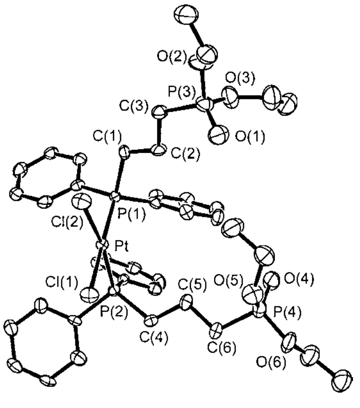


Fig. 1. ORTEP representation of complex **1** (thermal ellipsoids are shown at 30% probability; hydrogen atoms have been omitted for clarity).

Table 2
Selected bond lengths (Å) and bond angles (°) for compound **1**

Bond lengths			
Pt–P(1)	2.2567(9)	Pt–Cl(1)	2.3452(9)
Pt–P(2)	2.2507(9)	Pt–Cl(2)	2.3563(9)
P(1)–C(1)	1.828(4)	P(2)–C(4)	1.827(3)
P(3)–O(1)	1.452(3)	P(4)–O(4)	1.472(3)
P(3)–C(3)	1.766(4)	P(4)–C(6)	1.786(4)
P(3)–O(2)	1.583(3)	P(4)–O(5)	1.574(3)
P(3)–O(3)	1.574(4)	P(4)–O(6)	1.568(3)
Bond angles			
P(1)–Pt–P(2)	99.64(3)	P(2)–Pt–Cl(1)	83.06(3)
P(1)–Pt–Cl(1)	176.62(3)	P(2)–Pt–Cl(2)	169.60(3)
P(1)–Pt–Cl(2)	89.92(3)	Cl(1)–Pt–Cl(2)	87.54(4)
Pt–P(1)–C(1)	114.62(12)	Pt–P(2)–C(4)	112.99(13)
O(1)–P(3)–C(3)	116.02(19)	O(4)–P(4)–C(6)	114.64(19)
O(1)–P(3)–O(2)	113.98(19)	O(4)–P(4)–O(5)	115.56(19)
O(1)–P(3)–O(3)	114.6(2)	O(4)–P(4)–O(6)	115.29(17)

Complex **1** presents a *cis* square-planar geometry (Fig. 1) in which the phosphonate groups are not coordinated to the platinum atom. The square-planar geometry is slightly distorted around the platinum atom, as shown by the values of bond angles P(2)–Pt–Cl(1) (83.06(3)°) and P(1)–Pt–P(2) (99.64(3)°), P(1)–Pt–Cl(1) (176.62°), and P(2)–Pt–Cl(2) (169.60(3)°) (Table 2). Moreover the bond lengths Pt–P (2.2567(9) and 2.2507(9) Å), and Pt–Cl (2.3452(9) and 2.3563(9) Å) are close, but not equal. Solid-state ^{31}P-MAS NMR spectroscopy gave interesting informations owing to the coupling with ^{195}Pt ($I = 1/2$; 33.8%). The signal assigned to the phosphonate groups appeared as one singlet at 31.4 ppm, whereas the two signals assigned to the phosphine ligands, at 10.2 and -6.3 ppm (1/1 ratio), presented satellites with constants ^{1}J(PtP) of 3844 and 3556 Hz, respectively. The presence of two signals for the phosphorus atoms of the two phosphine ligands reflects their crystallographic non-equivalence and the distorted structure of complex **1**. Such a solid-state distortion is common for *cis* complexes of platinum [28]. Conversely the solution ^{31}P-NMR spectrum of complex **1** in a CH_2Cl_2–acetone-d_6 mixture presented only one singlet at 7.5 ppm with two ^{31}P–^{195}Pt satellites (^{1}J(PtP) = 3643 Hz) ascribed to the phosphine ligands, besides a sharp singlet at 30.2 ppm assigned to $P(O)(OEt)_2$ groups. Note that the coupling constants ${}^1J$(PtP) observed in the solid state as well as in solution are in the same range, higher than 3000 Hz as expected for a *cis* geometry [30].

Complex **2**, $PtCl_2L_2{\cdot}H_2O$, presents a *trans* geometry (Fig. 2) with a slightly distorted square-planar geometry around the platinum atom, as shown by the 175.27(3)° value of the Cl(1)–Pt–Cl(2) bond angle (Table 3). The oxygen atoms of the phosphoryl groups are not coordinated to the platinum atom, but they are bridged via hydrogen bonds to a molecule of adventitious water. Because of these hydrogen bonds the phosphonate groups must face each other, forming tongs, instead of being oriented away from the square plan. The lengths of the two hydrogen bonds are 1.90(4) and 1.94(5) Å. The bond angles O–H–O of 170(4) and 151(4)° indicate a distortion (Table 3). The literature [31] gives an example of a water molecule hydrogen bonded to two molecules of triphenylphosphine oxide, with H···O distances of 1.85 and 1.77 Å, and O–H–O angles of 161 and 168°.

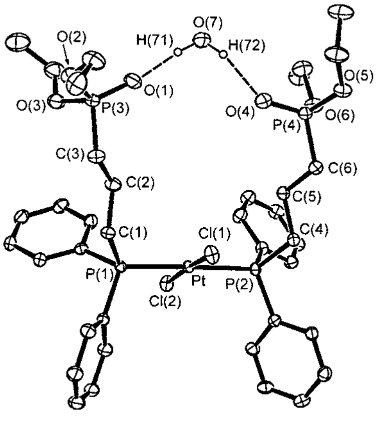


Fig. 2. ORTEP representation of complex **2** (thermal ellipsoids are shown at 30% probability; hydrogen atoms have been omitted for clarity).

Table 3
Selected bond lengths (Å) and bond angles (°) for compound **2**

Bond lengths			
Pt–P(1)	2.3256(8)	Pt–Cl(1)	2.3054(8)
Pt–P(2)	2.3269(8)	Pt–Cl(2)	2.3073(8)
P(1)–C(1)	1.830(3)	P(2)–C(4)	1.832(3)
P(3)–C(3)	1.795(3)	P(4)–C(6)	1.776(3)
P(3)–O(1)	1.465(3)	P(4)–O(4)	1.454(3)
O(7)–H(71)	0.91(5)	O(7)–H(72)	0.93(5)
O(1)–H(71)	1.90(4)	O(4)–H(72)	1.94(5)
O(1)–O(7)	2.797(4)	O(4)–O(7)	2.790(4)
Bond angles			
P(1)–Pt–P(2)	177.40(3)	P(2)–Pt–Cl(1)	89.78(3)
P(1)–Pt–Cl(1)	88.57(3)	P(2)–Pt–Cl(2)	90.26(3)
P(1)–Pt–Cl(2)	91.21(3)	Cl(1)–Pt–Cl(2)	175.27(3)
Pt–P(1)–C(1)	116.42(10)	Pt–P(2)–C(4)	115.50(11)
O(1)–P(3)–C(3)	115.03(18)	O(4)–P(4)–C(6)	114.66(17)
O(1)–P(3)–O(2)	114.02(16)	O(4)–P(4)–O(5)	113.03(17)
O(1)–P(3)–O(3)	115.95(17)	O(4)–P(4)–O(6)	115.98(17)
H(71)–O(7)–H(72)	104(4)	O(1)–H(71)–O(7)	170(4)
O(4)–H(72)–O(7)	151(4)		

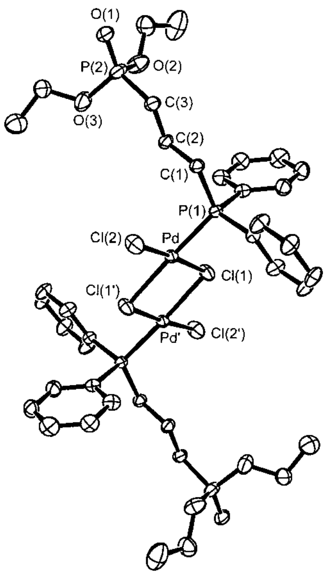


Fig. 3. ORTEP representation of complex **4** (thermal ellipsoids are shown at 30% probability; hydrogen atoms have been omitted for clarity).

2.2.2. Ligand L′

The treatment of $(PtCl_2(PhCN)_2)$ with two equivalents of ligand **L**′ led to complexes **3A** *cis* and **3B** *trans* as a mixture of white and yellow crystals. Attempts to separate them by crystallization remained unsuccessful. The ^{31}P-NMR spectrum in acetone-d_6 displayed two singlets with two ${}^{31}P-{}^{195}Pt$ satellites at 14.6 ppm (${}^1J$(PtP) = 3833 Hz) and at 21.3 ppm (${}^1J$(PtP) = 2469 Hz) in a 43:57 ratio, which were assigned to the *cis* (**3A**) and *trans* (**3B**) coordinated phosphines, respectively, and two singlets at 17.2 and 16.7 ppm ascribed to the phosphonate groups.

2.3. Complexes of palladium(II)

2.3.1. Ligand L

The reaction of $PdCl_2$ with two equivalents of **L** in THF led to a mixture of complexes **4** and **5**, which could be separated by successive crystallizations from CH_2Cl_2–pentane as orange and yellow crystals in 15 and 65% yields, respectively. The crystals obtained turned out to be suitable for structure determination by X-ray diffraction.

Compound **4** has a centrosymmetric dimeric structure in which the two metal centres are linked through bridging chlorine atoms (Fig. 3 and Table 4). The two palladium atoms adopt a quasi-square planar geometry in *trans* arrangement so that a centre of symmetry lies between them, as confirmed by ^{31}P-MAS NMR with only two peaks at 30.6 ppm (PO_3Et_2) and 28.7 ppm (PPh_2). The solution ^{31}P-NMR chemical shifts (30.8 and 30.3 ppm) point at a similar solution structure. These chemical shifts are in good agreement with literature values for dimeric complexes of palladium [32,33]. The ligands **L** are bonded to the palladium atoms through the trivalent phosphorus atoms of the phosphine groups, whereas the free phosphonate groups point out on each side of the plan formed by chlorine and palladium atoms to reduce steric repulsions. Such chlorine-bridged dimeric palladium complexes $[PdCl_2L]_2$ are known to form in the reaction of monometallic complexes L_2PdCl_2 with an excess of $PdCl_2$. Conversely the chloro bridges are cleaved by amines and phosphines and dimeric complexes are considered as intermediates in the synthesis of monometallic complexes with L–Pd ratios higher than 2 [34,35]. In complex **4**, the bond lengths between a palladium atom and either the terminal chlorine atom (2.2752(7) Å) or the bridging chlorine atoms (2.3273(7) and 2.4244(7) Å) are similar to those reported in the literature for chlorine-bridged dimeric palladium complexes [33,35–37], as are the Cl–Pd–Cl′ bond angles (85.66(2) and 91.89(2)°) (Table 4).

Complex **5** is monometallic. Its structure (Fig. 4) presents a *trans* square-planar geometry around the palladium atom. Actually complex **5** is isomorphous of complex **2**, with a slightly distorted square-planar geometry around the palladium atom: the P(1)–Pd–P(2) and Cl(1)–Pd–Cl(2) bond angles both depart from 180°, and P–Pd–Cl bond angles are slightly different from 90° (Table 5). ^{31}P-NMR spectroscopy in $CDCl_3$ confirm the *trans* arrangement with two peaks at 31.0 ppm (^4J(PP) = 2.5 Hz, PO_3Et_2) and at 16.4 ppm (^4J(PP) = 2.4 Hz, PPh_2) comparable with literature values for *trans* coordinated alkyldiarylphosphines [30,38,39]; there is no indication of an equilibrium between *cis*- and *trans*-complexes. As in complex **2**, a water molecule forms hydrogen bonds with the phosphoryl groups, forcing the two phosphonate groups to face each other. Distortion of the hydrogen bonds is reflected by the values of O(4)–H(72)–O(7) (140(3)°) and O(1)–H(71)–O(7) (173(3)°) bond angles.

Table 4
Selected bond lengths (Å) and bond angles (°) for compound **4**

Bond lengths			
P(2)–O(1)	1.4709(18)	P(1)–C(1)	1.828(2)
P(2)–O(2)	1.558(2)	P(1)–Pd	2.2171(6)
P(2)–O(3)	1.571(2)	Pd–Cl(1)	2.3273(7)
P(2)–C(3)	1.784(2)	Pd–Cl(2)	2.2752(7)
P(1)–C(8)	1.808(2)	Pd–Cl(1′)	2.4244(7)
P(1)–C(14)	1.807(2)		
Bond angles			
P(1)–Pd–Cl(1)	93.45(2)	Cl(1)–Pd–Cl(2)	175.68(2)
P(1)–Pd–Cl(2)	88.82(2)	Cl(1)–Pd–Cl(1′)	85.66(2)
P(1)–Pd–Cl(1′)	177.13(2)	Cl(2)–Pd–Cl(1′)	91.89(2)
Pd–P(1)–C(1)	116.76(7)	O(2)–P(2)–O(1)	115.14(11)
Pd–P(1)–C(8)	112.70(7)	O(2)–P(2)–C(3)	106.01(11)
Pd–P(1)–C(14)	108.66(7)	Pd–Cl(1)–Pd′	94.34(2)

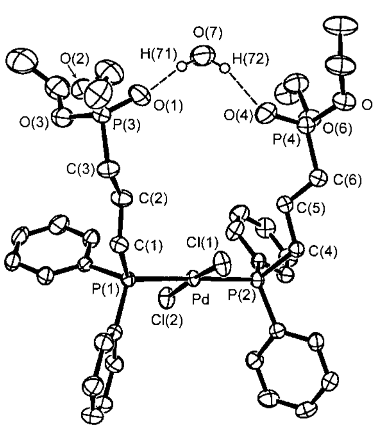


Fig. 4. ORTEP representation of complex **5** (thermal ellipsoids are shown at 30% probability; hydrogen atoms have been omitted for clarity).

Table 5
Selected bond lengths (Å) and bond angles (°) for compound **5**

Bond lengths			
P(3)–O(1)	1.4554(17)	P(1)–C(1)	1.824(2)
P(4)–O(4)	1.4578(19)	P(2)–C(4)	1.829(2)
P(3)–C(3)	1.780(2)	Pd–P(1)	2.3279(5)
P(4)–C(6)	1.768(2)	Pd–P(2)	2.3287(6)
Pd–Cl(2)	2.3027(6)	Pd–Cl(1)	2.3000(6)
O(7)–H(71)	0.90(3)	O(7)–H(72)	0.96(3)
O(1)–H(71)	1.89(3)	O(4)–H(72)	1.97(3)
O(1)–O(7)	2.789(3)	O(4)–O(7)	2.779(3)
Bond angles			
P(1)–Pd–P(2)	177.39(2)	Cl(1)–Pd–Cl(2)	175.10(2)
P(1)–Pd–Cl(1)	88.58(2)	P(2)–Pd–Cl(1)	89.75(2)
P(2)–Pd–Cl(2)	90.22(2)	P(1)–Pd–Cl(2)	91.26(2)
Pd–P(1)–C(1)	116.48(7)	Pd–P(2)–C(4)	115.51(7)
O(1)–P(3)–C(3)	114.98(12)	O(4)–P(4)–C(6)	115.01(11)
O(1)–P(3)–O(2)	113.91(10)	O(4)–P(4)–O(5)	113.22(11)
O(1)–P(3)–O(3)	116.13(11)	O(4)–P(4)–O(6)	115.63(11)
H(71)–O(7)–H(72)	95(3)	O(1)–H(71)–O(7)	173(3)
O(4)–H(72)–O(7)	140(3)		

2.3.2. Ligand L′

The treatment of palladium chloride $PdCl_2$ with two equivalents of ligand **L′** led to orange crystals of complex **6** ($PdCl_2L'_2 \cdot CH_2Cl_2$) after crystallization from a mixture CH_2Cl_2–pentane. Complex **6** has crystallographic inversion symmetry with the Pd on an inversion center (Fig. 5), which implies a precise planar coordination symmetry with close Pd–P (2.3400(7) Å) and Pd–Cl (2.2919(6) Å) bond lengths, and exact *trans* 180° angles (Table 6). This is confirmed by the presence of only two peaks in the ^{31}P-MAS NMR (15.5 ppm (PO_3Et_2), 21.8 ppm (PPh_2–Pd) values that are in agreement with those of *trans* triarylphosphines palladium complexes de-

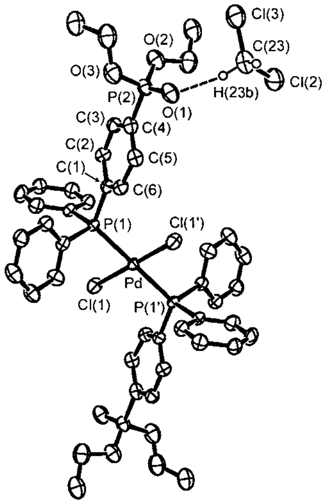


Fig. 5. ORTEP representation of complex **6** (thermal ellipsoids are shown at 30% probability; hydrogen atoms have been omitted for clarity).

Table 6
Selected bond lengths (Å) and bond angles (°) for compound **6**

Bond lengths			
P(2)–O(1)	1.445(2)	P(2)–O(2)	1.555(2)
P(2)–O(3)	1.565(2)	Pd–P(1)	2.3400(7)
P(2)–C(4)	1.770(3)	Pd–Cl(1)	2.2919(6)
P(1)–C(1)	1.815(2)	C(23)–O(1)	3.094(3)
C(23)–H(23B)	0.98	O(1)–H(23B)	2.14
Bond angles			
P(1)–Pd–P(1′)	180.0	Cl(1)–Pd–P(1′)	87.05(2)
P(1)–Pd–Cl(1)	92.95(2)	Pd–P(1)–C(1)	117.67(7)
O(1)–P(2)–O(2)	114.27(11)	O(1)–P(2)–C(4)	113.44(15)
C(23)–H(23B)–O(1)	164	O(1)–P(2)–O(3)	101.66(11)

scribed in the literature [38,40]. The ^{31}P-NMR spectrum in $CDCl_3$ displayed only two resonances (17.9 ppm (PO_3Et_2), 24.2 ppm (PPh_2–Pd)), which suggests a *trans* solution structure and that no *cis–trans* isomerization took place. The phosphonate groups lie on each part of the square plan, pointing away from the palladium center. The presence of a dichloromethane molecule bonded through a CH···O=P hydrogen bond to one phosphoryl group is noteworthy. In Table 7, the C···O and H···O separations in complex **6** are compared with some values reported in the literature for dichloromethane molecules hydrogen-bonded to acceptors of growing strength. It is well known [41–43] that the hydrogen bond length depends on both the acidity of the hydrogen bond donor and the basicity of the hydrogen bond acceptor. Accordingly, the strong polarization of the P=O bond is evidenced by the exceptionally short CH···O=P (2.14 Å) and C···O=P (3.03 Å) separations in complex **6**, as compared to the CH···O (2.27–2.6 Å) and C···O (3.21–3.51 Å) separations reported for various H-bonded acceptors and dichloromethane.

3. Experimental

3.1. General

All manipulations were carried out under an atmosphere of dry Ar using standard Schlenk and glovebox techniques. Solvents were purified by conventional procedures and distilled prior to use. Tetrahydrofuran was distilled from CaH_2 first, then from sodium pellets. Diethylether was distilled over sodium pellets. Dichloromethane was distilled over P_2O_5. Toluene, hexane and pentane were distilled over CaH_2. All the solvents were stored over molecular sieves (4 Å). Et_3N was distilled before use and Ph_2PK (0.5 M in THF) was used without further purification. Elemental analyses were performed at the laboratory of microanalysis of the CNRS in Vernaison (France). Solution ^{1}H- and ^{13}C-NMR were performed in a Bruker Avance DPX 200. ^{31}P-NMR analyses were performed using a Bruker AC 200 spectrometer. When CH_2Cl_2 was used as solvent for NMR experiments, samples were transferred under an Ar atmosphere into a 5 mm NMR tube and an acetone-d_6 capillary was used as a lock standard. ^{1}H-, ^{13}C-NMR chemical shifts are referenced to Me_4Si and ^{31}P-NMR chemical shifts to H_3PO_4 (85% in water). ^{31}P solid state NMR spectra were obtained with a Bruker Avance DPX300 spectrometer, using magic angle spinning (MAS) (spinning rate 10 kHz) and high-power proton decoupling; ^{31}P-MAS NMR spectra were recorded without cross-polarization (CP) using a 45° flip angle and a 10 s recycling delay; chemical shifts are referenced to H_3PO_4 (85% in water). FTIR spectrum was obtained in a Perkin–Elmer Spectrum 2000 spectrophotometer between NaCl windows. Mass spectra were recorded in a JEOL JMS D300 with the fast atom bombardment method using *m*-nitrobenzylic alcohol (NBA) or thioglycerol (GT) as matrices.

Table 7
Mean C···O and H···O distances (Å) for C–H···O hydrogen bonds from CH_2Cl_2 to P=O (in complex **6**) and other H-bond acceptors from the literature [42]

Acceptors	C–OH	C–O–C	S=O	NO_2	C=O	P=O (in **6**)
Mean C···O	3.51	3.43	3.3	3.32	3.21	3.03
Mean H···O	2.6	2.50	2.4	2.41	2.27	2.14

X-ray data were collected [44] in a Stoe Imaging Plate Diffractometer System (IPDS), equipped with an Oxford Cryosystems cooler device, at 203 K using Mo–K$_\alpha$ radiation with a graphite monochromator ($\lambda = 0.71073$ Å). In both cases, data were collected with a crystal-to-detector distance of 70 mm, in the 2θ range of 3.3–52.1° with a φ rotation movement ($\varphi = 0.0$–$250.6°$, $\Delta\varphi = 1.4°$ for **1**; $\varphi = 0.0$–$249.6°$, $\Delta\varphi = 1.6°$ for **3**) or with a φ oscillation movement ($\varphi = 0.0$–$200.4°$, $\Delta\varphi = 1.2°$ for **2**; $\varphi = 0.0$–$249.6°$, $\Delta\varphi = 1.6°$ for **4**; $\varphi =$ 0.0–200.2°, $\Delta\varphi = 1.1°$ for **5**). The structures were solved using the direct methods [45] and refined [46] by full-matrix least-squares F^2. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were found on a difference Fourier and introduced in calculations with a riding model, with U_{iso} equal to 1.1 times that of atom of attachment. The atomic scattering factors and anomalous dispersion terms were taken from the standard compilation [47].

3.2. Synthesis

$Br(CH_2)_3PO_3Et_2$ (I) [21] and $Br(4\text{-}C_6H_4PPh_2)$ (I′) [23] were prepared according to literature methods. Starting materials were characterized by ^1H-, ^{31}P-, and ^{13}C-NMR spectroscopy and mass spectrometry.

3.2.1. $Ph_2P(CH_2)_3PO_3Et_2$ (**L**)

A 250 ml three-necked round-bottom flask equipped with a pressure-equalizing addition funnel was charged under Ar with 12.95 g (0.05 mol) of bromopropyldiethylphosphonate (I) in 30 ml of dry THF. The mixture was cooled under stirring to 5 °C. A solution of potassium diphenylphosphide (100 ml, 0.5 M in THF) was added dropwise over 30 min. Then the reaction mixture was allowed to warm to room temperature (r.t.) and stirred for 15 h. Degassed water (3 × 50 ml) and EtOAc (100 ml) were added. The organic phase was separated and dried over Na_2SO_4. The solvent was removed under vacuum and the crude product chromatographed (SiO_2 column; EtOAc–hexane 80/20). The solvent was removed from the eluate under vacuum to give **L** as a pure colorless oil (15.58 g, 42.8 mmol, yield 86%). Anal. Found: C, 62.15; H, 7.19; O, 14.04; P, 16.35. Calc.: C, 62.64; H, 7.14; O, 13.19; P, 17.03%. ^{31}P-NMR (CH_2Cl_2–CD_3COCD_3): δ −17.5 (d, PPh_2, $J(PP) = 2.9$ Hz) and 30.9 (d, P=O, $J(PP) = 3.0$ Hz). ^1H-NMR ($CDCl_3$): δ 1.30 (t, 6H, CH_3), 1.73–2.00 (m, 4H, CH_2P), 2.19 (t, 2H, CH_2), 4.08 (q, 4H, CH_2) and 7.29–7.48 (m, 10H, aromatics). ^{13}C-NMR ($CDCl_3$): δ 16.9–16.8 (d, $J(PC) = 6.0$ Hz, CH_3), 19.9–19.46 (dd, $^2J(PC) = 12.0$ Hz, CH_2), 28.8–25.8 (dd, $^1J(PC) = 140$ Hz, CH_2), 29.6–29.12 (dd, $^1J(PC) = 18.0$ Hz, PCH_2), 61.9–61.7 (d, $J(PC) = 6.5$ Hz, OCH_2), 128.9–128.8 (d, $J(PC) = 6.7$ Hz), 129.0 (d, $J(PC) = 0.4$ Hz), 133.27–132.90 (d, $J(PC) = 18.6$ Hz) and 138.8–138.5 (d, $J(PC) = 12.7$ Hz) aromatics). FABMS; m/z: 365 ($[M+H]^+$, 100%).

3.2.2. $Ph_2P(4\text{-}C_6H_4PO_3Et_2)$ (**L′**)

A 100 ml three-necked flask under Ar was charged with **I′** (12.79 g, 37.5 mmol), diethylphosphite (5.69 g, 41.2 mmol), Et_3N (4.16 g, 41.2 mmol), toluene (20 ml), a stirrer bar and heated at 90 °C. Then, $Pd(PPh_3)_4$ (2.16 g, 1.87 mmol) was added. After the addition was complete, the reaction mixture was stirred at 90 °C for 72 h. After cooling, dry Et_2O (100 ml) was added and a precipitate immediately formed. After filtration, the filtrate was concentrated under vacuum. The residue was chromatographed on a silica column (toluene–THF gradient) to give **L′** as a yellow oil (7.76 g, 19.5 mmol, yield 52%). ^{31}P-NMR (CH_2Cl_2–CD_3COCD_3): δ −4.6 (PPh_2), 18.3 ($P(O)(OEt)_2$). ^1H-NMR ($CDCl_3$): δ 1.38 (t, 6H, CH_3), 4.15 (q, 4H, CH_2), 7.32–7.72 (m, 14H, aromatics). ^{13}C-NMR ($CDCl_3$): δ 16.83–16.78 (d, $J(PC) = 8.0$ Hz, CH_3), 63.19–63.16 (d, $J(PC) = 6.0$ Hz, CH_2), 128.49–128.51 (d, $J(PC) = 4$ Hz), 128.82–128.78 (d, $J(PC) = 8$ Hz), 130.60–130.51 (d, $J(PC) = 18$ Hz), 131.12–132.05 (d, $J(PC) = 186$ Hz), 133.05–133.14 (d, $J(PC) = 18$ Hz), 133.58–133.63 (d, $J(PC) = 10$ Hz), 137.4–137.0 (d, $J(PC) = 82$ Hz) 141.23–141.26 (d, $J(PC) = 6$ Hz) (aromatics). FABMS; m/z: 399 ($[M+H]^+$).

3.2.3. *cis*-$[PtCl_2\{Ph_2P(CH_2)_3P(O)(OEt)_2\}_2]$ (**1**) and *trans*-$[PtCl_2\{Ph_2P(CH_2)_3P(O)(OEt)_2\}_2 \cdot H_2O]$ (**2**)

$PtCl_2(PhCN)_2$ (0.325 g, 0.685 mmol) was added to a solution of compound **L** (0.5 g, 1.37 mmol) in dry CH_2Cl_2 (15 ml). The mixture was heated at 40 °C under stirring for 24 h, then cooled down to r.t., filtered and the solvent removed under vacuum. The crude yellow oil was crystallized from CH_2Cl_2–pentane under an Ar atmosphere to give, after filtration, compound **1** as white crystals (352 mg, 0.354 mmol, yield 58%). Anal. Found: C, 45.35; H, 5.07; Cl, 7.48; P, 11.70; Pt, 15.27. Calc.: C, 45.84; H, 5.23; Cl, 7.14; P, 12.47; Pt, 19.60%. ^{31}P-NMR (CH_2Cl_2–CD_3COCD_3): δ 7.5 (t, PPh_2, $^1J(PtP) = 3643$ Hz); 30.2 (P=O). ^{31}P-NMR (HPDEC MAS): δ −6.3 (PPh_2, $^1J(PtP) = 3556$ Hz); 10.2 (PPh_2, $^1J(PtP) = 3844$ Hz), 31.4 (P=O). ^1H-NMR ($CDCl_3$): δ 1.26 (t, 12H, CH_3), 1.58–1.90 (m, 8H, CH_2P), 2.47 (m, 4H, CH_2), 4.01 (q, 8H, OCH_2), 7.19–7.49 (m, 20H, aromatics). ^{13}C-NMR ($CDCl_3$): δ 16.92–16.82 (d, $J(PC) = 5.8$ Hz, CH_3), 19.24–19.17 (d, $J(PC) = 3.7$ Hz, CH_2), 27.40–25.85 (dd, $J(PC) = 139$ Hz, $P(O)CH_2$), 31.88–31.46 (dd, $J(PC) = 42$ Hz, P–CH_2), 62.02–61.92 (d, $J(PC) = 5$ Hz, OCH_2), 128.65–128.86 (t, $J(PC) = 10$ Hz), 129.87–129.93 (d, $J(PC) = 3$ Hz), 131.44 (s), and 133.67–133.87 (d, $J(PC) = 5$ Hz) (aromatics).

The filtrate was concentrated and the yellow oil crystallized from CH_2Cl_2–pentane under an Ar atmo-

Table 8
Crystal data and structure refinement parameters for compounds *cis*-$PtCl_2L_2$, **1**; *trans*-$PtCl_2L_2{\cdot}H_2O$, **2**; $[PdCl_2L]_2$, **4**; *trans*-$PdCl_2L_2{\cdot}H_2O$, **5**; and *trans*-$PdCl_2L'_2{\cdot}CH_2Cl_2$, **6**

Compound	1	2	4	5	6
Empirical formula	$C_{38}H_{52}Cl_2O_6P_4Pt$	$C_{38}H_{54}Cl_2O_7P_4Pt$	$C_{38}H_{52}Cl_4O_6P_4Pd_2$	$C_{38}H_{54}Cl_2O_7P_4Pd$	$C_{46}H_{52}Cl_6O_6P_4Pd$
Formula weight	994.67	1012.68	1083.28	923.99	1143.86
Temperature (K)	203	203	203	203	203
Crystal system	Triclinic	Monoclinic	Triclinic	Monoclinic	Triclinic
Space group	$P\bar{1}$ (no. 2)	$P2_1/c$ (no. 14)	$P\bar{1}$ (no. 2)	$P2_1/c$ (no. 14)	$P\bar{1}$ (no. 2)
Unit cell dimensions					
a (Å)	9.4292(13)	12.0208(12)	11.7497(16)	12.0144(14)	11.4884(13)
b (Å)	24.692(3)	28.105(3)	11.9417(18)	27.954(2)	14.0418(16)
c (Å)	9.3706(12)	13.9179(14)	8.2332(12)	13.8792(17)	9.1419(11)
α (°)	94.480(15)		96.432(17)		98.329(14)
β (°)	103.537(16)	111.616(11)	94.697(17)	111.556(13)	105.748(14)
γ (°)	80.323(15)		77.998(17)		66.043(12)
V (Å^3)	2089.2(5)	4371.4(8)	1120.8(3)	4335.3(8)	1296.1(3)
Z	2	4	1	4	1
μ (mm^{-1})	3.682	3.522	1.226	0.743	0.835
Total reflections	17 487	29 967	10 937	33 758	12 614
Independent reflections	7014	7927	4025	8181	4673
R_{int}	0.0331	0.0337	0.0307	0.0318	0.0318
R	0.0307	0.0352	0.0298	0.0356	0.0287

sphere to give after filtration, compound **2** as yellow crystals (110 mg, 0.11 mmol, yield 18%). Anal. Found: C, 44.98; H, 5.29; Cl, 6.94; P, 12.00; Pt, 17.90. Calc.: C, 45.03; H, 5.33; Cl, 7.01; P, 12.24; Pt, 19.26%. ^{31}P-NMR ($CDCl_3$): δ 12.4 (PPh_2, $^1J(PtP) = 2550$ Hz); 31.1 (P=O). ^{1}H-NMR ($CDCl_3$): δ 1.25 (t, 12H, CH_3), 1.72–1.86 (m, 8H, CH_2P), 2.50–2.59 (m, 4H, CH_2), 4.01 (q, 8H, OCH_2), 7.41–7.46 (m, 12H) and 7.74–7.81 (m, 8H) aromatics. ^{13}C-NMR ($CDCl_3$): δ 16.86–16.80 (d, $J(PC) = 5.9$ Hz, CH_3), 17.92–17.88 (d, $J(PC) = 4.1$ Hz, CH_2), 25.29–25.13 (dd, $J(PC) = 16$ Hz, P–CH_2), 26.28–27.68 (dd, $J(PC) = 140$ Hz, P(O)CH_2), 61.89–61.96 (d, $J(PC) = 6.3$ Hz, OCH_2), 128.65–128.75 (t, $J(PC) = 10$ Hz), 129.42–129.96 (t, $J(PC) = 54$ Hz), 130.99 (s) and 134.07–134.18 (t, $J(PC) = 11.5$ Hz) (aromatics).

3.2.4. *cis*-$[PtCl_2\{Ph_2PC_6H_4P(O)(OEt)_2\}_2]$ (**3A**) and *trans*-$[PtCl_2\{Ph_2PC_6H_4P(O)(OEt)_2\}_2]$ (**3B**)

$PtCl_2(PhCN)_2$ (0.347 g, 0.735 mmol) was added to a solution of compound **L**′ (0.587 g, 1. 47 mmol) in dry CH_2Cl_2 (30 ml). The mixture was heated under stirring at 40 °C for 24 h, then allowed to cool to r.t., filtered and the solvent removed under vacuum. The crude yellow oil was crystallized from CH_2Cl_2–pentane under an Ar atmosphere to give after filtration, compounds **3A** and **3B** as a mixture of white and yellow crystals (0.570 g, 0.536 mmol, yield 73%, *trans*/*cis*: 57:43).

^{31}P-NMR (CH_2Cl_2–CD_3COCD_3): **3A**: δ 14.6 (t, PPh_2, $^1J(PtP) = 3833$ Hz), and 16.7 (P=O). **3B**: δ 21.3 (t, PPh_2, $^1J(PtP) = 2469$ Hz) and 17.2 (P=O).

3.2.5. $[Pd_2Cl_4\{Ph_2P(CH_2)_3P(O)(OEt)_2\}_2]$ (**4**) and *trans*-$[PdCl_2\{Ph_2P(CH_2)_3P(O)(OEt)_2\}_2{\cdot}H_2O]$ (**5**)

$PdCl_2$ (0.121 g, 0.68 mmol) was added to a solution of compound **L** (0.5 g, 1.37 mmol) in THF (20 ml). The mixture was heated under stirring at 80 °C for 24 h, then cooled to r.t., filtered and evaporated under vacuum. The crude orange oil was crystallized from CH_2Cl_2–pentane under Ar to give after filtration complex **4** as orange crystals (110 mg, 0,101 mmol). Yield 15%. Elemental analysis: Found: C, 41.86; H, 4.90; Cl, 13.64; P, 11.0; Pd, 18.2. Calc.: C, 42.13; H, 4.84; Cl, 13.09; P, 11.44; Pd, 19.64%. ^{31}P-NMR ($CDCl_3$): δ 30.3 (PPh_2); 30.8 ($P(O)(OEt)_2$). ^{31}P-MAS NMR: δ 28.7 (PPh_2; 30.6 ppm ($P(O)(OEt)_2$). ^{1}H-NMR ($CDCl_3$): δ 1.44 (t, 12H, CH_3), 1.70–1.92 (m, 8H, CH_2P), 2.47–2.60 (m, 4H, CH_2), 4.4 (q, 8H, CH_2), 7.44–7.83 (m, 20H, aromatics). ^{13}C-NMR ($CDCl_3$): δ 16.9–16.83 (d, $J(PC) = 5.9$ Hz, CH_3), 18.02 (d, CH_2), 27.49–25.92 (dd, $J(PC) = 140$ Hz, P(O)CH_2), 28.39 (d, P–CH_2), 62.1–62.06 (d, $J(PC) = 6.2$ Hz, CH_2), 127.72, 127.15 (d, $J(PC) = 60$ Hz), 129.34, 129.23 (d, $J(PC) = 12$ Hz), 132.38 (s), 133.74–133.64 (d, $J(PC) = 9.7$ Hz) (aromatics).

The above filtrate was concentrated and the yellow oil crystallized from a CH_2Cl_2–pentane solution to give complex **5** as yellow needles (405 mg, 0.44 mmol, yield 65%). Elemental analysis: Found: C, 49.15; H, 5.82; Cl, 7.27; P, 13.0; Pd, 11.35. Calc.: C, 49.39; H, 5.89; Cl, 7.67; P, 13.41; Pd, 11.51%. ^{31}P-NMR ($CDCl_3$): δ 16.4 (PPh_2); 31.0 ($P(O)(OEt)_2$). ^{1}H-NMR ($CDCl_3$): δ 1.25 (t, 12H, CH_3), 1.71–1.92 (m, 8H, CH_2P), 2.54–2.63 (m, 4H, CH_2), 4.02 (q, 8H, OCH_2), 7.30–7.49 (m, 12H) and 7.69–7.79 (m, 8H) (aromatics). ^{13}C-NMR ($CDCl_3$): δ

15.39–15.45 (d, J(PC) = 6.0 Hz, CH_3), 16.78 (d, CH_2), 21.66 (dd, P(O)CH_2), 24.90 (d, P–CH_2), 60.46–60.53 (d, J(PC) = 6.2 Hz, OCH_2), 127.36 (s), 128.63–128.86 (d, J(PC) = 23 Hz), 129.6 (s) and 132.64–132.75 (d, J(PC) = 12 Hz) (aromatics). FABMS; m/z: 924 ([M + H]$^+$).

3.2.6. *trans-[$PdCl_2\{Ph_2PC_6H_4P(O)(OEt)_2\}_2 \cdot CH_2Cl_2$]* (**6**)

$PdCl_2$ (0.523 g, 2.94 mmol) was added to a solution of compound **L**′ (2.34 g, 5.87 mmol) in THF (40 ml). The reaction mixture was heated under stirring at 80 °C for 24 h; then cooled to r.t., filtered and the solvent was removed under vacuum. The crude orange oil was crystallized from a CH_2Cl_2–pentane solution under an Ar atmosphere, to give after filtration compound **6** as orange crystals (2.55 g, 2.23 mmol, yield 76%). Elemental analysis: Found: C, 48.28; H, 4.40; P, 10.50; Pd, 10.90. Calc.: C, 48.26; H, 4.55; P, 10.84; Pd, 9.30%. ^{31}P-NMR ($CDCl_3$): δ 24.2 (PPh_2); 17.9 ($P(O)(OEt)_2$). ^{1}H-NMR ($CDCl_3$): δ 1.36 (t, 12H, CH_3), 4.17 (q, 8H, OCH_2), 5.22 (s, 4H, CH_2Cl_2), 7.32–7.74 (m, 28H (aromatics). ^{13}C-NMR ($CDCl_3$): δ 16.7–16.8 (d, J(PC) = 6.3 Hz, CH_3), 53.84 (s, CH_2Cl_2), 62.8–60.86 (d, J(PC) = 5.6 Hz, OCH_2), 128.49–129.01 (m), 131.31–131.42 (t, J(PC) = 10 Hz) and 134.92–135.57 (m) (aromatics).

3.3. *X-ray crystallography*

Details of the structures of compounds **1**, **2**, **4**–**6** are given in Table 8.

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