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1-Diisopropylaminophospholes: synthesis and X-ray characterisations of new palladium and platinum complexes

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Dedicated to Dr François Mathey for his 60th birthday

Abstract

Starting from palladium precursor $[Pd(CH_3CN)_2Cl_2]$, 1-diisopropylaminophospholes give dinuclear complexes, $[Pd(phosphole)Cl_2]_2$, which proved to be intermediates in the formation of mononuclear complexes, *cis*-$[Pd(phosphole)_2Cl_2]$. In contrast with the platinum precursor, only mononuclear complexes, $[Pt(phosphole)_2Cl_2]$, are obtained with both *cis* and *trans* configurations. These new complexes were fully characterised by X-ray crystallography. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Phosphole; 1-Diisopropylaminophosphole; Complexes; Palladium; Platinum

1. Introduction

The chemistry of phospholes, phosphorus analogue of the classic five-membered heterocycles, pyrroles, furans and thiophenes, has been extensively investigated and reviewed [1]. Numerous phosphole derivatives have been prepared with various substituents at the ring positions. Among these phosphole derivatives, 1-phenylphospholes, in particular 3,4-dimethyl-1-phenyl-phosphole, have been studied extensively [2]. The reason is probably related to the easy preparation of this phosphole by Mathey's method of dehydrohalogenation of the Mc Cormak cycloadduct of 2,3-dimethylbutadiene and phenyl dichlorophosphine [3]. Although 1-functionalised phospholes, such as 1-alkoxy- [4], 1-alkylamino- [5], 1-aryl- [4,6] and 1-alkynyl- [4], could be obtained from 1-phenylphosphole, their coordination properties have received little attention.

As a part of our continuing interest in the design and synthesis of new phosphole derivatives as ligands for applications in catalysis [7], we decided to explore the potential of the 1-diisopropylaminophospholes [8]. The diisopropylamino group, which possesses different steric and electronic effects with respect to phenyl group, may induce different chemical behaviour in organic chemistry as well as in coordination chemistry.

Here, we report the coordination chemistry of 1-diisopropylaminophospholes towards the transition metals palladium and platinum. This work was sustained by the crystal structures of these new phosphole complexes, the bis[μ-chloro-chloro-(1-diisopropylamino-3,4-diphenylphosphole) palladium(II)] (**4**), the *cis*-dichloro-bis-(1-diisopropylamino-3,4-diphenylphosphole) palladium(II) (**6**), the *trans*-dichloro-bis(1-diisopropylamino-3,4-dimethylphosphole) platinum(II) (**7a**) and the *trans*-dichloro-bis-(1-diisopropylamino-3,4-diphenylphosphole) platinum (II) (**8a**).

2. Results and discussion

Phospholes which react as a two electron donor ligands are considered as good σ-donors and π-accep-

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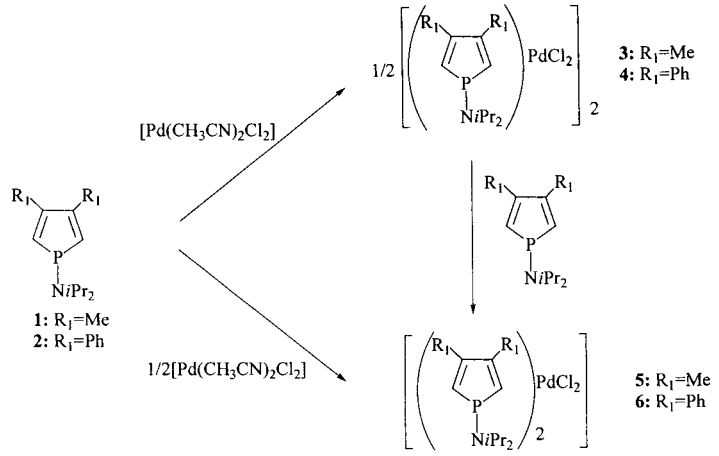


Scheme 1.

tors towards Pd(II) and Pt(II) [9]. However, the coordination ability may be modulated by changing the substituents on the phosphole ring and/or on the phosphorus atom. 1-Diisopropylaminophospholes, **1** (R = Me) and **2** (R = Ph), were prepared according to the new method we recently described [8]. They possess substituents with different electronic effects at the 3 and 4 position on the phosphole ring. The phosphole **1** was treated with 1 equivalent of $[Pd(CH_3CN)_2Cl_2]$ in dichloromethane at room temperature for 4 h. By following the course of the reaction by ^{31}P-NMR, we observed the disappearance of the signal at $\delta = +28$ ppm corresponding to the phosphole **1** concomitant with the appearance of two low field signals at $\delta = +49$ and $+53$ ppm corresponding to the formation of two new complexes in a ratio 25:75. These complexes, rather unstable, air and moisture sensitive, could not be separated. However, mass spectroscopy analysis of the reaction mixture allowed to identify the presence of the dinuclear complex **3**, $[Pd(phosphole)Cl_2Pd]_2$, ($m/z = 779$, $[MH^+]$) and the mononuclear complex **5**, $[Pd(phosphole)_2Cl_2]$, ($m/z = 601$, $[MH^+]$). Thus, an equilibrium could exist between these two complexes in solution as generally observed [10]. On the other hand, the mononuclear complex **5** ($\delta = +53$) could be quantitatively obtained from the reaction of an excess of phosphole **1** with palladium precursor in dichloromethane at room temperature (Scheme 1). This complex which could not be isolated in a pure form, has been partly characterised. According to ^{31}P- and ^{1}H-NMR analysis, the geometry of this complex should be square planar with a *cis* configuration. Indeed, the doublet observed at $\delta = 6.41$ ($^2J_{H-P} = 29$ Hz) for the α-methylene resonance is consistent with a *cis* geometry in solution [11].

With the phosphole **2**, analogous palladium complexes, **4** and **6**, have been obtained separately and proved to be stable. Each of them could be isolated and fully characterised. The reaction of 1 equivalent of phosphole **2** with 1 equivalent of $[Pd(CH_3CN)_2Cl_2]$, in dichloromethane at room temperature led to the immediate formation of complex **4** ($\delta = +48$) (Scheme 1). The ^{1}H- and ^{31}P-NMR spectra were consistent with the formation of a pure complex which could be isolated in 87% yield as an orange powder. This stable complex **4** is a dinuclear compound as indicated by elemental analysis, mass spectroscopy and X-ray crystallography. Although dinuclear complexes are known with bulky phosphines [10], to the best of our knowledge, complex **4** is the first reported example of a dinuclear palladium complex containing phosphole as ligand. The molecular structure of **4**, with atom labelling scheme, is presented in Fig. 1. Selected bond distances and angles are listed in Table 1. The dinuclear framework presents a symmetrical *trans* structure, the two phosphole ligands are in *trans* position with respect to the plane defined by the Pd and Cl atoms. Each palladium which is bonded through a double chloro bridge, presents a nearly perfect planar arrangement. The largest deviations from the best planes, Pd(1), P(1), Cl(12), Cl(11), Cl(21), and

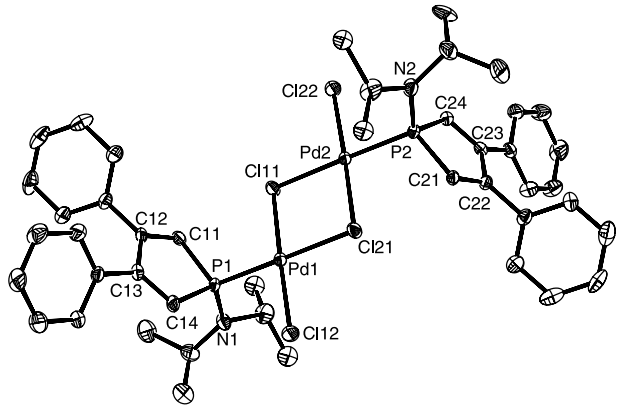


Fig. 1. Molecular structure of complex **4**. Ellipsoids are drawn at 30% probability.

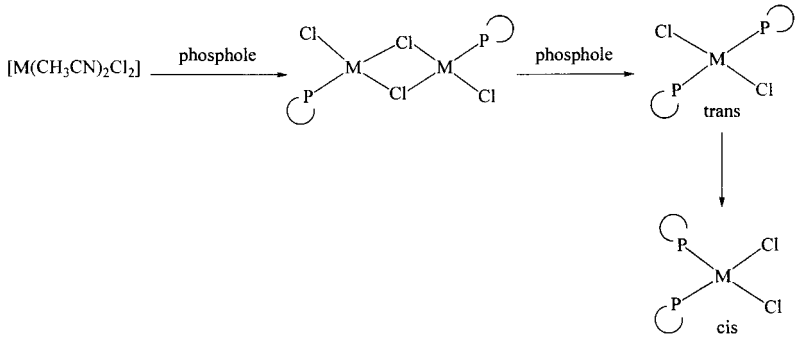
Table 1
Selected bond lengths (Å) and bond angles (°) for complexes **4**, **6**, **7a** and **8a**

Complex ***4***			
Pd(1)–P(1)	2.2103(15)	Pd(2)–P(2)	2.2079(15)
Pd(1)–Cl(12)	2.2829(17)	Pd(2)–Cl(22)	2.2745(17)
Pd(1)–Cl(11)	2.3257(15)	Pd(2)–Cl(11)	2.4219(14)
Pd(1)–Cl(21)	2.4326(14)	Pd(2)–Cl(21)	2.3303(15)
P(1)–N(1)	1.631(5)	P(2)–N(2)	1.631(5)
P(1)–C(14)	1.801(6)	P(2)–C(24)	1.785(6)
P(1)–C(11)	1.803(7)	P(2)–C(21)	1.788(6)
C(11)–C(12)	1.332(8)	C(21)–C(22)	1.347(8)
C(12)–C(13)	1.492(8)	C(22)–C(23)	1.517(8)
C(13)–C(14)	1.356(8)	C(23)–C(24)	1.341(8)
P(1)–Pd(1)–Cl(12)	86.18(6)	P(2)–Pd(2)–Cl(22)	86.05(6)
P(1)–Pd(1)–Cl(11)	93.69(5)	P(2)–Pd(2)–Cl(21)	94.27(5)
Cl(12)–Pd(1)–Cl(11)	175.78(7)	Cl(22)–Pd(2)–Cl(21)	175.25(7)
P(1)–Pd(1)–Cl(21)	179.44(6)	P(2)–Pd(2)–Cl(11)	177.18(6)
Cl(12)–Pd(1)–Cl(21)	94.03(6)	Cl(22)–Pd(2)–Cl(11)	93.63(6)
Cl(11)–Pd(1)–Cl(21)	86.14(5)	Cl(21)–Pd(2)–Cl(11)	86.28(5)
Pd(1)–Cl(11)–Pd(2)	93.99(5)	Pd(2)–Cl(21)–Pd(1)	93.59(5)
N(1)–P(1)–C(14)	114.4(3)	N(2)–P(2)–C(24)	114.7(3)
N(1)–P(1)–C(11)	114.7(3)	N(2)–P(2)–C(21)	113.5(3)
C(14)–P(1)–C(11)	92.2(3)	C(24)–P(2)–C(21)	92.4(3)
N(1)–P(1)–Pd(1)	111.01(17)	N(2)–P(2)–Pd(2)	112.07(17)
C(14)–P(1)–Pd(1)	112.8(2)	C(24)–P(2)–Pd(2)	111.22(19)
C(11)–P(1)–Pd(1)	110.5(2)	C(21)–P(2)–Pd(2)	111.4(2)
C(114)–N(1)–C(111)	117.6(5)	C(211)–N(2)–C(214)	116.9(5)
C(111)–N(1)–P(1)	115.8(4)	C(211)–N(2)–P(2)	117.0(4)
C(114)–N(1)–P(1)	124.7(4)	C(214)–N(2)–P(2)	125.0(4)
Complex ***6***			
Pd(1)–P(1)	2.2553(8)	Pd(1)–Cl(1)	2.3632(8)
P(1)–N(1)	1.649(2)	P(1)–C(1)	1.803(3)
P(1)–C(4)	1.792(3)	C(1)–C(2)	1.341(4)
N(1)–C(111)	1.489(4)	C(2)–C(3)	1.503(4)
N(1)–C(121)	1.482(3)	C(3)–C(4)	1.346(4)
P(1)–Pd(1)–P(1)′	95.98(4)	Cl(1)′–Pd(1)–Cl(1)	90.38(4)
P(1)–Pd(1)–Cl(1)′	172.06(2)	P(1)–Pd(1)–Cl(1)	87.30(3)
N(1)–P(1)–Pd(1)	113.05(9)	N(1)–P(1)–C(4)	111.06(12)
C(4)–P(1)–Pd(1)	120.17(9)	N(1)–P(1)–C(1)	119.12(13)
C(1)–P(1)–Pd(1)	101.10(9)	C(4)–P(1)–C(1)	90.50(12)
C(111)–N(1)–P(1)	123.79(19)	C(121)–N(1)–P(1)	120.43(18)
C(121)–N(1)–C(111)	115.8(2)		
Complex ***7a***			
Pt(1)–Cl(1)	2.3110(6)	Pt(1)–Cl(2)	2.3027(6)
Pt(1)–P(1)	2.3040(5)	Pt(1)–P(2)	2.3086(5)
P(1)–N(1)	1.6664(17)	P(2)–N(2)	1.6531(17)
P(1)–C(11)	1.8022(19)	P(2)–C(21)	1.798(2)
P(1)–C(14)	1.800(2)	P(2)–C(24)	1.799(2)
C(11)–C(12)	1.337(3)	C(21)–C(22)	1.347(3)
C(12)–C(13)	1.494(3)	C(22)–C(23)	1.481(4)
C(13)–C(14)	1.340(3)	C(23)–C(24)	1.333(4)
Cl(1)–Pt(1)–Cl(2)	176.42(2)	P(1)–Pt(1)–P(2)	173.937(16)
Cl(1)–Pt(1)–P(1)	92.39(2)	Cl(1)–Pt(1)–P(2)	88.87(2)
Cl(2)–Pt(1)–P(1)	89.82(2)	Cl(2)–Pt(1)–P(2)	89.23(2)
Pt(1)–P(1)–N(1)	120.24(7)	Pt(1)–P(2)–N(2)	111.78(7)
Pt(1)–P(1)–C(11)	111.07(7)	Pt(1)–P(2)–C(21)	111.46(7)
N(1)–P(1)–C(11)	107.82(9)	N(2)–P(2)–C(21)	114.7(1)
Pt(1)–P(1)–C(14)	111.63(7)	Pt(1)–P(2)–C(24)	111.70(8)
N(1)–P(1)–C(14)	110.85(9)	N(2)–P(2)–C(24)	114.3(1)
C(11)–P(1)–C(14)	91.4(1)	C(21)–P(2)–C(24)	91.48(11)
P(1)–N(1)–C(111)	116.44(14)	P(2)–N(2)–C(211)	124.62(15)
P(1)–N(1)–C(114)	125.14(15)	P(2)–N(2)–C(214)	119.31(15)
C(111)–N(1)–C(114)	117.24(17)	C(211)–N(2)–C(214)	116.03(18)
Complex ***8a***			
Pt(1)–Cl(1)	2.3065(8)	Pt(1)–P(1)	2.2908(8)
Pt(1)–N(1)	1.652(3)	P(1)–C(1)	1.798(3)
P(1)–C(4)	1.804(3)	C(1)–C(2)	1.340(4)
C(2)–C(3)	1.494(4)	C(3)–C(4)	1.338(4)
Cl(1)–Pt(1)–P(1)	90.17(3)	Cl(1)–Pt(1)–P(1)′	89.83(3)
Pt(1)–P(1)–N(1)	119.45(9)	Pt(1)–P(1)–C(1)	112.86(11)
Pt(1)–P(1)–C(4)	109.57(10)	Pt(1)–P(2)–C(21)	111.46(7)
C(1)–P(1)–C(4)	90.77(14)	P(1)–N(1)–C(111)	115.41(19)
P(1)–N(1)–C(121)	127.2(2)	C(111)–N(1)–C(121)	117.3(2)

Estimated S.D.s in parentheses refer to the last significant digit. Symmetry transformations used to generate equivalent atoms (′): $-x+1,\ y,\ -z+1/2$ for **6**; $-x+2,\ -y,\ -z+2$ for **8a**.

Pd(2), P(2), Cl(22), Cl(11), Cl(21) is −0.06 Å at Cl(12) and 0.08 Å at Cl(22), respectively. The Pd–P bond lengths (2.216 and 2.200 Å) are in good agreement with the values reported for dinuclear palladium complexes with other classical phosphines [12]. The phenyl and phosphole rings are planar within the experimental error. Both the amino groups PNC_2 are planar and they make a dihedral angle of 46.5° with the phosphole to which they are attached.

The mononuclear palladium complex **6** was obtained from the dinuclear complex **4** (Scheme 1) by a classical bridge-cleavage reaction. This was done by the addition of an excess of phosphole **2** to a dichloromethane solution of complex **4**, leading to the disappearance of the signal at $\delta = +48$ corresponding to the complex **4** and the appearance of a new signal at $\delta = +53$ ppm corresponding to the mononuclear complex **6**. As in the case of complex **5**, the ^{31}P- and ^{1}H-NMR analyses were consistent with the formation of a *cis* square planar complex in solution. Generally, the *trans* complex is the initial formed product of such bridge-cleavage reactions [13]. Thus, the obtention of the *cis* complex in this case might be due to a spontaneous *trans*–*cis* isomerisation [10] in solution at ambient temperature (Scheme 2), the *cis* isomer being thermodynamically more stable than the *trans* isomer as generally observed for the palladium phosphole complexes, $[Pd(phosphole)_2Cl_2]$ [11]. The stable complex **6**, isolated in 96% yield as an orange powder, was fully characterised by NMR spectroscopy, mass spectroscopy, elemental analysis and X-ray crystallography. In the solid state, the X-ray analysis confirmed the *cis* configuration of this complex as shown by the molecular structure presented in Fig. 2. The molecule possesses a crystallographic twofold axis going through the Pd atom which presents a square planar geometry. However, the coordination sphere around the Pd atom is somewhat distorted from the ideal square planar, as underlined by a dihedral angle of 10.2° between the planes defined by P(1)–Pd(1)–P(1′)



Scheme 2.

and Cl(1)–Pd(1)–Cl(1′). This tetrahedral distortion is larger than that of the structurally similar dichlorobis(3,4-dimethyl-1-phenyl-phosphole)palladium complex [11a] which exhibits an angle of 7.2° between the analogous plane. The deviations (in Å) of the coordinated atoms from the plane defined by P_2PdCl_2 are as follows: P(1) 0.15; Cl(1) −0.15. The Pd–P bond length of 2.2553(8) Å is slightly longer than that of 2.238(3) and 2.243(3) Å found in the dimethyl phosphole complex but is similar to the 2.260 and 2.266 Å reported for the bis(pyrimidyl)diphenylphosphine complex [14]. The phenyl and phosphole rings are planar within the experimental error. It is worth to point out that the amino groups PNC_2 which are also planar within the experimental error as in **4**, make a dihedral angle of 84.7° with the phosphole ring.

Phospholes **1** and **2** showed similar coordination behaviour towards palladium(II). These ligands reacted as two electron-donors to form dinuclear and mononuclear complexes. The ^{31}P coordination chemical shifts values ($\Delta\delta^{31}P = \delta^{31}P_{complex} - \delta^{31}P_{ligand}$), in particular for the mononuclear complexes **5** and **6**, which were, respectively, +25 and +18 and were comparable to those found for similar phosphole palladium complexes [9]. Furthermore, it is of interest to note that the value for complex **6** was smaller than for complex **5**. The small coordination chemical shifts values which reflected the existence of some π-backbonding between the palladium and the phosphole were in agreement with the fact that the ligand **2** with phenyl substituents in 3 and 4 positions possesses a π-acceptor character more important than ligand **1** with methyl substituents in 3 and 4 positions. This π-backbonding could be in part responsible for the greater stability observed for complex **6** relative to complex **5**.

Slightly different results were obtained with Pt(II). Phospholes **1** and **2** reacted under the same conditions with $[Pt(CH_3CN)_2Cl_2]$ precursor at room temperature in dichloromethane to afford only mononuclear complexes **7** and **8**, respectively (Scheme 3). In these cases, mass spectroscopy of the reaction mixture did not allow to identify the formation of dinuclear platinum complexes, analogous to palladium complexes **3** and **4**. Complexes **7** and **8** were obtained in solution as a mixture of *cis* and *trans* isomers in a ratio 15:85. Indeed, the ^{31}P- and ^{1}H-NMR spectra were consistent with the presence of *cis* and *trans* isomers. The $^{31}P\{^{1}H\}$ spectrum showed two signals with for each an overlapping doublet due to the 33.8% of the phosphorus nuclei coupled to ^{195}Pt. For the major complexes, the value of the $^{1}J_{P-Pt}$ (**7a**: $^{1}J_{P-Pt} = 2580$ Hz, **8a**: $^{1}J_{P-Pt} = 2625$ Hz) coupling constants are typical of *trans*-dichloro-bisphosphole-platinum complexes whereas the higher $^{1}J_{P-Pt}$ (**7b**: $^{1}J_{P-Pt} = 3645$ Hz, **8b**: $^{1}J_{P-Pt} = 3677$ Hz) coupling constants observed for the minor complex are typical of *cis*-dichloro-bisphosphole-platinum complexes [15]. In ^{1}H-NMR, the α-methylene resonances are also consis-

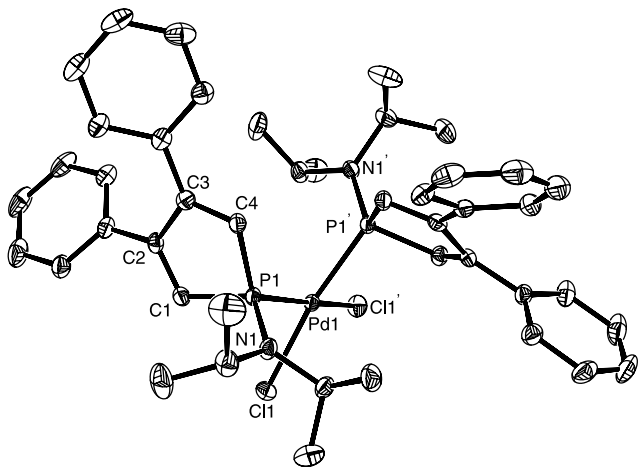
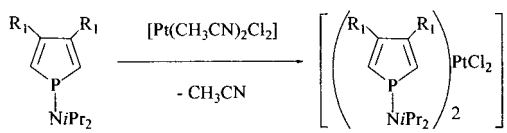


Fig. 2. Molecular structure of complex **6**. Ellipsoids are drawn at 30% probability.



1: R_1=Me
2: R_1=Ph

7: R_1=Me
8: R_1=Ph

Scheme 3.

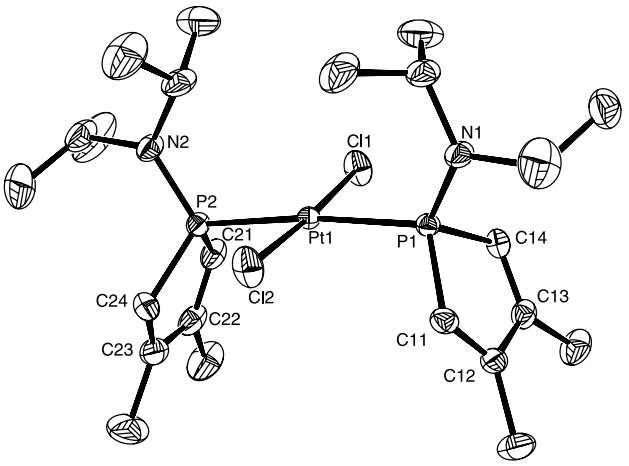


Fig. 3. Molecular structure of complex **7a**. Ellipsoids are drawn at 30% probability.

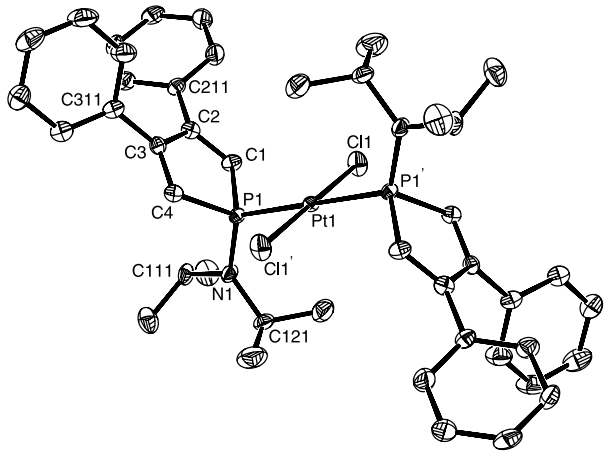


Fig. 4. Molecular structure of complex **8a**. Ellipsoids are drawn at 30% probability.

tent with the *cis* and *trans* geometry for these complexes in solution [11a]. The α-methylene resonances appeared as 1:2:1 triplet in the major *trans* complexes, those of the minor *cis* complexes appeared as 1:1 doublet. In the case of complex **7**, only the *trans* isomer **7a** could be isolated in 75% yield, as a yellow solid, and it was fully characterised by ^{1}H-, ^{31}P-, ^{13}C-NMR spectroscopy, mass spectroscopy and X-ray crystallography. In the solid state, the X-ray analysis confirmed the *trans* configuration of this complex as shown by the molecular structure presented in Fig. 3. The platinum coordination geometry is essentially planar with the largest deviation from the square plane being 0.03 Å. The N(1)–P(1)–P(2)–N(2) torsion angle is 11.5° which clearly indicates that the two phosphole rings are located on the same side of this plane. A similar arrangement was observed for the *trans* related 3,4-dimethyl-1-phenyl-phosphole palladium complex [11b]. The Pt–P and Pt–Cl bond lengths reflect the respective *trans* position of the ligands. Important bond distances and angles are given in Table 1. The Pt–P distances, 2.3040(5) and 2.3086(5) Å, are significantly longer than the value observed in the *cis*-3,4-dimethyl-1-phenyl-phosphole platinum complex [16], 2.239(2) and 2.227(1) Å, whereas the Pt–Cl distances are slightly shorter, 2.31106(6) and 2.3027(6) Å, with respect to the same *cis* complex, 2.336(2) and 2.360(2) Å [15b]. The phenyl and phosphole rings are planar within the experimental error. It is interesting to point out that the amino groups PNC_2 which are planar within the experimental error as in **4** and **6**, make a dihedral angle of 84.5 and 75.92° with the corresponding phosphole ring. Such a conformation, also observed in **6**, is found in the free ligand **1** [8].

In the case of complex **8**, the two isomers, separated by fractional crystallisation, were characterised by ^{1}H-, ^{31}P-, ^{13}C-NMR spectroscopy, mass spectroscopy. The structure of the *trans* isomer **8a** was determined by X-ray analysis. A view of this complex with atom labelling scheme is shown in Fig. 4. The platinum which is located on an inversion centre presents a nearly perfect square planar geometry with a Cl(1)–Pt–P(1′) angle of 90.17(2)°. Owing to the occurrence of the inversion centre, the two phosphole rings are located on each side of this plane. As observed in the other complexes, the amino moiety PNC_2 is nearly perpendicular to the phosphole ring making a dihedral angle of 95.07° with it.

According to the results obtained with the palladium complexes, we assumed that the formation of the mononuclear platinum **7** and **8** complexes as a mixture of *cis* and *trans* isomers proceeded via a dinuclear complex intermediate (Scheme 2). Then, the bridge-cleavage reaction by action of a second equivalent of phosphole led to the formation of the *trans* isomer which could isomerise slowly in solution, as generally observed for this type of platinum complexes [10], to give a small amount of the *cis* isomer.

3. Conclusions

1-Diisopropylaminophospholes **1** and **2** react like other phospholes to afford square planar palladium(II) and platinum(II) complexes with *trans* and/or *cis* configuration. However, the steric and electronic effects of the diisopropylamino group on the phosphorus position allow the formation of dinuclear complexes which have been characterised for the first time in the case of palladium and the electronic effects of the 3,4 substituents on the phosphole ring seem to influence the stability of these complexes. In addition, these dinuclear complexes appear to be intermediates in the formation of the mononuclear square planar complexes. Further studies are in progress in order to test the catalytic

activity of these new palladium and platinum mononuclear complexes.

4. Experimental

4.1. General

All reactions were carried out under an inert atmosphere of dry Ar by using Schlenk glassware and vacuum line techniques. 1-Diisopropylaminophospholes, **1** and **2**, was prepared as described in the literature [8]. Solvents were freshly distilled from standard drying agents. ^{1}H-, ^{31}P{^{1}H}- and ^{13}C{^{1}H,^{31}P}-NMR spectra were recorded in a Bruker AM 250 instrument operating at 250, 101, and 63 MHz, respectively. Chemical shifts are reported in parts per million (ppm) relative to Me_4Si (^{1}H and ^{13}C) or 85% H_3PO_4 (^{31}P). Mass spectra were obtained in a Mermag R10-10 instrument. Elemental analysis were performed by the 'service d'analyse du Laboratoire de Chimie de Coordination' at Toulouse.

4.2. Bis[μ-chloro-chloro-(1-diisopropylamino-3,4-diphenylphosphole)palladium(II)] (4)

A CH_2Cl_2 solution (5 ml) of phosphole **2** (0.210 g, 0.63 mmol) was added to a stirred suspension of $[PdCl_2(CH_3CN)_2]$ (0.080 g, 0.31 mmol) in CH_2Cl_2 (10 ml). The resulting mixture was stirred at room temperature (r.t.) for 24 h, filtered through a 0.45 μm PTFE filter and then concentrated under reduced pressure to give an orange solid residue. The solid was then washed three times with pentane, filtered and dried under vacuum. Yield: 0.230 g (87%). ^{31}P-NMR ($CDCl_3$): δ + 48.8. ^{1}H-NMR ($CDCl_3$): δ 1.32 (d, $J_{HH} = 6.3$ Hz, 24H, $(CH_3)_2CH$); 4.16 (m, 4H, $(CH_3)_2CH$); 6.80 (d, $J_{HP} =$ 29.8 Hz, 4H, C*H*P); 7.46–7.05 (m, 20H, Ph). ^{13}C-NMR ($CDCl_3$): δ 23.0 (s, $(CH_3)_2CH$); 51.7 (s, $(CH_3)_2CH$); 125.6–128.0 (m, Ph); 128.75 (d, $J_{C-P} = 21$ Hz, *C*HP); 135.3 (d, $J_{CP} = 16.7$ Hz, C_{ipso}); 149.8 (d, $J_{CP} = 18.6$ Hz, *C*Ph). DCIMS (CH_4); m/z (%): 1044 (100%) [MCH_5^+]. Anal. Found: C, 51.21; H, 4.33; N, 2.71. Calc. for $C_{44}H_{52}Cl_4N_2P_2Pd_2$ (1025.5): C, 51.54; H, 5.11; N, 2.73%. Crystals suitable for X-ray analysis were obtained by slow evaporation of a CH_2Cl_2 solution.

4.3. cis-Dichloro-bis(1-diisopropylamino-3,4-dimethylphosphole) palladium(II) (5)

The same procedure as described for **4** was used. Starting from **1** (0.145 g, 0.63 mmol) and $[PdCl_2(CH_3CN)_2]$ (0.073 g, 0.28 mmol), **5** was obtained as an orange solid. Yield: 0.130 g (80%). ^{31}P-NMR ($CDCl_3$): δ + 53.2. ^{1}H-NMR ($CDCl_3$): δ 1.18 (d, $J_{HH} = 6.8$ Hz, 24H, $(CH_3)_2CH$); 2.02 (d, $J_{HP} = 7.5$ Hz, 12H, CH_3); 3.85 (m, 4H, $(CH_3)_2CH$); 6.41 (d, $J_{HP} =$ 29.0 Hz, 4H, C*H*P).

4.4. cis-Dichloro-bis(1-diisopropylamino-3,4-diphenylphosphole) palladium(II) (6)

To a solution of palladium complex **4** (0.600 g, 0.58 mmol) in CH_2Cl_2 (10 ml) was added a solution of phosphole **2** (0.392 g, 1.16 mmol) in CH_2Cl_2 (2 ml). The resulting mixture was stirred at r.t. for 24 h, filtered through a 0.45 μm PTFE filter and then concentrated under reduced pressure to give a solid residue. This resulting solid was then dissolved in a small amount of CH_2Cl_2 and precipitated with a large excess of pentane. After filtration, the orange solid obtained was dried under vacuum. Yield: 0,944 mg (96%). ^{31}P-NMR ($CDCl_3$): δ + 53.5. ^{1}H-NMR ($CDCl_3$) δ: 1.03 (d, $J_{HH} = 6.25$ Hz, 24H, $(CH_3)_2CH$); 3,88 (m, 4H, $(CH_3)_2CH$); 7.06 (d, 4H, $J_{HP} = 27.1$ Hz, C*H*P) 7.12 (m, 6H, Ph), 7.34–7.24 (m, 14H, Ph). ^{13}C-NMR ($CDCl_3$): δ 23.0 (s, 2C, $(CH_3)_2CH$); 53.0 (d, $J_{CP} = 6$ Hz, $(CH_3)_2CH$); 128.1–128.8 (m, Ph); 135.6 (d, $J_{C-P} = 15.5$ Hz, C_{ipso}); 151.2 (b, *C*Ph). DCIMS (NH_3); m/z (%): 849 (24%) [MH^+]. Anal. Found: C, 62.59; H, 6.52; N, 3.12. Calc. for $C_{44}H_{52}Cl_2N_2P_2Pd$ (848.2): C, 62.31; H, 6.18; N, 3.30%. Crystals suitable for X-ray analysis were obtained by slow evaporation of a CH_2Cl_2 solution.

4.5. trans-Dichloro-bis(1-diisopropylamino-3,4-dimethylphosphole) platinum(II) (7a)

To a solution of phosphole **1** (0.200 g, 0.99 mmol) in CH_2Cl_2 (10 ml) was added solid $[Pt(CH_3CN)_2Cl_2]$ (0.176 g, 0.44 mmol). The reaction mixture turned yellow immediately. After 1 h of stirring at r.t., the resulting solution was filtered through a 0.45 μm PTFE filter, and then evaporated. The yellow solid obtained was washed with pentane and dried in vacuo. Yield: 0.130 mg (75%). ^{31}P-NMR ($CDCl_3$): δ 44.6. ^{1}H-NMR ($CDCl_3$): δ 1.18 (d, $J_{HH} = 6.8$ Hz, 24H, $(CH_3)_2CH$); 1.94 (s, 12H, CH_3); 4.04 (m, 4H, $(CH_3)_2CH$); 6.39 (t, $J_{HP} = 31.6$ Hz, 4H, C*H*P). ^{13}C{^{1}H}-NMR ($CDCl_3$): δ 17.74 (s, CH_3); 23.25 (s, $(CH_3)_2CH$); 50.0 (s, $(CH_3)_2CH$); 124.4 (t, $J_{CP} = 60.8$ Hz, *C*HP); 147.5 (t, $J_{CP} = 19.0$ Hz, *C*CH_3). DCIMS (NH_3); m/z (%): 689 (64) [MH^+]. Yellow crystals suitable for X-ray were obtained by slow evaporation of a CH_2Cl_2 solution.

4.6. cis- and trans-Dichloro-bis(1-diisopropylamino-3,4-diphenylphosphole) platinium(II) (8)

The procedure was analogous to that for **7**. The resulting solution was filtered through a 0.45 μm PTFE filter, concentrated to ~5 ml under reduced pressure and slow addition of ~10 ml of pentane gave the *cis*

complex **8b** as a yellow solid which was isolated by filtration, washed with pentane and dried under vacuum. The *trans* complex **8a** was obtained as a yellow powder by evaporation of the filtrate. Crystals were grown from a CH_2Cl_2 solution of the compound. **8a**: Yield: (62%). ^{31}P-NMR ($CDCl_3$): δ 46.65. ^{1}H-NMR (CD_2Cl_2): δ 1.30 (d, $J_{HH} = 6.8$ Hz, 24H, $(CH_3)_2CH$); 4.25 (m, 4H, $(CH_3)_2CH$); 6.90 (t, $J_{HP} = 27.3$ Hz, 4H, C*H*P); 7.00–7.25 (m, 20H, Ph). ^{13}C-NMR ($CDCl_3$): δ 23.23 (s, $(CH_3)_2CH$); 51.4 (s, $(CH_3)_2CH$); 128.5–127.9 (m, Ph); 129.5 (t, $J_{CP} = 59.4$ Hz, *C*HP); 149.5 (t, $J_{CP} = 20.3$ Hz, *C*Ph). DCIMS (NH_3); m/z (%): 937 (100) [MH^+].

8b: Yield: (10%). ^{31}P-NMR ($CDCl_3$): δ 33.38. ^{1}H-NMR (CD_2Cl_2): δ 1.06 (d, $J_{HH} = 6.8$ Hz, 24H, $(CH_3)_2CH$); 3.90 (m, 4H, $(CH_3)_2CH$); 6.89 (d, $J_{HP} = 27.3$ Hz, 4H, CHP); 7.07–7.32 (m, 20H, Ph). DCIMS (NH_3); m/z (%): 937 (100) [MH^+].

4.7. X-ray crystallographic study

Data for **4** were collected on a Bruker Smart 1000 diffractometer whereas a Stoe IPDS (imaging plate diffraction system) diffractometer was used for compounds **6**, **7a** and **8a**. The final unit cell parameters were obtained by the least-squares refinement of a large number of reflections (10 936 for the Smart and 8000 for the IPDS). Only statistical fluctuations were observed in the intensity monitors over the course of the data collections. The structure was solved by direct methods (SIR97 [16]) and refined by least-squares procedures on F^2. All H atoms attached to carbon were introduced in calculation in idealised positions [d(CH) = 0.96 Å] and treated as riding models. In complex **4**, the refinement of Flack's parameter did not allow to define properly the absolute structures and the occurrence of a twin by inversion (racemic twin) had to be considered. Moreover in this complex, two of the isopropyl groups are disordered over two positions. These disordered groups were treated using the available tools in SHELXL-97 [17]. Least-squares refinements were carried out by minimising the function $\Sigma w(F_o^2 - F_c^2)^2$, where F_o and F_c are the observed and calculated structure factors. The weighting scheme used in the last refinement cycles was $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$ where $P = (F_o^2 + 2F_c^2)/3$. Models reached convergence with $R = \Sigma(||F_o| - |F_c||)/\Sigma(|F_o|)$ and $wR_2 = \{\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2\}^{1/2}$, having values listed in Table 2. The calculations were carried out with the SHELXL-97 program [16] using the integrated system WINGX (1.63) [18]. Molecular view was realised with the help of ORTEP [19].

5. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic

Table 2
Crystal data and structural refinement parameters for complexes **4**, **6**, **7a** and **8a**

	4	**6**	**7a**	**8a**
Empirical formula	$C_{44}H_{50}Cl_4N_2P_2Pd_2$	$C_{23}H_{28}Cl_3NPPd_{0.5}$	$C_{24}H_{44}Cl_2N_2P_2Pt$	$C_{22}H_{26}ClNPPt_{0.5}$
Formula weight (g)	1023.4	508.98	688.54	468.40
Temperature (K)	193(2)	160(2)	160(2)	180(2)
Crystal system	Orthorhombic	Monoclinic	Monoclinic	Triclinic
Space group	$Pna2_1$	$C2/c$	$P2_1/c$	$P\bar{1}$
Unit cell dimensions				
a (Å)	22.1650(7)	23.345(5)	17.928(2)	8.3402(11)
b (Å)	8.1645(3)	8.573(2)	12.685(1)	11.4597(14)
c (Å)	24.7373(8)	24.282(5)	13.312(1)	12.2203(15)
α (°)				79.72(1)
β (°)		107.74(3)	101.92(1)	73.45(2)
γ (°)				73.74(1)
U (Å^3)	4476.6(3)	4628.6(17)	2962.1(5)	1068.6(2)
Z	4	8	4	2
D_{calc} (g cm^{-3})	1.518	1.461	1.544	1.456
μ (Mo–K$_\alpha$) (cm^{-1})	11.46	8.51	50.40	35.14
2θ range (°)	$3.30 < 2\theta < 52$	$5.1 < 2\theta < 48.3$	$4.74 < 2\theta < 51.9$	$5.26 < 2\theta < 52.18$
Reflections measured	48 639	17 946	22 683	10 509
Independent reflections (R_{int})	8780 (0.0670)	3504 (0.0476)	5716 (0.0324)	3874 (0.0299)
Reflections used ($I > 2\sigma(I)$)	7669	3237	5349	3237
R, wR_2 [$I > 2\sigma(I)$]	0.0396, 0.0954	0.0328, 0.0848	0.0179, 0.0434	0.0207, 0.0541
R, wR_2 (all data)	0.0510, 0.1068	0.0357, 0.0876	0.0202, 0.0441	0.0210, 0.0607
$(\Delta/\sigma)_{max}$	0.016	0.001	0.002	0.001
$\Delta\rho_{min}/\Delta\rho_{max}$	−0.59/1.62	−1.02/1.12	−0.45/0.54	−1.14/1.71
Goodness-of-fit	1.154	1.032	1.057	1.120
Variable parameters	492	262	292	236

Data Centre, CCDC nos. 163288–163291 for compounds **4**, **6**, **7a** and **8a**, respectively. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

Tables of anisotropic temperature factors, hydrogen coordinates and observed and calculated structure factors are available from the Cambridge Crystallographic Data Centre. Ordering information is given on any current masthead page.

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