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Syntheses and Coordination Chemistry of Bis(4-pyridyl)- and Mixed (4-Pyridyl) (2-pyridyl)-phospholes

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ABSTRACT: *The syntheses, spectroscopic characterizations, and X-ray structures of two new N,P,N-ligands* **1** *and* **2** *are described. These ligands are based on a central 2,5-substituted phosphole ring and have, respectively, two 4-pyridyl moieties, or one 4-pyridyl moiety and one 2-pyridyl moiety as substituents. The coordination chemistry of these ligands has been investigated. A Au(I)-complex* **5** *bearing ligand* **1** *as a P-donor and a Pt(II) complex* **6** *featuring ligand* **2** *as a P,N-chelate were obtained. Complex* **6** *spontaneously evolves to complex* **7** *bearing a 2-phospholene ring. Spectroscopic characterizations for complexes* **5–7** *as well as the X-ray crystal structure of* **7** *are described.* © 2011 Wiley Periodicals, Inc. Heteroatom Chem 22:339–347, 2011; View this article online at wileyonlinelibrary.com. DOI 10.1002/hc.20687

INTRODUCTION

Heteroditopic P,N-chelates have attracted considerable interest in coordination chemistry and homogeneous catalysis for several decades [1]. The importance of these mixed donor ligands arises from the different stereo-electronic properties of the two coordination sites providing unique reactivity to their metal complexes. Although different N-donors (imines, pyridines, quinolines, oxazolines, pyrazolines, oxazines, etc.) have been used for the design of P,N-chelates [1], less attention has been paid to the variation of the P-donors, the great majority of P,N-ligands bearing diarylphosphino fragments. In this context, phospholes are the most studied P-heterocycles due to their easy accessibility, good stability, and versatile chemical behavior [2]. This group 15 heteroles exhibits a limited aromatic character, owing to the inherent property of the P-atom (pyramidal geometry, inert s-pair effect) [3], resulting in a high reactivity of both their dienic- and heteroatom-moieties. This behavior, which is very different from that of their N-analogues, makes phospholes appealing derivatives for many purposes including coordination chemistry [2]. Indeed, phospholes act as classical terminal two-electron donors toward a large range of transition metals. Therefore, a variety of multidentate phosphole-containing ligands, including heteroditopic P,N-donors, have been reported as illustrated with selected examples depicted in Fig. 1 [2,4].

In this field, the coordination behavior of (2-pyridyl)-substituted phospholes ligands was recently explored in our group with the aim to obtain complexes with original structures and interesting physical properties. For example, 2-(2-pyridyl)phosphole-based chromophores **A–J** (Fig. 2) display extended π-conjugated systems and can act

Dedicated to Professor Kin-ya Akiba on the occasion of his 75th birthday.

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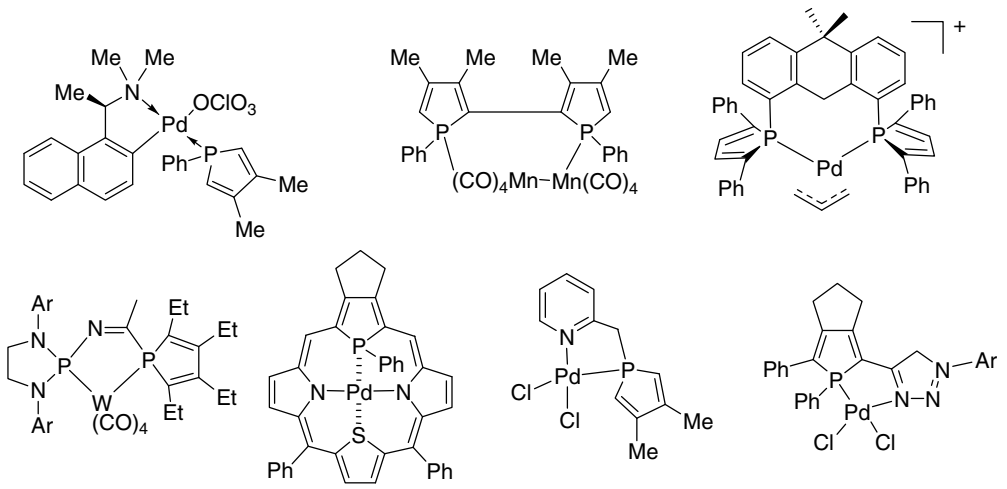


FIGURE 1 Selected examples of complexes bearing phosphole-based ligands.

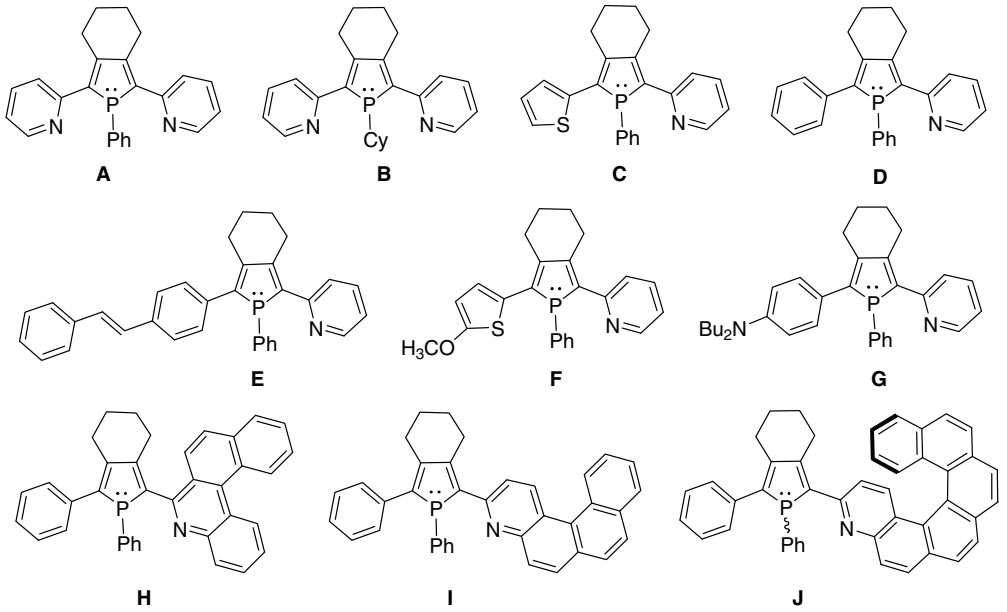


FIGURE 2 Selected examples of (2-pyridyl)-substituted phosphole ligands.

as heteroditopic P,N-chelates toward a large range of transition metals. Because of the different nature of the donor atoms (a soft P- and a hard N-centers according to the Pearson's classification) [5], they undergo highly stereoselective coordination processes to d^8 square-planar metal ions by virtue of the antisymbiotic rule. Furthermore, these heteroditopic P,N-ligands exhibit a hemilabile behavior, a dynamic property which is very important to obtain the thermodynamically more stable transition metal complex. The use of these appealing properties allowed the coordination-driven synthesis of C_2-symmetrical metallic complexes active in nonlinear optics [6] and chiral metal-bis(azahelicene phosphole) assemblies [7].

Two other remarkable properties of mixed pyridine–phosphole ligands are notable. The first one is the original coordination mode of bis(2-pyridyl)phosphole **A** (Fig. 2) that acts as a N,P,N-chelate with a bridging P-atoms to stabilize a variety of metal dimers [8] such as complexes **K** and **L** (Fig. 3a) [8d,e,9a]. These Cu^I-dimers are powerful "U-shape" molecular clips for the supramolecular synthesis of π-stacked [2,2]metallacyclophanes upon reaction with ditopic π-linkers [9]. The second one is the stereoselective isomerization of

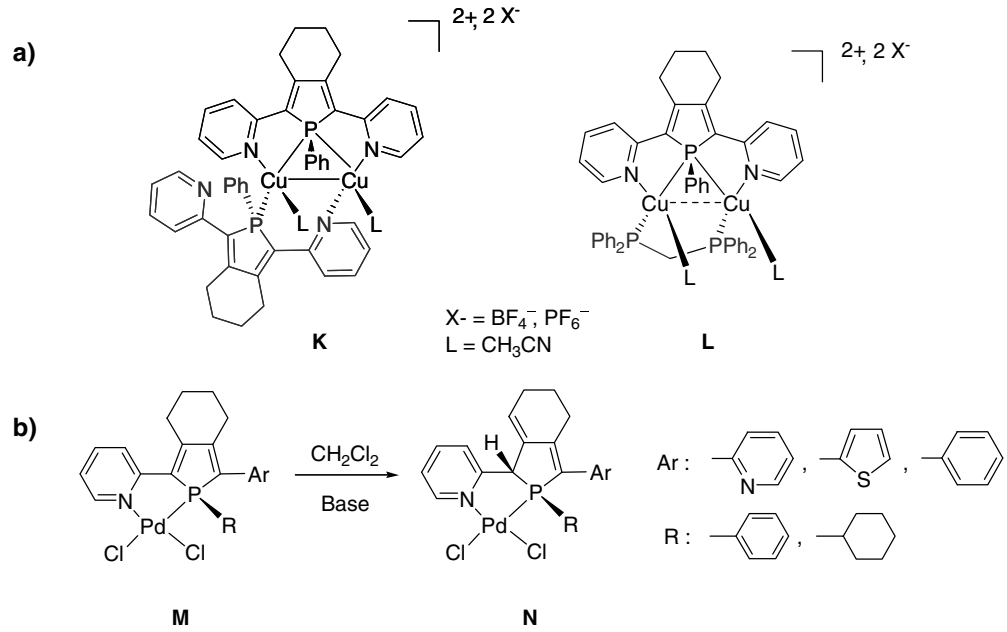


FIGURE 3 (a) Chemical structure of "U-shaped" molecular clips **K** and **L**, (b) Stereoselective isomerization of 2-pyridylphospholes into their corresponding 2-pyridyl-2-phospholenes in the coordination sphere of Pd(II) ions.

Pd(II)-coordinated 2-pyridylphosphole ligands into their corresponding 2-pyridyl-2-phospholene isomers in the presence of an organic base (pyridine, triethylamine, . . . ; Fig. 3b) [10]. This general transformation, involving a base-catalyzed [1,3]-H migration, gave access to enantiopure P,N-chelates that can be used as ligands for asymmetric homogeneous catalysis [11].

These results prompted us to extend our studies of mixed pyridine–phosphole ligands to phospholes substituted by a 4-pyridyl moiety. In this paper, we describe the synthesis and the coordination behavior of the new derivatives **1** and **2** (Fig. 4) in which the phosphole rings are substituted by two 4-pyridyl moieties, or by both a 4-pyridyl and a 2-pyridyl fragments.

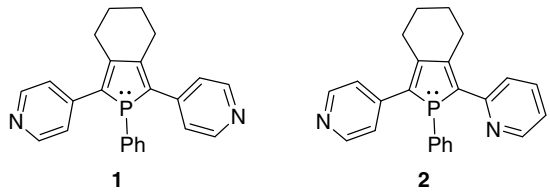
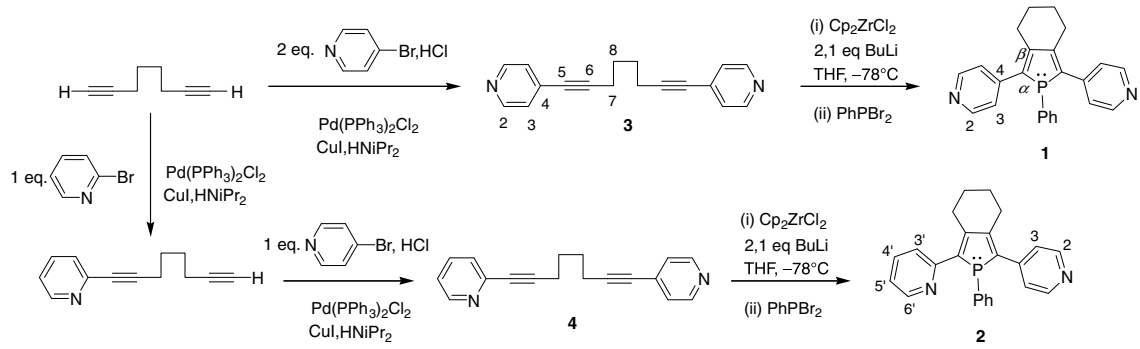


FIGURE 4 Chemical structure of (4-pyridyl)phospholes **1** and **2**.

RESULTS AND DISCUSSION

Syntheses and Characterizations of Derivatives **1** *and* **2**

Phospholes **1** and **2** were prepared via the "Fagan–Nugent method" (Scheme 1) [12], a general and an efficient organometallic route to phosphole moieties. Functionalized 1,7-diynes **3** and **4** were readily obtained via Sonogashira coupling reactions in good yields (Scheme 1). The intramolecular oxidative coupling of these diynes, possessing a $(CH_2)_4$ spacer to obtain the desired 2,5-substitution pattern, with "zirconocene" provides the corresponding zirconacyclopentadienes that were reacted in situ with dibromophosphine $PhPBr_2$ to give the corresponding phospholes **1** and **2** in moderate yields (**1**, 30%; **2**, 46%) as air-stable yellow powders. These new phosphole derivatives were characterized by multinuclear nuclear magnetic resonance (NMR) spectroscopies and mass spectrometry. Their ^{31}P NMR spectrum displays a sharp singlet at +14.2 ppm (**1**) and +13.6 ppm (**2**). These chemical shifts are typical of P-phenyl substituted λ^3,σ^3 phosphole ring [13]. The simplicity of the room temperature ^1H and ^{13}C NMR spectra of derivative **1** is fully consistent with a symmetrical structure. For example, the signal of the NCH protons of the (4-pyridyl) groups consists in a doublet of doublets at 8.49 ppm, and only one signal is recorded for the C^β carbon atoms (147.4 ppm, d, $^2J_{P\text{-}C} = 11.0$ Hz). As expected, in the ^1H NMR spectrum of mixed derivative **2**, two signals for the NCH protons are observed at 8.57 ppm (H2) and 8.46 ppm (H6′) with a relative integration ratio of 2:1. The unsymmetrical nature of phosphole **2** is



SCHEME 1 Syntheses of (4-pyridyl)phospholes **1** and **2**.

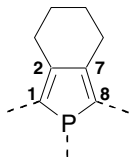
also proven by the ^{13}C NMR spectrum that displays a set of signals for each carbon atom of the phosphole ring and of the fused cyclohexyl ring.

The proposed structures for derivatives **1** and **2** were confirmed by X-ray diffraction studies. Single crystals of **1** and **2** suitable for X-ray analysis were obtained by slow evaporation of their CH_2Cl_2 solutions at room temperature (Table 1). Derivative **1** (Fig. 5a) crystallizes in the $P21/c$ space group of the monoclinic system, and compound **2** (Fig. 5b) crystallizes in the P-1 space group of the triclinic system. In both cases, one phosphole molecule is present in the unit cell. The metric parameters of the phosphole ring of these (4-pyridyl)-substituted derivatives (Table 2) are very similar to those of their corresponding (2-pyridyl) containing compounds **A** (Fig. 2) [13]. The central phosphole ring is almost planar, whereas the phosphorus atom's

TABLE 1 Crystal Data and Structure Refinement for Phospholes 1 and 2 and Complex 7

	1	***2***	***7***
Molecular formula	$C_{24}H_{30}N_2P_1$	$C_{24}H_{21}N_2P_1$	$C_{24}H_{21}N_2P_1Pt_1Cl_2$
CCDC number	794109	794106	794107
Molecular weight	368.40	368.40	634.39
A (Å)	9.2607(2)	9.350(3)	10.0311(2)
B (Å)	20.2677(5)	10.397(4)	16.1057(3)
C (Å)	9.9655(3)	11.050(3)	14.0646(2)
α°)	90	81.85(2)	90
β°)	91.5920(10)	65.55(2)	102.219(1)
γ°0	90	85.26(2)	90
V (Å^3)	1869.73(8)	967.6(6)	2220.77(7)
Z	4	2	4
ρ_{calcd} (Mg m^{-3})	1.309	1.264	1.897
Crystal system	Monoclinic	Triclinic	Monoclinic
Space group	$P21/c$	P-1	$P21/n$
T (K)	293(2)	293(2)	293(2)
Wavelength Mo $K\alpha$ (Å)	0.71069	0.71069	0.71069
Crystal size (mm)	0.32 × 0.30 × 0.30	0.35 × 0.15 × 0.15	0.42 × 0.35 × 0.35
μ (Mo Kα) (cm^{-1})	0.159	0.153	6.645
F(000)	776	388	1224
θ limit (°)	2.28–27.00	1.98–26.96	1.95–27.00
Index ranges hkl	$0 \le h \le 11$, $0 \le k \le 25$, $-12 \le l \le 12$	$0 \le h \le 11$, $-13 \le k \le 13$, $-12 \le l \le 14$	$0 \le h \le 12$, $0 \le k \le 20$, $-17 \le l \le 17$
Reflections collected	4057	4469	4841
Independent reflections	4057	4204	4841
Data/restraints/parameters	4057/0/244	4204/0/245	4841/0/272
Goodness-of-fit on F^2	1.040	0.887	1.073
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0520$ $wR_2 = 0.1241$	$R_1 = 0.0662$ $wR_2 = 0.1382$	$R_1 = 0.0345$ $wR_2 = 0.0880$
R indices (all data)	$R_1 = 0.0801$ $wR_2 = 0.1430$	$R_1 = 0.1663$ $wR_2 = 0.1571$	$R_1 = 0.0433$ $wR_2 = 0.0953$
Largest different peak and hole (e Å^{-3})	0.550 and −0.343	0.328 and −0.215	2.175 and −1.705

TABLE 2 Selected Bonds Lengths (Å) and Angles (°) of the Phosphole Moieties in Phospholes A [13], 1 and 2, and Complex 7



	$P-C^1$ $P-C^8$	C^1-C^3	C^2-C^7	C^7-C^8	C^7-C_{Py} C^8-C_{Py}	C^1-P-C^8
A	1.806(6) 1.806(6)	1.365(9)	1.478(9)	1.354(8)	1.466(9) 1.467(8)	90.5(3)
1	1.799(2) 1.818(2)	1.369(3)	1.469(3)	1.367(3)	1.467(3) 1.470(3)	91.29(10)
2	1.790(3) 1.799(3)	1.357(4)	1.472(4)	1.360(4)	1.478(4) 1.469(4)	91.05(16)
7	1.835(5) 1.810(5)	1.525(7)	1.469(7)	1.353(7)	1.497(7) 1.478(7)	93.2(2)

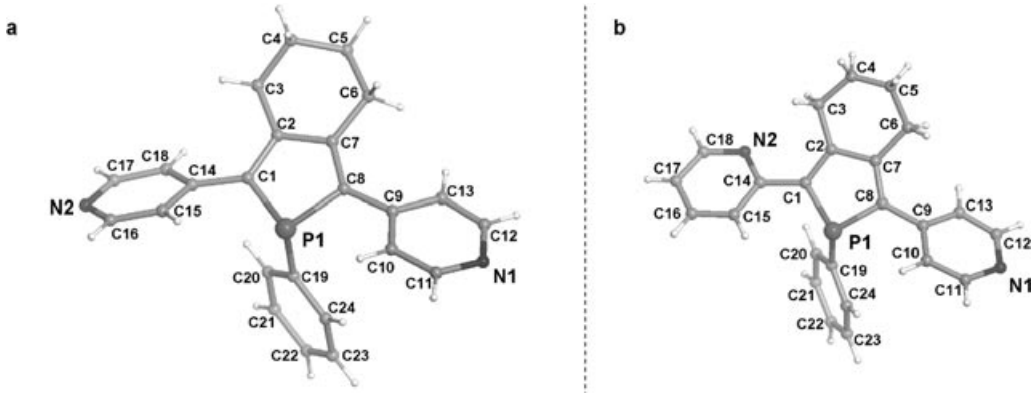
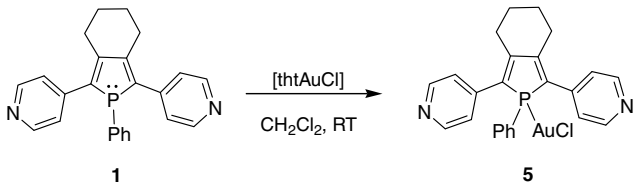


FIGURE 5 View of the X-ray crystal structures of phospholes **1** (a) and **2** (b).



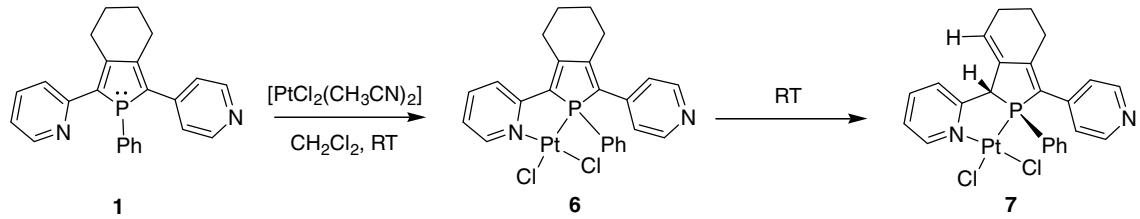
1 **5**

SCHEME 2 Synthesis of the complex **5**.

environment is strongly pyramidalized. The torsion angles between the central phosphole ring and the 2- or 4-pyridyl fragments range from 23.2° to 33.2°. They are slightly larger than those found in the solid-state structure of the bis(2-pyridyl)phosphole **A** (torsion angles, 0.5° and 26.1°) [13]. It is noteworthy that derivative **1** can be considered as "phosphole-modified" viologen (N1—C8—C1—N2, 1.9°).

Coordination Behavior of Bis(4-pyridyl) phosphole **1**

Derivative **1** potentially possesses two available coordination sites with different electronic properties (soft P-atom, hard N-atoms). It was thus interesting to study its coordination ability, and (tht)AuCl (tht = tetrahydrothiophene) was selected as Au(I) precursor with the hope to obtain a selective P-coordination. Compound **1** was reacted with 1 equiv of (tht)AuCl and, after workup, the novel complex **5** was isolated as an air-stable hygroscopic light yellow powder in a 91% yield (Scheme 2). The elemental analysis supports the formation of a (**1**)AuCl complex. Its $^{31}P\{^1H\}$ NMR spectrum displays a sharp singlet at +42.1 ppm. This chemical shift is typical of a terminal coordination of the phosphorus atom of λ^3, σ^3 phosphole ligands on a Au(I) center [14]. The room temperature ^1H NMR spectrum of **5** displays one set of signals only, which are very similar to those of the free ligand **1**, indicating a symmetric structure. These data clearly show that the Au(I) metal center coordinates exclusively to the phosphorus atom of ligand **1**. Indeed, this chemiselective modification opens the route to a variety of novel derivatives because the terminal N-atoms of complex **5** are potentially reactive sites for further functionalizations or coordination polymer formation. Preliminary experiments showed that



SCHEME 3 Synthesis of complexes **6** and **7**.

reacting **5** with ([$Cu(NO_3)_2$]. 2.5 H_2O, [$Cu(CH_3CN)_4$]PF_6, [$PdCl_2(CH_3CN)_2$], [$AgNO_3$], or [$AgCF_3SO_3$]) afforded materials that are insoluble in organic solvents (CH_2Cl_2, THF, CH_3OH, and acetone), probably due to their polymeric structure.

Coordination Behavior of (4-Pyridyl)(2-pyridyl) phosphole **2**

Ligand **2** was first reacted with 1 equiv of [$PtCl_2(CH_3CN)_2$] to form the complex **6** (Scheme 3). The $^{31}P\{^1H\}$ NMR spectrum of the resulting crude clear yellow solution displays one signal at +36.6 ppm. This $^{31}P\{^1H\}$ NMR chemical shift is low field shifted compared with that of the free ligand **2**, and typical for (2-pyridylphosphole)$PtCl_2$ complexes in which the organic ligand acts as a 1,4-P,N chelate [10b]. The coordination of the P-atom is also supported by the presence of a large $^1J_{PPt}$ coupling constant (3694 Hz), and that of the N-atoms of the 2-pyridyl moiety by the low field chemical shift of the ^1H NMR signal of the $H^{6'}$ proton ($\delta = 9.86$ ppm). Furthermore, the chemical shift of the H^2 proton of the 4-pyridyl moiety is almost unchanged ($\delta = 8.51$ ppm) compared with the free ligand **2** ($\delta = 8.46$ ppm). These data clearly support the proposed structure with ligand **2** acting as a P,N-chelate on the Pt(II) center in complex **6** (Scheme 3).

All attempts to isolate complex **6** in a pure form failed. Indeed, if this complex is left for a few minutes in solution at room temperature, a new signal appears at +40.5 ppm in the $^{31}P\{^1H\}$ NMR spectrum. This sharp singlet is associated with a $^1J_{PPt}$ coupling constant of 3815 Hz. After a few hours, the transformation is complete and the resulting light yellow solution does not evolve anymore. This observation suggests that the complex **6** undergoes in solution a spontaneous transformation into a new derivative **7** in which the phosphorus atom is still coordinated on the Pt(II) center. After evaporation of the solvent, derivative **7** (Scheme 3) is collected as a yellow powder. Its ^1H NMR spectrum shows a broad doublet at 4.7 ppm (J_{PH} = 8.H Hz, 1H) and a multiplet at 6.35 ppm (1H). The signal of the $H^{6'}$ proton of the

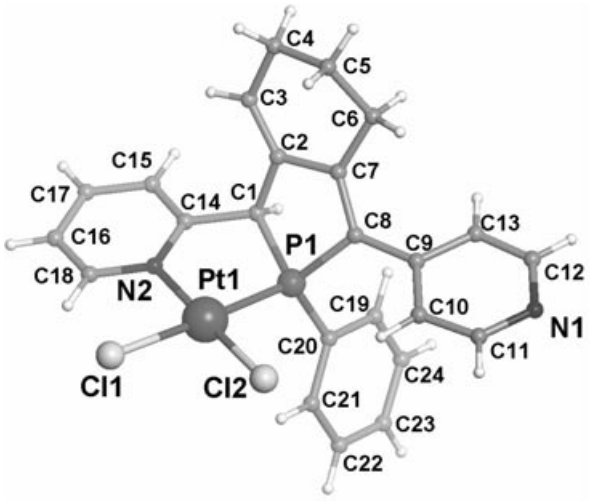


FIGURE 6 View of the X-ray crystal structure of complex **7**.

2-pyridyl moiety is low field shifted ($\delta = 10.15$ ppm), indicating that a P,N-chelate is still present in derivative **7**. These data reveal a profound modification of the phosphorus heterocycle structure and fit with a 2-phospholene structure [10]. This proposed structure was confirmed by X-ray diffraction studies (Fig. 6). Single crystals of derivative **7** suitable for X-ray diffraction analysis (Table 1) were obtained from a slow diffusion of pentane vapors into a CH_2Cl_2 solution of **7**. Complex **7** contains an almost square planar Pt(II) center linked to two chlorine atoms, a pyridine, and a 2-phospholene ring. Note that the pendant 4-pyridyl group of the ligand is not coordinated to any metal center (shortest intermolecular Pt-N(1) distance: 5.679 Å). The existence of the phospholene framework is clearly indicated by the tetrahedral geometry about the C(1) carbon atom and the C(1)-C(2) (1.525(7) Å) and C(7)–C(8) (1.353(7) Å) bond lengths, which are typical of single and double carbon–carbon links, respectively. The two endocyclic P—C distances (1.810(5) and 1.835(5) Å) are characteristic for single bonds. It is also noteworthy that the C(3) carbon atom has a planar geometry and that the C(2)–C(3) distance (1.324(8) Å) is consistent

with a double bond. Clearly, the fused carbocycle is now a cyclohexene fragment. These solid-state structural data are in full agreement with the NMR spectroscopic data recorded in solution.

The [1,3]-hydrogen shift leading to **7** (Scheme 3) creates a new stereogenic center (the C(1)-carbon atom), and the fact that only one diastereoisomer out of the two possible is detected by NMR spectroscopy reveals a stereoselective process. The solid-state studies show that the H-atom linked to the C(1) atom and the P-substituent are in a mutual cis configuration. This type of stereoselective process has already been observed with either Pd(II) or Pt(II) complexes bearing (2-pyridyl)-phosphole ligands (Fig. 3b) [10]. Note that in the present case (**6** → **7**, Scheme 3), it is very probable that the uncoordinated 4-pyridyl acts as a base to promote the [1,3]-hydrogen shift.

CONCLUSION

The syntheses, spectroscopic characterizations, and X-ray crystal structure study of two new stable N,P,N-ligands associating a central phosphole ring and 4-pyridyl termini have been described. The phosphorus atom of ligand **1** bearing two (4-pyridyl) fragments can be coordinated to a Au(I) metal center, affording a monometallic complex **5** in which the nitrogen atoms are free. Ligand **2**, having a (2-pyridyl)phosphole moiety, reacts with Pt(II) metal centers as a 1,4-chelate. It spontaneously isomerizes to a phospholene ring in the Pt(II)-coordination sphere. These results show that the new ligands **1** and **2** can be used for the synthesis of new coordination complexes having various structures.

EXPERIMENTAL

All experiments were performed under an atmosphere of dry argon using standard Schlenk techniques. Commercially available reagents were used as received without further purification. Solvents were freshly distilled under argon from sodium/benzophenone (diethylether) or from phosphorus pentoxide (dichloromethane, acetonitrile). ^{1}H, ^{13}C, and ^{31}P NMR spectra were recorded on Bruker AV300, DPX200, or AV500 spectrometers (Bruker AXS Inc., Madison, WI). ^{1}H and ^{13}C NMR chemical shifts were reported in parts per million (ppm) relative to Me_4Si as external standard. ^{31}P NMR downfield chemical shifts were expressed with a positive sign, in ppm, relative to external 85% H_3PO_4.

Synthesis of 1,8-Bis(4-pyridyl)octa-1,7-diyne **3**

Catalytic amounts of $[PdCl_2(PPh_3)_2]$ (0.11 g, 0.15 mmol) and CuI (0.03 g, 0.15 mmol) were added to a solution of 1,7-octadiyne (400 mg, 3.70 mmol) and 4-bromopyridine, hydrochloride (1.464 g, 7.4 mmol) in diisopropylamine (70 mL). The heterogeneous brown mixture was stirred for a night at 40°C. All volatiles materials were removed in vacuo, and the residue was extracted with diethylether (3 × 20 mL). After purification by column chromatography on silica gel (heptane/ether, 2/1), the product **3** was obtained as a pale yellow solid (yield 95%, 0.91 g, 3.55 mmol). NMR ^{1}H (200 MHz, $CDCl_3$): δ = 1.80 (m, 4H, C≡CCH$_2$CH_2), 2.50 (m, 4H, C≡CCH_2), 7.20 (dd, ^{3}J(H, H) = 4.5 Hz, ^{5}J(H, H) = 1.7 Hz, 4H, pyridyl H_3), 8.50 (dd, ^{3}J (H, H) = 4.5 Hz, ^{5}J(H, H) = 1.7 Hz, 4H, pyridyl H_2). NMR ^{13}C-{1H}(50 MHz, $CDCl_3$) : δ = 19.5 (s, C≡CCH$_2$CH_2), 27.9 (s, C≡CCH$_2$), 79.3 (s, C≡C-4py), 95.5 (s, C≡C-4py), 128.8 (s, pyridyl C_3), 150.0 (s, pyridyl C_2).

Synthesis of 1-(4-Pyridyl),8-(2′-pyridyl) octa-1,7-diyne **4**

Catalytic amounts of $[PdCl_2(PPh_3)_2]$ (0.180 g, 0.26 mmol) and CuI (0.050 g, 0.26 mmol) were added to a solution of 1-(2-pyridyl)octa-1,7-diyne [10] (1.574 g, 8.59 mmol) and 4-bromopyridine, hydrochloride (1.674 g, 8.59 mmol) in diisopropylamine (50 mL). The heterogeneous brown mixture was stirred overnight at 40°C. All volatile materials were removed in vacuo, and the residue was extracted with diethylether (3 × 20 mL). After purification by column chromatography on silica gel (heptane/ether, 2/1), the product **4** was obtained as a pale yellow solid (yield 72%, 1.60 g, 6.1 mmol). NMR ^{1}H (200 MHz, $CDCl_3$): δ = 1.60 (m, 4H, C≡CCH$_2$CH_2), 2.30 (m, 4H, C≡CCH_2), 6.86 (ddd, ^{3}J (H, H) = 7.7 Hz, ^{4}J = 7.7 Hz, ^{3}J (H, H) = 1.2 Hz,1H, pyridyl $H_{5'}$), 7.06 (dd, ^{3}J (H, H) = 4.4 Hz, ^{5}J(H, H) = 1.6 Hz, 2H, pyridyl H_3), 7.08 (ddd, ^{3}J (H, H) = 7.7 Hz, ^{4}J (H, H) = 1.8 Hz, ^{5}J (H, H) = 1.2 Hz, 1H, pyridyl H_3), 7.29 (ddd, ^{3}J (H, H) = 7.7 Hz, ^{3}J (H, H) = 7.7 Hz, ^{4}J (H, H) = 1.8 Hz, 1H, pyridyl H_4), 8.32 (dd, ^{3}J H, H) = 4.4 Hz, ^{5}J(H, H) = 1.6 Hz, 2H, pyridyl H_2), 8.35 (m, 1H, pyridyl $H_{6'}$). NMR ^{13}C-{1H}(50 MHz, $CDCl_3$): δ = 19.4 (s, C≡CCH$_2$CH_2), 19.5 (s, C≡CCH$_2$CH_2), 27.6 (s, C≡CCH$_2$), 27.8 (s, C≡CCH$_2$), 79.1 (s, C≡C-4py), 81.2 (s, C≡C-2py), 90.5 (s, C≡C-2py), 95.6 (s, C≡C-4py), 122.7 (s, pyridyl $C_{5'}$), 126.1 (s, pyridyl C_3), 127.1 (s, pyridyl $C_{3'}$),132.4 (s, pyridyl C_4),136.4 (s, pyridyl $C_{4'}$), 144.0(s, pyridyl $C_{2'}$), 150.0 (s, pyridyl C_2), 150.1 (s, pyridyl $C_{6'}$). HR-MS (EI): *m/z* measured 260.1302 $[M]^+$; $C_{18}H_{16}N_2$calculated 260.13135.

Synthesis of 1-Phenyl-2,5-di(4-pyridyl) phosphole **1**

To a tetrahydrofuran (THF) solution (20 mL) of Cp_2ZrCl_2 (874 mg, 3 mmol) and 1,8-bis(4-pyridyl)octa-1,7-diyne **3** (782 mg, 0.3 mmol), was added dropwise (ca. 1 min), at −78°C, a hexane solution of *n*-BuLi (1.6 M, 3.9 mL, 6 mmol). The solution was warmed to room temperature, and stirred over night. To this solution, freshly distilled $PhPBr_2$ (620 μL, 0.3 mmol) was added at −78°C. The solution was allowed to warm to room temperature and stirred for 6 h. The solution was filtered on basic alumina (THF), and the volatile materials were removed under vacuo. The desired product was washed with pentane and obtained as a yellow solid (yield 30%, 332 mg, 0.09 mmol). NMR^{1}H (200 MHz, $CDCl_3$): δ = 1.60–1.90 (m, 4H, C≡CCH$_2$CH_2), 2.55–2.80 (m, 2H, C≡CCH_2), 2.90–3.1 (m, 2H, C≡CCH$_2$), 7.05–7.12 (m, 5H, H_{Ph}), 7.26 (dd, ^3J (H, H) = 4.6 Hz, ^5J(H, H) = 1.6 Hz, 4H, pyridyl H_3), 8.49 (dd, ^3J H, H) = 4.6 Hz, ^5J(H, H) = 1.6 Hz, 4H, pyridyl H_2). NMR^{13}C-{1H} (50 MHz, $CDCl_3$): δ = 23.3 (s, C=CCCH$_2$CH_2), 28.4 (s, C=C*C*H$_2$), 123.3 (d, ^2J(P, C) = 5.6 Hz, pyridyl C_3), 124.0 (d, ^3J(P, C) = 9.6 Hz, pyridyl C_2), 129.2 (d, ^3J(P, C) = 8.5 Hz, phenyl C_{meta}), 130.3 (s, phenyl C_{para}), 133.8 (d, ^2J(P, C) = 19.1 Hz, phenyl C_{ortho}), 143.2 (s, P–C=C), 144.9 (d, ^1J(P, C) = 19.2 Hz, phenyl C_{ipso}), 147.4 (d, ^2J(P, C) = 11.0 Hz, P–C=C), 150.2 (s, pyridyl C_2). NMR^{31}P-{1H}(81 MHz, $CDCl_3$): δ = +14.2. HR-MS (EI): *m/z* measured 368.1426 [M]$^+$; $C_{24}H_{21}N_2P$ calculated 368.14424.

Synthesis of 1-Phenyl-2,5-(4-pyridyl),8-(2′-pyridyl)phosphole **2**

To a THF solution (20 mL) of Cp_2ZrCl_2 (0.85 g, 2.91 mmol) and 1-(4-pyridyl),8-(2′-pyridyl)octa-1,7-diyne **4** (0.76 g, 2.91 mmol) was added dropwise (ca. 1 min), at −78°C, a hexane solution of *n*-BuLi (1.6 M, 3.82 mL, 6.11 mmol). The solution was warmed to room temperature and stirred overnight. To this solution, freshly distilled $PhPBr_2$ (0.6 mL, 2.91 mmol) was added at −78°C. The solution was allowed to warm to room temperature and stirred for 6 h. The solution was filtered on basic alumina (THF), and the volatile materials were removed under vacuo. The desired product was washed with pentane and obtained as a yellow solid (yield 46%, 0.49 g, 1.33 mmol). NMR^{1}H (200 MHz, $CDCl_3$): δ = 1.72 (m, 4H, C=CCH$_2$CH$_2$), 2.80 (m, 3H, C=CCH$_2$), 3.40 (m, 1H, C=CCH$_2$), 7.01(ddd, ^3J (H, H) = 7.3 Hz, ^4J (H, H) = 4.9 Hz, ^5J (H, H) = 1.3 Hz, 1H, pyridyl $H_{5'}$), 7.06–7.15 (m, 3H, phenyl H_{meta}, H_{para}), 7.25 (td, ^3J (H, H) = 8.0 Hz, ^5J (H, H) = 2.0 Hz, 1H, phenyl H_{ortho}), 7.29 (dd, ^3J(H, H) = 4.5 Hz, ^4J(H, H) = 1.6 Hz, 2H, pyridyl H_3), 7.44 (bd, ^3J(H, H) = 8.0 Hz, 1H, pyridyl $H_{3'}$), 7.56 (dd, ^3J(H, H) = 7.9 Hz, ^4J(H, H) = 1.8 Hz, 1H, pyridyl $H_{4'}$), 8.46 (dd, ^3J(H, H) = 4.6 Hz, ^4J (H, H) = 1.6 Hz, 2H, pyridyl H_2), 8.57 (ddd, ^3J (H, H) = 4.9 Hz, ^4J (H, H) = 1.8 Hz, ^5J(H, H) = 0.9 Hz, pyridyl $H_{6'}$). RMN ^{13}C-{1H} (50 MHz, $CDCl_3$): δ = 23.4 (s, C=CCCH$_2$CH_2), 23.5 (s, C=CCCH$_2$CH_2), 28.6 (s, C=C*C*H$_2$), 29.0 (s, C=C*C*H$_2$), 121.2 (s, pyridyl $C_{5'}$), 123.7 (d, ^3J(P, C) = 8.1 Hz, pyridyl $C_{3'}$), 124.1 (d, ^3J(P, C) = 9.0 Hz, pyridyl C_3), 128.9 (d, ^2J(P, C) = 8.2 Hz, phenyl C_{meta}), 129.8 (s, phenyl C_{para}), 131.5 (d, ^1J(P, C) = 11.9 Hz, phenyl C_{ipso}), 133.9 (d, ^2J(P, C) = 18.6 Hz, phenyl C_{ortho}), 136.4 (s, pyridyl $C_{4'}$), 145.2 (s, P–*C*=C), 145.3 (s, P–*C*=C), 147.8 (d, ^2J(P, C) = 10.0 Hz, P–C=C), 147.3 (d, ^2J (P, C)=11.0 Hz, P–C=C), 150.0 (s, pyridyl $C_{6'}$), 150.1 (s, pyridyl C_2), 155.8 (d, ^2J(P, C) = 18.1 Hz, pyridyl $C_{2'}$). NMR^{31}P-{1H}(81 MHz, $CDCl_3$): δ = +13.6. HR-MS (EI): *m/z* measured 368.1426 [M]$^+$; $C_{24}H_{21}N_2P$ calculated 368.14424.

Synthesis of the Derivative **5**

To a CH_2Cl_2 solution (5 mL) of the ligand **2** (0.040 g, 0.11 mmol), a CH_2Cl_2 solution (5 mL) of (tht)AuCl (0.035 g, 0.11 mmol) was added at room temperature. After 1 h, the solvent was evaporated. The residue was washed with pentane, and a yellow powder of **6** was recovered (yield 91%, 0.060 g, 0.10 mmol). NMR ^{1}H (200 MHz, $CDCl_3$): δ = 1.7–1.9 (m, 4H, C=CCH$_2$CH$_2$) 2.6–3.0). (m, 4H, C=CCH$_2$), 7.3–7.5 (m, 9H, pyridyl H_3, H_{Ph}), 8.4–8.6 (bs, 4H, pyridyl H_2). NMR ^{31}P{1H} (81 MHz, $CDCl_3$): δ = 42.1. elemental analysis (%) calcd for $C_{24}H_{21}N_2P_1Au_1Cl_1$: C 47.98, H 3.52, N 4.66; found: C 47.69, H 3.33, N 4.89.

Synthesis of the Derivative **6**

To a CH_2Cl_2 solution (5 mL) of the ligand **2** (0.040 g, 0.11 mmol), a CH_2Cl_2 solution (5 mL) of [$PtCl_2(CH_3CN)_2$] (0.038 g, 0.11 mmol) was added at room temperature. After 2 min, the solvent was evaporated. The residue was washed with pentane, and a yellow powder of **6** was recovered (yield 85%, 0.059 g, 0.09 mmol). NMR^{1}H (200 MHz, $CDCl_3$): δ = 1.8 (m, 4H, C=CCH$_2$CH_2), 2.5 (m, 2H, C=CCH$_2$CH_2), 2.9 (m, 1H, C=CCH_2), 3.2 (m, 1H, C=CCH$_2$), 7.24 (m, 3H, pyridyl $H_{5'}$, phenyl H_{meta}), 7.60 (d, ^3J (H, H) = 6.6 Hz, 2H, pyridyl H_3), 7.66 (m, 4H, pyridyl $H_{3'}$, phenyl H_{ortho}, phenyl H_{para}), 8.01 (bt, ^3J (H, H) = 8.0 Hz, ^4J (H, H) = 1.0 Hz, 1H, pyridyl $H_{4'}$), 8.51 (bd, ^3J(H, H) = 6.6 Hz, 2H, pyridyl H_2), 9.86 (bd, ^3J (H, H) = 5.6 Hz, 1H, pyridyl $H_{6'}$). NMR^{31}P{1H} (81 MHz, $CDCl_3$): δ = 36.6 ($^1J_{P-Pt}$ = 3694 Hz).

Synthesis of the Derivative **7**

To a CH_2Cl_2 solution (5 mL) of the ligand **2** (0.020 g, 0.055 mmol), a CH_2Cl_2 solution (5 mL) of $[PtCl_2(CH_3CN)_2]$ (0.019 g, 0.055 mmol) was added at room temperature. After 36 h, the solvent was evaporated. The residue was washed with pentane, and a yellow powder of **7** was recovered (yield 80%, 0.028 g, 0.04 mmol). NMR ^{1}H (200 MHz, $CDCl_3$): δ 1.9 (m, 4H, C=CCH$_2$C*H*$_2$), 2.9 (m, 2H, C=CCH$_2$), 4.66 (bd, ^2J(P, H) = 8.4 Hz, C=C*H*), 6.3 (m,1H, PC*H*), 6.9–8.0 (m, 11H, pyridyl H$_{3'}$, pyridyl H$_2$, pyridyl H$_3$, pyridyl H$_{5'}$, phenyl H$_{ortho}$, phenyl H$_{meta}$, phenyl H$_{para}$), 8.20 (bt, 1H, ^3J (H, H) = 5.6 Hz, pyridyl H$_{4'}$), 10.15 (d, ^3J(H, H) = 7 Hz, pyridyl H$_{6'}$). NMR ^{31}P{1H}(81 MHz, $CDCl_3$): δ = 40.5 ($^1J_{P\text{-}Pt}$ = 3815 Hz); elemental analysis (%) calcd for $C_{24}H_{21}N_2P_1Pt_1Cl_2$: C 45.44, H 3.34, N 4.42; found: C 45.69, H 3.12, N 4.09.

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