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Journal of Organometallic Chemistry 643–644 (2002) 4–11

Journal of Organometallic Chemistry

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Palladium(II) ion promoted hydroamination of di(phenylethynyl)phenylphosphine and aniline: a facile synthesis of a six-membered P–N heterocycle

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Received 3 May 2001; accepted 21 June 2001

Dedicated to Professor F. Mathey on the occasion of his 60th birthday, with our best wishes and most sincere congratulations

Abstract

The six-membered aromatic heterocycle 1,4-2H-1,2,4,6-tetraphenyl-1,4-azaphosphabenzene was generated efficiently via a $[PdCl_2(NCMe)_2]$ promoted hydroamination between $PhP(C{\equiv}CPh)_2$ and aniline. The heterocyclization reaction adopts a stepwise mechanism during which the unstable intermediate imino complex *cis*-dichloro{1,2-diphenyl-3-phenyl(phenylethynyl)phosphino-1-aza-1-propene}palladium(II) is formed. The end product of the cyclization reaction is a palladium complex in which the six-membered aromatic P–N heterocyclic ring is coordinated to the metal center as a typical monodentate ligand via phosphorus. The azaphospha heterocycle can subsequently be liberated from the palladium reaction activator as an air-stable yellow solid by treating the palladium complex with KCN. In contrast to the intermediate imino-complex, where the C=N is readily hydrolyzed by HCl, the aromatic heterocycle is stable in strongly acidic environments.

Keywords: Azaphospha heterocycle; Phosphinoalkyne; Hydroamination reaction; Imino-phosphine; Acid hydrolysis; Crystal structures

1. Introduction

The syntheses and the reactions of heterocyclic phosphorus compounds have been extensively studied over many years by Mathey and his co-workers [1]. These heterocycles have been shown to have rich metal–ligand chemistry. For example, they are able to form the classic P–M bonds and participate in the π-accepting "ring to metal" bonding [2]. Among the various families of phospha-heterocycles, the heteroaromatic five-membered phosphole core is perhaps the best-studied system, both by the synthetic and theoretical chemists. Similarly, the six-membered phosphinine core has also received considerable attention and has been the subject of a number of theoretical investigations [3]. In particular, studies have been focused on their chemical relationships with analogous pyridine derivatives, and on their phosphorus–carbon double bond characters in the conjugative interaction [4]. More recently, studies have shown that successive replacement of the aromatic-carbons in phosphinine by phosphorus [5] or nitrogen [6] significantly affects the aromaticity of the six-membered ring, enhancing the ring reactivity markedly. However, the syntheses of these interesting six-membered heterocycles generally involve inefficient multi-step processes. The literature methods generally involved the initial oxidation and hydrolysis of bis-alkynylphosphines into the corresponding diketo phosphine oxides followed by the silane compound promoted reductive couplings between the diketo-phosphine oxides and the selected amines under prolonged and strong heating conditions [7]. In some cases, it was necessary to conduct the reductive coupling reaction in boiling toluene for 3 days. In this article, we report a simple and efficient approach for the preparation of a

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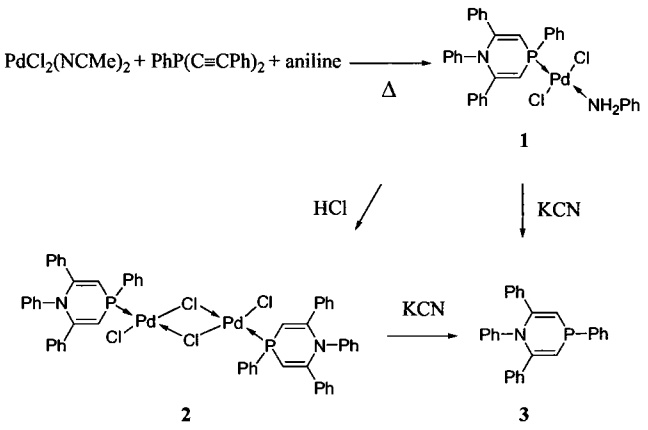
0022-328X/02/$ - see front matter
PII: S0022-328X(01)01074-9

six-membered P–N heterocycle 1,4-2H-1,2,4,6-tetraphenyl-1,4-azaphosphinine from the palladium(II) ion promoted heterocyclization reaction between di(phenylethynyl)phenylphosphine and aniline.



Scheme 1.

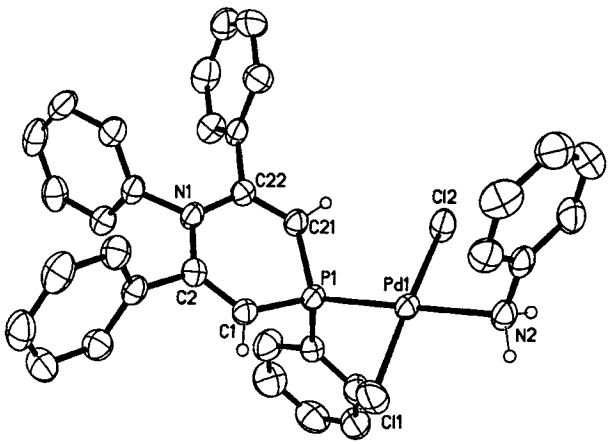


Fig. 1. Molecular structure of complex **1**.

Table 1
Selected bond distances (Å) and angles (°) of complex **1**

Bond lengths			
Pd(1)–P(1)	2.231(1)	Pd(1)–N(2)	2.147(2)
Pd(1)–Cl(1)	2.296(1)	Pd(1)–Cl(2)	2.302(1)
P(1)–C(15)	1.821(2)	P(1)–C(21)	1.766(2)
P(1)–C(1)	1.770(2)	C(1)–C(2)	1.351(3)
C(21)–C(22)	1.342(3)	N(1)–C(2)	1.392(3)
N(1)–C(22)	1.398(3)	N(1)–C(9)	1.463(3)
Bond angles			
P(1)–Pd(1)–Cl(1)	90.1(1)	P(1)–Pd(1)–N(2)	179.0(1)
P(1)–Pd(1)–Cl(2)	91.1(1)	Cl(1)–Pd(1)–N(2)	90.7(1)
Cl(1)–Pd(1)–Cl(2)	176.8(1)	N(2)–Pd(1)–Cl(2)	88.0(1)
C(15)–P(1)–Pd(1)	107.5(1)	C(1)–P(1)–C(15)	109.0(1)
C(1)–P(1)–C(21)	98.8(1)	C(21)–P(1)–Pd(1)	115.3(1)
C(1)–P(1)–Pd(1)	118.2(1)	C(1)–P(1)–C(15)	109.0(1)
C(22)–C(21)–P(1)	125.4(2)	C(2)–C(1)–P(1)	124.9(2)
C(2)–N(1)–C(22)	122.0(2)	C(2)–N(1)–C(9)	120.0(2)
C(9)–N(1)–C(22)	116.0(2)	Pd(1)–N(2)–C(29)	112.5(1)
C(1)–N(2)–N(1)	124.2(2)	N(1)–C(22)–C(21)	124.0(2)

2. Results and discussion

2.1. Formation of a 1,4-azaphosphabenzene heterocycle

No reaction between di(phenylethynyl)phenylphosphine and aniline was observed in the absence of a transition metal ion. However, in the presence of $PdCl_2(NCMe)_2$ as the reaction promoter, the cyclization reaction between di(phenylethynyl)phenylphosphine and excess aniline proceeded smoothly in acetonitrile at 75 °C (Scheme 1). The reaction was monitored by ^{31}P-NMR spectroscopy and was found to be complete within 3 h. The ^{31}P-NMR spectrum of the crude reaction mixture in $CDCl_3$ exhibited only one singlet at δ −10.8, thus indicating the generation of a sole product in this reaction. The product was purified by column chromatography and re-crystallized from dichloromethane–diethyl ether and was obtained as orange prisms in 59% yield, m.p. > 225 °C. Fig. 1 shows the X-ray structure of the product palladium(II) complex **1** which contains the monodentate P–N heterocycle, a coordinated aniline from the excess reagent used, and two *trans*-orientated chloro ligands. Selected bond distances and angles are given in Table 1. The X-ray structural analysis thus establishes unambiguously that the palladium(II) ion promoted hydroamination reaction between di(phenylethynyl)phenylphosphine and aniline indeed occurred and the desired six-membered P–N heterocycle was generated. The geometry at palladium is slightly distorted square plane with angles in the ranges of 88.0(1)–91.1(1)° and 176.8(1)–179.0(1)° and a mean deviation from planarity of 0.025 Å. The Pd(1)–P(1) [2.231(1) Å], Pd(1)–N(2) [2.147(2) Å], Pd(1)–Cl(1) [2.296(1) Å], and Pd(1)–Cl(2) [2.302(1) Å] bond distances are typical. The geometry at phosphorus is distorted tetrahedral with angles in the range of 98.8(1)–118.2(1)°. The distortions involve the contraction of C(1)–P(1)–C(21) to 98.8(1)° and the drastic enlargement of C(1)–P(1)–Pd(1) and C(21)–P(1)–Pd(1) to 118.2(1) and 115.3(1)°, respectively. Most importantly, the six atoms in the heterocyclic ring lie in one plane, with a maximum deviation of only 0.03 Å. Furthermore, the geometry at N(1) is trigonal-planar with angles in the range of 116.0(2)–122.0(2)°, indicating that the nitrogen atom in the six-membered ring adopts the classic sp^2 hybridization. These structural features are consistent with the aromatic nature of the P–N heterocycle. In agreement with the solid state structural studies, the ^{1}H-NMR spectrum of **1** in $CDCl_3$ recorded a doublet for the two identical PC*H* protons in the low field region (δ 7.73, $^2J_{PH} = 13.7$ Hz).

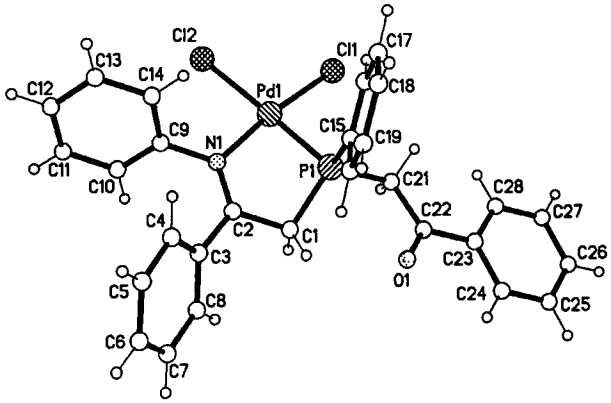


Fig. 2. Molecular structure of complex **2**.

Table 2
Selected bond distances (Å) and angles (°) of complex **2**

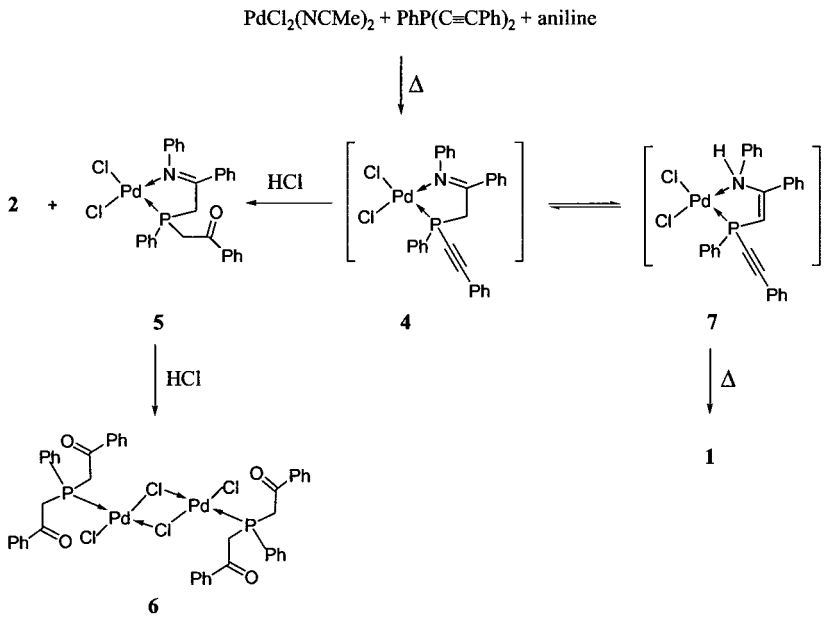
Bond lengths			
Pd(1)–Cl(1)	2.332(2)	C(21)–C(22)	1.337(8)
Pd(1)–Cl(1C)	2.458(2)	C(2)–N(1)	1.412(8)
Pd(1)–Cl(2)	2.271(2)	C(22)–N(1)	1.398(8)
Pd(1)–P(1)	2.204(2)	C(2)–C(3)	1.520(9)
P(1)–C(1)	1.767(6)	C(22)–C(23)	1.507(9)
P(1)–C(21)	1.753(6)	N(1)–C(9)	1.457(8)
C(1)–C(2)	1.330(8)	P(1)–C(15)	1.804(7)
Bond angles			
Cl(1)–Pd(1)–Cl(1C)	86.2(1)	C(15)–P(1)–Pd(1)	109.0(2)
Cl(1)–Pd(1)–Cl(2)	178.4(1)	P(1)–C(1)–C(2)	126.1(5)
Cl(1)–Pd(1)–P(1)	93.9(1)	C(1)–C(2)–N(1)	123.7(6)
Pd(1)–Cl(1)–Pd(1A)	93.8(1)	C(1)–C(2)–C(3)	118.8(6)
P(1)–Pd(1)–Cl(1C)	176.4(1)	C(3)–C(2)–N(1)	117.4(6)
P(1)–Pd(1)–Cl(2)	86.7(1)	C(2)–N(1)–C(22)	120.9(5)
Cl(2)–Pd(1)–Cl(1C)	93.3(1)	C(2)–N(1)–C(9)	119.2(5)
Pd(1)–Cl(1C)–Pd(1A)	93.8(6)	C(9)–N(1)–C(22)	119.7(5)
Cl(1)–Pd(1A)–Cl(1C)	86.2(1)	N(1)–C(22)–C(21)	125.2(6)
C(1)–P(1)–Pd(1)	116.2(2)	N(1)–C(22)–C(23)	119.1(6)
C(1)–P(1)–C(21)	98.8(3)	C(23)–C(22)–C(21)	115.6(6)
C(21)–P(1)–C(15)	108.6(3)	C(22)–C(21)–P(1)	125.1(5)
C(21)–P(1)–Pd(1)	117.4(2)	C(1)–P(1)–C(15)	105.9(3)
C(1)–P(1)–C(15)	105.9(3)	P(1)–C(15)–C(16)	118.5(5)

The coordinated aniline ligand in complex **1** could be removed chemoselectively by treatment with concentrated hydrochloric acid to generate the dimeric complex **2**. The highly crystalline dimer **2** readily crystallized from dichloromethane–diethyl ether as orange prisms in 95% yield. The ^{31}P-NMR spectrum of **2** in DMSO-d_6 exhibits a sole singlet at δ −9.1. A single crystal X-ray structural analysis of **2** was achieved (Fig. 2). Selected bond distances and angles are given in Table 2. The structural studies of **2** reveal that the chloro-bridged dipalladium(II) complex has crystallographic inversion symmetry, with each palladium atom coordinated to one P–N heterocycle and two bridging and one terminal chloro ligands. The monodentate P–N heterocycle ligands adopt a *trans* geometry in solid state. The four-membered di-μ-chlorobispalladium bridging unit is planar. The palladium coordination sphere, however, is distorted slightly from the square-planar with the angles in the ranges of 86.2(1)–93.9(1) and 176.4(1)–178.4(1)°. Similar to that observed in the monomeric complex **1**, the six-membered heterocyclic rings in **2** adopt a near-planar geometry, the maximum deviation from planarity being 0.02 Å. The nitrogen center is trigonal-planar and adopts the sp^2 hybridization, with angles in the range of 119.7(5)–120.9(5)°. It is important to note that the isolation of **2** from the hydrochloric acid reaction with **1** unambiguously established that the P–N heterocycle is stable in strong acidic conditions.

The six-membered P–N heterocycle could be liberated quantitatively both from the monomeric complex **1** and from the dimeric species **2** by treatment with aqueous potassium cyanide. Thus the P–N heterocycle **3** was obtained as air-stable yellow solids. The ^{31}P-NMR spectrum of the liberated heterocycle in $CDCl_3$ exhibits a singlet at δ −41.6.

2.2. Mechanistic investigations

From a mechanistic standpoint, the formation of the six-membered P–N heterocycle involves a hydroamination reaction between aniline and both alkyne groups in di(phenylethynyl)phenylphosphine. It has been well established that this class of hydroamination process can be activated via metal complexation at the amine function or at the alkyne moiety [8]. In the above reaction, however, the kinetic activation step may have involved the coordination of both di(phenylethynyl)phenylphosphine and aniline on the palladium(II) activator, although the thermodynamic heterocyclic product was isolated as a simple monodentate phosphorus ligand. Furthermore, the two alkyne groups could adopt a concerted hydroamination reaction mechanism to form the P–N ring or proceeded the heterocyclization process via a step-wise fashion. In order to establish the reaction mechanism for this cyclization reaction, we attempted to isolate and identify all possible intermediates generated in the reaction. To facilitate the isolation of these reactive species, a similar palladium(II) promoted cyclization reaction was repeated in which only two molar equivalents of aniline were used and the reaction mixture was heated in acetonitrile at 75 °C for 0.5 h (Scheme 2). At this stage, the ^{31}P-NMR spectrum of the reaction mixture in $CDCl_3$ exhibited only one new singlet at δ 12.0. This signal had not been observed previously and could be due to a key intermediate generated at the early stage of the heterocyclization reaction. Unfortunately, attempts to isolate this intermediate were unsuccessful as it was found to be a chemically reactive species that transformed slowly into the heterocyclic complex **1**, even at room temperature. The reaction could however, be quenched with acid. Thus when this reactive material was briefly treated



Scheme 2.

with concentrated hydrochloric acid, the dimeric complex **2** was obtained in 34% yield. In addition, the acid treatment also produced a novel imino-phosphine complex **5** as a minor product in 5% isolated yield. The molecular structure of **5** is depicted in Fig. 3. Selected bond distances and angles are given in Table 3. The structural investigations reveal that **5** is a *cis*-dichloro palladium complex containing a novel 5-membered imino-phosphine chelate. The geometry at palladium is slightly distorted square planar with angles at palladium in the ranges of 81.2(1)–95.2(1) and 172.5(1)–175.4(1)°. The N(1)–C(2) [1.294(6) Å] and O(1)–C(22) [1.220(5) Å] distances are typical for the nitrogen–carbon and oxygen–carbon double bonds, respectively. On the other hand, the C(1)–C(2) distance [1.496(6) Å] is typical for a carbon–carbon single bond. Consistent with the formation of a keto and a imino functions, the IR spectrum (KBr) of **5** exhibited strong absorption signals at 1670.1 cm^{-1} ($\nu_{C=O}$) and 1591.8 cm^{-1} ($\nu_{C=N}$).

In $CDCl_3$ the ^{31}P-NMR spectrum of **5** exhibited a singlet at δ 41.7. The ^{1}H-NMR signals due to the four non-equivalent PC*H* protons in **5** were observed as individual doublet of doublet at δ 4.12 ($^2J_{HH} = 18.5$ Hz, $^2J_{PH} = 14.4$ Hz), 4.39 ($^2J_{HH} = 16.9$ Hz, $^2J_{PH} = 12.5$ Hz), 4.91 ($^2J_{HH} = 16.9$ Hz, $^2J_{PH} = 10.8$ Hz) and 5.13 ($^2J_{HH} = 18.5$ Hz, $^2J_{PH} = 12.9$ Hz). The presence of these ^{1}H-NMR signals confirm that the imino-phosphine chelate is stable in solution and does not undergo the imine–enamine tautomeric transformation rapidly into its enamino counterpart [9]. Furthermore, the complex is found to be stable towards prolonged heating. The ^{31}P-NMR studies confirmed that the complex remained unchanged after it had been heated in acetonitrile at 75 °C for 3 h. Addition of aniline to this reaction sample also did not initiate any further transformation. However the imino-phosphine chelate in **5** is unstable in strong acidic conditions. For example, further treatment of **5** with hydrochloric acid resulted in the cleavage of the Pd–N and the imino C=N bonds to form the monodentate keto phosphine ligands in complex **6**. The dimeric keto-phosphine complex was obtained as orange prisms in 85% yield. The molecular connectivity of **6** has been established unambiguously by X-ray crystallography and shows the structure to be the centrosymmetric dimer as illustrated in Fig. 4. The planar Pd_2Cl_2 ring has asymmetric Pd–Cl linkages with that *trans* to Cl(2) [2.325(1) Å] being significantly shorter than that *trans* to phosphorus [2.412(1) Å]; the Pd–Cl(2) distance is 2.271(1) Å. The Pd–P bond length [2.220(1) Å] is marginally longer than the analogous distance in **2**. The palladium coordination plane is planar to within only 0.053 Å reflecting the non-linear P–Pd–Cl(1) angle of

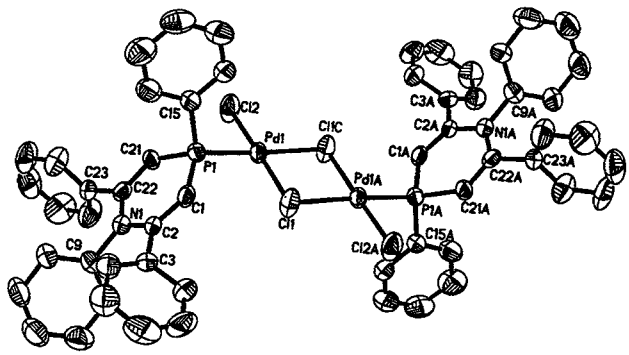


Fig. 3. Molecular structure of complex **5**.

Table 3
Selected bond distances (Å) and bond angles (°) of complex **5**

Bond lengths			
Pd(1)–Cl(1)	2.295(1)	P(1)–C(21)	1.818(4)
Pd(1)–Cl(2)	2.367(1)	C(21)–C(22)	1.511(6)
Pd(1)–P(1)	2.190(1)	C(22)–O(1)	1.220(5)
Pd(1)–N(1)	2.068(3)	N(1)–C(9)	1.451(5)
P(1)–C(1)	1.817(4)	C(2)–C(3)	1.485(6)
C(1)–C(2)	1.496(6)	P(1)–C(15)	1.811(4)
N(1)–C(2)	1.294(6)	C(22)–C(23)	1.485(6)
Bond angles			
Cl(1)–Pd(1)–Cl(2)	92.2(1)	C(1)–C(2)–C(3)	115.7(4)
Cl(1)–Pd(1)–N(1)	172.5(1)	C(2)–C(1)–P(1)	106.6(3)
Cl(1)–Pd(1)–P(1)	91.4(1)	C(1)–P(1)–Pd(1)	99.7(2)
Cl(2)–Pd(1)–N(1)	95.2(1)	C(1)–P(1)–C(15)	107.8(2)
Cl(2)–Pd(1)–P(1)	175.4(1)	C(15)–P(1)–C(21)	108.3(2)
N(1)–Pd(1)–P(1)	81.2(1)	Pd(1)–P(1)–C(21)	120.4(2)
Pd(1)–N(1)–C(9)	120.5(3)	P(1)–C(21)–C(22)	113.9(3)
Pd(1)–N(1)–C(2)	120.0(3)	C(21)–C(22)–O(1)	120.3(4)
C(2)–N(1)–C(9)	119.4(4)	C(21)–C(22)–C(23)	118.3(4)
N(1)–C(2)–C(1)	118.2(4)	O(1)–C(22)–C(23)	121.4(4)
N(1)–C(2)–C(3)	126.0(4)	C(1)–P(1)–C(21)	111.3(2)

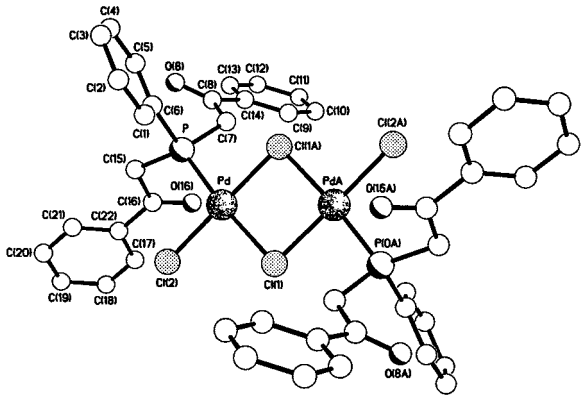


Fig. 4. Molecular structure of complex **6**.

174.5(1)°. The angles at phosphorus range between 103.6(2) and 117.2(2)°, the largest departure from tetrahedral being that for Pd–P–C(15) and reflecting the steric interaction between Cl(2) and the C(15) methylene group. There are no packing interactions of note, the shortest intermolecular contact being 2.94 Å between O(8) and its symmetry related counterpart; the geometry of this approach, however, does not indicate a carbonyl···carbonyl dipole···dipole interaction.

The isolation of both imino-phosphine **5** and keto-phosphine complex **6** unveiled several crucial mechanistic issues regarding the formation of the P–N heterocycle. For instance, the isolation of the imino-phosphine chelate in **5** confirmed that only one of the two alkyne substituents in di(phenylethynyl)phenylphosphine was initially involved in the hyroamination reaction with aniline. Thus the heterocyclization reaction between coordinated di(phenylethynyl)phenylphosphine and aniline proceeds via a stepwise reaction mechanism. Thus we believe that the sole reactive intermediate that is initially generated is the imino-phosphine complex **4** or its enamino analogue **7**, or an equilibrium mixture of both tautomeric complexes **4** and **7** (Scheme 2). We have recently reported a similar imine–enamine tautomerism with several chiral palladium(II) complexes containing the bidentate ligand $Ph_2PCH_2C(Ph)$=NPh [9]. In principle, complex **7** can undergo the heterocyclization reaction. Sterically, however, it is unlikely that the second intra-chelate hydroamination reaction can occur while both phosphorus and nitrogen donors are coordinated to the palladium activator. It is noteworthy, however, that bidentate P–N ligands frequently form labile complexes with palladium(II) [10]. We therefore also believe that the Pd–N bond in **7** is kinetically labile, and thus the enamino-nitrogen can easily leave the metal activator and undergo a further hydroamination reaction with the second alkyne substituent on phosphorus to form the P–monodentate heterocycle. The vacant coordination site generated from the original Pd–N bond cleavage is then taken up by aniline to form complex **1**. On the other hand, when the intermediate **4** was briefly quenched with hydrochloric acid, the remaining alkyne substituent was hydrolyzed to form the ketone function but the imino-phosphine chelate remained intact. Considering the structure of the hydrolyzed complex **5**, it is interesting to note that a combination of the double bond rearrangement and a simple intramolecular condensation reaction between the keto group and the imine function may also result in the formation of the six-membered P–N heterocycle. However, attempts to carry out this intra-molecular heterocyclization reaction under a variety of viable conditions were not successful. We therefore infer that complex **5** is not one of the possible intermediates in the current heterocycle synthesis.

In conclusion, the present study provides a novel and efficient synthetic route to the preparation of the six-membered P–N heterocycles via the hydroamination of the prochiral phosphinoalkyne. Currently, we are applying this methodology to the synthesis of a range of substituted azaphosphinines.

3. Experimental

Reactions involving air-sensitive compounds were performed under a positive pressure of purified nitrogen. NMR spectra were recorded at 25 °C on Bruker ACF300 and AMX500 spectrometers. Elemental analyses were performed by the Elemental Analysis Laboratory of the Department of Chemistry at the National University of Singapore. The phosphinoalkyne phenyl(diphenylethynyl)phosphine was prepared by the literature method [11].

3.1. Heterocyclization reaction: synthesis of the monomeric complex **1**

A mixture of $PdCl_2(NCMe)_2$ (1.0 g, 3.86 mmol), $PhP(C{\equiv}CPh)_2$ (1.2 g, 3.86 mmol) and aniline (1.8 g, 19.30 mmol) in MeCN (250 ml) was refluxed at 75 °C for 3 h. The solvent was the removed under reduced pressure to give a black residue. The crude product was purified by silica gel column chromatography (EtOAc–hexane 1:1, v/v). The product was obtained as orange crystals after crystallization from CH_2Cl_2–Et_2O (1.5 g, 58.8%) ^{31}P-NMR ($CDCl_3$) δ −10.8 (s). ^{1}H-NMR ($CDCl_3$) δ 7.73 (d, 2H, $^2J_{PH} = 13.7$ Hz, =CH), 8.73–9.50 (m, 23 H, aromatics), 10.08 (dd, 2H, $^3J_{HH} = 7.4$ Hz, $^3J_{PH} = 12.6$ Hz, *o*-P*Ph*). Anal. Found: C, 60.4; H, 4.1; N, 4.5. Calc. for $C_{34}H_{29}N_2Cl_2PPd$: C, 60.6; H, 4.3; N, 4.1%.

3.2. Acid hydrolysis of monomer **1** and synthesis of the dimer **2**

The monomeric complex **1** (0.5 g, 0.74 mmol) was treated with concentrated HCl (20 ml) in CH_2Cl_2 (50 ml) for 15 min. The solution was washed with water, and dried over anhydrous $MgSO_4$. Crystallization of the crude product from CH_2Cl_2–Et_2O gave the dimeric complex **2** as orange prisms (0.42 g, 94.7%). ^{31}P-NMR (DMSO-d_6) δ −9.1 (s). ^{1}H-NMR (DMSO-d_7) δ 5.66 (d, 4H, $^2J_{PH} = 12.5$ Hz, =CH), 6.89–7.66 (m, 36H, aromatics), 8.17 (dd, 4H, $^3J_{HH} = 6.4$ Hz, $^3J_{PH} = 12.0$ Hz, *o*-P*Ph*). Anal. Found: C, 57.5; H, 4.0; N, 2.4. Calc. for $C_{56}H_{44}N_2Cl_4P_2Pd_2$: C, 57.9; H, 3.8; N, 2.4%.

3.3. Liberation of the six-membered P–N heterocycle. Isolation of 1,4-2H-1,2,4,6-tetraphenyl-1,4-azaphosphabenzene (3)

A solution of complex **1** (0.12 g, 0.18 mmol) in CH_2Cl_2 (20 ml) was stirred vigorously with a saturated aqueous solution of KCN (0.5 g, 7.69 mmol) for 30 min. The resulting yellow organic layer was separated, washed with water, and dried over anhydrous $MgSO_4$. Upon removal of the solvent, the product was obtained as air-stable pale yellow solids (72 mg, 72%). ^{31}P-NMR ($CDCl_3$) δ −41.6 (s). ^{1}H-NMR ($CDCl_3$) δ 5.79 (d, 2H, $^2J_{PH} = 5.6$ Hz, 2 × =CH), 6.78–7.70 (m, 20H, aromatics). Anal. Found: C, 83.8; H, 5.1; N, 3.1. Calc. for $C_{28}H_{22}NP$: C, 83.4; H, 5.5; N, 3.5%. The heterocycle could be liberated similarly from the dimer **2**.

Table 4
Selected bond distances (Å) and bond angles (°) of the complex **6**

Bond lengths			
Pd–P	2.220(1)	P–C(15)	1.814(4)
Pd–Cl(1A)	2.325(1)	P–C(6)	1.813(2)
Pd–Cl(1)	2.412(1)	P–C(7)	1.833(5)
Pd–Cl(2)	2.271(1)	C(7)–C(8)	1.514(6)
Bond angles			
P–Pd–Cl(2)	92.6(1)	P–Pd–Cl(1A)	89.6(1)
Cl(2)–Pd–Cl(1A)	177.3(1)	P–Pd–Cl(1)	174.5(1)
Cl(2)–Pd–Cl(1)	91.9(1)	Cl(1)–Pd–Cl(1A)	86.0(1)
Pd–Cl(1)–PdA	94.1(1)	C(6)–P–C(15)	103.6(2)
C(6)–P–C(7)	109.4(2)	C(15)–P–C(7)	110.0(2)
C(6)–P–Pd	111.8(1)	C(15)–P–Pd	117.2(2)
C(7)–P–Pd	104.8(2)	P–C(7)–C(8)	119.6(3)

3.4. Isolation of the dichloro imino-phosphine complex **5**

A mixture of $PdCl_2(NCMe)_2$ (0.5 g, 1.93 mmol), $PhP(C{\equiv}CPh)_2$ (0.6 g, 1.93 mmol) and aniline (0.4 g, 3.86 mmol) in MeCN (75 ml) was refluxed at 75 °C for 0.5 h. The reaction was allowed to cool to room temperature (r.t.) and the solvent was removed immediately under reduced pressure to give a black residue. The residue was redissolved in CH_2Cl_2 (30 ml) and treated with concentrated HCl (10 ml) for 15 min. The solution was washed with water, and dried over anhydrous $MgSO_4$. Both the dimeric complex **2** (0.25 g, 34%) and the hydrolyzed imino-phosphine complex **5** were obtained separately by the slow fractional crystallization of the residue from CH_2Cl_2–Et_2O. Complex **5** was isolated as highly crystalline yellow prisms (15 mg, 5%). ^{31}P-NMR (CD_2Cl_2): δ 41.7(s). ^{1}H-NMR (CD_2Cl_2) δ 4.12 (dd, 1H, $^2J_{HH} = 18.5$ Hz, $^2J_{PH} = 14.4$ Hz, C_aHH), 4.39 (dd, 1H, $^2J_{HH} = 16.9$ Hz, $^2J_{PH} = 12.5$ Hz, C_bHH), 4.91 (dd, 1H, $^2J_{HH} = 16.9$ Hz, $^3J_{PH} = 10.8$ Hz, C_bHH), 5.13 (dd, 1H, $^2J_{HH} = 18.5$ Hz, $^2J_{PH} = 12.9$ Hz, C_aHH), 6.87–7.95 (m, 18H, aromatics); 8.02 (dd, 2H, $^3J_{HH} = 6.0$ Hz, $^3J_{PH} = 12.8$ Hz, *o*-P*Ph*). IR (cm^{-1}, KBr) 1670.1, 1591.8, 1445.4, 1288.0, 1186.1, 986.5, 743.4, 692.7. Anal. Found: C, 55.8; H, 4.1; N, 2.4. Calc. for $C_{28}H_{24}NCl_2OPPd$: C, 56.2; H, 4.0; N, 2.3%.

3.5. Acid hydrolysis of **5** and isolation of the dimeric keto-complex **6**

A solution of the dichloro complex **5** (50 mg, 0.08 mmol) in CH_2Cl_2 (25 ml) was treated with concentrated HCl (10 ml) at r.t. for 2 h. The organic layer was separated, washed with water and then dried over anhydrous $MgSO_4$. Removal of the solvent gave a yellow residue. The dimer **6** (Table 4) was obtained as orange prisms by crystallization of the residue from CH_2Cl_2–Et_2O (37 mg, 85%). ^{31}P-NMR ($CDCl_3$) δ 16.6 (s). ^{1}H-NMR ($CDCl_3$) δ 4.40 (ABX, 4H, $^2J_{PH} = 16.5$, $^2J_{HH} = 13.7$, 2 × CH_2), δ 4.67 (ABX, 4H, $^2J_{PH} = 16.7$, $^2J_{HH} = 10.8$, 2 × CH_2), 7.40–7.92 (m, 26H, aromatics), 8.02 (dd, 4H, $^3J_{PH} = 12.7$, $^3J_{HH} = 7.2$, *o*-PPh × 2) Anal. Found: C, 50.2; H, 3.7. Calc. for $C_{28}H_{24}NCl_2O_4PPd$: C, 50.5; H, 3.7%.

Table 5
Crystallographic data for complexes **1**, **2**, **5** and **6**

	1	**2**	**5**	**6**
Formula	$C_{34}H_{29}Cl_2N_2PPd$	$C_{56}H_{44}Cl_4N_2P_2Pd_2{\cdot}2CH_2Cl_2$	$C_{28}H_{24}Cl_2NOPPd{\cdot}CH_2Cl_2$	$C_{44}H_{38}O_4P_2Cl_4Pd_2$
Formula weight	673.86	1331.32	683.68	1047.28
Space group	$P2_1/c$	$P2_1/c$	$P\bar{1}$	$P\bar{1}$
Crystal system	Monoclinic	Monoclinic	Triclinic	Triclinic
Unit cell dimensions				
a (Å)	14.119(1)	11.807(1)	9.820(2)	9.533(1)
b (Å)	17.495(1)	16.211(1)	12.586(2)	10.273(1)
c (Å)	13.266(1)	15.007(1)	14.066(3)	11.466(2)
α (°)	–	–	113.843(3)	77.019(9)
β (°)	111.410(1)	91.038(1)	99.531(3)	86.180(12)
γ (°)	–	–	103.087(3)	80.614(10)
V (Å^3)	3050.7(3)	2872.0(2)	1482.8(5)	1079.1(3)
Z	4	2	2	1
T (K)	223	223	173	293
D_{calc} (g cm^{-3})	1.467	1.540	1.531	1.612
λ (Å)	0.71073	0.71073	0.71073	1.54178
μ (cm^{-1})	8.62	10.93	10.63	100.4
R_1	0.0298	0.0834	0.0432	0.0389
Rw	0.0665	0.1407	0.1263	0.1025

3.6. Crystal structure determination of *1*, *2*, *5* and *6*

Crystal data for all complexes and a summary of the crystallographic analyses are given in Table 5. For compounds **1**, **2** and **5**, diffraction data were collected at the National University of Singapore on a Siemens SMART OCD diffractometer with Mo–K_α radiation (graphite monochromator) using ω-scans. Compound **6** was analyzed at the Imperial College using a Siemens P4/PC diffractometer with Cu–K_α radiation (graphite monochromator) using ω-scans. For all four compounds, semiempirical absorption corrections were applied and refinements by full-matrix least-square were based on SHELXL 93 [12]. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were introduced at fixed distance from carbon and nitrogen atoms and were assigned fixed thermal parameters.

4. Supplementary material

Crystallographic data for the structural analysis have been deposited in cif format with the Cambridge Crystallographic Data Centre, CCDC nos. 162699, 162700, 162701 and 162702 for compounds **1**, **2**, **5** and **6**, respectively. Copies of this data 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).

Acknowledgements

We are grateful to the National University of Singapore for the financial support, a Research Fellowship to S.S. and a PhD research scholarship to X.M.L. We express our appreciation to Professor G. Bertrand for his invitation to take part in this occasion.

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