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# Reaction of $\mu$ -ethynediyl dipalladium complexes with phenyl isocyanide in the presence of trialkylphosphines and the molecular structure of $\text{Cl}(\text{Et}_3\text{P})_2\text{PdC}(=\text{NPh})\text{C}\equiv\text{CC}(=\text{NPh})\text{Pd}(\text{PEt}_3)_2\text{Cl}$

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## Abstract

The reaction of  $\mu$ -ethynediyl dipalladium complexes (1) with 2 equiv of phenyl isocyanide in the presence of trialkylphosphines results in the insertion of one molecule of the isocyanide into each of the two Pd–C bonds and produces a new complex  $\text{Cl}(\text{R}_3\text{P})_2\text{PdC}(=\text{NPh})\text{C}\equiv\text{CC}(=\text{NPh})\text{Pd}(\text{PR}_3)_2\text{Cl}$  (3). Complex 3 was characterized by IR and mass, and <sup>1</sup>H, <sup>13</sup>C, and <sup>31</sup>P NMR spectra. No further insertion of the isocyanide into the Pd–C bonds of 3 was observed. The structure of  $\text{Cl}(\text{Et}_3\text{P})_2\text{PdC}(=\text{NPh})\text{C}\equiv\text{CC}(=\text{NPh})\text{Pd}(\text{PEt}_3)_2\text{Cl}$  (3a) has been established by a single-crystal X-ray diffraction analysis. The crystal data are as follows: space group  $P\bar{1}$ ,  $a = 12.840(3)$ ,  $b = 11.447(5)$ ,  $c = 9.069(2)$  Å,  $\alpha = 104.03(2)^\circ$ ,  $\beta = 100.02(2)^\circ$ ,  $\gamma = 105.76(3)^\circ$ ,  $V = 1202.7(7)$  Å<sup>3</sup>, and  $Z = 1$ .

**Key words:** Palladium; Acetylide; Imino; Isocyanide; Ethynediyl; Crystal structure

## 1. Introduction

The chemistry of hydrocarbon-bridged multi-nuclear transition metal complexes is a subject of intense research activity, because information on the chemical behaviour of hydrocarbon fragments in the complexes will help towards understanding the activation of substrates in the surface chemistry of heterogeneous catalysts [1]. Though several  $C_1$ -bridged dinuclear complexes are already known [2], there have appeared only a few reports of dinuclear complexes having a  $C_2$ -hydrocarbon bridge. The  $C_2$  bridges present the additional possibility of linking the two metals by a carbon–carbon single, double or triple bond [3–5]. Dinuclear complexes having C=C and C≡C bridges may be expected to exhibit unique properties owing to interaction between the two metals through a  $\pi$ -conjugated system.

We have been studying  $\mu$ -ethynediyl dinuclear complexes, in which two metal atoms are linked together by one acetylene unit [6]. Recently we have shown that two molecules of aryl isocyanides selectively insert into just one of the two Pd–C bonds of  $\mu$ -ethynediyl dipalladium complexes (1) (eqn. (1)) [7]. This reactivity is peculiar to the  $\mu$ -ethynediyl dinuclear complexes since other dipalladium complexes in which two metals are linked by conjugated acetylenes such as butadiyne and diethynylbenzene, as well as mononuclear acetylide complexes, gave a normal single-insertion product. Thus we have investigated the mechanism of selective double-insertion of isocyanides, and also examined the effect of additives such as excess isocyanides [8] and phosphines. Here we wish to report the reaction of  $\mu$ -ethynediyl dipalladium complexes with phenyl isocyanide in the presence of trialkylphosphines.

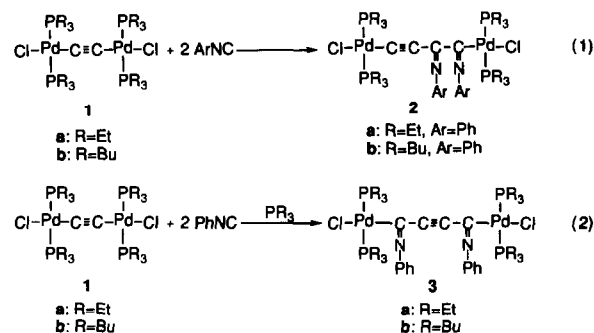
## 2. Results and discussion

The reaction of  $\mu$ -ethynediyl dipalladium complexes 1a with 2 equiv of aryl isocyanides selectively gives the double-insertion product 2 and, with a large excess of isocyanides under more severe conditions, produces

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isocyanide polymers in high yields [8]. When a free trialkylphosphine was added the reaction, however, gave neither the double-insertion product nor the polymeric product. In order to investigate this dramatic effect of the additive on the reaction, we carried out the reaction in the presence of phosphines and tried to isolate the reaction product.



Treatment of  $\mu$ -ethynediyl dipalladium complex (**1a**) with 2 equiv of phenyl isocyanide in the presence of 0.2 equiv of triethylphosphine in dichloromethane at room temperature produced a yellow complex (**3a**) along with a small amount of **2a**. Complex **3a** is air-stable and soluble in common organic solvents except aliphatic hydrocarbons. The FD mass spectrum of **3a** exhibited the molecular ion ( $m/z = 987$ ) corresponding to a product derived from one molecule of **1a** and two molecules of phenyl isocyanide. This composition of the molecule suggested that the yellow product might be **2a**. However, the IR spectrum of **3a** showed no absorption attributable to  $\nu(\text{C}\equiv\text{C})$ , but  $\nu(\text{C}=\text{N})$  absorption at  $1535 \text{ cm}^{-1}$ , while absorptions due to  $\nu(\text{C}\equiv\text{C})$  and  $\nu(\text{C}=\text{N})$  were clearly observed at  $2080 \text{ cm}^{-1}$  and  $1570 \text{ cm}^{-1}$ , respectively, for **2a** [7]. The Raman spectrum of **3a** exhibited an absorption at  $2160 \text{ cm}^{-1}$  due to  $\nu(\text{C}\equiv\text{C})$  as well as a signal at  $1522 \text{ cm}^{-1}$  due to  $\nu(\text{C}=\text{N})$ . These data indicate that **3a** must be symmetrical around the acetylene group. The symmetrical structure of complex **3a** was also supported by  $^{31}\text{P}$ ,  $^{13}\text{C}$  and  $^1\text{H}$  NMR spectrometry. The  $^{31}\text{P}$  NMR spectrum showed a single peak at  $\delta 19.4$ , suggesting that all the phosphine ligands are equivalent. In the  $^{13}\text{C}$  NMR spectrum characteristic resonances appeared at  $\delta 173.69$  for the imino carbons and at  $\delta 96.75$  for the acetylenic carbons as a single peak indicating a symmetrical structure of **3a**. Furthermore both the  $^1\text{H}$  and  $^{13}\text{C}$  spectra groups revealed that the two phenyl attaching to the imino nitrogens must be magnetically equivalent. On the basis of these spectroscopic data, complex **3a** could be identified as a symmetrical dinuclear di-imino complex which would be produced by the insertion of one molecule of isocyanide into each of the two Pd-C bonds (eqn. 2). Similarly the reaction of **1b** with

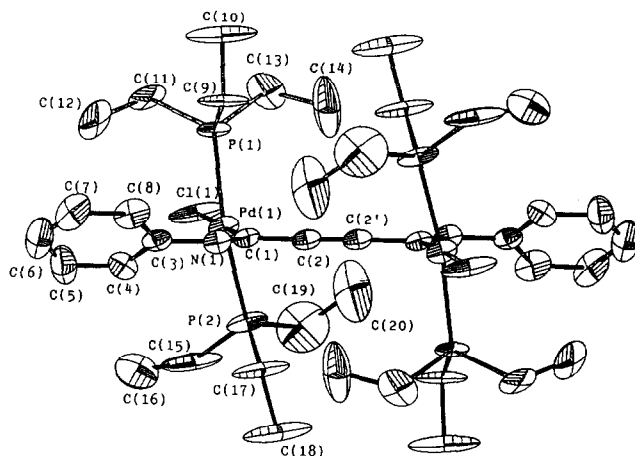


Fig. 1. A perspective view of  $\text{Cl}(\text{Et}_3\text{P})_2\text{PdC}(\text{=NPh})\text{C}\equiv\text{CC}(\text{=NPh})\text{Pd}(\text{PEt}_3)_2\text{Cl}$  (**3a**) showing the atom numbering scheme.

phenyl isocyanide in the presence of tributylphosphine gave complex **3b**.

The molecular structure of **3a** has been confirmed by a single-crystal X-ray diffraction study (Fig. 1). The crystallographic data and positional parameters are summarized in Tables 1 and 2, and selected bond distances and angles are listed in Table 3. As suggested by the spectroscopic analyses, **3a** has indeed a symmetrical structure around the acetylene bridge which is formed from the selective insertion of one molecule of the isocyanide into each of the two Pd-C bonds of **1a**. The molecule of **1a** is oriented around the crystallographic centre of symmetry. Therefore, the two  $\text{PdClP}_2\text{C}$  planes are parallel, in contrast with the dihe-

TABLE 1. Crystallographic data for **3a**

formula	$\text{C}_{40}\text{H}_{70}\text{Cl}_2\text{N}_2\text{P}_4\text{Pd}_2$
fw	986.65
crystal syst.	triclinic
space group	$\text{P}\bar{1}$
$a, \text{\AA}$	12.840(3)
$b, \text{\AA}$	11.447(5)
$c, \text{\AA}$	9.069(2)
$\alpha, \text{deg}$	104.03(2)
$\beta, \text{deg}$	100.02(2)
$\gamma, \text{deg}$	105.76(3)
$V, \text{\AA}^3$	1202.7(7)
$Z$	1
$D_{\text{calc}}, \text{g cm}^{-3}$	1.362
$\mu(\text{Mo K}\alpha), \text{cm}^{-1}$	10.03
$2\theta$ range, deg	$3 < 2\theta < 55$
no. of data collected	5530
no. of data with $F_o > 3\sigma(F_o)$	5049
no. of parameters	227
$R$	0.044
$R_w$	0.075

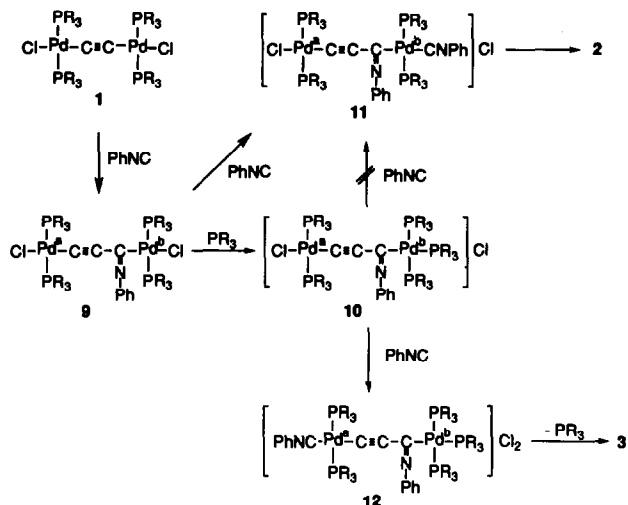
TABLE 2. Positional parameters and equivalent  $B$  values for complex **3a**

Atom	$x$	$y$	$z$	$B_{eq}, \text{\AA}^2$
Pd(1)	0.23232(2)	0.31493(2)	0.40942(3)	3.16(1)
Cl(1)	0.0584(1)	0.2851(2)	0.4828(2)	6.6(1)
P(1)	0.2720(1)	0.1811(1)	0.5496(1)	3.53(3)
P(2)	0.1990(1)	0.4738(1)	0.3071(2)	4.63(4)
N(1)	0.4079(2)	0.2683(3)	0.2446(3)	3.0(1)
C(1)	0.3781(3)	0.3380(3)	0.3518(4)	2.6(1)
C(2)	0.4658(3)	0.4518(3)	0.4537(4)	2.9(1)
C(3)	0.3329(3)	0.1256(3)	0.1359(4)	3.2(1)
C(4)	0.2216(4)	0.1317(4)	0.0693(4)	4.1(1)
C(5)	0.1574(4)	0.0151(5)	-0.0463(5)	5.4(1)
C(6)	0.2036(5)	-0.0791(5)	-0.0906(6)	5.9(2)
C(7)	0.3138(5)	-0.0593(4)	-0.0213(6)	5.7(2)
C(8)	0.3809(4)	0.0568(4)	0.0893(5)	4.7(1)
C(9)	0.4006(4)	0.1398(6)	0.5454(6)	5.2(2)
C(10)	0.4251(7)	0.0602(9)	0.655(1)	8.7(4)
C(11)	0.1589(4)	0.0308(5)	0.5095(6)	5.3(2)
C(12)	0.1335(7)	-0.0573(6)	0.3425(8)	8.2(3)
C(13)	0.2887(5)	0.2567(6)	0.7574(5)	6.1(2)
C(14)	0.3893(7)	0.3822(8)	0.8241(7)	9.0(3)
C(15)	0.0525(5)	0.4284(7)	0.176(1)	8.0(3)
C(16)	0.0264(7)	0.3238(9)	0.028(1)	10.0(3)
C(17)	0.2901(4)	0.5293(6)	0.1884(9)	6.7(2)
C(18)	0.2734(7)	0.6362(9)	0.121(1)	9.9(4)
C(19)	0.193(1)	0.6064(9)	0.454(1)	11.8(5)
C(20)	0.290(1)	0.6567(9)	0.596(1)	13.3(5)

dral angle of  $54.4(1)^\circ$  between the two  $\text{PdClP}_2\text{C}$  planes of **2a** [7b] and that of  $89.8(3)^\circ$  between the two  $\text{PtClP}_2\text{C}$  planes of  $\text{I}(\text{Me}_3\text{P})_2\text{PtC}\equiv\text{C}(\text{PMe}_3)_2\text{I}$  (**4**) [6b]. The  $\text{Pd}(1)-\text{C}(1)$  bond length of  $1.997(4) \text{ \AA}$  is comparable with those of  $1.992(8) \text{ \AA}$  in **2a** [7b] and  $1.98(1) \text{ \AA}$  in *trans*- $\text{PdCl}\{\text{C}(\text{N}=\text{C}_6\text{H}_4\text{OMe})\text{C}(\text{Me})=\text{NC}_6\text{H}_4\text{OMe}\}$ - $(\text{PPh}_3)_2$  (**5**) [9], and slightly longer than that of  $1.956(6) \text{ \AA}$  in  $\text{Pd}\{\text{C}(\text{=NR})\text{C}(\text{=NR})\text{C}(\text{=NR})\text{C}(\text{=NR})\text{CH}(\text{=NR})\}$ - $(\text{CNR})\text{Cl}$  (**6**) [10]. The imino N atom is found at a distance of  $3.008(3) \text{ \AA}$  from the  $\text{Pd}(1)$  atom. This is clearly a non-bonding distance. The dihedral angles between  $\text{Pd}(1)$  coordination plane and  $\text{Pd}(1)\text{C}(1)\text{N}(1)-\text{C}(2)\text{C}(3)$  or the phenyl group  $\text{C}(3)-\text{C}(8)$  are  $78.05$  and  $74.16^\circ$ , respectively. The former is similar to that of  $79.72^\circ$  in *trans*- $\text{Pt}\{\text{C}(\text{Me})=\text{NC}_6\text{H}_4\text{Cl}\}(\text{PEt}_3)_2$  (**7**), but the latter is slightly smaller than that of  $81.52^\circ$  in **7** [11]. The  $\text{C}\equiv\text{C}$  bond distance of  $1.209(5) \text{ \AA}$  is comparable

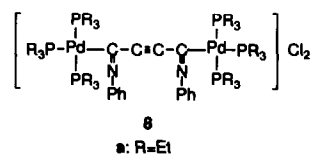
TABLE 3. Selected bond distances ( $\text{\AA}$ ) and angles (deg) for **3a**

$\text{Pd}(1)-\text{Cl}(1)$	2.400(2)	$\text{Pd}(1)-\text{P}(1)$	2.316(1)
$\text{Pd}(1)-\text{P}(2)$	2.335(2)	$\text{Pd}(1)-\text{C}(1)$	1.997(4)
$\text{C}(1)-\text{C}(2)$	1.441(4)	$\text{C}(1)-\text{N}(1)$	1.283(5)
$\text{C}(2)-\text{C}(2)$	1.209(5)		
$\text{Cl}(1)-\text{Pd}(1)-\text{P}(1)$	88.6(1)	$\text{Cl}(1)-\text{Pd}(1)-\text{P}(2)$	89.0(1)
$\text{Cl}(1)-\text{Pd}(1)-\text{C}(1)$	178.8(1)	$\text{P}(1)-\text{Pd}(1)-\text{P}(2)$	170.90(4)
$\text{P}(1)-\text{Pd}(1)-\text{C}(1)$	90.2(1)	$\text{P}(2)-\text{Pd}(1)-\text{C}(1)$	92.2(1)
$\text{Pd}(1)-\text{C}(1)-\text{N}(1)$	131.7(2)	$\text{Pd}(1)-\text{C}(1)-\text{C}(2)$	113.2(3)

Scheme 1. Reaction of **1** with phenyl isocyanide in the presence and in the absence of trialkylphosphine.

with that of  $1.20(1) \text{ \AA}$  in **2a** [7b] and slightly longer than that of  $1.18(5) \text{ \AA}$  in **4** [6b], due to the conjugation with the imino groups.

It should be noted that the reaction of **3a** with phenyl isocyanide did not give further insertion products, but that **3a** was recovered. In addition, **3a** did not isomerize to **2a**, and **2a** was not transformed into **3a**, suggesting that **3a** is not an intermediate of the selective double-insertion of isocyanide giving **2a**. On treatment of **1a** with 2 equiv of phenyl isocyanide in the presence of 2 equiv of triethylphosphine, a cationic complex **8a** was formed, though it could not be isolated in a pure form.



The complex was characterized by spectral analyses. The IR spectrum showed a  $\nu(\text{C}=\text{N})$  at  $1525 \text{ cm}^{-1}$  and the  $^{31}\text{P}$  NMR exhibited a doublet ( $J(\text{pp}) = 28 \text{ Hz}$ ) at  $\delta$  26.8 and a triplet at 19.9 in a 2:1 integral ratio. The formation of the phosphine-coordinated cationic complex implies that the reaction may proceed through a pathway leading to **3** as tentatively proposed in Scheme 1. A separate experiment traced by means of  $^{31}\text{P}$  NMR spectroscopy has shown that in the absence of free phosphines the double-insertion reaction proceeds through stepwise insertion of isocyanides into the  $\text{M}-\text{C}$  bonds of **1**, that is, the reaction of **1** with  $\text{RNC}$  gives the single-insertion product **9** at the first step, followed

by the coordination of RNC to Pd<sup>b</sup> and the subsequent insertion of RNC into the Pd<sup>b</sup>-C(=NR) bond to afford **2** [12]. In the case of the presence of free trialkylphosphines in the system the formation of **3** suggests, instead of **11**, an intermediate **10** in which the phosphine occupies the coordination site on Pd<sup>b</sup> and prevents the coordination of RNC on it. The coordination of RNC on Pd<sup>a</sup> of **10** leads to the formation of **3**, though the reason why the phosphine added prefers coordination on the Pd<sup>b</sup> to that on the Pd<sup>a</sup> has not yet been made clear.

### 3. Experimental section

All reactions were carried out under an atmosphere of nitrogen, but the workup was performed in air. <sup>1</sup>H and <sup>13</sup>C NMR were measured in CDCl<sub>3</sub> on a Bruker AM-360 spectrometer using SiMe<sub>4</sub> as an internal standard, and <sup>31</sup>P NMR (in CD<sub>2</sub>Cl<sub>2</sub>/CH<sub>2</sub>Cl<sub>2</sub> = 1/1) spectra on a JEOL FX-100 spectrometer against an external PPh<sub>3</sub> (in C<sub>6</sub>D<sub>6</sub>) reference. FD mass spectra were obtained on a JMS-01SG-2 spectrometer, and IR spectra on a Hitachi 295 spectrophotometer. Elemental analyses were performed by the Material Analysis Center, ISIR, Osaka University.

$\mu$ -Ethynediyl dipalladium complexes were prepared by the method described previously [6], and phenyl isocyanide was prepared by the literature method [13].

#### 3.1. Preparation of Cl(Et<sub>3</sub>P)<sub>2</sub>PdC(=NPh)C≡CC(=NPh)Pd(PEt<sub>3</sub>)<sub>2</sub>Cl (**3a**)

Complex **1a** (156 mg, 0.2 mmol) was treated with phenyl isocyanide (41 mg, 0.4 mmol) and a 0.1 M benzene solution of triethylphosphine (0.4 ml, 0.04 mmol) in dichloromethane (20 ml) at room temperature. After being stirred for 20 h, the solvent was evaporated under reduced pressure and the residue purified by column chromatography on alumina using dichloromethane as an eluent. Recrystallization from dichloromethane-hexane gave yellow crystals (53 mg, 27%) of **3a**.

M.p. 163–165°C (dec.); IR  $\nu$ (C=N) 1535 cm<sup>-1</sup>; Raman  $\nu$ (C≡C) 2160,  $\nu$ (C=N) 1522 cm<sup>-1</sup>; <sup>1</sup>H-NMR  $\delta$  7.89 (4H, d,  $J$  = 8 Hz, Ph), 7.35 (4H, dd,  $J$  = 8 Hz, Ph), 7.19 (2H, t,  $J$  = 7 Hz, Ph), 1.90–1.66 (24H, m, CH<sub>2</sub>), 1.11 (36H, dt,  $J_{P-H}$  = 16,  $J_{H-H}$  = 8 Hz, CH<sub>3</sub>); <sup>13</sup>C NMR  $\delta$  173.69 (s, PdC(=N)), 151.56 (s, Ph), 128.65 (s, Ph), 126.00 (s, Ph), 120.69 (s, Ph), 96.75 (t,  $J_{P-C}$  = 7 Hz, C≡), 15.53 (vt,  $J$  = 12 Hz, PCH<sub>2</sub>), 8.25 (s, CH<sub>3</sub>); <sup>31</sup>P NMR  $\delta$  19.4 (s); Mass  $m/z$  = 987 (M<sup>+</sup>); Anal. Calcd. for C<sub>40</sub>H<sub>70</sub>N<sub>2</sub>P<sub>4</sub>Cl<sub>2</sub>Pd<sub>2</sub>: C, 48.70; H, 7.15; N, 2.84; Cl, 7.19; P, 12.56. Found: C, 48.40; H, 6.97; N, 2.83; Cl, 6.98; P, 12.43%.

#### 3.2. Preparation of Cl(Bu<sub>3</sub>P)<sub>2</sub>PdC(=NPh)C≡CC(=NPh)Pd(PBu<sub>3</sub>)<sub>2</sub>Cl (**3b**)

Phenyl isocyanide (62 mg, 0.6 mmol) was added to a solution of complex **1b** (335 mg, 0.3 mmol) and tributylphosphine (121 mg, 0.6 mmol) in dichloromethane (20 ml) at room temperature. After 15 h the solvent was removed *in vacuo*, and the residue purified by chromatography on alumina with benzene as an eluent. Recrystallization from hexane gave yellow crystals (226 mg, 57%) of **3b**.

M.p. 155–157°C; IR  $\nu$ (C=N) 1530 cm<sup>-1</sup>; <sup>1</sup>H-NMR  $\delta$  7.98 (4H, d,  $J$  = 8 Hz, Ph), 7.33(4H, dd,  $J$  = 8 Hz, Ph), 7.20 (2H, t,  $J$  = 7 Hz, Ph), 1.90–1.27 (72H, m, CH<sub>2</sub>), 0.88 (36H, t,  $J$  = 7 Hz, CH<sub>3</sub>); <sup>13</sup>C NMR  $\delta$  174.44 (s, PdC(=N)), 151.57 (s, Ph), 128.45 (s, Ph), 126.04 (s, Ph), 120.92 (s, Ph), 95.90 (t,  $J_{P-C}$  = 8 Hz, C≡), 26.21 (s, CH<sub>2</sub>CH<sub>3</sub>), 24.56 (vt,  $J$  = 7 Hz, PCH<sub>2</sub>CH<sub>2</sub>), 22.50 (vt,  $J$  = 12 Hz, PCH<sub>2</sub>), 13.80 (s, CH<sub>3</sub>); <sup>31</sup>P NMR  $\delta$  11.8 (s); Mass  $m/z$  = 1324 (M<sup>+</sup>); Anal. Calcd. for C<sub>64</sub>H<sub>118</sub>N<sub>2</sub>P<sub>4</sub>Cl<sub>2</sub>Pd<sub>2</sub>: C, 58.09; H, 8.99; N, 2.12; Cl, 5.36; P, 9.36. Found: C, 58.11; H, 8.79; N, 2.13; Cl, 5.47; P, 9.20%.

#### 3.3. Crystallographic data collection and structure refinement

Crystals suitable for an X-ray diffraction analysis were obtained by slow evaporation of a dichloromethane-hexane solution of **3a** at 0°C. The dimensions of the crystals were approximately 0.50 × 0.50 × 0.80 mm. The crystal was mounted on glass fibre with epoxy resin. Diffraction measurement was made on a Rigaku ACF-5FOS diffractometer using graphite-monochromated Mo K $\alpha$  radiation ( $\lambda$  = 0.7107 Å) with  $\omega$  scan technique with a scan rate of 8 deg min<sup>-1</sup>. The unit cell was determined and refined by a least-squares method using 25 independent reflections with 34 < 2 $\theta$  < 36. Three standard reflections were monitored every 55 measurements, and no damage was observed. Intensities were corrected for Lorentz and polarization effects and no absorption correction was made. The position of the Pd atom was determined by a heavy-atom method. The other non-hydrogen atomic positions were subsequently found from a series of difference Fourier synthesis. The positions of non-hydrogen atoms were refined anisotropically by using block-diagonal least-squares techniques minimizing  $\sum w(|F_o| - |F_c|)^2$ , where  $w = (\sigma^2 - 0.01396 |F_o| + 0.00603 |F_o|^2)^{-1}$ . No attempt was made to locate the hydrogen atoms.

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