

# Cyclopalladated Compounds with Bulky Phosphine (dppm): Synthesis, Characterization, and X-ray Diffraction <sup>†</sup>

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**Abstract:** The reaction between a cholro-bridged dinuclear compound (a, b) and a diphosphine (dppm) ligand in a molar ratio of 1:2 yielded a mononuclear compound  $[\text{Pd}[\text{R}-\text{C}_6\text{H}_3\text{C}(\text{H})=\text{NCy}]\{\text{Ph}_2\text{PCH}_2\text{PPh}_2-\text{P},\text{P}\}][\text{PF}_6]$   $\{\text{R} = 3\text{-CHO (1a), 4-CHO (1b)}\}$ . The compounds were characterized using IR, <sup>1</sup>H, and <sup>31</sup>P–{<sup>1</sup>H} NMR spectroscopy, and compound **1b** was identified using X-ray diffraction.

**Keywords:** palladacycle; imine ligands; dppm; X-ray diffraction

## 1. Introduction

One of the classic ways to activate C–H bonds in hetero-substituted organic compounds is through the cyclometallation reaction, which is a well-known procedure [1]. The first cyclometallated compounds were discovered in the mid–1960s [2], and since then, this reaction has received a lot of attention because of the many applications of metallacycles, such as organic synthesis, catalysis, metallomesogen design, asymmetric synthesis, racemic ligand resolution, C–H bond activation, the synthesis and reactivity of organometallic compounds with biologically active ligands, and medical chemistry. In recent years, phosphine ligands have received a lot of attention [3–5], such as bis[diphenylphosphino]methane (dppm) ligands, which are widely employed in transition metal chemistry as chelating and bridging coordination modes ligands [6]. However, in square planar metal complexes with a d<sup>8</sup> configuration, the tendency for chelation of diphosphine ligands is very strong [7–9], hence several mononuclear dppm–type compounds have shown interest in homogeneous catalysis [10–13]. These bidentate diphosphine ligands are useful in metal-catalyzed processes. Over the last 30 years, metal–catalyzed cross-coupling reactions have grown in prominence, particularly as convenient procedures for forming C–C bonds [14,15]. Palladium-catalyzed reactions have piqued curiosity [16,17]. The Suzuki–Miyaura reaction, which is catalyzed by palladium, is one of the most important ways for the formation of C–C bonds under very mild experimental conditions and is particularly useful for the creation of biaryls [18]. In the Suzuki cross-coupling reaction, both nitrogen-based ligands (amines or imines) and bulky phosphines (phosphorus ylides) have been successfully described (Figure 1) [19]. New catalysts are needed for current technologies that are low-cost, easily available, moisture- and air-stable, and most critically, extremely effective at low catalyst loading [20,21].



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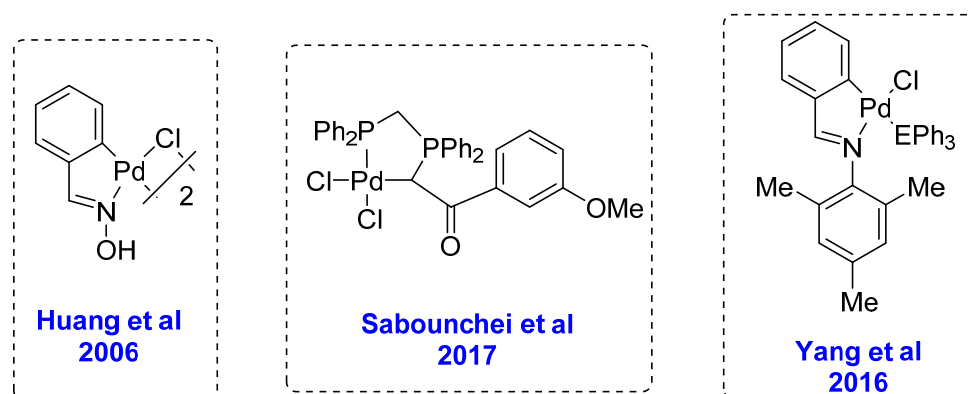
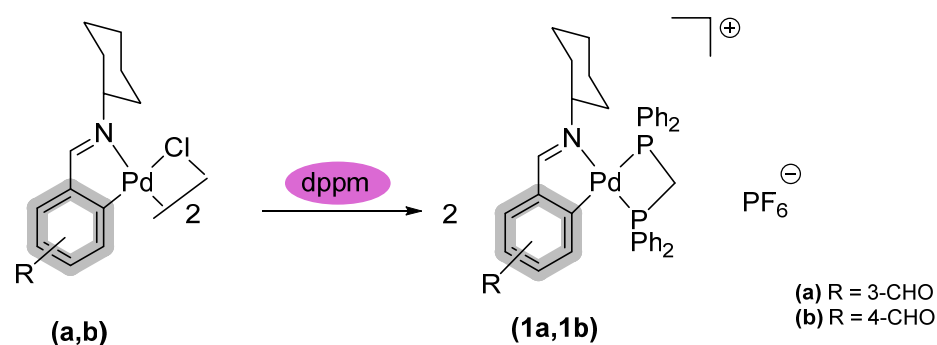


Figure 1. Palladacycle catalysts in activity [20–22].

## 2. Result and Discussion

The mononuclear compounds were obtained by treating the halide-bridged dinuclear compound **a** and **b** with bis(diphenylphosphino)methane (dppm) in the existence of  $\text{NH}_4\text{PF}_6$  in a 1:2 molar ratio (Scheme 1). The IR spectra revealed a shift in the C=N stretch's direction. Compared to the free Schiff base, the lower wavenumber nitrogen coordination of the C=N ligand group in the  $^1\text{H}$  NMR spectra, the HC=O resonance shows a singlet signal at  $\delta$  9.87 for **1a** and  $\delta$  9.53 for **1b**, and the HC=N resonance appears as a doublet ca.  $\delta$  8.43 by connecting to only the  $^{31}\text{P}$  nucleus trans to nitrogen for both compounds. The proton H5, coupled to both phosphorus nuclei, was assigned a doublet at  $\delta$  6.90 for **1a** [ $^4J(\text{H5P}) = 7.9$  Hz] and  $\delta$  6.80 for **1b** [ $^4J(\text{H5P}) = 6.4$  Hz]. In the  $^{31}\text{P}$ – $^1\text{H}$  NMR spectra, two doublets were seen for the two non-equivalent phosphorus atoms. The doublets were assigned based on the idea that a ligand with more trans influence causes the resonance of the phosphorus atoms trans to it to shift to a lower frequency [22].

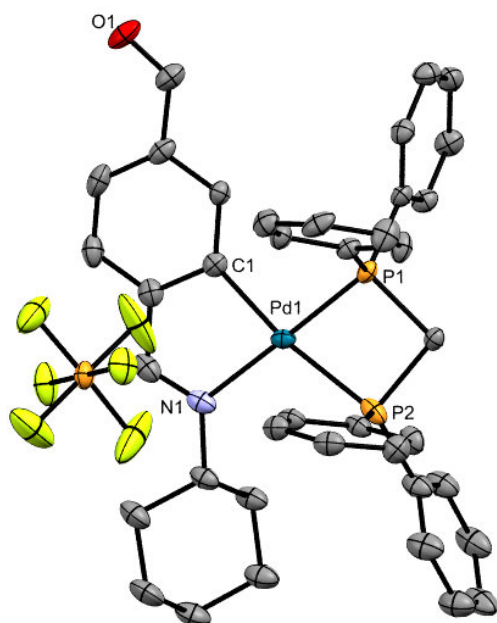


Scheme 1. dppm, acetone, r.t.

The crystal structure of **1b** (Figure 2) includes a mononuclear molecule and a hexafluorophosphate anion. A (N1) from the imine group, (C1) an ortho carbon atom from the phenyl ring, and (P1,P2) two phosphorus atoms from a chelating dppm form the coordination sphere surrounding the palladium atom. At a palladium, the sums of angles are nearly  $360^\circ$ , with the distortions being more visible at the slightly reduced “bite” angles C1–Pd1–N1 [ $81.02^\circ$ ], resulting from chelation. The bond angles P(1)–Pd(1)–P(2) are forced to  $70.15^\circ$  by the demands of the four-membered chelate ring of phosphine. The Pd1–N1 bond length is  $2.097 \text{ \AA}$ , and the Pd1–C1 bond length is  $2.025 \text{ \AA}$ . The Pd1–N1 bond length is  $2.097 \text{ \AA}$ , and the Pd1–C1 bond length is  $2.025 \text{ \AA}$ . The Pd(1)–P(2), and trans to nitrogen, Pd(1)–P(1), [ $2.463(13) \text{ \AA}$  versus  $2.248(11) \text{ \AA}$ ] clearly indicate the contrasting influence of the phenyl carbon and imine nitrogen atoms (Table 1).

The hydrogen bonding between the adjacent molecules in the  $\text{C}8 \cdots \text{H}18\text{--C}18_{\text{aryl}}$  and  $\text{O}1 \cdots \text{H--C}$  intermolecular contact causes weak interactions, as shown in Figure 3. Weak  $\text{C}8 \cdots \text{H}24$ ;  $2.874 \text{ \AA}$ ,  $\text{C}8\text{--C}24$ ;  $3.191 \text{ \AA}$ ,  $\text{O}1 \cdots \text{H}27a$ ;  $2.298 \text{ \AA}$  and  $\text{O}1 \cdots \text{H}29$ ;  $2.658 \text{ \AA}$  (Table 2)

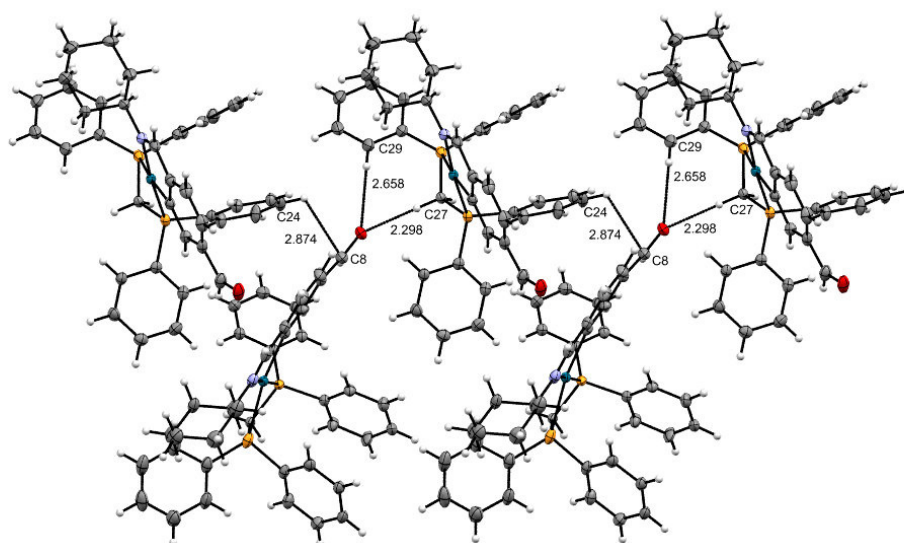
connect the crystal structure **1b**, resulting in a bifurcated hydrogen bond that extends along the crystallographic direction. Symmetry code # $1/2 + x, 1.5 - y, -1/2 + z$ .



**Figure 2.** Crystal structure of compound **1b**. Solvent molecules and hydrogen atoms have been omitted for clarity.

**Table 1.** Bond lengths are given in [Å] and angles in [°] of **1b**.

Pd(1)-N(1)	2.097(4)	C(1)-Pd(1)-N(1)	81.02(16)
Pd(1)-C(1)	2.025(4)	P(1)-Pd(1)-N(1)	175.10(10)
Pd(1)-P(1)	2.248(11)	N(1)-Pd(1)-P(2)	109.25(11)
Pd(1)-P(2)	2.463(13)	P(1)-Pd(1)-C(1)	98.97(12)
P(1)-Pd(1)-P(2)	70.15(4)	C(1)-Pd(1)-P(2)	167.36(12)



**Figure 3.** The packing view in complex **1b** shows intermolecular interaction (C–H···C<sub>aryl</sub>) and (C–H···O) the PF<sub>6</sub> ions have been omitted for clarity.

**Table 2.** C–H...C<sub>aryl</sub> interactions [ $\text{\AA}$ ,  $^\circ$ ] of 1b.

C–H...C <sub>aryl</sub>	C–H	H...C <sub>aryl</sub>	C–C <sub>aryl</sub>	$\angle(\text{C–H...C}_{\text{aryl}})^\circ$
C8–H24–C24	2.874	0.95	3.191	100.78
C–H...O1	C–H	H...O	C–O	$\angle(\text{C–H...O})^\circ$
C27–H27a–O1	0.99	2.298	3.337	128.91
C29–H29–O1	0.95	2.658	3.288	178.46

Table S1 shows Crystal data and structure refinement for 1b.

### 3. Experimental Part

The synthesis of  $[\text{Pd}\{3\text{-(COH)C}_6\text{H}_3\text{C(H)=NCy}\}(\mu\text{-Cl})_2]$  (**a**) and  $[\text{Pd}\{4\text{-(COH)C}_6\text{H}_3\text{C(H)=NCy}\}(\mu\text{-Cl})_2]$  (**b**) were reported previously by our group [23].

*Preparation of  $[\text{Pd}\{R\text{-C}_6\text{H}_3\text{C(H)=NCy}\}[\text{PPh}_2\text{CH}_2\text{PPh}_2][\text{PF}_6]$  {R= 3-CHO, 4-CHO}. (1a, 1b)*

To a solution of **a** or **b** (50 mg, 0.070 mmol), dppm (53.8 mg, 0.0140 mmol), in acetone 15 mL was added. The mixture was mixed at room temperature for 2 h, following which ammonium hexafluorophosphate (23 mg, 0.0140 mmol) was added, the solution was stirred for another 1 h, water ca. 20 mL was added dropwise, and the mixture was stirred for another 2 h. A precipitate was produced, which was then filtered, washed with water, and dried in vacuo. The required compound was recrystallized as pale-yellow microcrystals in  $\text{CH}_2\text{Cl}_2$ /n-hexane. **1a**: Yield 73 %, IR =  $1693\text{ cm}^{-1}$  (C=O),  $1617\text{ cm}^{-1}$  (C=N),  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  9.87 (s, 1H, HC=O), 8.42 (d,  $^4J$  = 6.9 Hz, 1H, Hi), 7.95 (s, 1H, H2), 7.75–7.37 (m, 20H,  $\text{PPh}_2$ ), 6.90 (d,  $^4J$  = 8.0 Hz, 1H, H5), 4.30 (t,  $^2J$  = 9.8 Hz, 2H,  $\text{CH}_2$ ), 3.37 (m, 1H, N-CH-Cy), 0.6–2.0 (m, 20H, Cy) (Figure S1).  $^{31}\text{P}$  NMR ( $\text{CDCl}_3$ , 162 MHz) –4.8 (d,  $J$  = 63.9 Hz), –28.2 (d,  $J$  = 63.9 Hz), –141.7 (h,  $\text{PF}_6$ ) (Figure S2).

**1b**: Yield 82 %, IR =  $1692\text{ cm}^{-1}$  (C=O),  $1624\text{ cm}^{-1}$  (C=N),  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  9.53 (s, 1H, HC=O), 8.43 (d,  $^4J$  = 7.3 Hz, 1H, Hi), 7.86–7.32 (m, 20H,  $\text{PPh}_2$ ), 7.11 (t,  $^3J$  = 8.4 Hz, 1H, H3), 6.80 (d,  $^4J$  = 6.4 Hz, 1H, H5), 4.30 (dd,  $^2J$  = 11.3, 8.2 Hz, 2H,  $\text{CH}_2$ ), 3.38 (m, 1H, N-CH-Cy), 0.6–2.30 (m, 20H, Cy) (Figure S1).  $^{31}\text{P}$  NMR ( $\text{CDCl}_3$ , 162 MHz) –4.8 (d,  $J$  = 64.5 Hz), –28.2 (d,  $J$  = 64.5 Hz), –141.5 (h,  $\text{PF}_6$ ).

**Supplementary Materials:** The following supporting information can be downloaded at <https://www.mdpi.com/article/10.3390/ecsoc-26-13563/s1>. Figure S1:  $^1\text{H}$  NMR of compounds 1a and 1b in  $\text{CDCl}_3$ ; Figure S2:  $^{31}\text{P}$  [ $^1\text{H}$ ]NMR of compound 1a in  $\text{CDCl}_3$ ; Table S1: Crystal data and structure refinement for 1b.

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