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Proceeding Paper

Cyclopalladated Compounds with Bulky Phosphine (dppm): Synthesis, Characterization, and X-ray Diffraction

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Abstract: The reaction of cholro-bridged dinuclear compound (a, b) with diphosphine (dppm) ligand in molar ratio 1:2 yielded a mononuclear compound [{Pd[R-$C_6H_3C(H)$=NCy]{$Ph_2PCH_2PPh_2$-P,P}][PF_6] {R = 3-CHO (1a), 4-CHO (1b)}. The compounds were characterized using IR, ^1H and ^{31}P–{^1H} NMR spectroscopy, and compound **1b** was identified using X-ray diffraction.

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

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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 gotten 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^8 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 diphosphines 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].

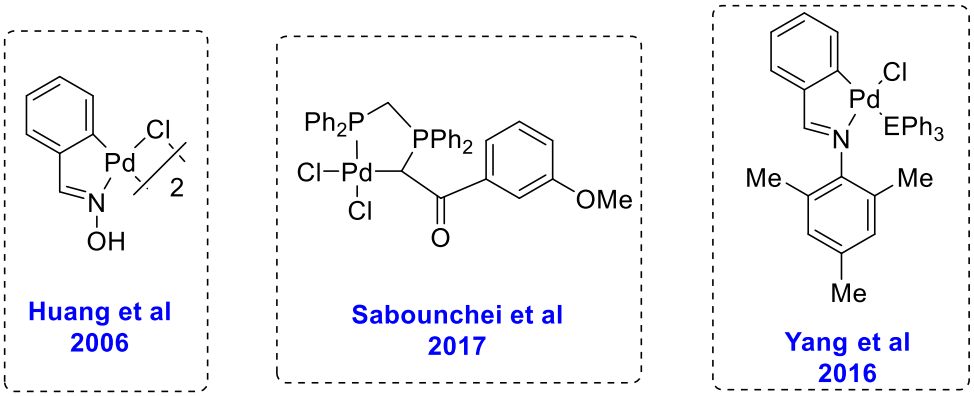
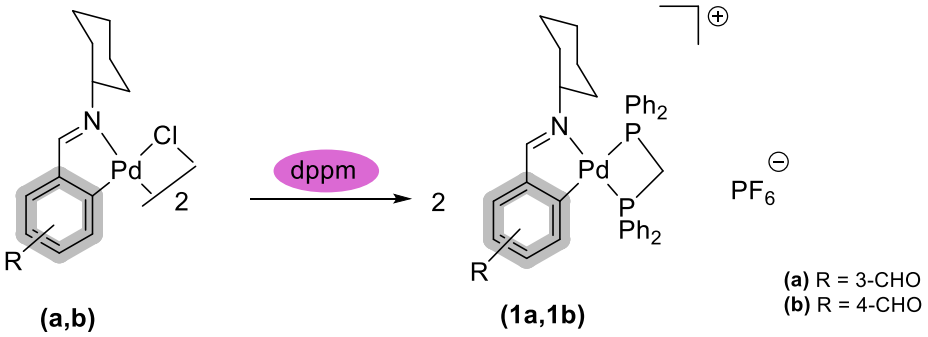


Figure 1. Palladacycle catalysts in activity.

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 NH_4PF_6 in a 1:2 molar ratio. The IR spectra revealed a shift in the C=N stretch's direction. Compared to the free Schiff base, lower wavenumbers nitrogen coordination of the C=N ligand group. In the ^{1}H NMR spectra, the HC=O resonance shows a singlet signal at δ 9.87 for 1a and δ 9.53 for 1b, and HC=N resonance appears as a doublet ca. δ 8.43 by connecting to only the ^{31}P nucleus trans to nitrogen for both compounds. The proton H5, coupled to both phosphorus nuclei, was assigned a doublet at δ 6.90 for 1a [^4J(H5P) = 7.9 Hz]and δ 6.80 for 1b [^4J(H5P) = 6.4 Hz]. In the ^{31}P–{^{1}H} NMR spectra, two doublets were seen for the two non-equivalent phosphorus. 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** 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 palladium, the sums of angles are nearly 360°, with the distortions being more visible at the slightly reduced "bite" angles C1–Pd1–N1 [81.02]°, resulting from chelation. The bond angles P(1)–Pd(1)–P(2) is forced to 70.15 by the demands of the four-membered chelate ring of phosphine. The Pd1–N1 bond length is 2.097 Å, and the Pd1–C1 bond length is 2.025 Å. The Pd–P distance trans to carbon, Pd(1)–P(2), and trans to nitrogen, Pd(1)–P(1), [2.463(13) Å versus 2.248(11) Å] clearly indicate the contrasting influence of the phenyl carbon and imine nitrogen atoms.

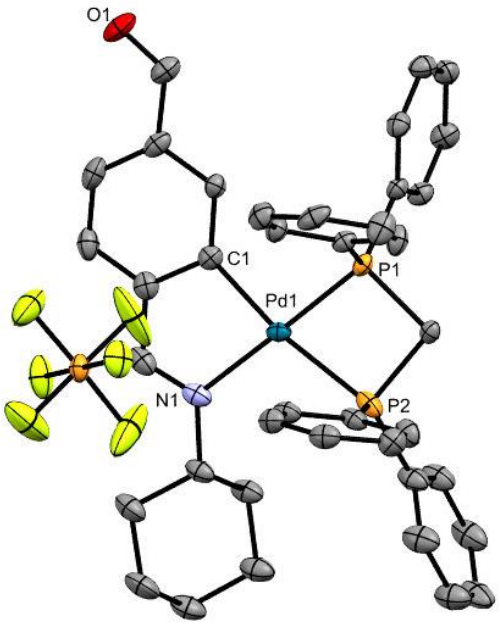


Figure 1. Crystal structure of compound **1b**. Solvent molecules and hydrogen atoms have been omitted for clarity.

The hydrogen bonding between adjacent molecules in the C8···H18−C18$_{aryl}$ and O1···H−C intermolecular contact causes weak interactions, as shown in Figure 2. Weak C8···H24; 2.874 Å, C8−C24; 3.191 Å, O1···H27a; 2.298 Å and O1···H29; 2.658 Å 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.

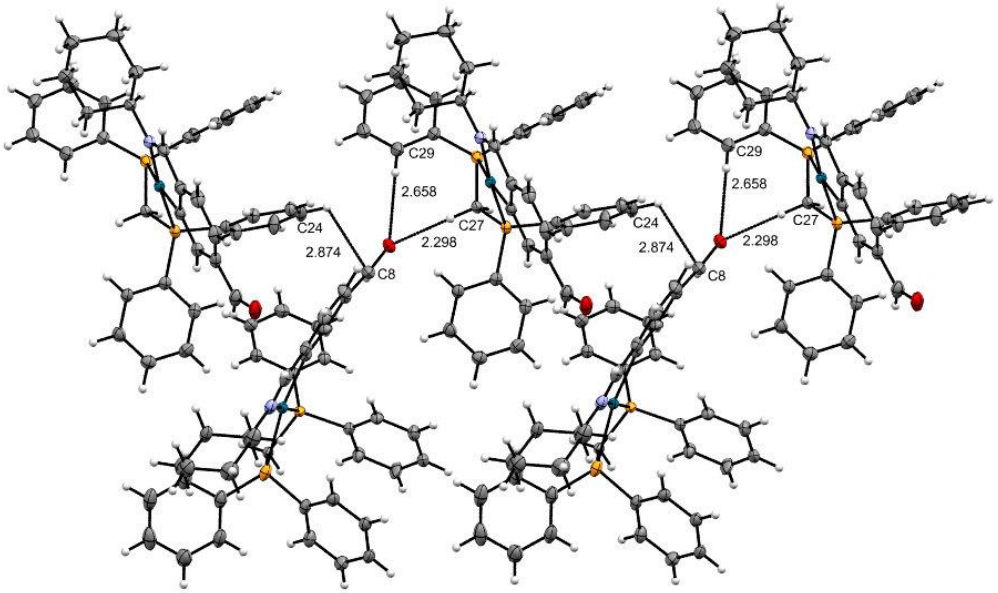


Figure 2. The packing view in complex 1b shows intermolecular interaction (C−H···C$_{aryl}$) and (C−H···O). The PF_6 ions have been omitted for the clarity.

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)

Table 2. C–H···C_{aryl} interactions [Å, °] of 1b.

C–H···C_{aryl}	**C–H**	**H···C_{aryl}**	**C–C_{aryl}**	**<(C–H···C_{aryl})°**
C8–H24–C24	2.874	0.95	3.191	100.78
C–H···O1	**C–H**	**H···O**	**C–O**	**<(C–H···O)°**
C27–H27a–O1	0.99	2.298	3.337	128.91
C29–H29–O1	0.95	2.658	3.288	178.46

3. Experimental Part

The synthesis of [Pd{3-(COH)C_6H_3C(H)=NCy}(μ-Cl)]$_2$ (**a**) and [Pd{4-(COH)C_6H_3C(H)=NCy}(μ-Cl)]$_2$ (**b**) were reported previously by our group [23].

3.1. Preparation of [Pd{R-C_6H_3C(H)=NCy}{$PPh_2CH_2PPh_2$}[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 CH_2Cl_2/n-hexane. **1a**: Yield 73 %, IR = 1693 cm^{-1} (C=O), 1617 cm^{-1} (C=N), ^{1}H NMR (400 MHz, $CDCl_3$) δ 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, PPh_2), 6.90 (d, ^4J = 8.0 Hz, 1H, H5), 4.30 (t, ^2J = 9.8 Hz, 2H, CH_2), 3.37 (m, 1H, N-CH-Cy), 0.6 5–2.0 (m, 20H, Cy). ^{31}P NMR ($CDCl_3$, 162 MHz)–4.8 (d, J = 63.9 Hz), −28.2 (d, J = 63.9 Hz), −141.7 (h, PF_6).

1b: Yield 82 %, IR = 1692 cm^{-1} (C=O), 1624 cm^{-1} (C=N), ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.53 (s, 1H, HC=O), 8.43 (d, ^4J = 7.3 Hz, 1H, Hi), 7.86 –7.32 (m, 20H, 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, CH_2), 3.38 (m, 1H, N-CH-Cy), 0.6–2.30 (m, 20H, Cy). ^{31}P NMR ($CDCl_3$, 162 MHz)–4.8 (d, J = 64.5 Hz), −28.2 (d, J = 64.5 Hz), −141.5 (h, PF_6).

Supplementary Materials: The following supporting information can be downloaded at: www.mdpi.com/xxx/s1, Figure S1: ^{1}H NMR of compounds 1a and 1b in $CDCl_3$; Figure S2: ^{31}P {^{1}H}NMR of compound 1a in $CDCl_3$; Table S1: Crystal data and structure refinement for 1b.

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Conflicts of Interest:

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Supplementary Material.

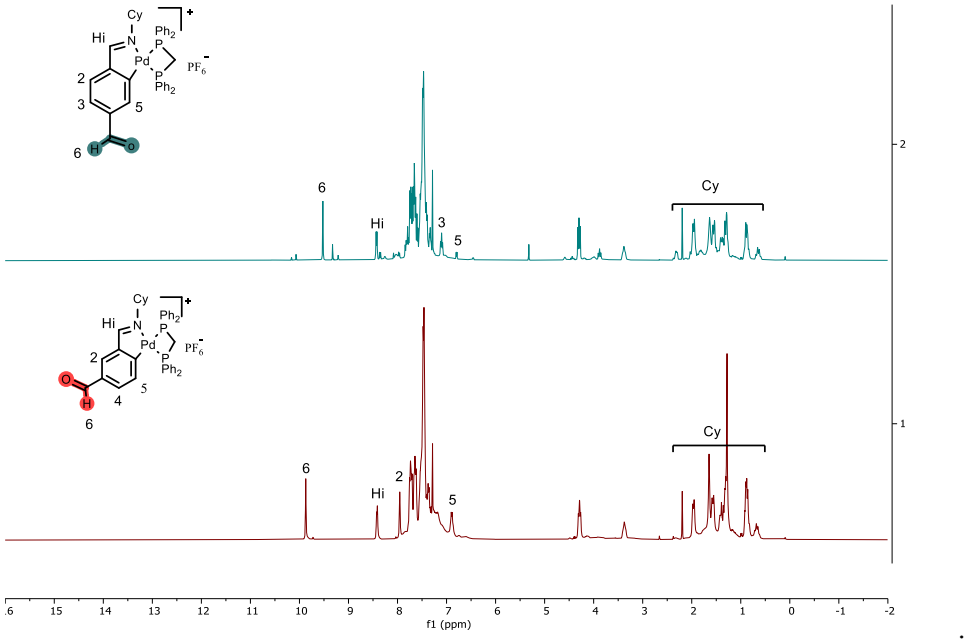

Figure S1. ^{1}H NMR of compounds 1a and 1b in $CDCl_3$.

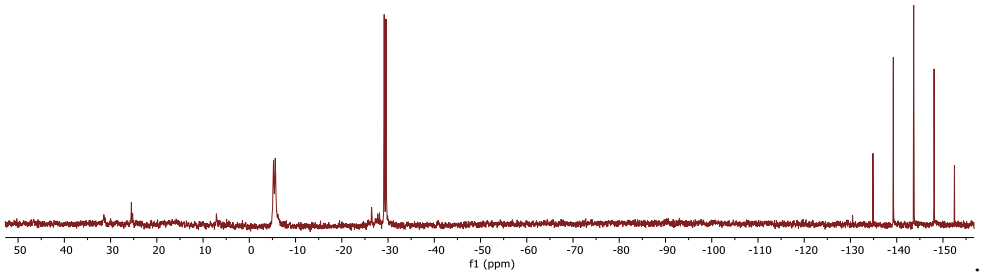

Figure S2. ^{31}P $\{^{1}H\}$NMR of compound 1a in $CDCl_3$.

Table 3. Crystal data and structure refinement for 1b.

Molecular formula.	$C_{39}H_{38}F_6NOP_3Pd$..
Formula weight.	850.01..
Temperature/K.	100.00..
Crystal system.	monoclinic..
Space group.	$P2_1/n$..
a/Å.	10.0932(6)..
b/Å.	33.4658(18)..
c/Å.	11.4492(6)..
α/°.	90..
β/°.	110.580(2)..
γ/°.	90..
Volume/Å^3.	3620.5(3)..
Z.	4..
ϱ_{calc}g/cm^3.	1.559..
μ/mm^{-1}.	0.710..
F(000).	1728.0..
Crystal size/mm^3.	0.9 × 0.07 × 0.04..

Radiation.	MoKα (λ = 0.71073)..
θ range for data collection/°.	4.48 to 56.554..
Index ranges.	$-13 \leq h \leq 13$, $-44 \leq k \leq 44$, $-15 \leq l \leq 15$..
Reflections collected.	149704..
Independent reflections.	8997 [R_{int} = 0.0551, R_{sigma} = 0.0214]..
Data/restraints/parameters.	8997/0/461..
Goodness-of-fit on $F^{2.}$	1.194..
Final R indexes [I>=2σ (I)].	R_1 = 0.0595, wR_2 = 0.1224..
Final R indexes [all data].	R_1 = 0.0661, wR_2 = 0.1255..
Largest diff. peak/hole / e $Å^{-3.}$	2.50/-1.83..