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Synthesis and X-ray diffraction of cyclopalladated compounds derived from imine ligands †

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Abstract: The crystal structures of mononuclear cyclopalladated compounds with phosphine ligands are investigated. The reaction of five-membered cyclopalladated dinuclear complexes $[Pd(L)(\mu\text{-}Cl)]_2$ with the mono phosphine ligand (PPh_3) and diphosphine (dppm) in molar ratio 1:2 and ammonium hexafluoride in case of compound b gave mononuclear complexes [Pd{2,3,4-$(CHO)C_6H_3C(H)$=NCy}{PPh_3}[Cl] (**1a**) and [Pd{2,3,4-$(CHO)C_6H_3C(H)$=NCy}{$Ph_2PCH_2PPh_2$-P,P}][PF6] (**1b**).

Keywords: Cyclometallated; Palladium; imine; X-ray diffraction

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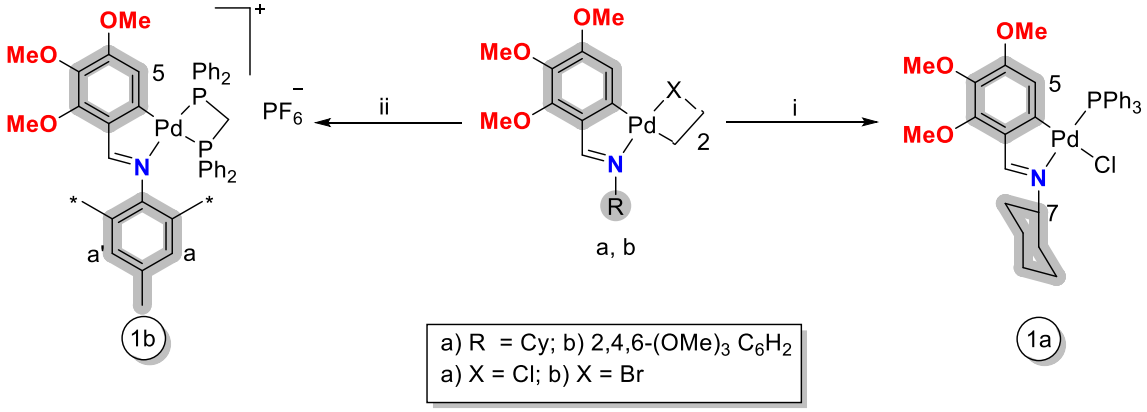
1. Introduction

The possible application of palladium compounds in medicine has become a particularly active and attractive study issue in bioinorganic and biological chemistry [1]. The use of chelating ligands in the development of physiologically active palladium compounds with improved kinetic stability is a well-established design principle [2]. Since the existence of a strong Pd–C bond in the [C, N] palladacycle enhances the stability of the organometallic complex, orthometallated N–donor ligands, such as imines, have been successfully employed for this purpose [3]. Nitrogen-donor ligands palladacycles are gaining popularity due to their numerous applications in organic synthesis, antitumoral drugs, asymmetric synthesis, intermolecular aromatic C–H bond activation, synthesis, and reactivity of organometallic complexes with biologically important ligands, and drug delivery [4]. Therefore, we report herein the synthesis and characterization of cyclopalladated compounds of the general formula [Pd{2,3,4-$(MeO)_3C_6HC(H)$=N-R}{R = Cy, 2,4,6-MeC_6H_2}(X = Cl, Br)] with PPh_3 and dppm ligands.



Scheme 1. (**i**) PPh_3, r.t, 3h; (**ii**) dppm, NH_4PF_6, r.t, 3h.

2. Result and Discussion

Treatment of halogen-bridged ligand compound **a** with the PPh_3 in molar ratio 1:2 produced monomer palladium(II) compound with PPh_3 ligand and compound **b** with the diphosphine dppm and NH_4PF_6 1:2 molar ratio gave a monomer palladium(II) compound with phosphine chelated ligand. Compounds were characterized by $^{31}P\{^1H\}$ and ^1H NMR spectroscopy. In the ^1H NMR, the proton H(5) for compounds **1a** and **1b** appears as a doublet by coupling ^{31}P. A doublet resonance of HC=N proton is coupled to ^{31}P nucleus trans to nitrogen for compound **1a** at 8.26 ppm [^4J(PHi) = 9.1 Hz] and for compound **1b** at 8.20 ppm [^4J(PHi) = 7.6 Hz]. The OMe(C4) NMR resonance for compounds **1a** and **1b** is shifted to a lower frequency, due to the shielding effect of the phosphine phenyl ring. The two inequivalent OMe(C4) groups would have two different resonances in an antiparallel configuration, as one of them would not be impacted by the phosphine's phenyl ring. In the ^{31}P-$\{^1H\}$ NMR, a singlet was ascribed for compound **1a** to the ^{31}P nucleus shifted to a lower field ca. 43 ppm, which is consistent with a phosphorus trans to nitrogen arrangement. Whereas for compound **1b**, the two inequivalent phosphorus nuclei are represented by two doublets at -4.33 [d, J = 62.9 Hz], -27.53 [d, J = 62.9 Hz]. The phosphorus nucleus trans to the phenyl carbon C(6), has the lower frequency doublet, while the phosphorus nucleus trans to the imine nitrogen has the higher frequency doublet. This is predicated on the notion that a ligand with a higher trans influence shifts the phosphorus nucleus trans ^{31}P resonance to a lower frequency.

3. X-ray Diffraction

Mononuclear molecules (one molecule per asymmetric unit) in **1a** and **1b**, and a hexafluorophosphate anion is present in the case of crystal structure **1b**. The coordination sphere enclosing the palladium atom in crystal structures **1a** and **1b** is formed by a nitrogen atom from the imine group, an ortho carbon atom from the phenyl ring (C1), one phosphor atom from a PPh_3, a chlorine atom in case the crystal structure of **1a**, and two phosphorus atoms from a chelating dppm in case the crystal structure of **1b**. The Pd1–C1, 2.027(5) Å for **1a**, and 2.036(3) Å for **1b** are in agreement with the partial multiple-bond character of the Pd–C bond [5]. The Pd(1)-N(1) bond length, 2.112(5) Å for **1a**, and 2.096(2) Å for **1b**, is longer than the single bond predicted value of 2.011, which has an impact on the phosphine ligand's trans effect [6]. It can be noticed in Figure 5 that there intermolecular interaction for compound 1b, result a C_{sp3}···H···C weak interaction. The bond and angel interaction C38···H10···C10 are 2.838 Å and 113.36°, respectively, and C38···C10 bond interaction 3.331 Å.

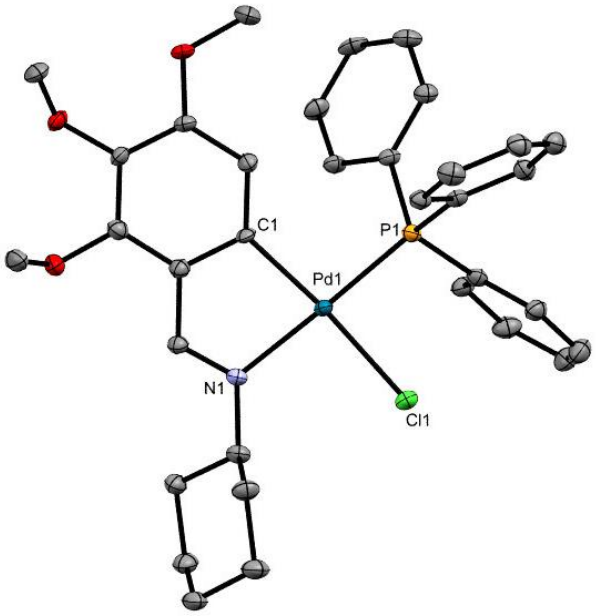


Figure 1. Molecular structure of compound **1a (Thermal ellipsoid at probability 50%)**. selected bond distances and angles: Pd1-N1 2.112(5), Pd1-C1 2.027(5), Pd1-P1 2.262(14), Pd1-Cl1 2.379(13), C1-Pd1-N1 81.41(2), C1-Pd1-P1 97.15(16), N1-Pd1-Cl1 93.07(13), P1-Pd1-Cl1 89.95(5).

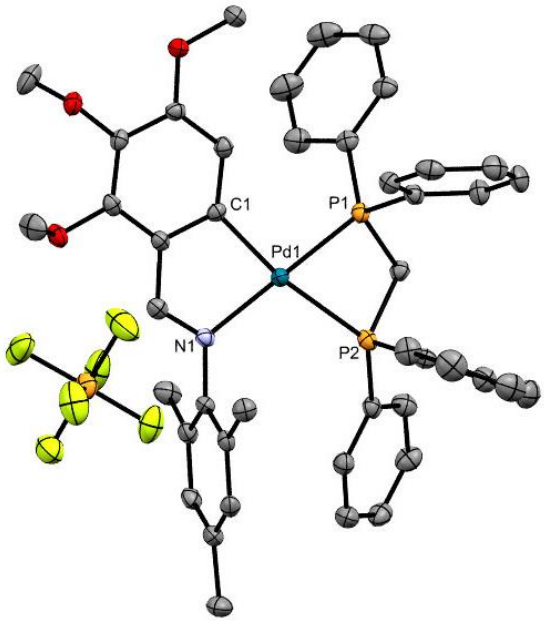


Figure 2. Molecular structure of compound **1b (Thermal ellipsoid at probability 50%).** selected bond distances and angles: Pd(1)-N(1) 2.096(2), Pd(1)-C(1) 2.036(3), Pd(1)-P(1) 2.251(8), Pd(1)-P(2) 2.408(8), N(1)-Pd(1)-P(1) 179.49(7), C(1)-Pd(1)-N(1) 80.47(11), P(1)-Pd(1)-P(2) 70.88(3), N(1)-Pd(1)-P(2) 108.80(7), P(1)-Pd(1)-C(1) 99.86(9), C(1)-Pd(1)-P(2) 170.54(9).

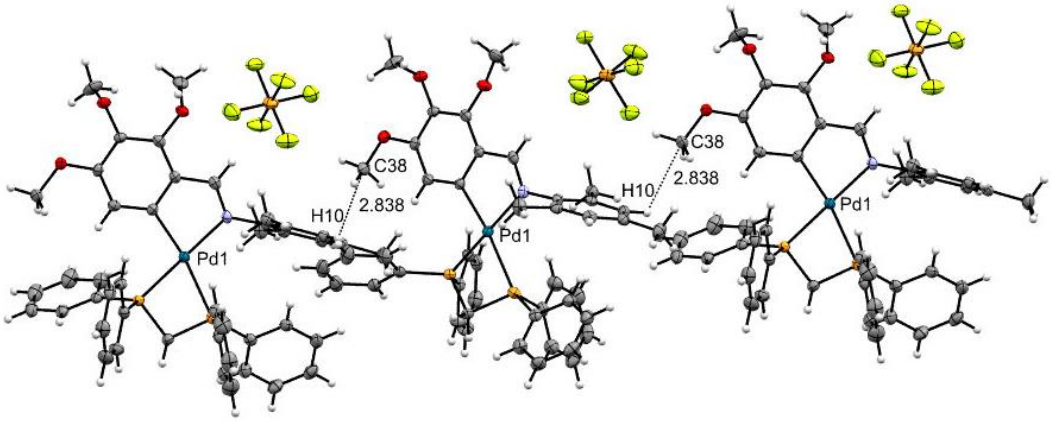


Figure 3. Intermolecular interaction (C_{sp3}···H···C) of compound 1b.

4. Experimental Part

Compounds **a** and **b** has been prepared in the same manner [7].

4.1. Synthesis of [Pd{2,3,4-(MeO)$_3$C$_6$HC(H)=N-C$_6$H$_2$}{PPh$_3$}]. (1a)

(25 mg, 0.029 mmol) compound **a** was added in acetone (10 cm^3). The required quantity of triphenylphosphine was added (in a 1:2 molar ratio) and the mixture was agitated for 3 h at room temperature. The solution was reduced to a low volume, and the solid was recrystallized from dichloromethane/n-Hexane and dried in vacuo. Yield 50%. IR = ν(C=N) 1569 cm^{-1}, ν(Pd–Cl) 298 cm^{-1}. NMR ^{1}H (400 MHz, $CDCl_3$)) δ 8.26 (d, ^4J(PHi) = 9.1 Hz, 1H, Hi), 7.67 (t, ^3J(HH) = 7.6 Hz, 6H, PPh_3), 7.35 (t, ^3J(HH) = 7.6 Hz, 3H, PPh_3), 7.29 (d, ^3J(HH) = 7.6 Hz, 6H, PPh_3), 5.65 (d, ^4J(H5P) = 6.4 Hz, 1H, H5), 4.33 (m, ^3J(HH) = 11.1 Hz, 1H, N-CH-Cy), 3.86 (s, 3H, OMe), 3.61 (s, 3H, OMe), 2.72 (s, 3H, OMe), 2.17-0.79 (m, 10H, Cy). ^{31}P NMR (δ ppm, $CDCl_3$) δ 42.86.

4.2. Synthesis of [Pd{2,3,4-(MeO)$_3$C$_6$HC(H)=N-2,4,6-Me$_3$C$_6$H$_2$}{Ph$_2$PCH$_2$PPh$_2$-P,P}](PF$_6$). (1b)

(25 mg, 0.025 mmol) compound **b** was added in acetone (10 cm^3). The appropriate amounts of dppm and NH_4PF_6 were added in molar ratio (1:2), and the mixture was stirred for 3 h at room temperature. The orange precipitate formed was filtered off, recrystallized from dichloromethane/n-Hexane and dried in vacuo. Yield 85%. IR = ν(C=N) 1565 cm^{-1}. NMR ^{1}H (400 MHz, $CDCl_3$) δ 8.20 (d, ^4J(PHi) = 7.6 Hz, 1H, Hi), 8.06–6.99 (m, 20H, PPh_2), 6.68 (s, 2H, Ha, Ha'), 6.03 (dd, ^4J(H5P$_{trans}$) = 10.4 Hz, ^4J (H5P$_{cis}$) = 7.6 Hz, 1H, H5), 4.27 (dd, ^2J(HP) = 12.0, 8.0 Hz, 2H, PCH_2P), 3.99 (s, 3H, OMe), 3.79 (s, 3H, OMe), 3.17 (s, 3H, OMe), 2.25 (s, 3H, Me), 2.18 (s, 6H, Me*). ^{31}P-{^{1}H} NMR ($CDCl_3$, δ ppm) -6.0 [d, J = 66.5], -30 [d, J = 66.5], -141 [h, PF_6^-].

Supplementary Materials: The following are available online at www.mdpi.com/xxx/s1, Figure 4. ^{1}H NMR of compound 2a in $CDCl_3$; Figure 5. ^{1}H NMR of compound 2b in $CDCl_3$.

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