chemistry proceedings

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Proceeding Paper

Synthesis and X-ray Diffraction of Cyclopalladated Compounds Derived from Imine Ligands †

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† Presented at the 26th International Electronic Conference on Synthetic Organic Chemistry, 15–30 November 2022; Available online: https://sciforum.net/event/ecsoc-26.

Abstract: The crystal structures of mononuclear cyclopalladated compounds with phosphine ligands are investigated. The reactions of the five-membered cyclopalladated dinuclear complexes [Pd(L)(μ-Cl)]$_2$ with the monophosphine ligand (PPh_3) and diphosphine ligand (dppm) in the molar ratio of 1:2, and ammonium hexafluoride in the case of compound b, result in the 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

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]. The nitrogen-donor ligands, palladacycles, are gaining popularity due to their numerous applications in organic synthesis, antitumoral drug synthesis, asymmetric synthesis, intermolecular aromatic C–H bond activation, synthesis and reactivity of organometallic complexes with biologically important ligands, and drug delivery [3]. Therefore, we report herein the synthesis and characterization of cyclopalladated compounds of the general formula [Pd{2,3,4-$(MeO)_3C_6$HC(H)=N-R}{R = Cy, 2,4,6-MeC_6H_2}(X = Cl, Br)] with PPh_3 and dppm ligands.

2. Result and Discussion

The treatment of the halogen-bridged ligand compound **a** with the PPh_3 in the molar ratio of 1:2 produced a monomer palladium(II) compound with PPh_3 ligand, and the treatment of compound **b** with the diphosphine dppm and NH_4PF_6 in a 1:2 molar ratio gave a monomer palladium(II) compound with phosphine chelated ligand (Scheme 1). The compounds were characterized by using $^{31}P\{^1H\}$ and ^1H NMR spectroscopy. In the ^1H NMR, the proton H(5) for compounds **1a** and **1b** appears as a doublet by coupling to ^{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's phenyl ring. The two inequivalent OMe(C4) groups have two different resonances in an antiparallel configuration, as one of them is not impacted by the phosphine's phenyl ring. In the $^{31}P\text{-}\{^1H\}$ NMR, a singlet ascribed to the coupling of compound **1a** to the ^{31}P nucleus is shifted to a lower field ca. 43 ppm,

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Citation: Al Janabi, B.; Ortigueira, J.M.; Vila, J.M. Synthesis and X-ray Diffraction of Cyclopalladated Compounds Derived from Imine Ligands. *Chem. Proc.* **2022**, *12*, 52. https://doi.org/10.3390/ecsoc-26-13699

Academic Editor: Julio A. Seijas

Published: 18 November 2022

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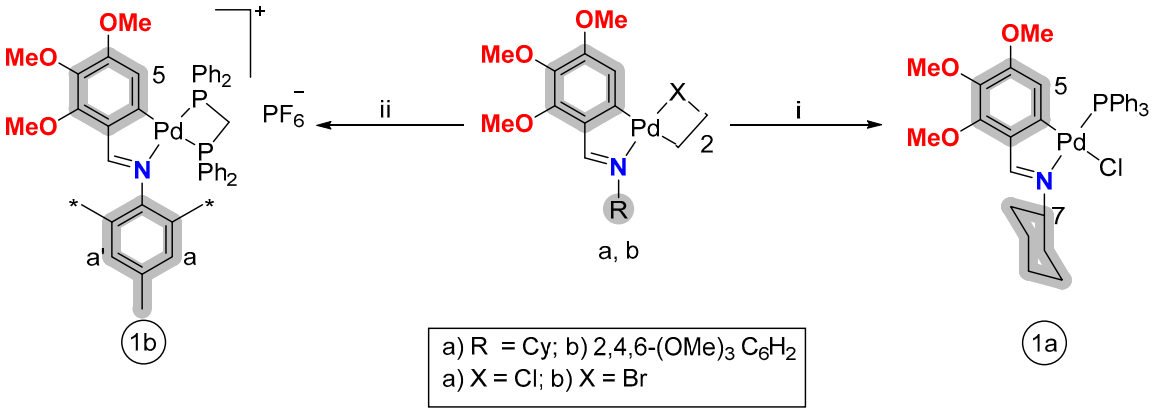
which is consistent with a phosphorus trans to nitrogen arrangement. In contrast, for compound **1b**, the two inequivalent phosphorus nuclei are represented by two doublets at −4.33 [d, J = 62.9 Hz] and −27.53 [d, J = 62.9 Hz]. The phosphorus nucleus trans to the phenyl carbon C(6) has the lower-frequency 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.



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

3. X-ray Diffraction

The mononuclear molecules (one molecule per asymmetric unit) are present in **1a** (Figure 1) and **1b**, and a hexafluorophosphate anion is present in the case of the crystal structure **1b** (Figure 2). The coordination sphere enclosing the palladium atom in the crystal structures **1a** and **1b** is formed by a nitrogen atom from the imine group, an ortho carbon atom from the phenyl ring (C1), a phosphor atom from a PPh_3, a chlorine atom in the case of the crystal structure of **1a**, and two phosphorus atoms from a chelating dppm in the case of the crystal structure of **1b**. The Pd1–C1, which is 2.027(5) Å for **1a** and 2.036(3) Å for **1b,** is in agreement with the partial multiple-bond character of the Pd–C bond [4]. The Pd(1)-N(1) bond length, which is 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 [5]. It can be noticed in that there is an intermolecular interaction for compound 1b, resulting in a C_{sp3}···H···C weak interaction. The bond and angel interaction C38···H10···C10 are 2.838 Å and 113.36°, respectively, and the C38···C10 bond interaction is 3.331 Å (Figure 3). Table S1 lists specifics regarding the structure's refinement and the final reliability factors.

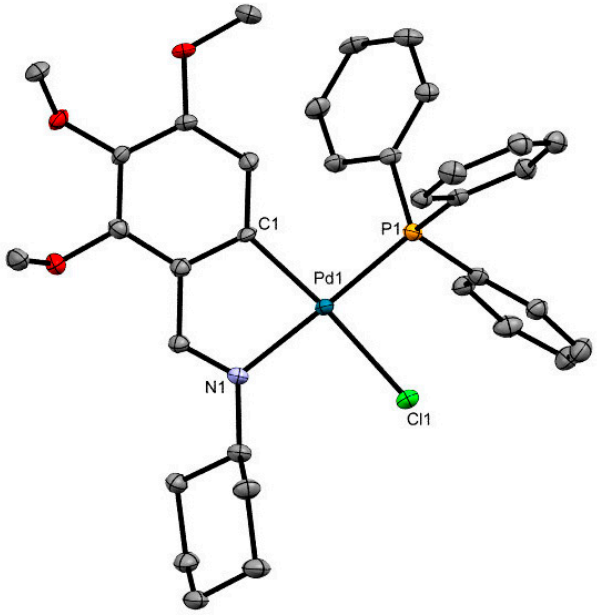


Figure 1. Molecular structure of compound **1a** (Thermal ellipsoid at the probability of 50%). Selected bond distances and angles: Pd1-N1 2.112(5), Pd1-C1 2.027(5), Pd1-P1 2.262(14), Pd1-Cl1 2.379(13), C1-Pd1-N1 81.41(2), C1-Pd1-P1 97.15(16), N1-Pd1-Cl1 93.07(13), and P1-Pd1-Cl1 89.95(5).

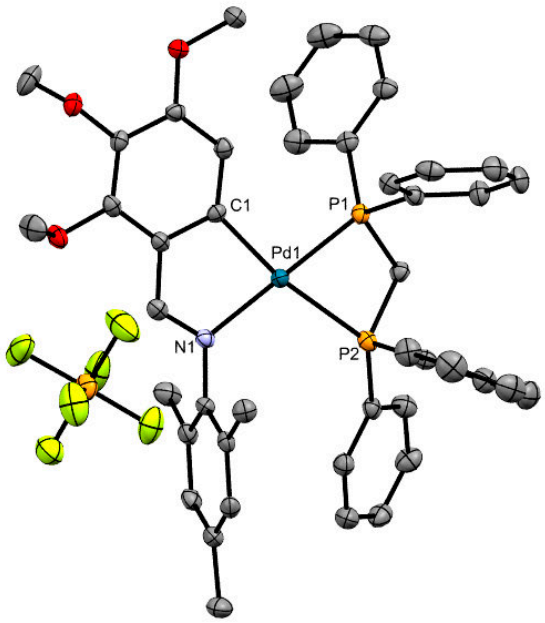


Figure 2. Molecular structure of compound **1b** (Thermal ellipsoid at the probability of 50%). Selected bond distances and angles: Pd(1)-N(1) 2.096(2), Pd(1)-C(1) 2.036(3), Pd(1)-P(1) 2.251(8), Pd(1)-P(2) 2.408(8), N(1)-Pd(1)-P(1) 179.49(7), C(1)-Pd(1)-N(1) 80.47(11), P(1)-Pd(1)-P(2) 70.88(3), N(1)-Pd(1)-P(2)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

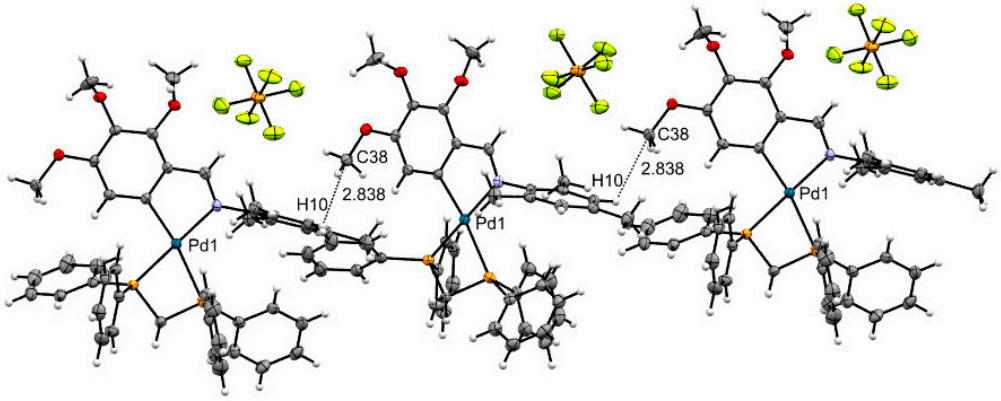


Figure 3. Intermolecular interaction (C_{Sp3}···H···C) of compound **1b**.

4. Experimental Part

Compounds **a** and **b** were prepared in the same manner [6].

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

A total of (25 mg, 0.029 mmol) of compound **a** was added to 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. The yield was 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) (Figure S1**)**. ^{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**)*

A total of (25 mg, 0.025 mmol) of compound **b** was added to acetone (10 cm^3). The appropriate amounts of dppm and NH_4PF_6 were added in a molar ratio of (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. The yield was 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*) (Figure S2). ^{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 https://www.mdpi.com/article/10.3390/ecsoc-26-13699/s1, Figure S1: ^{1}H NMR of compound **1a** in $CDCl_3$, Figure S2: ^{1}H NMR of compound **1b** in $CDCl_3$, Table S1: Crystal data and structure refinement for compounds **1a** and **1b**.

Author Contributions: Formal analysis, B.A.J.; Methodology, B.A.J.; Writing original draft, B.A.J.; writing—review and editing, B.A.J., J.M.V. and J.M.O. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by the Xunta de Galicia. GRC2019/14.

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: Not applicable.

Acknowledgments: We would like to thank the Xunta de Galicia (Galicia, Spain) and the Competitive Reference Groups GRC2019/14 for their financial support.

Conflicts of Interest: The authors declare no conflict of interest.

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