

Proceeding Paper

Palladacycles as Functionalized Metal-Ligand Precursors, Contain Tridentate [Csp², N, S] Ligands †

Basma Al janabi *, Jose Manuel Vila * and Juan M. Ortigueira

Department of Inorganic Chemistry, Faculty of Chemistry, University of Santiago de Compostela, Avd. das Cienciam s/n, 15782 Santiago de compostela, Spain; e-mail@e-mail.com

* Correspondence: josemanuel.Vila@usc.es, juanm.ortigueira@usc.es

†

Abstract: The reactivity of R-CH=N-(C₆H₄-2-SMe) with R=4-Br-C₆H₅, R=3-Br-C₆H₅, R=2-Cl-C₆H₅ with palladium (II) salts has been investigated. We were able to prepare and characterize the cyclometalation complexes. The thioimines act as a [Csp², phenyl, N, S] tridentate group, according to the X-ray crystal structures of the latter complex.

Keywords: Palladium; cyclometalation; imine ligand

Citation: Al janabi, B.; Vila, J.M.; Ortigueira, J.M. Palladacycles as Functionalized Metal-Ligand Precursors, Contain Tridentate [Csp², N, S] Ligands. *Chem. Proc.* **2021**, *3*, x. <https://doi.org/10.3390/xxxxx>

Academic Editor: Julio A. Seijas

Published: 15 November 2021

Publisher's Note: MDPI stays neutral with regard to jurisdictional claims in published maps and institutional affiliations.



Copyright: © 2021 by the authors. Submitted for possible open access publication under the terms and conditions of the Creative Commons Attribution (CC BY) license (<http://creativecommons.org/licenses/by/4.0/>).

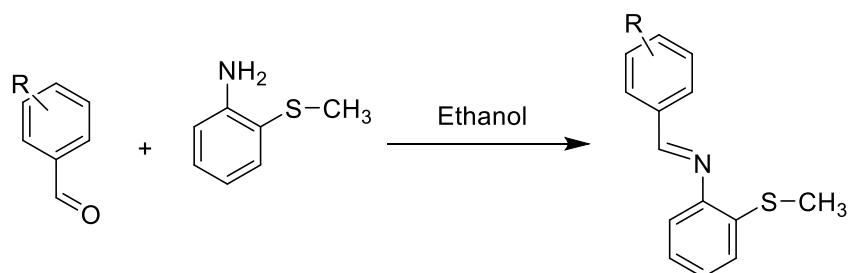
1. Introduction

Due to their applications in a variety of fields, the study of cyclopalladated compounds has sparked a lot of interest in the last decade [1]. So far, a large number of palladacycles with a $\sigma(\text{Pd}/\text{Csp}^2)$ or $\sigma(\text{Pd}/\text{Csp}^3)$ bond and a bidentate [C,X]- {X= N, P, O} ligand or a tridentate [C,X,Y]- or [X,C,Y]- {X, Y= N, P, O} group have been described [2,3]. Few articles, however, focus on cyclopalladated compounds containing tridentate [C, N, S] ligands [4,5]. Some researchers were reported the activation of the δ (Csp², aryl-H) bond of the thioimine: C₆H₅-CH=N-CH₂-CH₂-Set, which led to the syntheses and characterization of the mononuclear compounds: [M{C₆H₄-CH=N-CH₂-CH₂-Set}Cl] {M=Pd, Pt} [6]. In our interest we decided to study the replacement of the -CH₂-CH₂- moiety by a less flexible backbone between the two heteroatoms (N and S) could be important in determining the nature of the final product and/or the ease with which the $\sigma(\text{C}-\text{H})$ bond is activated. On this basis, we were inspired to make the ligands X-R-CH=N-(C₆H₄-2-SMe) with [X= Br, Cl], [R=C₆H₅], and test their reactivity against palladium(II) salts. We present a general procedure for activating the $\sigma(\text{Csp}^2-\text{H})$ bond of thioimines using palladium(II) salts in this paper, which has allowed us to isolate and characterize the first mononuclear cyclopalladated complex containing a $\sigma[\text{Csp}^2, \text{N}, \text{S}]$ tridentate ligand.

2. Material and Methods

2.1. 1-Synthesis of a-c

4-Br-benzaldehyde (a), 3-Br-benzaldehyde (b), and 2-Cl-benzaldehyde (c) were added to ethanol with a corresponding amount of 2-methylthioaniline. The solution was then refluxed for 4 h. After that time, the solvent evaporated and the mixture was allowed to cool to room temperature.



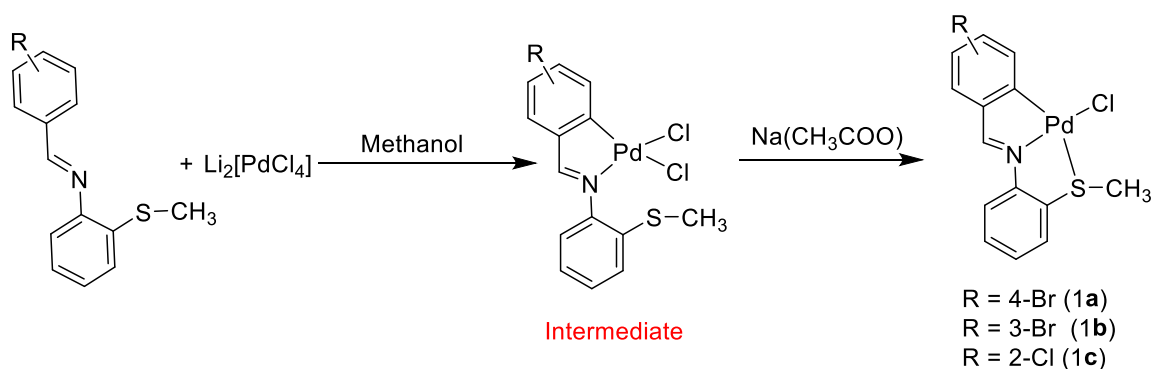
R = (a) 4-bromobenzene

R = (b) 3-bromobenzene

R = (c) 2-chlorobenzene

2.2. 2-Synthesis of 1a–1c

To begin, prepare a $\text{Li}_2[\text{PdCl}_4]$ solution. In methanol, palladium chloride was added to lithium chloride for 3 h. The appropriate amount of the corresponding ligand was then added, and the mixture was then refluxed at 70°C for 1 h. Allow for a few minutes of cooling before adding the sodium acetate (15 equivalents). During the addition, solid precipitates are formed.

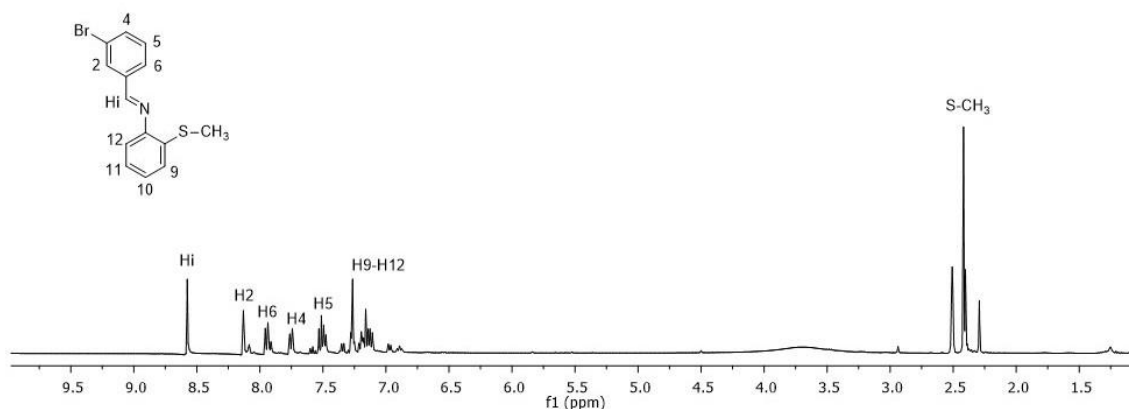


3. Result and Discussion

3.1. 1-Synthesis a-c

The ^1H NMR spectra of the Schiff bases **a–c** reveal a common and representative feature of this class of organic compounds: the presence of a singlet at approximately for **a** and **b** 8.50, and 8.80 ppm for **c**, caused by the proton of the imine group, $\text{HC}=\text{N}$. The different benzyl ring substitutions in each ligand determine the number, position, and multiplicity of the corresponding signals in the benzyl ring. It's also important to note that the H6 proton's signal resonates at higher frequencies than the H5 proton's in proton NMR spectra, which is consistent with the strong unshielded effect caused by the imine group's proximity, $\text{HC}=\text{N}$. The high field singlet corresponds to the signal from the thiomethyl group. In the

6.56–7.40 ppm multiplet, the phenyl protons H9–H12 have overlapping signals.



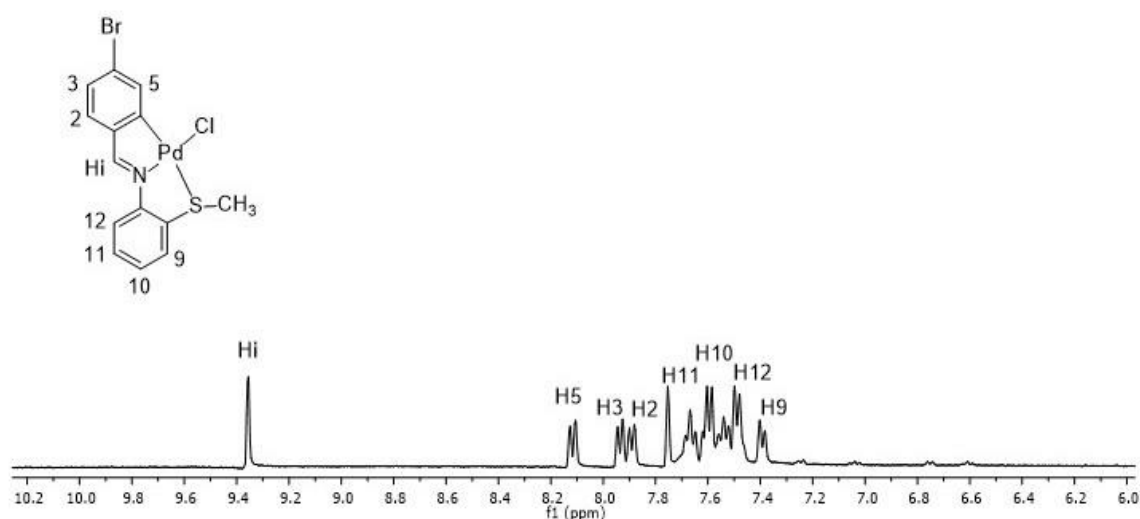
^1H NMR spectrum of ligand **b** in DMSO-d_6 .

3.2. 2-Synthesis **1a-1c**

The most notable feature of the proton NMR spectrum of the derivatives **1a-1c** is the signal decoupling of the imine proton in comparison to the free Schiff base. This behavior has previously been observed in other cyclopaladated compounds [C, N, S] [7,8].

The activation of the C-H bond, which leads to the formation of the metalacycle, is confirmed by the variation in the integration and multiplicity of the protons signals in the aromatic zone. The loss of the signal corresponding to the proton H6 and the decrease in the multiplicity of the proton H5 signal due to the formation of the (M-C) bond indicates the formation of the ortho-metalated species.

In the ^1H NMR spectra, the signal due to the imine proton appeared at lower fields of three compounds than for the free ligands, which were assigned at ca. 9.30 ppm for **1a** and **1c**, and 9.23 for **1b**. The proton H5 of **1a-1c** forms an AB system ($J_{\text{HH}} = 8.2\text{Hz}$) as a doublet for **1a** and **1b**, at 8.12, 8.06, and 8.22 ppm for **1c**.



^1H NMR spectrum of compound **1a** in DMSO-d_6 .

4. X-ray Diffraction

The crystal structure of compound **1c** determined by X-ray diffraction, confirms the spectroscopic data. The structure is constructed of $[\text{Pd}\{\text{C}_6\text{H}_4\text{-2-Cl-(H)C=N(C}_6\text{H}_4\text{-2-SMe)}\}\text{Cl}]$ from discrete molecules. The molecule contains a tetracyclic system composed of an aryl ring that shares a C-C bond with the chelate ring, which is formed by the

coordination of two heteroatoms (N and S) to the palladium, a five-membered palladacycle in structure, and the other phenyl ring. Palladium atom is bound to chlorine, sulfur, imine nitrogen, and C(14) for 1c atom in a slightly distorted square/planar environment. This proved that the thioimines bind to palladium(II) in a specific way.

The lengths of the C=N bonds 1.307(6) Å in 1c are comparable to those found in related palladacycles derived from Schiff bases [9]. The distance between the Cl and the H(5) atom in compound 1c [2.914 Å and 2.904 Å] also indicates a weak Cl... H...C(5) intramolecular interaction [10]. Figures 1 and 2 show the molecular structure of 1c, as well as their atom labeling schemes. Table 2 shows a variety of bond lengths and bond angles for the structure.

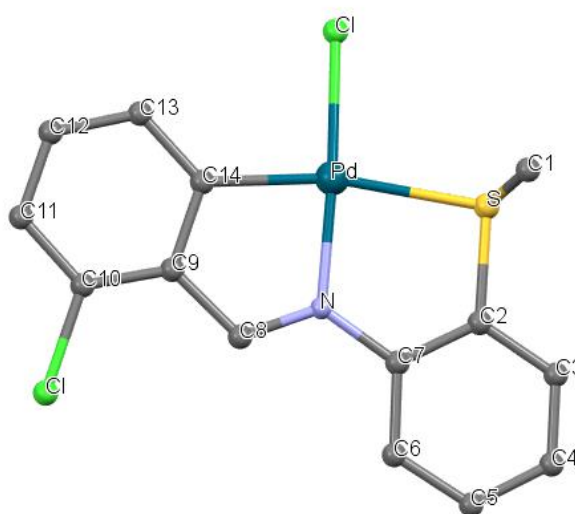


Figure 1. Molecular structure and atom labeling scheme for (1c).

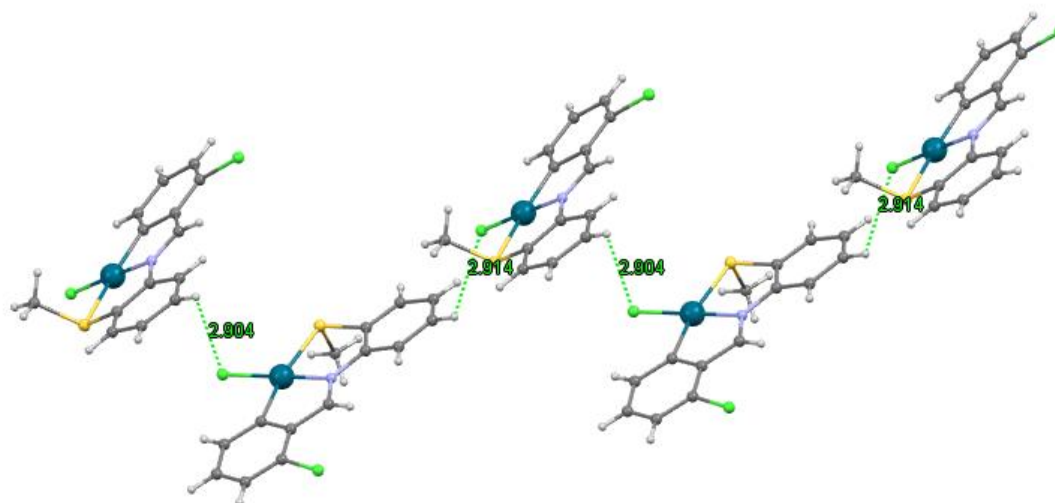


Figure 2. Intermolecular interaction Cl...H...C(5) of molecular structure (1c).

Table 1. Crystal data and structure refinement for 1c.

Empirical formula	C ₁₄ H ₁₁ Cl ₂ NPdS
Formula weight	402.63

Temperature/K	100.0
Crystal system	triclinic
Space group	P-1
a/Å	10.9824(2)
b/Å	18.2981(3)
c/Å	14.3485(3)
α /°	90
β /°	99.9460(10)
γ /°	90
Volume/Å ³	2840.10(9)
Z	8
$\rho_{\text{calc}}/\text{cm}^3$	1.876
μ/mm^{-1}	15.235
F(000)	1572.0
Crystal size/mm ³	0.1 × 0.05 × 0.03
Radiation	CuK α (λ = 1.54184)
2 θ range for data collection/°	4.83 to 149.41
Index ranges	-13 ≤ h ≤ 13, -22 ≤ k ≤ 22, -17 ≤ l ≤ 17
Reflections collected	83138
Independent reflections	11,516 [R _{int} = 0.0899, R _{sigma} = 0.0514]
Data/restraints/parameters	11516/0/690
Goodness-of-fit on F ²	1.040
Final R indexes [I ≥ 2 σ (I)]	R ₁ = 0.0369, wR ₂ = 0.0803
Final R indexes [all data]	R ₁ = 0.0583, wR ₂ = 0.0881

Table 2. Bond length (Å) and bond angles (°) for molecular structure 1c.

Bond Lengths			
Pd-C(14)	1.986 (5)	Pd-N	2.008 (4)
Pd-Cl	2.304 (1)	Pd-S	2.375 (1)
S-C(2)	1.783 (6)	S-C(1)	1.812 (7)
N-C(8)	1.307 (7)	N-C(7)	1.416 (7)
C(2)-C(7)	1.400 (8)	C(2)-C(3)	1.393 (8)
C(3)-C(4)	1.364 (7)	C(4)-C(5)	1.380 (8)
C(5)-C(6)	1.386 (8)	C(6)-C(7)	1.400 (7)
C(8)-C(9)	1.441 (8)	C(9)-C(10)	1.393 (8)
C(9)-C(14)	1.422 (8)	C(10)-C(11)	1.387 (8)
C(10)-Cl	1.751 (6)	C(11)-C(12)	1.376 (7)
C(13)-C(14)	1.395 (8)	C(12)-C(13)	1.397 (8)
Bond angles			
N-Pd-S	85.33 (1)	C(14)-Pd-Cl	95.09 (1)
S-C(2)-C(3)	119.89 (4)	Cl-S-Pd	103.03 (2)
N-C(8)-C(9)	115.52 (4)	C(7)-C(2)-S	120.15 (4)
C(2)-C(7)-N	118.3 (4)	N-Pd-C(14)	82.10 (2)

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

Reference

1. Jairton, D.; Pfeffer, M.; Spencer, J. *Eur. J. Inorg. Chem.* **2001**, 2001.8, 1917–1927.
2. (a) Fernández-Rivas, C.; et al. *Organometallics* **2001**, 20.14, 2998–3006.
(b) Vicente, J.; et al. *Organometallics* **2001**, 20.13, 2704–2715.
3. (a) Cativiela, C.; et al. *New J. Chem.* **2001**, 25.2, 344–352.
(b) Stark, M.A.; Jones, G.; Christopher, J.R. *Organometallics* **2000**, 19.7, 1282–1291.
(c) Zucca, A.; et al. *Organometallics* **2000**, 19.21, 4295–4304.
4. (a) Chattopadhyay, S.; et al. *Organometallics* **1991**, 10.4, 1135–1139.
(b) Pal, C.K.; et al. *J. Organomet. Chem.* **1992**, 439.1, 9199.
(c) Chittaranjan, S.; Bandyopadhyay, D.; Chakravorty, A. *Inorg. Chem.* **1988**, 27.7, 1173–1178.
5. Ankersmit, H.A.; et al. *Inorganic Chemistry* **1996**, 35.21, 6053–6063.
6. (a) Riera, X.; et al. *J. Organomet. Chem.* **2001**, 629, 97.
(b) Riera, X.; et al. *Organometallics* **2000**, 19.7, 1384–1390.
7. Basuli, F.; Chattopadhyay, P.; Sinha, C. *Polyhedron* **1996**, 15.14, 2439–2444.
8. Albert, J.; Granell, J. *Trends Organomet. Chem* **1999**, 3, 99.
9. Albert, Joan. Granell, Jaume. Sales, and Solans, Xavier. *Organometallics* **1990**, 9, 1536.
10. (a) Mason, R. *Acta Crystallographica Section B: Structural Crystallography and Crystal Chemistry* **1974**, 30.8, 2077–2078.
(b) van Bondi, A. *Journal Phys. Chem.* **1964**, 68.3, 441–451.