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# Palladacycles as Functionalized Metal-Ligand Precursors, Contain Tridentate [Csp$^2$, N, S] Ligands †

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**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 was investigated in this study. We were able to prepare and characterize the cyclometallation complexes. The thioimines act as a [Csp2, phenyl, N, S] tridentate group, according to the X-ray crystal structures in the latter complex.

**Keywords:** palladium; cyclometallation; imine ligand



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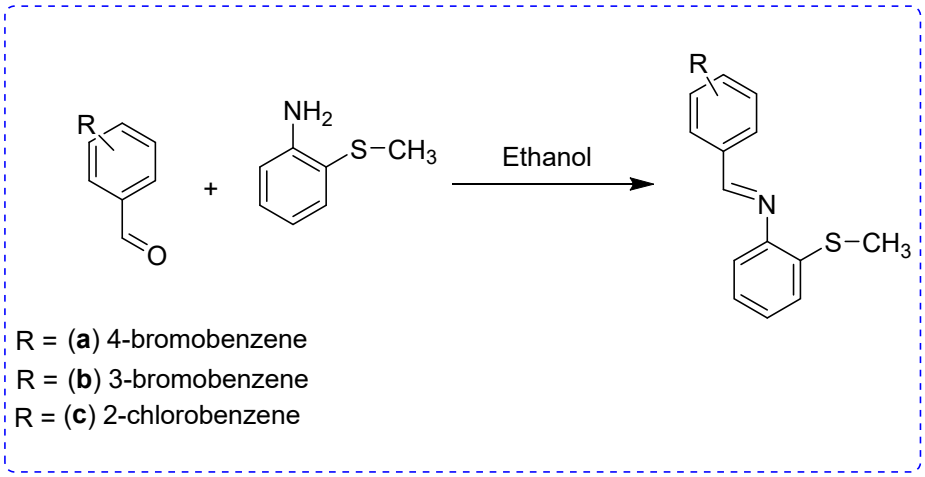
## 1. Introduction

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 σ(Pd/Csp$^2$) or σ(Pd/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 [2–6]. Few articles, however, focus on cyclopalladated compounds containing tridentate [C, N, S] ligands [7–10]. Some researchers reported the activation of the δ (Csp$^2$, aryl–H) bond of the thioimine: $C_6H_5$–CH=N–$CH_2$–$CH_2$–Set, which led to the syntheses and characterization of the mononuclear compounds: [M{$C_6H_4$–CH=N–$CH_2$–$CH_2$–Set}Cl] {M = Pd, Pt} [11,12]. In our interest, we decided to study the replacement of the –$CH_2$–$CH_2$– moiety, as 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 σ(C–H) bond is activated. On this basis, we were inspired to make the ligands X–R–CH=N–($C_6H_4$–2–SMe) with [X = Br, Cl], [R = $C_6H_5$], and test their reactivity against palladium(II) salts. We present a general procedure for activating the σ(Csp$^2$–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 σ[Csp$^2$, N, S] tridentate ligand.

## 2. Material and Methods

### 2.1. Synthesis of **a**–**c**

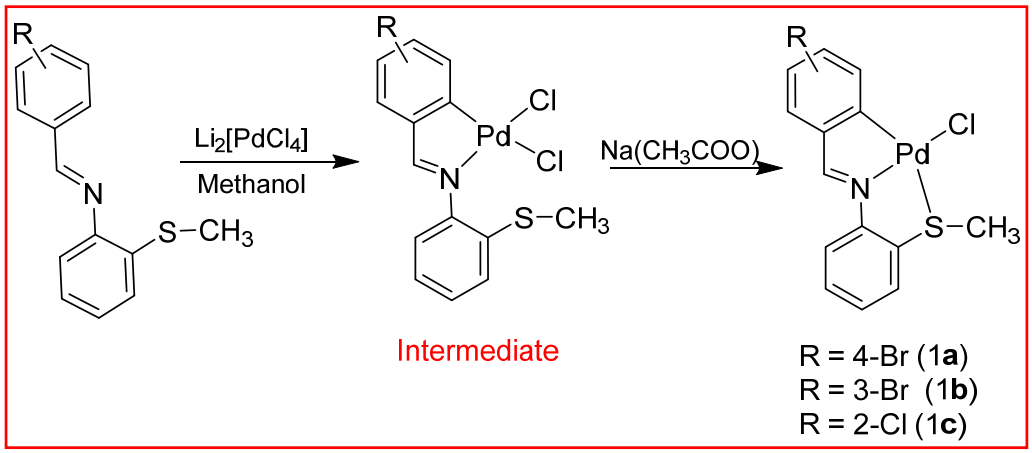
4-Br-benzaldehyde (**a**), 3-Br-benzaldehyde (**b**), and 2-Cl-benzaldehyde (**c**) were added to ethanol with a corresponding amount of 2-methylthioaniline. The solution was then refluxed for 4 h. After that time, the solvent evaporated and the mixture was allowed to cool to room temperature (Scheme 1).




**Scheme 1.** Synthesis of Schiff bases ligands [C, N, S].

*2.2. Synthesis of* **1a–1c**

To begin, we prepared a $Li_2[PdCl_4]$ 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. We allowed for a few minutes of cooling before adding the sodium acetate (15 equivalents). During the addition, solid precipitates are formed (Scheme 2).




**Scheme 2.** Synthesis of cyclometallated compounds.

## 3. Result and Discussion

*3.1. 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** (Figure 1), 8.50, and 8.80 ppm for **c**, caused by the proton in the imine group, HC=N. The different benzyl ring substitutions in each ligand determine the number, position, and multiplicity of the corresponding signals in the benzyl ring. It is 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, HC=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.

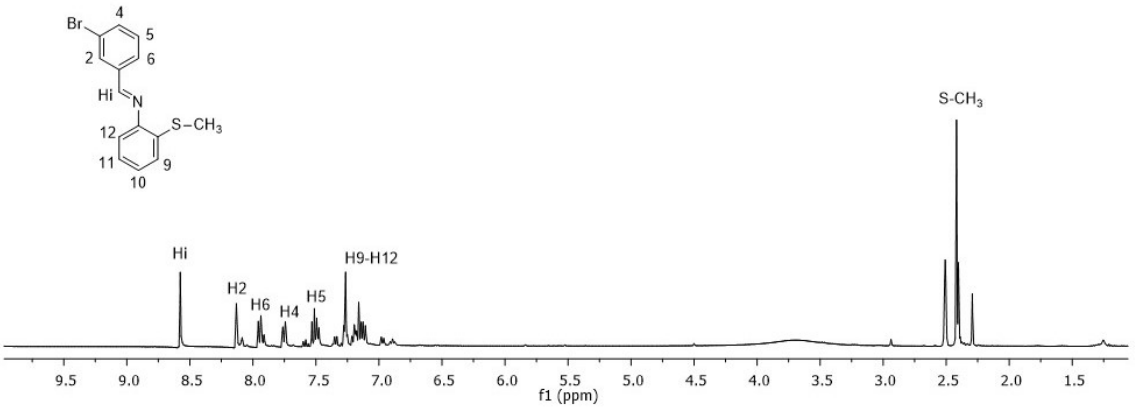



**Figure 1.** $^{1}$H NMR spectrum of ligand **b** in DMSO-d6.

### *3.2. 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 (Figure 2). This behavior has previously been observed in other cyclopalladated compounds [C, N, S] [13,14].

The activation of the C-H bond, which leads to the formation of the metallacycle, 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-metallated species. In the $^{1}$H 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 ($J_{HH}$ = 8.2 Hz) as a doublet for **1a** and **1b**, at 8.12, 8.06, and 8.22 ppm for **1c**.

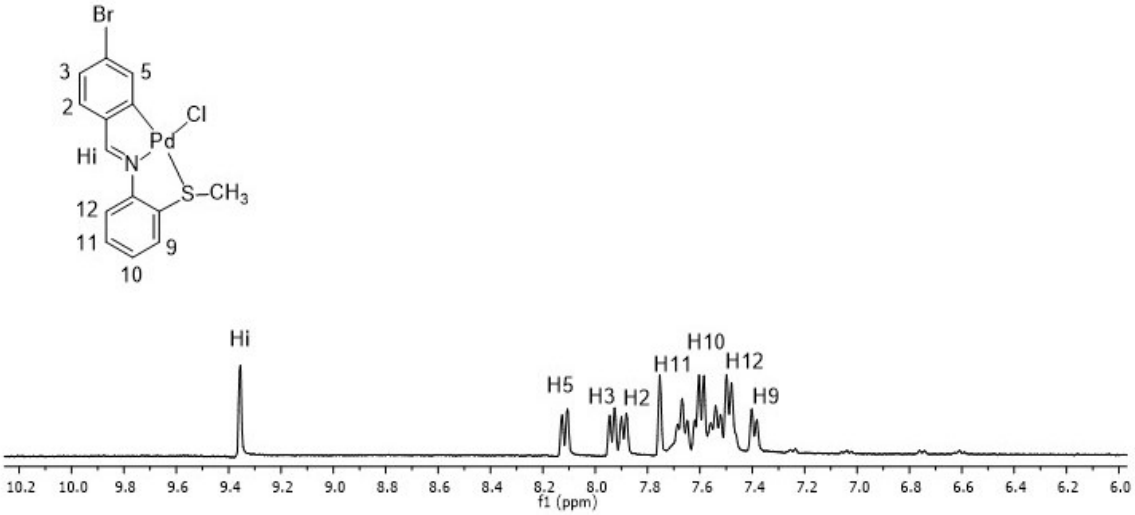



**Figure 2.** $^{1}$H NMR spectrum of compound **1a** in DMSO-d6.

## 4. X-ray Diffraction

The crystal structure of compound **1c**, determined by X-ray diffraction, confirms the spectroscopic data. The structure is constructed of [Pd{$C_6H_4$–2–Cl–(H)C=N($C_6H_4$–2–SMe)}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. The palladium atom is bound to chlorine, sulfur,

imine nitrogen, and C(14) for the **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 [15]. 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 [16]. Figures 3 and 4 show the molecular structure of **1c**, as well as their atom–labeling schemes. Tables 1 and 2 show the crystallographic data and a variety of bond lengths and bond angles for structure **1c**.

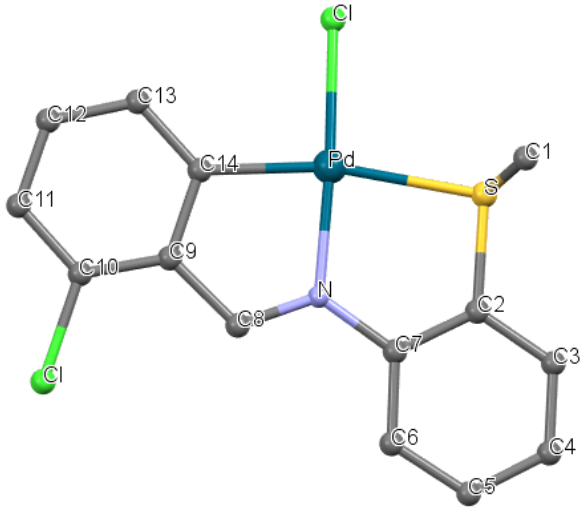



**Figure 3.** Molecular structure and atom–labeling scheme for (**1c**).

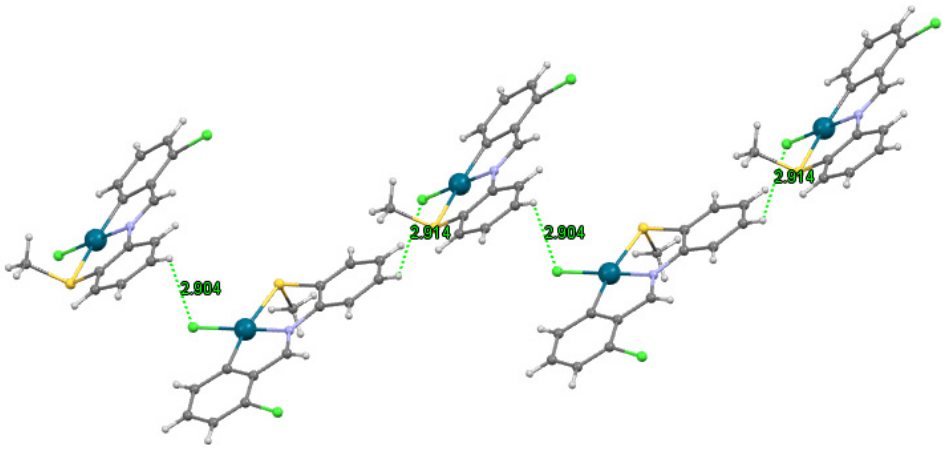



**Figure 4.** Intermolecular interaction Cl···H···C(5) of molecular structure (**1c**).

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

| | |
|---|---|
| Empirical formula | $C_{14}H_{11}Cl_2NPdS$ |
| 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 |

**Table 1.** *Cont.*

| | |
|---|---|
| Volume/Å$^3$ | 2840.10(9) |
| Z | 8 |
| $\rho_{calc}$ (g/cm$^3$) | 1.876 |
| $\mu$/mm$^{-1}$ | 15.235 |
| F(000) | 1572.0 |
| Crystal size/mm$^3$ | 0.1 × 0.05 × 0.03 |
| Radiation | CuK$\alpha$ ($\lambda$ = 1.54184) |
| $\theta$ range for data collection/° | 4.83 to 149.41 |
| Index ranges | $-13 \leq h \leq 13$, $-22 \leq k \leq 22$, $-17 \leq l \leq 17$ |
| Reflections collected | 83,138 |
| Independent reflections | 11,516 [$R_{int}$ = 0.0899, $R_{sigma}$ = 0.0514] |
| Data/restraints/parameters | 11,516/0/690 |
| Goodness-of-fit on F$^2$ | 1.040 |
| Final R indexes [I >= 2$\sigma$ (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 (**º**) 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 Angels** | | | |
| 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) |

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