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Palladacycles derivates of diimine ligands [*N*,*C*,*C*,*N*][†]

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Abstract: This paper presents the preparation, characterization and structural study of novel tridentate [*C*,*N*,*S*] biscyclopalladated complexes with ligands derived from the condensation of a primary amine −2-(methylthio)aniline− with the corresponding aromatic dialdehyde −terephthalaldehyde−. The compounds are also interesting due to their close-to-planarity arrangement and to the presence of seven fused rings in their structure.

Keywords: Diimines; Palladium; Tridentate Ligands.

1. Introduction

In past years extensive work has been published related to cyclometallated complexes containing two independent metallated phenyl rings [1-5]. But there are fewer studies dealing with double metallation of the same phenyl ring, namely, dicyclopalladation reactions on the same phenyl ring for ligands, such as diamines [6,7], diimines [8-10], pyrazines [11], pyridazines [12,13], tetrazines [14], bis(phenoxypyridines) [15], bis(imidazole) [16], bis(oxazolines) [17], bis(oximes) [6] and bis(pyrazoles) [19], have been described. Accordingly, it is necessary for the ligand to contain two substituents with potentially donor atoms, such as nitrogen or sulfur, which allow the formation of two five− or six− membered chelate rings.

2. Materials and Methods

2.1. General comments

Microanalyses were carried out at the Servicio de Análisis Elemental at the University of Santiago using a FISONS elemental analyzer, Model 1108. IR spectra were recorded as KBr pellets or polythene discs on BRUKER Model IFS-66v and IR-FT MATTSON Model CYGNUS-100 spectrophotometers. NMR spectra were obtained as $CDCl_3$ or DMSO-d_6 solution and referenced to $SiMe_4$ (^1H) or 85 % H_3PO_4 (^{31}P-{^1H}) and were recorded on BRUKER DPX 250 and Varian Inova 400 spectrometers.

2.1. Synthesis of Schiff base ligand

2.1.1. $[(2\text{-}(SMe)C_6H_4)_2N{=}C(H)\{\mu\text{-}C_6H_4\}]$ (a)

The synthesis of $[(2\text{-}(SMe)C_6H_4)_2N{=}C(H)\{\mu\text{-}C_6H_4\}]$ was performed by refluxing a dry chloroform solution of the appropriate quantities of terephthalaldehyde and 2-(methylthio)aniline in a Dean-Stark apparatus for 8 h under dry nitrogen. The solution was concentrated on an evaporator to give white solid (99 % yield). $C_{22}H_{20}N_2S_2$ (376.53). Analysis CHNS: calculated, C, 70.2; H, 5.4; N, 7.4; S, 17.0; experimental, C, 68.0; H, 5.4; N, 7.4; S, 17.3. IR (KBr, ν/cm^{-1}): 1622 (C=N). ^{1}H NMR (250 MHz, $CDCl_3$, 298 K): δ_H (ppm): 2.48 (s, 6H, S*CH*$_3$); 7.01-7.26 (m, 8H, H3, H4, H5, H6); 8.05 (s, 4H, Ha); 8.45 (s, 2H, *H*C=N).

2.2. Preparation of the complex

2.2.1. Synthesis of [(Pd{2-(SMe)C_6H_4N=C(H)κ*C*κ*N*κ*S*}(O_2CMe))$_2$(μ- C_6H_4)] (1a)

To a Schlenk tube with ligand **a** (0.3 g; 0.79 mmol) and palladium acetate (II) (0.4 g; 1.59 mmol), dry acid acetic (15 cm^3) was added. The mixture was heated to 95 °C for 4 hours. After this, the resulting solution was filtered off and the red solid washed through a Soxhlet with dichloromethane. The resultant red solution was dried with anhydrous sodium sulfate, and the solvent removed. (71 % yield). $C_{26}H_{24}N_2O_4Pd_2S_2$ (705.45). Analysis CHNS: calculated, C, 44.3; H, 3.4; N, 4.0; S, 9.1; experimental, C, 44.7; H, 3.3; N, 3.9; S, 9.1. IR (KBr, ν/cm^{-1}): 1614 (C=N), 1584 (COO)$_{as}$, 1384 (COO)$_s$.^{1}H NMR (250 MHz, DMSO-*d*$_6$, 298 K): δ_H (ppm): 1.95 (s, 3H, O*CH*$_3$); 2.84 (s, 6H, S*CH*$_3$); 7.42-7.54 (m, 8H, H3, H6, H10, H11); 7.80 (d, 2H, H12); 8.09 (d, 2H, H9); 9.23 (s, 2H, *H*C=N).

2.2.2. [(Pd{2-(SMe)C_6H_4N=C(H)κ*C*κ*N*κ*S*}(Cl))$_2$(μ- C_6H_4)] (2a)

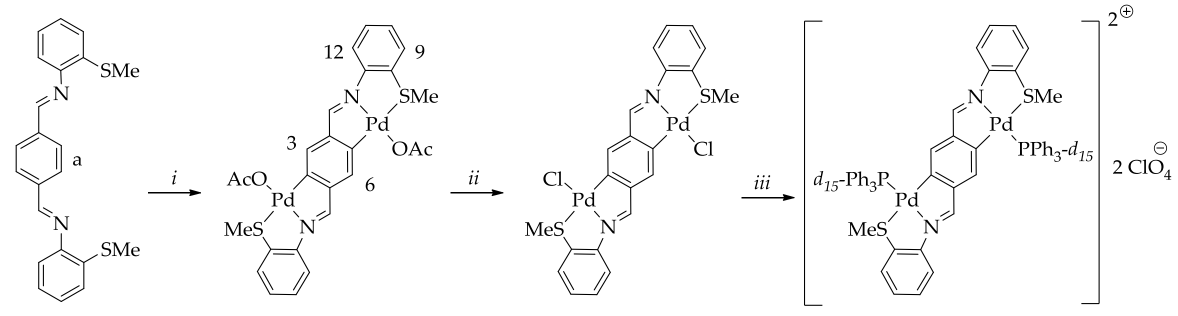
Compound **1a** (100 mg; 0.44 mmol) in acetone (15 cm^3) was treated with a solution of sodium chloride $5{\cdot}10^{-2}$ M. The resulting mixture was allowed to stir at room temperature for 24 h. After this, a red solid was separated by filtration and air dried. (33 % yield). $C_{22}H_{18}Cl_2N_2Pd_2S_2$ (658.27). Analysis CHNS: calculated, C, 40.1; H, 2.8; N, 4.3; S, 9.7; experimental, C, 40.7; H, 2.7; N, 4.3; S, 9.5. IR (KBr, ν7cm^{-1}): 1615 (C=N). IR (Nujol, ν7cm^{-1}): 470 (Pd-Cl$_t$ *trans*-N).^{1}H NMR (250 MHz, DMSO-*d*$_6$, 298 K): δ_H (ppm): 2.79 (s, 6H, S*CH*$_3$); 7.56 (m, 4H, H10, H11); 7.70 (s, 2H, H3, H6); 7.88 (d, 2H, H12, ^3J(H12H11) = 7,2 Hz); 8.13 (d, 2H, H9, ^3J(H9H10) = 7.1 Hz); 9.39 (s, 2H, *H*C=N).

2.2.3. [(Pd{2-(SMe)C_6H_4N=C(H)κ*C*κ*N*κ*S*}(PPh_3-*d*$_{15}$))$_2$(μ- C_6H_4)](ClO_4)$_2$ (3a)

Triphenylphoshine (0.42 g; 0.152 mmol) was added to a suspension of **2a** (0.05 g; 0.076 mmol) in acetone (15 cm^3) in a 1 to 2 molar ratio. The resulting mixture was stirred at room temperature for 12 h. Solvent removal *in vacuo* led to the precipitation of a yellow solid. (46 % yield). $C_{58}H_{18}D_{30}Cl_2N_2O_8P_2Pd_2S_2$ (1341.02). Analysis CHNS: calculated, C, 52.0; H, 5.9; N, 2.1; S, 4.8; experimental, C, 51.8; H, 6.1; N, 2.4; S, 5.1. IR (KBr, $\bar{\nu}$/cm^{-1}): 1591 (C=N).^{1}H NMR (400 MHz, DMSO-*d*$_6$, 298 K): δ_H (ppm): 1.92 (s, 6H, S*CH*$_3$); 6.66 (d, 2H, H3, H6, ^4J(HP) = 4.8 Hz); 7.47 (t, 2H, H11, ^3J(H11H12) = 7.2 Hz); 7.53 (t, 2H, H10, ^3J(H10H9) = 7.1 Hz); 7.70 (d, 2H, H9, ^3J(H9H10) = 7.1 Hz); 8.05 (d, 2H, H12, ^3J(H12H11) = 7.2 Hz); 8.73 (d, 2H, HC=N, ^4J(HP) = 8.2 Hz). ^{31}P RMN (400 MHz, DMSO-*d*$_6$, 298 K): δ_P (ppm): 39.07 (s).

3. Results and Discussion

For the convenience of the reader, the compounds and reactions are shown in Figure 1. The compounds described in this paper were characterized by elemental analysis, IR spectroscopy (data in the experimental section), and by ^{1}H, ^{31}P-{^{1}H}.



a **1a** **2a** **3a**

Figure 1. Reagents and conditions: *i*) $Pd(OAc)_2$ in molar ratio $Pd(OAc)_2$/diimine 2:1, dry acetic acid, 95 ºC, 4 h. *ii*) NaCl, acetone, rt. i*ii*) PPh_3-d_{15} in molar ratio complex:phosphine (1:2), $AgClO_4$ in molar ratio 1:2, acetone, rt., 12 h.

Reaction of ligand **a** with palladium(II) acetate in dry acetic acid gave the cyclometallated compound **1a** as a red air-stable solid. The *H*C=N proton resonance in the ^{1}H NMR spectrum of **1a** was shifted upfield as compared to that of the free ligand, in agreement with the endocyclic nature of the complex, and corroborates coordination of the palladium atom *via* the lone pair of the nitrogen atom. One singlet at 2.00 ppm was assigned to the acetate group; the monodentate coordination mode of the latter was confirmed by the presence of two bands at 1584 and 1344 cm^{-1} in the IR spectrum assigned to ν_{as}(C–O) and ν_s(C–O), respectively. The absence of the H5 proton resonance and the lack of symmetry in the ring

Reaction of **1a** with aqueous sodium chloride yielded the complex **2a**. The ^{1}H NMR spectrum showed only one set of signals for the H3, H6 and *H*C=N proton resonances. The H3 and H6 resonances appeared at 7.70 ppm shifted downfield as compared to complex **1a**. Treatment of **2a** with triphenylphosphine in a 1:2 molar ratio yield a dinuclear complex in which each metal atom is coordinated to a chlorine atom and a phosphine ligand. A resonance in the ^{1}H NMR spectrum (Figure 2) {δ8.73 [d, ^4J(PH) = 8.2 Hz]} was assigned to the *H*C=N proton coupled to the ^{31}P nucleus. The H3 and H6 resonances appeared as a doublet at 6.66 ppm, shifted to lower frequency compared to complex **2a** as a result of the coordination of triphenylphosphine. The ^{31}P-{^{1}H} NMR spectrum showed a singlet at 40.0 ppm. This shift is in the range expected for cyclometallated compounds of molecular formula *trans-N,P*-[Pd($\overset{\frown}{C\ N}$)(PPh_3)Cl] with a five membered palladacycle where a $C_{sp^2\text{-}phenyl}$ has been activated.

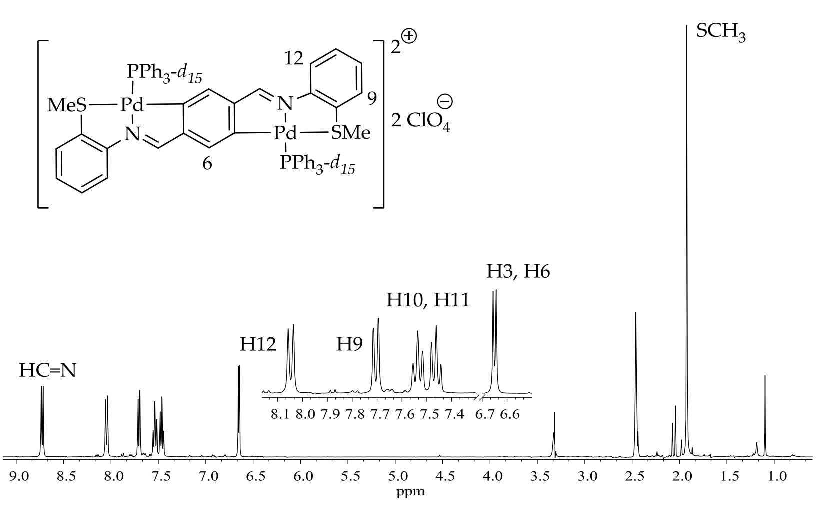


Figure 2. NMR ^{1}H spectrum (400 MHz, DMSO-d_6, 298 K) of **3j** complex.

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

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