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cis-Palladium(II) complexes of derivatives of di-(2-pyridyl)methane: Study of the influence of the bridge group in the coordination mode

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Abstract

Palladium(II) complexes containing di-(2-pyridyl)-*N*-methylimine (**1**), di-(2-pyridyl)methanol (**2**) and di-(2-pyridyl)methyl-*N*,*N*-diethyldithiocarbamate (**4**) ligands were synthesized and characterized by ^{1}H and ^{13}C NMR in solution, IR and X-ray single crystal diffraction. Crystal structures of *cis*-dichloro[di-(2-pyridyl)-*N*-methylimine]palladium(II) (**5**), *cis*-dichloro[di-(2-pyridyl)methanol]palladium(II) (**6**) and *cis*-dichloro[di-(2-pyridyl)methyl-*N*,*N*-diethyldithiocarbamate]palladium(II) (**7**) showed a bidentate coordination mode of the di-(2-pyridyl)methane derivatives **1**, **2** and **4**. In these complexes is observed the formation of a five-membered chelate ring with the iminic ligand **1** and six-membered chelate rings with the pyridinic ligands **2** and **4**. In all complexes the palladium atom displays a distorted square planar geometry.

Keywords: Pd(II) complexes; Di-(2-pyridyl)methane derivatives; X ray diffraction; NMR

1. Introduction

Several palladium(II) complexes derived from bidentate *N*,*N*′-ligands of the type I containing 2-pyridyl substituents (Fig. 1) have been described as stable catalysts for different carbon–carbon and carbon-nitrogen bond-forming reactions [1–6]. In these complexes, the di-2-pyridyl ligands have amino and amide groups as bridging moieties that mainly lead to the formation of six-membered chelate rings. Complexes of similar structure containing *cis*-dibromo- and dichloropalladium(II) fragments have also been reported [7,8]. On the other hand, dipyridinic analogues containing unsubstituted or substituted methylene as bridge groups have been widely studied in coordination chemistry [9–13] and only some dichloropalladium(II) complexes have been structurally characterized by means of X-ray diffraction; in these complexes the ligand coordination mode is formally bidentate [6,9,13–17]. The paucity of these structural studies in palladium chemistry prompt us to evaluate the coordinative behavior of di-(2-pyridyl)methane ligands **1**, **2** and **4**, where the bridge carbon contains *N*-methylimine, hydroxy and *N*,*N*-diethyldithiocarbamate groups, respectively. In the present work, we report on the synthesis, mass spectra, NMR and crystal characterization of di-(2-pyridyl)methylchloride (**3**) and di-(2-pyridyl)methyl-*N*,*N*-diethyldithiocarbamate (**4**) ligands and *cis*-dichloro[di-(2-pyridyl)-*N*-methylimine]palladium(II) (**5**), *cis*-dichloro[di-(2-pyridyl)-methanol]palladium(II) (**6**) and *cis*-dichloro[di-(2-pyridyl)methyl-*N*,*N*-diethyldithiocarbamate]palladium(II) (**7**) complexes, Fig. 2.

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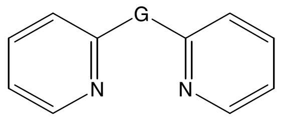


G= CH_2, $C(OH)_2$, C(OH)(OMe), C=O, NH, O, S

Fig. 1. Di-(2-pyridyl) ligands.

2. Experimental

2.1. Reagents and general procedures

All manipulations of air and moisture sensitive materials were carried out under dinitrogen using Schlenk techniques. Solvents were dried before use by standard methods. Di-(2-pyridyl)ketone, $NaS_2CNEt_2 \cdot 3H_2O$ and $PdCl_2$ were obtained commercially (Aldrich) and used as received. Melting points were recorded on a Mel-Temp II apparatus and are uncorrected. EI mass spectra were recorded on a Hewlett Packard 5989A spectrometer and FAB-mass spectra on a Jeol JMS-AX505HA mass spectrometer. Elemental analyses were performed on a Finnigan Flash EA 1112NC. IR spectra were recorded on a FT-IR 200 Perkin–Elmer spectrophotometer in the 4000–400 cm^{-1} range using KBr and CsI pellets. NMR spectra were recorded on a Jeol GSX 400 spectrometer. ^{1}H (399.78 MHz) and ^{13}C (100.53 MHz) spectra were obtained in DMSO-d_6. Chemical shifts (ppm) are relative to $Si(CH_3)_4$. NMR assignments of **1**–**7** were made by two-dimensional heteronuclear and homonuclear correlation experiments (hetcor, coloc and cosy). Single-crystal X-ray structures determination of compounds **3**–**7** were performed at room temperature on a Bruker Smart 6000 CCD diffractometer using graphite monochromated Mo Kα radiation (0.71073 Å). Structures of compounds **3**–**6** were solved by direct methods and the structure of the compound **7** was solved by Patterson method (SHELXTL NT 5.10) [18]. All non-hydrogen atoms were refined anisotropically. The positions of the hydrogen atoms were kept fixed with a common isotropic displacement parameter.

2.2. Synthesis of di-(2-pyridyl)methane ligands 1–4

Ligands **1** [19], **2** and **3** [20] were prepared as previously described; these ligands were characterized by means of NMR in $CDCl_3$ solution; for the sake of this work we have characterized them in DMSO-d_6 solution and reported below.

2.2.1. Di-(2-pyridyl)-N-methylimine (1)

Moisture-sensitive yellow solid. M.p. 67–68 °C. ^{1}H NMR (DMSO-d_6) δ: 8.66 (dd, 1H, H-12, $^{3}J_{H12-H11} = 4.85$ Hz, $^{4}J_{H12-H10} = 1.83$ Hz), 8.43 (dd, 1H, H-6, $^{3}J_{H6-H5} = 4.76$ Hz, $^{4}J_{H6-H4} = 1.83$ Hz), 8.14 (d, 1H, H-9, $^{3}J_{H9-H10} = 8.05$ Hz), 7.89 (m, 2H, H-4, H-10), 7.42 (m, 2H, H-5, H-11,), 7.32 (dd, 1H, H-3, $^{3}J_{H3-H4} = 7.68$, $^{4}J_{H3-H5} = 1.09$ Hz), 3.19 (s, 3H, N-CH_3); ^{13}C {^{1}H} NMR (DMSO-d_6) δ: 168.4 (C-13), 157.0 (C-2), 155.3 (C-8), 149.8 (C-12), 148.9 (C-6), 137.2 (C-4), 136.7 (C-10), 125.0 (C-5), 124.2 (C-3), 123.6 (C-11), 121.8 (C-9), 41.3 (N-CH_3).

2.2.2. Di-(2-pyridyl)methanol (2)

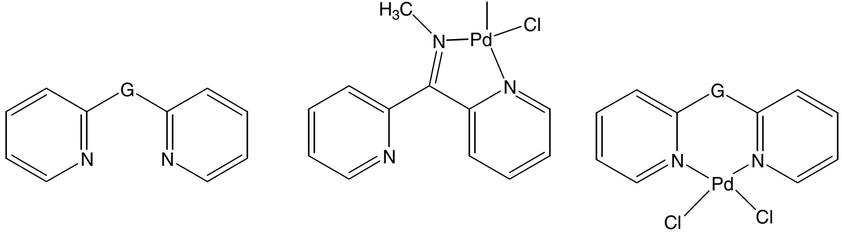
Yellow oil. ^{1}H NMR (DMSO-d_6) δ: 8.47 (d, 1H, H-6, $^{3}J_{H6-H5} = 4.40$ Hz), 7.78 (dd, 1H, H-4, $^{3}J_{H4-H3} = 7.68$, $^{3}J_{H4-H5} = 7.72$ Hz), 7.57 (d, 1H, H-3, $^{3}J_{H3-H4} = 7.68$ Hz), 7.22 (ddd, 1H, H-5, $^{3}J_{H5-H6} = 4.40$ Hz, $^{3}J_{H5-H4}$=7.72 Hz, $^{4}J_{H4-H6} = 1.48$ Hz), 6.28 (d, 1H, OH, $^{3}J_{OH14-H13} = 4.76$ Hz), 5.83 (d, 1H, CH-13, $^{3}J_{H13-OH14} = 5.12$ Hz); ^{13}C {^{1}H} NMR (DMSO-d_6) δ: 163.2 (C-2), 148.9 (C-6), 137.2 (C-4), 122.9 (C-5), 121.7 (C-3), 77.5 (C-13).

2.2.3. Di-(2-pyridyl)methylchloride (3)

Colorless solid. Dec. 67–69 °C. ^{1}H NMR (DMSO-d_6) δ: 9.03 (d, 1H, H-6, $^{3}J_{H6-H5} = 5.12$ Hz); 8.19 (dd, 1H, H-4, $^{3}J_{H4-H3} = 7.32$ Hz, $^{3}J_{H4-H5} = 7.60$ Hz); 7.95 (d, 1H, H-3, $^{3}J_{H3-H4} = 7.32$ Hz); 7.68 (dd, 1H, H-5, $^{3}J_{H5-H6} = 5.12$ Hz, $^{3}J_{H5-H4} = 7.60$ Hz); 7.18 (s, 1H, CH-13). ^{13}C {^{1}H} NMR (DMSO-d_6) δ: 155.3 (C-6); 151.9 (C-2); 142.0 (C-4); 126.8 (C-5); 126.6 (C-3); 60.8 (C-13).

2.2.4. Di-(2-pyridyl)methyl-N,N-diethyldithiocarbamate (4)

A mixture of **3** (0.100 g, 0.443 mmol) and sodium diethyldithiocarbamate trihydrate (0.120 g, 0.532 mmol) in



1 G= CNMe
2 G= CH(OH)
3 G= CH(Cl)
4 G= $CH(S_2CNEt_2)$

5

6 G= CH(OH)
7 G= $CH(S_2CNEt_2)$

Fig. 2. Ligands and complexes synthesized.