

Contents lists available at ScienceDirect

Polyhedron

journal homepage: www.elsevier.com/locate/poly

Monodentate *S*-vs. bidentate 1,5-*O,S*-coordination of *N*-phosphoryl-*N'*-(*R*)-thioureas with Pd(II)

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ARTICLE INFO

Article history:

Received 26 February 2008

Accepted 14 March 2008

Available online 2 May 2008

Keywords:

Complex

Crown-ether

Monodentate coordination

Palladium(II)

Thiourea

ABSTRACT

Reaction of *N*-phosphorylated thioureas of common formula RNHC(S)NHP(O)(OiPr)₂ (R = *t*Bu, **HL**^I; R = Ph, **HL**^{II}; R = 4'-benzo-15-crown-5, **HL**^{III}) with Pd(PhCN)₂Cl₂ in acetonitrile leads to complexes of the structure Pd(**HL**^{I-S})₂Cl₂ (**1**), Pd(**HL**^{II-S})₂Cl₂ (**2**) and Pd(**HL**^{III-S})₂Cl₂ (**3**). Reaction of *N*-phosphorylated thioureas of common formula RC(S)NHP(O)(OiPr)₂ (R = Et₂N, **HL**^{IV}; R = morpholine-*N*-yl, **HL**^V) in the same conditions leads to complexes Pd(**L**^{IV-O,S})₂ (**4**) and Pd(**L**^{V-O,S})₂ (**5**), where the palladium(II) atoms are coordinated in a square-planar fashion by the C=S sulfur atoms and the P=O oxygen atoms of two anionic ligands. The crystal structure of complex **1** has been investigated by X-ray crystallography. It was established that the thiourea ligands are in a *trans*-configuration and the palladium(II) cation is coordinated by the sulfur atoms of the C=S groups and the chlorine atoms. Complex **1** is the first example of palladium(II) complex in which the potentially chelating *N*-phosphorylated thiourea ligand is bound through the sulfur atom only.

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1. Introduction

The coordination chemistry of polyfunctional ligands, capable to realize different coordination modes with metal cations [1] is of interest for synthesis of new selective complexing agents and analytical reagents. Koch and others have shown that the coordination of *N,N*-dialkyl-*N'*-aroylthioureas leads to bidentate-*O,S*-coordination to Pd(II) [2,3]. It was also shown that the coordination mode of *N*-alkyl-*N'*-aroylthioureas depends on an intramolecular hydrogen bond between the donor oxygen atom of the carbonyl group and the hydrogen atom of the NH group [2].

We have become interested in the coordination chemistry of *N*-phosphorylated thioureas RR'NC(S)NHP(O)(OiPr)₂ (R = R' = alkyl; R = H, R' = alkyl, aryl) towards various transition metal cations [4] in view of their application in metals separation [5]. Recently, we reported, that in the square-planar complexes of *N*-phosphorylthioureas M[RNHC(S)NP(O)(OiPr)₂]₂, where (M = Ni(II), R = Ph [6], *p*-MeOC₆H₄, *p*-BrC₆H₄, *t*Bu, *i*Pr, *c*-Hex [7]; M = Pd(II), R = Ph [6], *i*Pr [7]; M = Cu(II), R = Ph, *c*-Hex [6]), 1,3-*N,S*-coordination of the anionic ligand is realized.

Recently, we reported some synthetic results presented here as a preliminary communication [8]. Herein, we report the comparative study on the complexes of the Pd(II) ions with *N*-phospho-

rylthioureas, containing secondary (Scheme 1) and tertiary (Scheme 2) nitrogen at the *N*-thioacylamidophosphate moiety C(S)NHP(O)(OiPr)₂. The crystal structure of *trans*-Pd(**HL**^{I-S})₂Cl₂, the first example of *N*-phosphorylthiourea coordinated to Pd(II) only through the S atom in the monodentate fashion, is also reported.

2. Experimental

2.1. Synthesis of **HL**^I-**HL**^V

N-Diisopropoxyphosphorylthioureas were prepared according to the previously described methods [9].

2.2. Synthesis of **1–5**

A portion of Pd(PhCN)₂Cl₂ (0.192 g, 0.5 mmol) dissolved in 30 mL of acetonitrile was added dropwise to 30 mL of a well stirred solution containing **HL**^{I-V} (0.296, 0.316, 0.506, 0.295 or 0.310 g; 1 mmol) in the same solvent. The mixture was stirred at room temperature for a further 10 h. The solvent was then removed *in vacuo*. A precipitate was isolated from dichloromethane by *n*-hexane.

2.2.1. Pd(**HL**^{I-S})₂Cl₂ (**1**)

Yield: 0.331 g (86%). M.p. 128–129 °C. ¹H NMR (CDCl₃): δ 1.38–1.43 (m, 12H, CH₃), 1.49–1.53 (m, 9H, CH₃, *t*Bu), 4.58–4.73 (m, 2H,

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