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# Intramolecular hydrogen bond controlled monodentate S-coordination of *N*-phosphoryl-*N'*-(*R*)-thioureas with Pd(II)

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## Abstract

Reaction of *N*-phosphorylated thioureas RNHC(S)NHP(O)(OiPr)<sub>2</sub> (R = *t*Bu, **HL**<sup>I</sup>; R = Ph, **HL**<sup>II</sup>; R = 4'-benzo-15-crown-5, **HL**<sup>III</sup>) with Pd(PhCN)<sub>2</sub>Cl<sub>2</sub> in acetonitrile leads to complexes of formulae Pd(HL<sup>I</sup>-S)<sub>2</sub>Cl<sub>2</sub> (**1**), Pd(HL<sup>II</sup>-S)<sub>2</sub>Cl<sub>2</sub> (**2**) and Pd(HL<sup>III</sup>-S)<sub>2</sub>Cl<sub>2</sub> (**3**). 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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The coordination chemistry of polyfunctional ligands, capable to realize different coordination modes with metal cations [1], is of interest for the 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)<sub>2</sub> (R = R' = alkyl; R = H, R' = alkyl, aryl) towards various transition metal cations [4] in view of their application in metals separations [5]. Recently, we reported, that in the square-planar complexes of *N*-phosphorylthioureas M[RNHC(S)NP(O)(OiPr)<sub>2</sub>]<sub>2</sub>, where M = Ni(II), R = Ph

[6], *p*-MeOC<sub>6</sub>H<sub>4</sub>, *p*-BrC<sub>6</sub>H<sub>4</sub>, *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.

Herein, we report the comparative study on the complexes of the Pd(II) ions with *N*-phosphorylthioureas, containing secondary nitrogen at the *N*-thioacylamidophosphate moiety C(S)NHP(O)(OiPr)<sub>2</sub> (Scheme 1). The crystal structure of *trans*-Pd(HL<sup>I</sup>-S)<sub>2</sub>Cl<sub>2</sub>, the first example of *N*-phosphorylthiourea coordinated to Pd(II) only through the S atom in the monodentate fashion, is also reported.

*N*-Phosphorylated thioureas were prepared as previously described [8] and purified by recrystallization from dichloromethane-*n*-hexane mixtures.

Complexes **1–3** were prepared by the following procedure: Pd(PhCN)<sub>2</sub>Cl<sub>2</sub> was dissolved in acetonitrile and added to a solution containing the corresponding ligand in the same solvent (Scheme 1) [9]. The compounds obtained are crystalline solids that are soluble in most polar solvents.

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