

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

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Reaction of *N*-phosphorylated thioureas $\text{RNHC(S)NHP(O)(OiPr)}_2$ ($\text{R} = t\text{Bu}$, **HL^I**; $\text{R} = \text{Ph}$, **HL^{II}**; $\text{R} = 4'$ -benzo-15-crown-5, **HL^{III}**) with $\text{Pd(PhCN)}_2\text{Cl}_2$ in acetonitrile leads to complexes of formulae $\text{Pd(HL^I-S)}_2\text{Cl}_2$ (**1**), $\text{Pd(HL^{II}-S)}_2\text{Cl}_2$ (**2**) and $\text{Pd(HL^{III}-S)}_2\text{Cl}_2$ (**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 CS 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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