

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

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Rok wydania

2008

Czasopismo

Polyhedron

Numer woluminu

27

Strony

1995-1998

DOI

10.1016/j.poly.2008.03.012

Kolekcja

Naukowa

Język

Angielski

Typ publikacji

Artykuł

Streszczenie

Reaction of *N*-phosphorylated thioureas of common formula $\text{RNHC(S)NHP(O)(OiPr)}_2$ ($\text{R} = t\text{Bu}$, **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 the structure $\text{Pd(HL^I-S)}_2\text{Cl}_2$ (**1**), $\text{Pd(HL^{II}-S)}_2\text{Cl}_2$ (**2**) and $\text{Pd(HL^{III}-S)}_2\text{Cl}_2$ (**3**). Reaction of *N*-phosphorylated thioureas of common formula $\text{RC(S)NHP(O)(OiPr)}_2$ ($\text{R} = \text{Et}_2\text{N}$, **HL^{IV}**; $\text{R} = \text{morpholine-}N\text{-yl}$, **HL^V**) in the same conditions leads to complexes $\text{Pd(L^{IV}-O,S)}_2$ (**4**) and Pd(L^V-O,S)_2 (**5**), where the palladium(II) atoms are coordinated in a square-planar fashion by the CS sulfur atoms and the PO 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 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.

Adres publiczny

<https://doi.org/10.1016/j.poly.2008.03.012>

Strona internetowa wydawcy

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