

**(4-*tert*-Butyl-2-methylthiosemicarbazido)-  
(*O*-methyldithiophosphato)palladium(II)****Michal Janča, Jan Taraba and Jiří Příhoda\***

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**Key indicators**

Single-crystal X-ray study

 $T = 120$  KMean  $\sigma(\text{C}-\text{C}) = 0.009$  Å $R$  factor = 0.060 $wR$  factor = 0.110

Data-to-parameter ratio = 16.6

For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

The title Pd complex,  $[\text{Pd}(\text{C}_6\text{H}_{14}\text{N}_3\text{S})(\text{CH}_3\text{O}_2\text{PS}_2)]$ , is formed from  $\text{Pd}(\text{acetate})_2$  and 5-*tert*-butylamino-4-methyl-2-sulfoxo-2-thioxo-1,3,4,2 $\lambda^5$ -thiadiazaphospholan-5-onium, (1), in methanol. The Pd atom is coordinated to two different ligands which are generated *in situ* as a result of methanolysis of the starting compound (1). Thus, Pd is complexed by the *O*-methyldithiophosphate ligand and by 2-methyl-4-*tert*-butylthiosemicarbazide. Two molecules of the Pd chelate are linked by two intermolecular  $\text{N}-\text{H} \cdots \text{O}$  hydrogen bonds, the  $\text{N} \cdots \text{O}$  distances of which are 3.361 and 2.827 Å.

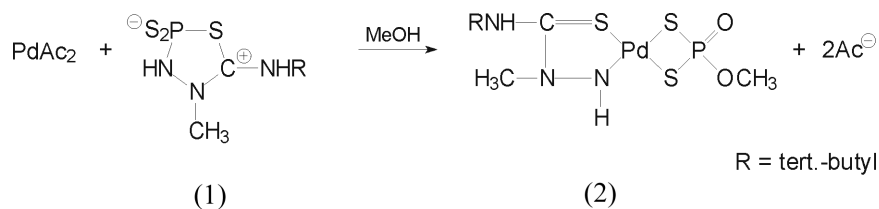
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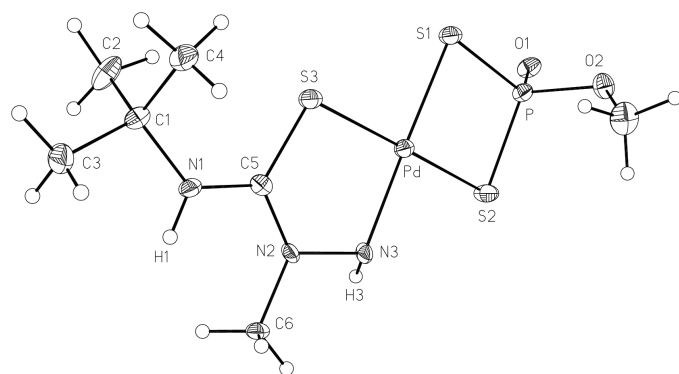
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**Comment**

Chlorodithiophosphoric acid pyridiniumbetaine,  $\text{PyPS}_2\text{Cl}$ , reacts with the thiosemicarbazide derivative  $(\text{RNH})(\text{H}_2\text{N}-\text{NMe})\text{CS}$  ( $R$  is *tert*-butyl), in acetonitrile in the absence of any HCl-acceptor, to yield a new compound, (1), with a five-membered heterocycle (Janča *et al.*, 2001). This substance was used in an attempt to complex palladium in acetonitrile solution, but no complex formation was observed. Therefore, we used methanol as the reaction solvent. We isolated a solid product in the form of dark-orange crystals. An X-ray diffraction experiment revealed this substance to be the title complex, (2). The unexpected complex formation can be explained by the reaction of the starting complexing agent (1) with methanol, in which two ligands, *O*-methyldithiophosphate and 2-methyl-4-*tert*-butylthiosemicarbazide, are generated *in situ*. These ligands react further with  $\text{Pd}(\text{acetate})_2$ . The formation of the palladium(II) complex is shown in the scheme below.



Selected bond lengths and angles are given in Table 1 and the molecular structure is shown in Fig. 1. The palladium environment is approximately planar. This is confirmed by the values of bond angles  $\text{S1}-\text{Pd}-\text{N3}$  [177.91 (16)°],  $\text{S2}-\text{Pd}-\text{S3}$  [175.90 (7)°],  $\text{S1}-\text{Pd}-\text{S2}$  [84.41 (6)°],  $\text{S2}-\text{Pd}-\text{N3}$  [95.67 (14)°],  $\text{N3}-\text{Pd}-\text{S3}$  [84.92 (14)°] and  $\text{S3}-\text{Pd}-\text{S1}$  [95.15 (6)°]. The greatest deviation from the Pd/S1/S2/S3/N3 plane is for atom S2 (0.0821 Å). *O*-Methyldithiophosphate is bonded to the Pd centre through atoms S1 and S2. The Pd—S1 bond [2.3069 (17) Å], in a *trans* position with respect to atom N3, is shorter than the Pd—S2 distance [2.3457 (18) Å]. This



**Figure 1**  
The structure of (4-*tert*-butyl-2-methylthiosemicarbazido)(*O*-methylthiophosphato)palladium(II). Displacement ellipsoids are drawn at the 50% probability level.

difference can be explained by a stronger *trans* influence of nitrogen compared with sulfur. A similar difference in bond distances between a central atom and a donor S atom was observed in the case of a non-symmetric palladium complex of dithiolate and *N,N*-dimethylbenzylamine (Narayan *et al.*, 1997), where the Pd–S1 distance is 2.3303 (12) Å and Pd–S2 is 2.458 (2) Å. The Pd–S1–S2–P ring is also approximately planar, the exception being the P atom, which deviates slightly from the plane (0.0678 Å). The P atom environment is, in accordance with our expectations, tetrahedral. The lengths of the P–S1 [2.033 (2) Å] and P–S2 [2.024 (2) Å] bonds correspond to single-bond character. Similar distances can be found in a nickel(II) complex with *O*-methylthiophosphate [2.032 (4) and 2.024 (4) Å; Gastaldi *et al.*, 1974].

From the other side, the palladium is complexed by a neutral molecule of 2-methyl-*tert*-butylthiosemicarbazide. The donor atoms of the ligand are amide atom N3 and S3 in the thiocarbonyl group of the ligand. A five-membered Pd/N3/N2/C5/S3 heterocycle is formed. The bond distances in the ring are: Pd–N3 2.060 (5), N3–N2 1.433 (7), N2–C5 1.345 (8), C5–S3 1.714 (6) and S3–Pd 2.2762 (17) Å. Similar rings have already been described in the literature, *e.g.* by Neumuller *et al.* (1999) and Ghassemzadeh *et al.* (2000), where the corresponding distances are Pd–N 2.079 (5), N–N 1.443 (6), N–C 1.353 (7), C–S 1.692 (6) and S–Pd 2.274 (2) Å. The Pd–N3–N2–C5–S3 ring can be considered planar; only atom N3 deviates slightly from the plane of the ring (0.0675 Å). The C5–S3 bond [1.714 (6) Å] has almost double-bond character compared with the C=S bond in 2,4-methylthiosemicarbazide (1.697 Å; Valente *et al.*, 1998). The values for C–S bonds are in the region 1.82–1.86 Å (*International Tables for Crystallography*, 1995, Vol. C, p. 685). Two molecules of the Pd complex are linked by two intermolecular hydrogen bonds, N3–H3⋯O1<sup>i</sup> [2.827 (6) Å] and N1–H1⋯O2<sup>ii</sup> [3.361 (7) Å] (Fig. 2; see Table 2 for symmetry codes).

## Experimental

The title palladium complex was prepared by the reaction of Pd(acetate)<sub>2</sub> (0.04 mol) with the complexing agent (1) (0.08 mol) in 20 ml of methanol. The reaction mixture was intensively stirred for

24 h at room temperature. The crystals were grown from the solution after partial evaporation of the solvent. A dark-orange crystal was chosen for the X-ray structure determination.

## Crystal data

[Pd(C<sub>6</sub>H<sub>14</sub>N<sub>3</sub>OS)(CH<sub>3</sub>O<sub>2</sub>PS<sub>2</sub>)]  
*M<sub>r</sub>* = 408.79  
 Monoclinic, *P*2<sub>1</sub>/*c*  
*a* = 12.889 (3) Å  
*b* = 10.854 (2) Å  
*c* = 11.120 (2) Å  
 β = 105.23 (3)°  
*V* = 1501.0 (5) Å<sup>3</sup>  
*Z* = 4

*D<sub>x</sub>* = 1.809 Mg m<sup>−3</sup>  
 Mo *K*α radiation  
 Cell parameters from 50 reflections  
 θ = 11.0–20.8°  
 μ = 1.75 mm<sup>−1</sup>  
*T* = 120 (2) K  
 Prism, orange  
 0.10 × 0.05 × 0.02 mm

## Data collection

Kuma KM-4 CCD diffractometer  
 with an Oxford Cryosystems low-temperature device  
 ω scans  
 9041 measured reflections  
 2636 independent reflections

2249 reflections with *I* > 2σ(*I*)  
*R*<sub>int</sub> = 0.078  
 θ<sub>max</sub> = 25.0°  
*h* = −15 → 13  
*k* = −12 → 12  
*l* = −11 → 13

## Refinement

Refinement on *F*<sup>2</sup>  
*R*[*F*<sup>2</sup> > 2σ(*F*<sup>2</sup>)] = 0.060  
*wR*(*F*<sup>2</sup>) = 0.110  
*S* = 1.16  
 2636 reflections  
 159 parameters  
 H-atom parameters constrained

*w* = 1/[σ<sup>2</sup>(*F<sub>o</sub>*<sup>2</sup>) + (0.0398*P*)<sup>2</sup> + 3.35*P*]  
 where *P* = (*F<sub>o</sub>*<sup>2</sup> + 2*F<sub>c</sub>*<sup>2</sup>)/3  
 (Δ/σ)<sub>max</sub> = 0.001  
 Δρ<sub>max</sub> = 1.18 e Å<sup>−3</sup>  
 Δρ<sub>min</sub> = −1.04 e Å<sup>−3</sup>

**Table 1**

Selected geometric parameters (Å, °).

Pd–N3	2.060 (5)	O2–C7	1.449 (8)
Pd–S3	2.2762 (17)	N1–C5	1.341 (8)
Pd–S1	2.3069 (17)	N1–C1	1.493 (8)
Pd–S2	2.3457 (18)	N1–H1	0.880
P–O1	1.489 (5)	N2–C5	1.345 (8)
P–O2	1.610 (5)	N2–N3	1.433 (7)
P–S2	2.024 (2)	N2–C6	1.461 (8)
P–S1	2.033 (2)	N3–H3	0.988
S3–C5	1.714 (6)		
N3–Pd–S3	84.92 (14)	C5–S3–Pd	98.8 (2)
N3–Pd–S1	177.91 (16)	C7–O2–P	120.4 (4)
S3–Pd–S1	95.15 (6)	C5–N1–C1	128.9 (5)
N3–Pd–S2	95.67 (14)	C5–N1–H1	115.6
S3–Pd–S2	175.90 (7)	C1–N1–H1	115.6
S1–Pd–S2	84.41 (6)	C5–N2–N3	119.4 (5)
O1–P–O2	105.0 (3)	C5–N2–C6	124.5 (5)
O1–P–S2	117.3 (2)	N3–N2–C6	114.9 (5)
O2–P–S2	108.92 (19)	N2–N3–Pd	114.4 (4)
O1–P–S1	114.8 (2)	N2–N3–H3	106.3
O2–P–S1	109.88 (18)	Pd–N3–H3	103.4
S2–P–S1	100.81 (10)	N1–C5–N2	117.0 (5)
P–S1–Pd	87.34 (8)	N1–C5–S3	122.5 (5)
P–S2–Pd	86.50 (8)	N2–C5–S3	120.5 (5)

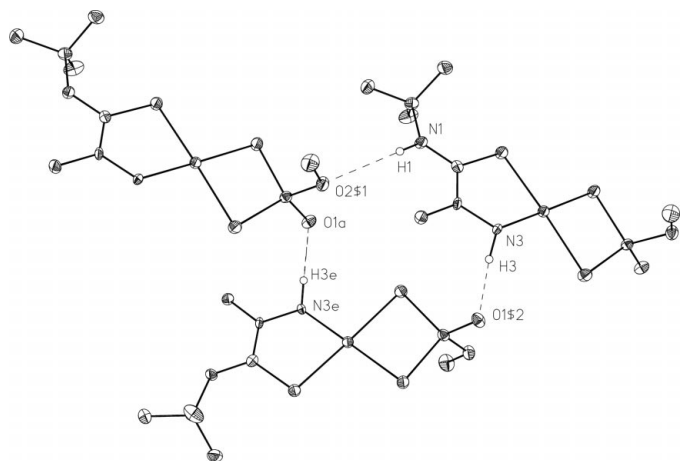
**Table 2**

Hydrogen-bonding geometry (Å, °).

<i>D</i> –H⋯ <i>A</i>	<i>D</i> –H	H⋯ <i>A</i>	<i>D</i> ⋯ <i>A</i>	<i>D</i> –H⋯ <i>A</i>
N3–H3⋯O1 <sup>i</sup>	0.99	1.88	2.827 (6)	160
N1–H1⋯O2 <sup>ii</sup>	0.88	2.56	3.361 (7)	151

Symmetry codes: (i) 2 − *x*, *y* − ½, ½ − *z*; (ii) *x*, *y* − 1, *z*.

H atoms were placed in calculated positions and refined as riding.



**Figure 2**

Hydrogen bonding in the title palladium(II) complex. Displacement ellipsoids are drawn at the 50% probability level.

Data collection: *KM-4 Software* (Kuma, 1997); cell refinement: *KM-4 Software*; data reduction: *KM-4 Software*; program(s) used to

solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *XP* in *SHELXTL* (Sheldrick, 1997).

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## References

- Gastaldi, L., Porta, P. & Tomlinson, A. A. G. (1974). *J. Chem. Soc. Dalton Trans.* pp. 1424–1429.
- Ghassemzadeh, M., Bolourchain, M., Chitsaz, S., Neumuller, B. & Heravi, M. M. (2000). *Eur. J. Inorg. Chem.* **8**, 1877–1882.
- Janča, M., Nečas M., Žák, Z. & Příhoda, J. (2001). *Polyhedron*, **20**, 2823–2828.
- Kuma (1997). *KM-4 Software*. Version KM4b8. Kuma Diffraction, Wrocław, Poland.
- Narayan, S., Jain, V. K. & Butcher, R. J. (1997). *J. Organomet. Chem.* **549**, 73–80.
- Neumuller, B., Heravi, M. M. & Ghassemzadeh, M. (1999). *Z. Anorg. Allg. Chem.* **625**, 1908–1911.
- Sheldrick, G. M. (1997). *SHELXS97*, *SHELXL97* and *SHELXTL*. University of Göttingen, Germany.
- Valente, E. J., Zubkowski, J. D., Jabalameli, A., Mazhari, S., Venkatraman, R. & Sullivan, R. H. (1998). *J. Chem. Crystallogr.* **28**, 27–33.