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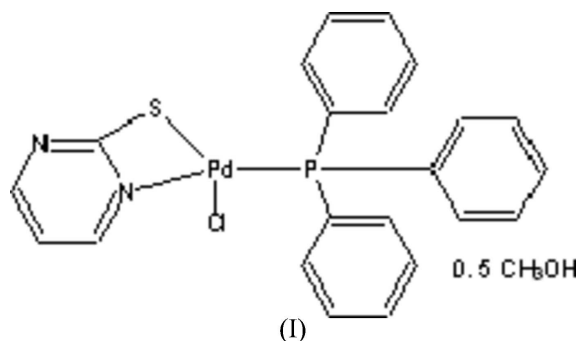
## Key indicators

Single-crystal X-ray study  
 $T = 233$  K  
Mean  $\sigma(\text{C}-\text{C}) = 0.004$  Å  
H-atom completeness 91%  
Disorder in solvent or counterion  
 $R$  factor = 0.033  
 $wR$  factor = 0.074  
Data-to-parameter ratio = 18.4For details of how these key indicators were  
automatically derived from the article, see  
<http://journals.iucr.org/e>.Chloro(pyrimidine-2-thiolato- $\kappa^2N,S$ )-  
(triphenylphosphine- $\kappa P$ )palladium(II)  
methanol hemisolvate

In the title compound,  $[\text{Pd}(\text{C}_4\text{H}_3\text{N}_2\text{S})\text{Cl}(\text{C}_{18}\text{H}_{15}\text{P})] \cdot 0.5\text{CH}_3\text{OH}$ , the Pd atom is four-coordinate and exhibits a slightly distorted square-planar geometry with the S atom of the pyrimidine-2-thiolate ligand *trans* to the chloro ligand and the coordinated N atom *trans* to the phosphine. The compound crystallizes with two unique molecules and a disordered methanol solvent molecule in the asymmetric unit.

## Comment

Palladium(II) complexes with heterocyclic thione ligands are of current interest for the synthesis of clinically useful drugs (Raper *et al.*, 1985). The crystal structures of four-coordinate palladium(II) complexes with N- and S-donor heterocyclic 2-thionate ligands, such as  $\text{Pd}_2(2\text{-Me}_2\text{NCH}_2\text{C}_6\text{H}_4)_2(\mu\text{-OH})(\mu\text{-Br})$  (Ruiz *et al.*, 1996) and (2-benzylpyridinethiosemicarbazone)palladium(II) have been extensively investigated (Rebolledo *et al.*, 2005). The title compound, (I), exhibits antibacterial and antitumor activity (Krischner *et al.*, 1966) due to the N—C—S group generated by deprotonation of the heterocyclic thione (Santana *et al.*, 2000). It has also been used as a pesticide (Fackler, 2002) and an antimicrobial agent (Ronconi *et al.*; 2005).



In the title compound, each Pd atom of the two unique molecules in the asymmetric unit is four-coordinate and exhibits a slightly distorted square-planar geometry (Fig. 1). The two molecules are similar except for the conformational orientation of the triphenylphosphine ligand, shown by the torsion angles  $\text{S1}-\text{Pd1}-\text{P1}-\text{C5}$  [ $5.4(1)^\circ$ ] and  $\text{S2}-\text{Pd2}-\text{P2}-\text{C27}$  [ $-19.9(1)^\circ$ ]. The pyrimidine-2-thiolate ligand acts as a bidentate chelate, coordinating to Pd *via* the S1 atom and the adjacent pyrimidine N1 atom. Atom S1 is *trans* to the chloro ligand and N1 is *trans* to the triphenylphosphine ligand (Table 1). The slightly distorted square-planar geometry of the Pd atoms is also revealed by the displacements of the Pd atoms from the mean planes through the ligand donor atoms of

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0.0876 (7) Å for Pd1 and 0.0893 (6) Å for Pd2. These deviations may be related to weak intermolecular interactions between Pd1 and N3 [3.660 (2) Å], and between Pd2 and S1 [3.9498 (9) Å].

## Experimental

Pyrimidine-2-thione (0.16 g, 1.14 mmol) dissolved in CH<sub>2</sub>Cl<sub>2</sub> (10 ml) was added dropwise to a suspension of [PdCl<sub>2</sub>(PPh<sub>3</sub>)] (0.5 g, 1.14 mmol) (Kitano *et al.*, 1983) in CH<sub>2</sub>Cl<sub>2</sub> (20 ml). The resulting solution was refluxed for 2–3 h and a clear solution was obtained. Yellow crystals were obtained by slow evaporation of the solvent at room temperature.

### Crystal data

[Pd(C<sub>4</sub>H<sub>3</sub>N<sub>2</sub>S)Cl(C<sub>18</sub>H<sub>15</sub>P)]·  
0.5CH<sub>2</sub>O  
*M<sub>r</sub>* = 531.29  
Monoclinic, *P*2<sub>1</sub>/*c*  
*a* = 16.1340 (2) Å  
*b* = 9.7020 (1) Å  
*c* = 29.0480 (4) Å  
*β* = 102.617 (1)°  
*V* = 4437.14 (10) Å<sup>3</sup>  
*Z* = 8

*D<sub>x</sub>* = 1.591 Mg m<sup>-3</sup>  
Mo *Kα* radiation  
Cell parameters from 26420  
reflections  
*θ* = 1.0–27.5°  
*μ* = 1.14 mm<sup>-1</sup>  
*T* = 233 (2) K  
Prism, yellow  
0.35 × 0.25 × 0.08 mm

### Data collection

Nonius KappaCCD diffractometer  
*φ* and *ω* scans  
Absorption correction: none  
26420 measured reflections  
9812 independent reflections  
8231 reflections with *I* > 2σ(*I*)

*R<sub>int</sub>* = 0.033  
*θ<sub>max</sub>* = 27.5°  
*h* = –20 → 20  
*k* = –12 → 12  
*l* = –37 → 36

### Refinement

Refinement on *F*<sup>2</sup>  
*R* [*F*<sup>2</sup> > 2σ(*F*<sup>2</sup>)] = 0.033  
*wR* (*F*<sup>2</sup>) = 0.074  
*S* = 1.02  
9812 reflections  
532 parameters  
H-atom parameters constrained

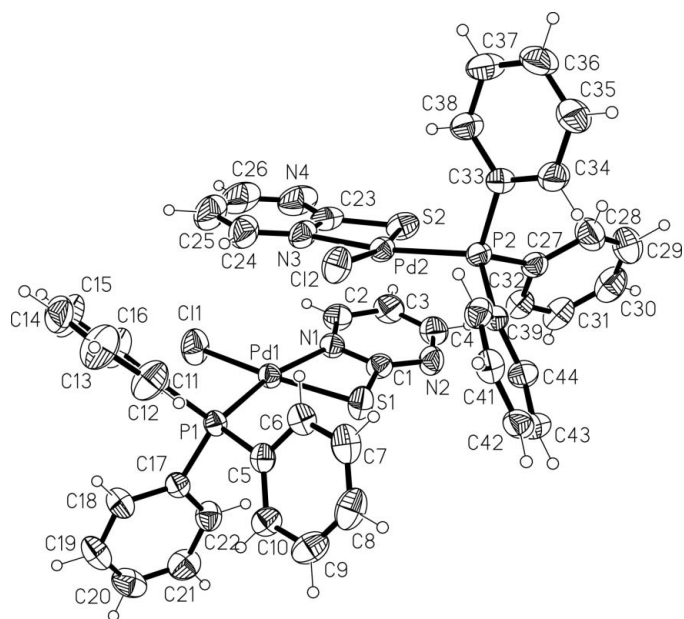
$w = 1/[\sigma^2(F_o^2) + (0.0217P)^2 + 4.762P]$   
where  $P = (F_o^2 + 2F_c^2)/3$   
(*Δ*/*σ*)<sub>max</sub> = 0.002  
*Δρ*<sub>max</sub> = 0.39 e Å<sup>-3</sup>  
*Δρ*<sub>min</sub> = –0.63 e Å<sup>-3</sup>

**Table 1**

Selected geometric parameters (Å, °).

Pd1–N1	2.071 (2)	Pd2–Cl2	2.3104 (7)
Pd1–P1	2.2467 (7)	S1–C1	1.747 (3)
Pd1–S1	2.2975 (7)	S2–C23	1.740 (3)
Pd1–Cl1	2.3225 (8)	N1–C1	1.345 (3)
Pd2–N3	2.082 (2)	N2–C1	1.320 (3)
Pd2–P2	2.2424 (7)	N3–C23	1.342 (4)
Pd2–S2	2.3100 (7)	N4–C23	1.333 (4)
N1–Pd1–P1	166.81 (6)	S2–Pd2–Cl2	166.96 (3)
N1–Pd1–S1	70.26 (6)	C1–S1–Pd1	81.03 (9)
P1–Pd1–S1	96.84 (2)	C23–S2–Pd2	80.59 (10)
N1–Pd1–Cl1	95.41 (6)	C1–N1–Pd1	100.12 (16)
P1–Pd1–Cl1	97.16 (3)	C23–N3–Pd1	88.62 (16)
S1–Pd1–Cl1	164.78 (3)	N2–C1–N1	126.1 (2)
N3–Pd2–P2	169.30 (7)	N2–C1–S1	125.3 (2)
N3–Pd2–S2	70.10 (7)	N1–C1–S1	108.54 (19)
P2–Pd2–S2	100.22 (3)	N4–C23–N3	125.1 (3)
N3–Pd2–Cl2	97.40 (7)	N4–C23–S2	125.3 (3)
P2–Pd2–Cl2	91.91 (3)	N3–C23–S2	109.6 (2)

All C-bound H atoms were refined using a riding model, with C–H = 0.94 Å and *U*<sub>iso</sub>(H) = 1.2*U*<sub>eq</sub>(C). The asymmetric unit contains a



**Figure 1**

The structures of the two unique complex molecules of (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level. The solvent molecule has been omitted.

disordered methanol solvent molecule. The disorder, with fixed occupancy of 0.75 for O1 and 0.25 for O1A, was resolved by varying the occupancy factors of both O-atom positions until their isotropic displacement parameters refined to a similar value. A final refinement was accomplished with fixed occupancy factors and anisotropic displacement parameters for the O-atom positions. The H atoms of this solvent molecule, which would have poor resolution and large displacement parameters, were not included in this refinement.

Data collection: *COLLECT* (Nonius, 1998); cell refinement: *SCALEPACK* (Otwinowski & Minor, 1997); data reduction: *DENZO* (Otwinowski & Minor, 1997) and *SCALEPACK*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997a); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997a); molecular graphics: *SHELXTL* (Sheldrick, 1997b); software used to prepare material for publication: *SHELXL97*.

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