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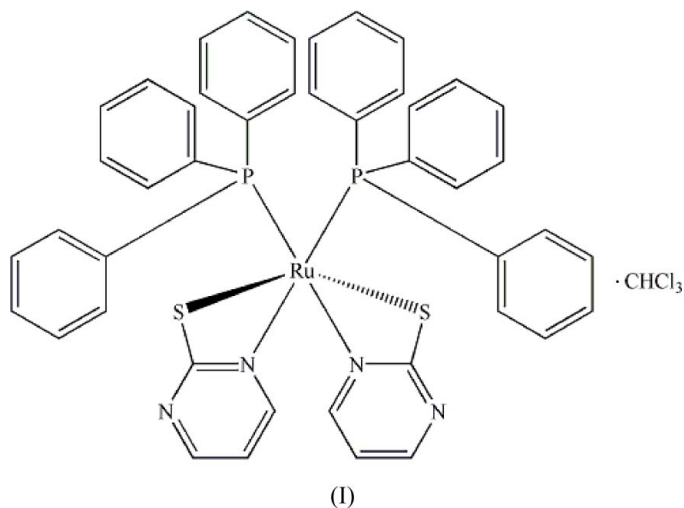
## Key indicators

Single-crystal X-ray study  
 $T = 294$  K  
Mean  $\sigma(\text{C}-\text{C}) = 0.005$  Å  
Disorder in solvent or counterion  
 $R$  factor = 0.040  
 $wR$  factor = 0.083  
Data-to-parameter ratio = 18.7For details of how these key indicators were  
automatically derived from the article, see  
<http://journals.iucr.org/e>.Bis(pyrimidine-2-thiolato)bis(triphenylphosphine)-  
ruthenium(II) chloroform solvate

In the title compound,  $[\text{Ru}(\text{C}_4\text{H}_3\text{N}_2\text{S})_2(\text{C}_{18}\text{H}_{15}\text{P})_2]\cdot\text{CHCl}_3$ , the Ru atom has a distorted octahedral environment formed by two S and two N atoms from the pyrimidine-2-thiolate ligands and two P atoms from the triphenylphosphine ligands. Intramolecular  $\pi-\pi$  interactions between the pyrimidine and phenyl rings of triphenylphosphine are observed.

## Comment

The ruthenium(II) complexes of heterocyclic ligands, such as pyridine and pyrazole, have various applications in photochemistry, photophysics and biochemistry (Chan & Wong, 1995). Some of the ruthenium(II) complexes are known to target DNA with preferential attack at purine bases (guanines) (Chen *et al.*, 2002). Thus, their important applications as probes of DNA structure, DNA-mediated electron transfer, DNA footprinting and sequence-specific cleaving agents have been developed (Dandliker *et al.*, 1997; Fletcher & Skapski, 1972; Gonzalez *et al.*, 2000). Among the ligands used, 2-mercaptopyridine and its analogues have attracted attention due to their activities against some types of human cancers when coordinated to metals (Gonzalez *et al.*, 2000; Hong *et al.*, 2002).



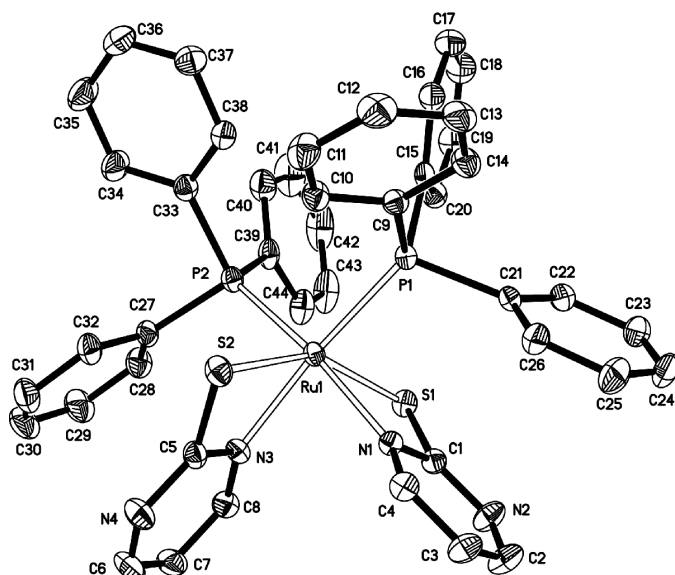
Unlike the reported 2-mercaptopyridine ligand, which may act only as a bidentate ligand, 2-mercaptopyrimidine has versatile coordination modes that lead to diverse potential biological activities (Lobana *et al.*, 1998; Gonzalez *et al.*, 2000). In continuation of our study of such complexes, the title compound, (I), was prepared by the reaction of 2-mercaptopyrimidine with  $[\text{Ru}(\text{PPh}_3)_3\text{Cl}_2]$ .

The molecular structure of the ruthenium(II) complex is shown in Fig. 1. The two bulky triphenylphosphine groups are

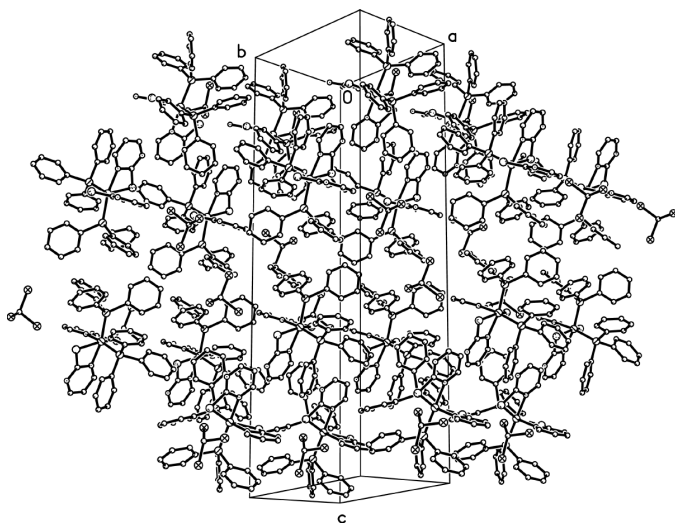
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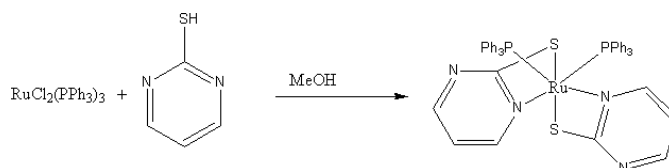
**Figure 1**  
View of the title compound, with displacement ellipsoids drawn at the 30% probability level. The chloroform solvent molecule and H atoms are not shown for clarity.



**Figure 2**  
View of the crystal packing without the H atoms. Only the major component of the disordered chloroform molecule is shown.

in the *cis* configuration. Both of the pyrimidine-2-thiolate ligands are bidentate; each contributes an S atom and one of its two N atoms to coordinate the central metal. No interactions are observed between the metal ion and the remaining N atoms. The S atoms are *trans* to each other, whereas the N-atom donors are *trans* to the P atoms. The mean Ru—P distance (2.325 Å; Table 1) is in good agreement with those in the pyridine analogue [2.326 (1) Å]. The Ru—N distances of 2.106 (2) and 2.109 (2) Å (Table 1) are slightly shorter than those in the pyridine analogue [2.115 (2) and 2.132 (2) Å]. The Ru—S distances [2.436 (1) Å] are normal. The C—S bond distances of 1.735 (3) and 1.732 (3) Å are significantly longer than the normal C=S double bond distance of 1.62 Å, but shorter than a C—S single bond of 1.81 (2) Å, suggesting

partial double-bond character of the C—S bonds. Two four-membered rings are constructed by means of an Ru ion with S and N atoms from the same pyrimidine-2-thiolate ligand, tolerating considerable strain to achieve an octahedral coordination of ruthenium. As a result, the Ru—N—C and N—C—S angles are distorted from 120° for  $sp^2$ -hybridized atoms to 103 and 110°, respectively. The S atoms are displaced from the equatorial plane, suggesting the weak bent bonds with their consequent inferior orbital overlaps. This is consistent with the rather longer Ru—S distances and slightly shorter Ru—N bond lengths, which indicate that the N atom of pyrimidine-2-thiolate has a stronger coordinating ability than that of pyridine.



In the crystal structure, intramolecular  $\pi$ – $\pi$  stacking interactions exist between the pyrimidine rings (N1/C1/N2/C2/C3/C4 and N3/C5/N4/C6/C7/C8) and phenyl rings of triphenylphosphines (C21–C26 and C27–C32). The distances between the centres of the pyrimidine and corresponding phenyl rings are 3.576 (8) and 3.539 (7) Å, respectively, while the dihedral angles between the two interacting rings are 22.7 (3) and 20.9 (3)°, respectively. These  $\pi$ – $\pi$  interactions and the presence of *d* electrons cause a distortion of the coordination configuration. The crystal packing (Fig. 2) is mainly stabilized by van der Waals interactions.

## Experimental

A mixture of  $[\text{Ru}(\text{PPh}_3)_3\text{Cl}_2]$  (0.2 g, 0.2 mmol), 2-mercaptopyrimidine (0.05 g, 0.44 mmol) and methanol (20 ml) was refluxed under argon for 10 h. A red solid was obtained after removal of most of the solvent to give the product in 78% yield. Single crystals suitable for X-ray analysis were obtained by evaporation of a  $\text{CHCl}_3$  solution. Analysis calculated for  $\text{C}_{45}\text{H}_{37}\text{Cl}_3\text{N}_4\text{P}_2\text{RuS}_2$ : C 55.87, H 3.83, N 5.79%; found: C 56.15, H 3.77, N 6.12%.

## Crystal data

$[\text{Ru}(\text{C}_4\text{H}_3\text{N}_2\text{S})_2(\text{C}_{18}\text{H}_{15}\text{P})_2] \cdot \text{CHCl}_3$	$D_x = 1.465 \text{ Mg m}^{-3}$
$M_r = 967.27$	Mo $K\alpha$ radiation
Monoclinic, $P2_1/n$	Cell parameters from 12257 reflections
$a = 11.7340$ (19) Å	$\theta = 1\text{--}27.5^\circ$
$b = 10.3824$ (17) Å	$\mu = 0.75 \text{ mm}^{-1}$
$c = 36.162$ (6) Å	$T = 294$ (2) K
$\beta = 95.382$ (3)°	Prism, yellow
$V = 4386.1$ (12) Å <sup>3</sup>	$0.38 \times 0.24 \times 0.22 \text{ mm}$
$Z = 4$	

## Data collection

Bruker SMART CCD area-detector diffractometer	10086 independent reflections
$\varphi$ and $\omega$ scans	6790 reflections with $I > 2\sigma(I)$
Absorption correction: multi-scan (SADABS; Sheldrick, 1996)	$R_{\text{int}} = 0.044$
$T_{\text{min}} = 0.765$ , $T_{\text{max}} = 0.853$	$\theta_{\text{max}} = 27.6^\circ$
29059 measured reflections	$h = -14 \rightarrow 15$
	$k = -13 \rightarrow 13$
	$l = -47 \rightarrow 43$

## Refinement

Refinement on  $F^2$

$$R[F^2 > 2\sigma(F^2)] = 0.040$$

$$wR(F^2) = 0.083$$

$$S = 1.03$$

10086 reflections

540 parameters

H-atom parameters constrained

$$w = 1/[\sigma^2(F_o^2) + (0.03P)^2]$$

$$\text{where } P = (F_o^2 + 2F_c^2)/3$$

$$(\Delta/\sigma)_{\max} = 0.001$$

$$\Delta\rho_{\max} = 0.58 \text{ e } \text{\AA}^{-3}$$

$$\Delta\rho_{\min} = -0.62 \text{ e } \text{\AA}^{-3}$$

**Table 1**

Selected geometric parameters ( $\text{\AA}$ ,  $^\circ$ ).

Ru1–N1	2.106 (2)	Ru1–P2	2.3294 (9)
Ru1–N3	2.109 (2)	Ru1–S1	2.4366 (7)
Ru1–P1	2.3212 (8)	Ru1–S2	2.4378 (7)
N1–Ru1–N3	82.25 (9)	P1–Ru1–P2	99.96 (3)
N1–Ru1–P1	88.76 (6)	N1–Ru1–S1	67.24 (5)
N3–Ru1–P1	168.33 (6)	N3–Ru1–S1	92.76 (5)
N1–Ru1–P2	167.75 (5)	P1–Ru1–S1	90.60 (2)
N3–Ru1–P2	90.09 (6)	P2–Ru1–S1	103.84 (2)
N1–Ru1–S2	89.96 (5)	P1–Ru1–S2	105.46 (2)
N3–Ru1–S2	67.2995 (3)	P2–Ru1–S2	95.87 (2)
S1–Ru1–S2	152.05 (3)		

H atoms were positioned geometrically and refined as riding, with C–H = 0.93  $\text{\AA}$  and  $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ . In the solvent molecule, each of the three Cl atoms is disordered over two positions with refined occupancies of 0.834 (3) and 0.166 (3).

Data collection: *SMART* (Bruker, 1997); cell refinement: *SAINT* (Bruker, 1997); data reduction: *SAINT* and *SHELXTL* (Sheldrick,

1998); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

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