DOI: 10.1002/zaac.200700482

Variable Bonding Modes of Pyrimidine-2-thione in Pd^{II}/Pt^{II} Complexes $[M(\eta^2\text{-N, S-pymS})(\eta^1\text{-S-pymS})(PPh_3)]$ and $[M(\eta^1\text{-S-pymS})_2(L\text{-L})]$ (L-L = dppm, dppe)

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Received August 3rd, 2007; accepted October 12th, 2007.

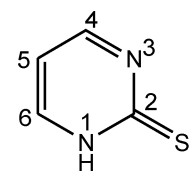
Abstract. Reactions of pyrimidine-2-thione (HpymS) with Pd^{II}/Pt^{IV} salts in the presence of triphenyl phosphine and bis(diphenylphosphino)alkanes, $Ph_2P\text{-}(CH_2)_m\text{-}PPh_2$ (m = 1, 2) have yielded two types of complexes, viz. (a) $[M(\eta^2\text{-N, S- pymS})(\eta^1\text{-S- pymS})(PPh_3)]$ (M = Pd, **1**; Pt, **2**), and (b) $[M(\eta^1\text{-S-pymS})_2(L\text{-L})]$ {L-L, M = dppm (m = 1) Pd, **3**; Pt, **4**; dppe (m =2), Pd, **5**; Pt, **6**}. Complexes have been characterized by elemental analysis (C, H, N), NMR spectroscopy (^1H, ^{13}C, ^{31}P), and single crystal X-ray crystallography (**1**, **2**, **4**, and **5**). Complexes **1** and **2** have terminal η^1-S and chelating η^2-N, S-modes of $pymS^-$, while other Pd/Pt complexes have only terminal η^1-S modes. The solution state ^{31}P NMR spectral data reveal dynamic equilibrium for the complexes **3**, **5** and **6**, whereas the complexes **1**, **2** and **4** are static in solution state.

Keywords: Pyrimidine-2-thione; Triphenylphosphine; Heterocyclic thioamides; Diphosphines; Crystal structures

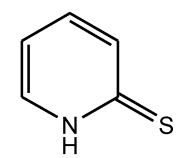
Introduction

The interaction of heterocyclic thioamides with the transition, post-transition and main group metals has been the focus of several investigations because these compounds contain chemically active, -N(H)-C(=S)- ⇔ -N=C(-SH)- groups, and bind to the metals both as the neutral and deprotonated ligands and have formed monomers, dimers, oligomers and polymers [1−4]. Pyrimidine-2-thione, pyridine -2-thione, 2- thiouracil and 6 − mercaptopurine are the thio analogs of nucleobases, such as purine and pyrimidine [1−4], and these find use in clinical drugs, as antimetabolite andantitumour drug [5−13]. They also exhibit bacteriocidal and fungicidal activity [14, 15].

Pyrimidine-2-thione (pymSH, I) is similar to pyridine-2-thione (pySH, II), but its chemistry is much less explored. Pyrimidine −2-thiones have formed several palladium(II) and platinum(II) complexes of nuclearity ranging from mononuclear, dinuclear to polynuclear [16−25] with different bonding modes. For example, neutral pymSH forms S − bonded complexes (III) [16], while, deprotonate $dpymS^-$ or its derivatives have shown η^1-S − bonding (IV) [17], N, S− chelation (V) [18], and N, S- bridging (VI) modes [20].



I



II

There are a few complexes of pyrimidine-2-thione with monotertiary phosphines as co-ligands, namely, $[Pd(\eta^1\text{-S-pymS})_2(PPh_3)_2](ClO_4)$ [18], and $[Pd(\eta^2\text{ -N,S-pymS})(PMe_3)Cl]_2$ [20], and none with ditertiary phosphines. In this paper, we report Pd(II) and Pt(II) complexes with pymSH in the presence of triphenylphosphine(PPh_3),1,1-bis(diphenylphosphino)methane (dppm) and 1, 2-bis(diphenylphosphino)ethane (dppe) as co-ligands.

Experimental Section

Material and Techniques

Pyrimidine−2−thione (pymSH), bis(diphenylphosphino)methane (dppm), PPh_3, $PtCl_4$, H_2PtCl_6 and $PdCl_2$ were procured from Sigma Aldrich Ltd. The 1,2- bis(diphenylphosphino)ethane (dppe) was prepared by a reported method [26]. The precursors, namely, trans-$PdCl_2(PPh_3)_2$ or cis-$PdCl_2(L\text{-}L)_2$ (L-L = dppm, dppe) were prepared by the addition of a phosphine to a solution of $PdCl_2$ in acetonitrile followed by refluxing for 5-6 h [27]. The melting points were determined with a Gallenkamp electrically heated apparatus. The elemental analysis for C, H, N were carried out using a thermoelectron FLASHEA1112 analyzer. The ^1H, ^{13}C, ^{31}P NMR spectra were recorded in $CDCl_3$ using a JEOL spectrometer at 300 MHz, 75.45 MHz and 121.5 MHz, respectively. For ^1H and ^{13}C NMR,

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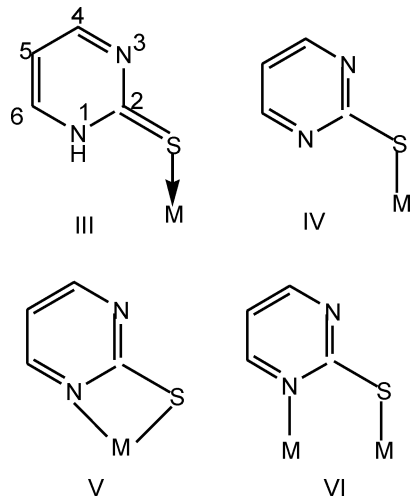


TMS is used as an internal reference, while for ^{31}P NMR, {$(CH_3O)_3P$} is the external reference, taken as zero position

Synthesis of complexes

[Pd(η²-N,S-pymS)(η¹-S-pymS) (PPh_3)] (1). To the solid pymSH (0.080 g, 0.07 mmol) placed in round bottom flask was added a solution of sodium hydroxide (NaOH) (0.002 g) in distilled water (2 cm^3), which formed a clear light yellow solution. To this solution was added a suspension of $PdCl_2(PPh_3)_2$ (0.025 g, 0.035 mmmol) in ethanol, and the contents were refluxed for 10 h. The colour of the reaction mixture became bright yellow and NaCl formed was filtered off. The filtrate was allowed to crystallize at room temperature and dark yellow crystals of compound **1** were formed over a period of 5 d. It is soluble in chloroform, dichloromethane and acetone. Mp. 170-175 °C, Yield, 60 %. Anal. Calcd $C_{26}H_{21}N_4PPdS_2$ (590.96); C 53.4(calc.52.7); H, 3.76(3.96); N, 9.53(9.47) %.

Main IR bands (KBr, cm^{-1}); ν(C − H), 3060; ν(C − C) + ν(C − N), 1575, 1480; ν (C−S), 850w, 800w; ν(P − C), 1090. **^{1}H NMR** (ppm, *J*Hz, $CDCl_3$): 8.58 [d, 1H, J_{HH} 4.8, H^4], 8.14 [d, 1H, J_{HH} 5.1, H^6], 7.26 [t, 1H, J_{HH} 11.4, H^5],7.70 [m, 6H, o-H],7.60 [m, 6H, m-H], 7.49 [m, 3H, p-H], **^{13}C NMR** (ppm, J_{Hz} $CDCl_3$): 185.0 [s, C^2], 155.6 [s, C^4, C^6], 138.2 [s, i-C], 96.6 [s, C^5], 134.3 [d, o- & p-C], 128.3 [s, m-C]. **^{31}P NMR** ($CDCl_3$, δ): −74.9. Δδ ($\delta_{complex} - \delta_{ligand}$) = 38.3 ppm.

[Pt(η²-N,S- pymS)(η¹-S- pymS) (PPh_3)] (2). To the solid pymSH (0.024 g, 0.11 mmol) suspended in dry benzene (5 cm^3) in a round bottom flask was added a solution of platinic acid, H_2PtCl_6 (0.05 g, 0,116 mmol) in dry ethanol (15 cm^3) in presence of Et_3N base (2 cm^3). The contents were stirred for 2 h until turbidity appeared and to this was added solid PPh_3 (0.061 g, 0.116 mmol). The clear orange colour solution formed was stirred overnight and $Et_3NH^+Cl^-$ formed was filtered off, and the filtrate was allowed to crystallize at room temperature. The brown crystals of compound **2** were formed in a period of 6 d. It is soluble in chloroform, dichloromethane and acetone. Mp. 180 °C, Yield, 65 %. Anal. Calcd $C_{26}H_{21}N_4PPtS_2$ (679.65); C 44.19 (calc. 44.8); H, 3.59 (3.52); N, 9.05 (8.75) %.

Main IR bands (KBr, cm^{-1}); ν(C − H), 3060; ν(C − C) + ν(C − N), 1537, 1481; ν(C−S), 923m, 860w; ν(P − C), 1087. **^{1}H NMR** (ppm, J_{Hz} $CHCl_3$ −d): 8.58 [d, 1H, J_{HH} 4.8, H^6], 7.09 [t, 1H, J_{HH} 4.8, H^4], 6.99 [t, 1H, J_{HH} 1.8, H^4], 7.47 [m, 6H, o-H], 7.67 [m, 6H, m-H], 7.70 [m, 3H, p-H], **^{13}C NMR** (ppm, J_{Hz} $CHCl_3$ −d): 157.9 [s, C^4, C^6], 134.1 [s, i-C], 133.1 [s, o-C], 132.0 [dd, p-C], 128.4 [d, m-C], 45.8 [s, CH_2]. **^{31}P NMR** ($CDCl_3$, δ): −78.7. Δδ ($\delta_{complex} - \delta_{ligand}$) = 34.5 ppm.

[Pd(η¹-S-pymS)₂(dppm)] (3). To the solid pymSH (0.025 g, 0.22 mmol) placed in round bottom flask was added a solution of sodium hydroxide (NaOH) (0.008 g) in distilled water (2 cm^3), which formed a clear light yellow solution. To this solution was added a suspension of $PdCl_2$(dppm) (0.062 g, 0.11 mmol) in ethanol, and the contents were refluxed for 10 h. The colour of the reaction mixture became orange and NaCl formed was filtered off. The filtrate was allowed to crystallize at room temperature and dark yellow crystals of compound **3** were formed over a period of 5 d. It is soluble in chloroform, dichloromethane and acetone. Mp. 180-185 °C, Yield, 70 %. Anal. Calcd $C_{33}H_{36}N_4P_2PdS_2$ (715); C 55.4 (calc. 55.38); H, 3.76 (3.81); N, 7.60 (7.83) %.

Main IR bands (KBr, cm^{-1}); ν(C − H), 3049m; ν(C − C) + ν(C − N), 1562, 1481; ν (C−S), 885m, 850w; ν(P−C), 1084m. **^{1}H NMR** (ppm, J_{Hz} $CHCl_3$ −d): 8.58 [d, 1H, J_{HH} 4.8, H^6], 8.18 [d, 1H, J_{HH} 4.8, H^4], 7.09 [b, 1H, H^5], 7.68 [m, 6H, o-H], 7.44 [m, 6H, m-H], 7.35 [m, 3H, p-H], 3.72 [q, J_{HH} 11.4, CH_2]. **^{13}C NMR** (ppm, J_{Hz} $CHCl_3$ −d): 188.7 [s, C^2], 163.9 [s, C^4, C^6], 132.6 [s, i-C], 131.8 [s, o-C], 131.2 [d, m-C], 128.7 [d, p-C], 48.0 [s, -CH_2]. **^{31}P NMR** ($CDCl_3$, δ): −77.6, −82.8. Δδ ($\delta_{complex} - \delta_{ligand}$) = 52.4, 47.4 ppm.

[Pt(η¹-S- pymS)₂(dppm)] (4). To the solid pymSH (0.033 g, 0.148 mmol) suspended in dry benzene (5 cm^3) in a round bottom flask was added a solution of platinium chloride, $PtCl_4$ (0.050 g, 0.148 mmol) in dry ethanol (15 cm^3) in presence of Et_3N base (2 cm^3). The contents were stirred for 2 h until turbidity appeared and to this was added solid dppm (0.056 g, 0.148 mmol). The clear orange colour solution formed was stirred overnight and $Et_3NH^+Cl^-$ formed was filtered off, and the filtrate was allowed to crystallize at room temperature. The light yellow crystals of compound **4** were formed in a period of 5 d. It is soluble in chloroform, dichloromethane and acetone. Mp. 190 °C, Yield, 65 %. Anal. Calcd $C_{33}H_{28}N_4P_2PtS_2$ (801.74); C 48.8 (calc. 49.2); H, 3.43 (3.48); N, 7.05 (6.97) %.

Main IR bands (KBr, cm^{-1}); ν(C − H), 3040; ν(C − C) + ν(C − N), 1558, 1481; ν (C−S), 877m, 820w; ν(P − C), 1100m. **^{1}H NMR** (ppm, J_{Hz} $CHCl_3$ −d): 8.58 [d, 2H, J_{HH} 4.8, H^4, H^6], 7.08 [t, 1H, J_{HH} 4.8, H^4], 6.70 [dd, 1H, H^4], 7.33 [m, 6H, o-H], 7.49 [m, 6H, m-H], 7.73 [m, 3H, p-H], **^{13}C NMR** (ppm, J_{Hz} $CHCl_3$ −d): 185.0 [s, C^2], 157.9 [s, C^4, C^6], 118.2 [s, C^5], 131.0 [d, o- & p-C], 128.4 [s, m-C], 45.9 [s, CH_2]. **^{31}P NMR** ($CDCl_3$, δ): −114.9. Δδ ($\delta_{complex} - \delta_{ligand}$) = 15.19 ppm.

[Pd(η¹-S- pymS)₂(dppe)] (5). To the solid pymSH (0.0197 g, 0.175 mmol) placed in round bottom flask was added a solution of sodium hydroxide (NaOH) (0.006 g) in distilled water (2 cm^3), which formed a clear light yellow solution. To this solution was added a suspension of $PdCl_2$(dppe) (0.050 g, 0.086 mmol) in ethanol, and the contents were refluxed for 10 h. The colour of the reaction mixture became bright yellow and NaCl formed was filtered off. The filtrate was allowed to crystallize at room temperature and dark yellow crystals of compound **5** were formed over a period of 6 d. It is soluble in chloroform, dichloromethane and acetone. Mp. 200-210 °C, Yield, 70 %. Anal. Calcd $C_{34}H_{30}N_4P_2PdS_2$ (727.08); C 55.01 (calc. 55.06); H, 4.05 (4.115); N, 7.35 (7.68) %.

Main IR bands (KBr, cm^{-1}); ν(C − H), 3049; ν(C − C) + ν(C − N), 1562, 1485; ν (C − S), 879m, 819s; ν(P − C), 1101s. **^{1}H NMR** (ppm, J_{Hz} $CHCl_3$ −d): 8.58 [dd, 2H, J_{HH} 4.8, H^4, H^6], 7.09 [t, 1H, H^5], 7.88 [m, 6H, o-H], 7.83 [m, 6H, m-H], 7.41 [m, 3H, p-H], 4.65 [b, 4H, -CH_2-CH_2] **^{13}C NMR** (ppm, J_{Hz} $CHCl_3$ −d): 185.0 [s, C^2], 155.7 [s, C^4, C^6], 131.7 [s, i-C], 114.6 [s, C^5], 133.0 [d, o-C], 130.7 [d, p-C], 128.6 [t, m-C]. **^{31}P NMR** ($CDCl_3$, δ): −75.3, −79.8 ($\delta_{complex} - \delta_{ligand}$) = 44.7, 40.2 ppm.

[Pt(η¹-S- pymS)₂(dppe)] (6). To the solid pymSH (0.0245 g, 0.11 mmol) suspended in dry benzene (5 cm^3) in a round bottom flask was added a solution of platinic acid, H_2PtCl_6 (0.050 g, 0.11 mmol) in dry ethanol (15 cm^3) in presence of Et_3N base

($2\ cm^3$). The contents were stirred for 2 h until turbidity appeared and to this was added solid dppe (0.046 g, 0.11 mmol). The clear orange colour solution formed was stirred overnight and $Et_3NH^+Cl^-$ formed was filtered off, and the filtrate was allowed to crystallize at room temperature. The light yellow crystalline compound **6** was formed in a period of 4 d. It is soluble in chloroform, dichloromethane and acetone. Mp. 190 °C, Yield, 65 %. Anal. Calcd $C_{34}H_{30}N_4P_2PtS_2$ (818); C 49.6 (calc. 50.00); H, 3.26 (3.50); N, 5.95 (5.86) %.

Main IR bands (KBr, cm^{-1}); ν(C − H), 3049; ν(C − C) + ν(C − N), 1552, 1477; ν (C-S), 879m, 850w; ν(P − C), 1103s. **^{1}H NMR** (ppm, J_{Hz} $CHCl_3$ −d): 8.58 [dd, 2H, J_{HH} 4.8, H^4, H^6], 7.09 [t, 1H, J_{HH} 4.8, H^4], 7.86 [m, 6H, o-H], 7.73 [m, 6H, m-H], 7.67 [m, 3H, p-H], **^{13}C NMR** (ppm, J_{Hz} $CHCl_3$ −d): 185.0 [s, C^2], 157.9 [s, C^4, C^6], 132.1 [s, i-C], 118.2 [s, C^5], 130.8 [d, o- & p-C], 128.8 [d, m-C]. **^{31}P NMR** ($CDCl_3$, δ): −74.6, −66.5. Δδ ($\delta_{complex} - \delta_{ligand}$) = 45.4, 53.5 ppm.

Ligands' ^{31}P NMR Spectra ($CDCl_3$, δ): −113.15, PPh_3; −130.21, dppm; −120.30, dppe relative to $\{(CH_3O)_3P\}$ as the external reference taken as zero position.

X-ray Crystallography

The data for compounds **1** and **2** were collected at 293 K on a Siemens P4 diffractometer. The θ−2θ technique was used to measure the intensities up to a maximum of 2θ = 50° with graphite monochromatised Mo-K_α radiation (λ = 0.71073 Å). Cell parameters were refined in the θ range, 10-12.5° using XSCANS [28] The data were corrected for Lorentz and polarization factors. An empirical psi absorption correction was applied. The structure was solved by the direct methods and refined by full matrix least squares methods based on F^2. All hydrogen atoms were refined anisotropically, fixed geometrically, and were not refined. Scattering factors from the International Tables for X-ray crystallography were used [29]. Data reduction, structure solution, refinement and molecular graphics were performed using SHELXTL-PC [30] and WinGX [31].

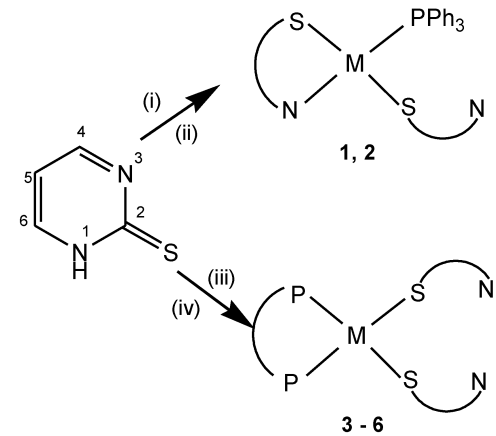
Colourless crystals of compound **4** were mounted on an automatic Enraf Nonius CAD-4 diffractometer equipped with graphite monochromator and Mo-K_α radiation (λ = 0.71073 Å). The unit cell dimensions and intensity data were measured at 103 K. The structures were solved by direct methods and refined by full matrix least squares method based on F^2. All nonhydrogen atoms were refined anisotropically using XCAD-49 (data reduction) and SHELXL [32]. The hydrogen atoms were calculated using structure factor calculations in their idealized positions.

A yellow prismatic crystal of **5** was mounted on a glass fiber and used for data collection. Crystal data were collected at 293(2) K, using a Bruker SMART CCD 1000 diffractometer. Graphite monochromated Mo-K_α radiation (λ = 0.71073 Å) was used throughout. The data were processed with SAINT [33] and corrected for absorption using SADABS (transmissions factors: 1.000−0.791) [34]. The structure was solved by direct methods using the program SHELXS-97 [35] and refined by full-matrix least-squares techniques againts F^2 using SHELXL-97 [35]. Positional and anisotropic atomic displacement parameters were refined for all nonhydrogen atoms. Hydrogen atoms were included in geometrically idealized positions employing appropriate riding models. Atomic scattering factors from "International Tables for Crystallography" [36]. Molecular graphics from PLATON [37] and SCHAKAL [38].

Results and Discussion

Synthesis and IR spectroscopy

Scheme 1 depicts the formation of complexes **1**−**6** with pyrimidine-2-thione in the presence of PPh_3, dppm, and dppe as co-ligands. Compound **1** was formed by the reaction $PdCl_2(PPh_3)_2$ precursor with pymSH (1 : 2 molar ratio) in the presence of aqueous NaOH as a base. Compounds **3** and **5** were similarly prepared using $PdCl_2$(L-L) precursors (L-L = dppm, dppe). Reactions of platinic acid or platinum tetrachloride with pymSH in the presence of Et_3N base yielded compounds **2**, **4** and **6**. Complexes are soluble in the organic solvents such as chloroform, dichloromethane, acetone and ethyl alcohol and melt in a wide range, 170-230 °C. X-ray crystallography (vide infra) has revealed that in complexes **1** and **2** one $pymS^-$ moiety is η^2-N, S- chelating, and the second is η^1-S- bonded. However, in the presence ofchelating dppm and dppe, both the $pymS^-$ moieties are η^1-S- bonded with pendant pyrimidine rings (**3**−**6**).



Scheme 1 (i) $PdCl_2(PPh_3)_2$ **1** (ii) H_2PtCl_6 + $2PPh_3$ **2**
(iii) $PdCl_2$(dppm) **3** / $PdCl_2$(dppe) **5**
(iv) $PtCl_4$ + dppm **4** / H_2PtCl_6 + dppe **6**

The IR spectra of complexes **1**−**6** did not show bands due to ν(N-H) in the region, 3400 − 3100 cm^{-1} and it suggested deprotonation of pyrimidine-2-thione ligand in complexes. The ν(C − H) bands in the complexes lie in the region 3040-3060 cm^{-1} and show high energy shifts relative to the free ligand {ν(C − H) at 2900 cm^{-1}}. The diagnostic ν(C = S) band at 1130 cm^{-1} in the free ligand appeared as a pair of bands in the region 800 to 925 {weak to strong bands} and are listed in the experimental section. The ν(C − C) + ν(C − N), bands show insignificant shifts as compared with the free ligands.The ν(P − C_{Ph}) bands in the region 1084 to 1103 cm^{-1} showed the presence of PPh_3 in complexes.

Crystal structures of complexes 1, 2, 4 and 5

The atomic numbering schemes for complexes **1**, **2**, **4** and **5** are given in figures 1-4 respectively. The crystal data are given in Table 1, and the selected bond angles / bond

Table 1 Crystal data of compounds **1**, **2**, **4**, and **5**.

	1	**2**	**4**	**5**
Empirical Formula	$C_{26}H_{21}N_4PPdS_2$	$C_{26}H_{21}N_4PPtS_2$	$C_{33}H_{28}N_4P_2PtS_2$	$C_{34}H_{30}N_4P_2PdS_2$
Formula weight	590.96	679.65	801.74	727.08
Wavelength /Å	0.71069	0.71073	0.71073	0.71073
Crystal System / Space Group	monoclinic, $P2_1/n$	monoclinic, $P2_1/n$	triclinic, $P\bar{1}$	monoclinic, P2(19/c)
Unit Cell dimensions	a = 10.774(5) Å b = 15.134(5) Å c = 15.221(5) Å β =96.310(5)°	A = 10.791(1) Å b = 15.126(2) Å c = 15.232(1) Å □ = 96.51(1)°	a = 8.8941(11) Å b = 11.1734(14) Å c = 15.736(2) Å α = 84.493(2)° β = 83.537(2)° γ = 80.810(2)°	a = 8.5596(6) Å b = 10.5787(8) Å c = 35.291(3) Å β = 90.520(2)°
Volume /Å^3	2466.8(16)	2470.2(4)	1529.0(3)	3195.4(4)
Z	4	4	2	4
Density, calcd /(mg/m^3)	1.591	1.828	1.741	1.511
Absorption Cofficient /mm^{-1}	1.009	5.937	4.861	0.843
F(000)	1192	1320	788	1480
Crystal Description	yellow	yellow	yellow prismatic	yellow prismatic
Crystal Size /mm	0.18 x 0.18 x 0.16	0.20 x 0.20 x 0.18	0.10 x 0.33 x 0.35	0.82 x 0.25 x 0.22
θ range for data collection	1.90 to 25.49°	1.90 to 25.00°	2.18 to 28.35°	2.01 to 27.98°
Index range	0≤h≤11, 0≤k≤18, −18≤l≤18	0≤h≤10, 0≤k≤17, −18≤l≤17	−11≤h≤11, −14≤k≤14, −19≤l≤21	−11≤h≤11, −13≤k≤13, −34≤l≤46
Reflections collected	4703	4390	12030	19622
Unique reflection, R_{int}	4450, 0.0360	4148, 0.0863	7283, 0.0446	7420, 0.0261
Reflns. with [$I>2\sigma(I)$]	3594	3148	6946	6111
R indices	R = 0.0314, wR = 0.0743	R = 0.0730, wR = 0.2011	R = 0.0293, wR = 0.0731	R = 0.0356, wR = 0.0758
Goodness of fit on F^2	1.027	1.231	1.049	1.097
Largest diff peak and hole /e.Å^{-3}	0.359 and −0.440	0.889 and −7.643	2.436 and −2.345	0.302 and −0.754

lengths are listed in Table 2. Complexes crystallized in monoclinic (**1**, **2** and **5**) or triclinic (**4**) crystalsystems.

Palladium Complexes

Complex **1** has two pyrimidine-2-thiolates (pymS$^-$) and one PPh_3 ligands coordinating to the Pd center (Figure 1). One pymS$^-$ anion is chelating via N^1, S −donor atoms forming a four membered metallacyclic ring, with a N(1)−Pd−S(1) bite angle of 69.21(8)°, and second pymS$^-$ anion is S-bonded. This bite angle is close to 67.2° observed in an analogous octahedral complex $[Ru(pymS)_2(PPh_3)_2]$ **7** with a similar bonding pattern [39]. The trans bond angles, S(1)-Pd-S(2) {166.02(3)°} and N(1)-Pd-P {167.74(8)°} reveal that the geometry is severely distorted from a square plane. For the chelating pymS$^-$, the Pd-S(1)-C(19) bond angle of 80.60(12)° is much shorter than 103.48(12)° {Pd-S(2)-C(23)} observed for the η^1-S- bonded pymS$^-$. The Pd−donor atom distances {Pd-S, 2.3458(12), 2.3213(11), Pd-N, 2.093(3), Pd-P, 2.2500(11) Å} are comparable with the similar distances {Pd-S, 2.293(1)}, Pd-N, 2.143(3), Pd-P, 2.236(1) Å} reported for $[Pd_2(pymS)_2Cl_2(PMe_3)_2]$ **8** [20].

Two pyrimidine-2-thiolates (pymS$^-$) and one dppe ligand coordinate to the Pd center in complex **5** (Figure 4). Both the pymS$^-$ anions adopt η^1-S-bonding due to chelation by dppe. The trans bond angles, P-Pd-S, 172.91(2)° and 175.04(2)° reveal that the structure is less distorted than that of compound **1**. The P(1)-Pd-P(2), bite angle {84.84(2)°} is close to 85.19(8)° reported for a similar complex $[Pd(\eta^1\text{-S- pyS})_2(dppe)]$ **9** (pyS$^-$ = pyridine -2-thiolate) [40]. All the four cis-angles around Pd lie in the range, 84.84(2)°−95.68(2)°. The Pd-S(1)-C(11) and Pd-S(2)-C(21)

Table 2 Selected bond lengths /Å and bond angles /° for compounds **1**, **2**, **4**, and **5**.

1			
Pd−N(1)	2.093(3)	Pd−S(1)	2.3458(12)
Pd−P	2.2500(11)	Pd−S(2)	2.3213(11)
S(2)−C(23)	1.739(4)	S(1)-C(19)	1.740(3)
N(1)-Pd-P	167.74(8)	N(1)-Pd-S(1)	69.21(8)
S(1)-Pd-S(2)	166.02(3)	N(I)-Pd-S(2)	96.96(8)
P-Pd−S(1)	103.38(4)	Pd−S(1)−C(19)	80.60(12)
P-Pd−S(2)	89.86(5)	Pd−S(2)−C(23)	103.48(12)
2			
Pt−N(1)	2.064(15)	Pt − P1	2.231(5)
Pt-S(1)	2.353(5)	S(1)−C(19)	1.73(2)
Pt−S(2)	2.324(5)	S(2)−C(23)	1.75(2)
N(I)-Pt-S(2)	95.9(5)	S(1)-Pt-S(2)	164.2(2)
P(1)-Pt-S(2)	91.3(2)	N(1)-Pt-P(1)	169.1(5)
N(1)-Pt-S(1)	68.5(5)	Pt-S(1)-C(19)	80.9(7)
P(1)-Pt-S(1)	103.9(2)	Pt-S(2)-C(23)	104.8(6)
4			
Pt-P(2)	2.2683(8)	Pt-S(1B)	2.3479(8)
Pt-P(1)	2.2727(8)	S(1B)-C(1B)	1.751(3)
Pt-S(1A)	2.3445(8)	S(1A)-C(1A)	1.742(3)
P(1)-Pt-S(1A)	103.96(3)	P(2)-Pt-S(1B)	103.02(3)
S(1A)-Pt-S(1B)	79.35(3)	C(1A)-S(1A)-Pt	113.41(11)
P(1)-Pt-S(1B)	175.27(3)	C(1B)-S(1B)-Pt	113.15(11)
P(2)-Pt-S(1A)	177.47(3)	Pt-S(1A)-P(1)	103.96(3)
P(2)-Pt-P(1)	73.73(3)	Pt-S(1B)-P(2)	103.02(3)
5			
Pd(1)-P(2)	2.2767(6)	Pd(1)-S(1)	2.3822(7)
Pd(1)-P(1)	2.2773(7)	S(1)−C(11)	1.745(3)
Pd(1)-S(2)	2.3793(7)	S(2)- C(21)	1.740(3)
P(1)−Pd(1)−S(2)	90.82(2)	P(1)−Pd(1)−S(1)	175.04(2)
P(2)−Pd(1)−S(1)	95.68(2)	S(2)−Pd(1)−S(1)	89.13(3)
P(1)−Pd(1)−P(2)	84.84(2)	Pd-S(2)-C(21)	102.11(9)
P(2)−Pd(1)−S(2)	172.91(2)	Pd-S(1)-C(11)	97.91(9)

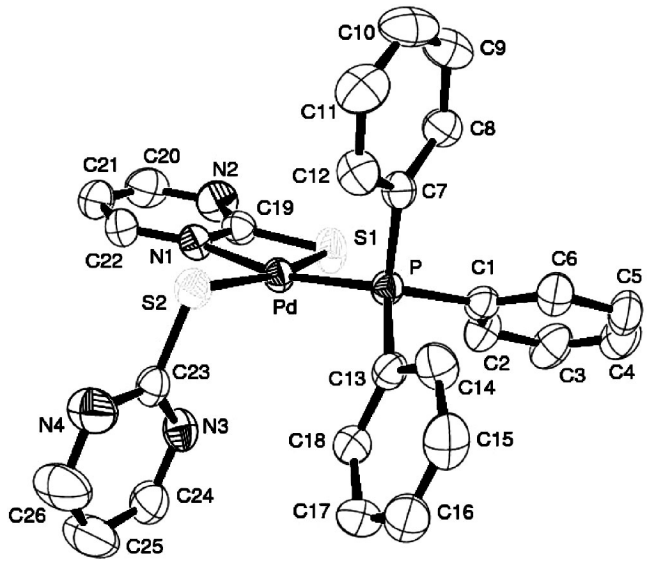


Fig. 1 Structure of compound **1** with numbering scheme.

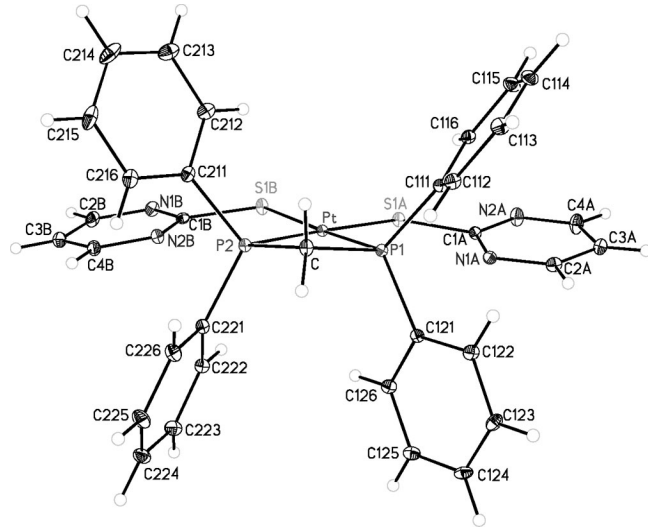


Fig. 3 Structure of compound **4** with numbering scheme.

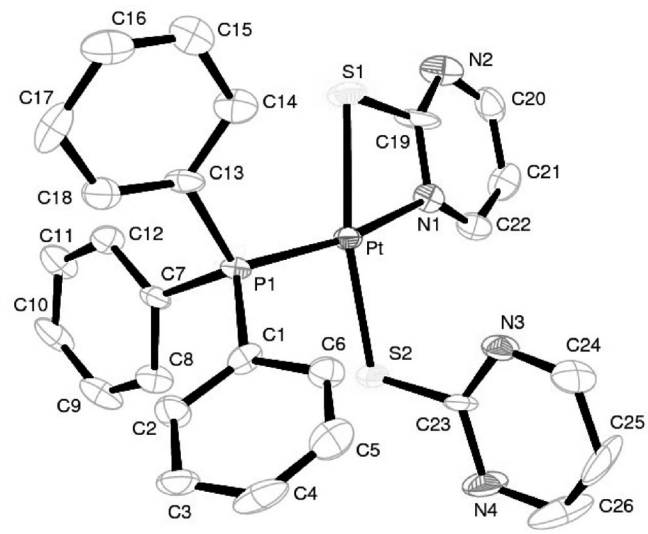


Fig. 2 Structure of compound **2** with numbering scheme.

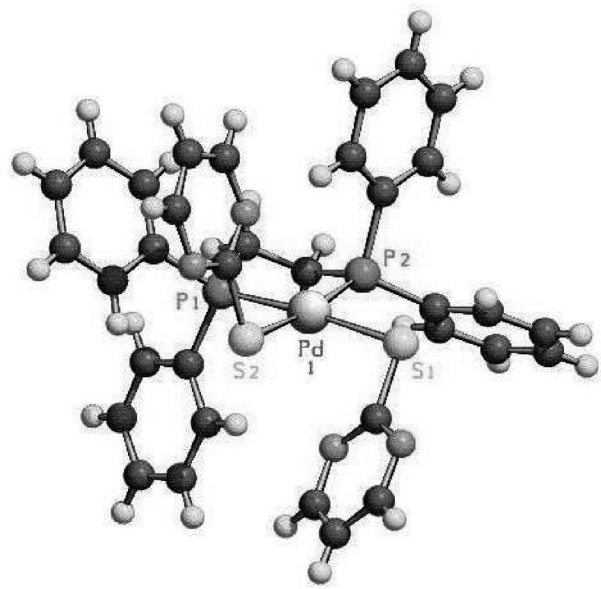


Fig. 4 Structure of compound **5** with numbering scheme.

bond angles of 97.91(9)°, 102.11(9)° are similar to 103.48(12)° observed for compound **1** with η^1-S-bonded $pymS^-$ ligand. The Pd-P distances, {2.2767(6), 2.2773(7) Å} are somewhat longer than 2.250(11) Å observed for compound **1**, but are similar with those observed for compound **9** {2.297(2), 2.263(2) Å} [40]. Similarly, the Pd−S distance of {2.3793(7), 2.3822(7) Å} is longer than that found for compound **1**.

Platinum complexes

The composition of compound **2** is similar to that of compound **1** and thus ligands are similarly bonded. It has two $pymS^-$ anionic and one PPh_3 ligands coordinating to the Pt atom (Fig. 2). One $pymS^-$ anion is chelating via N^1, S-donor atoms forming a four membered metallacyclic ring with a N(1)-Pt-S(1) bite angle of 68.5(5)°, and second $pymS^-$ anion is η^1-S-bonded. The bite angle of this complex is close to 67.2° observed in complex **1**. The trans bond angles, S(1)-Pt-S(2) {164.2(2)°} and N(1)-Pt-P {169.1(5)°} reveal that the geometry is severely distorted from a square plane. The pattern of the bond angles, Pt-S(1)-C(19) {80.9(7)°} and Pt-S(2)-C(23) {104.8(6)°} is similar to that observed for compound **1**. The Pt−S {2.353(5), 2.324(5) Å} and Pt-N distances {2.065(15) Å} are somewhat longer than those {Pt-S, 2.301(8), Pt-N, 2.046(23) Å} observed for $[Pt_2Cl(pymS)_5]$ (**10**) [24]. The Pt-P bond distance of 2.231(5) Å is similar to the literature values [40].

In Complex **4** two pyrimidine-2-thiolate ($pymS^-$) and one dppm ligands coordinate to the Pt atom (Figure 4).

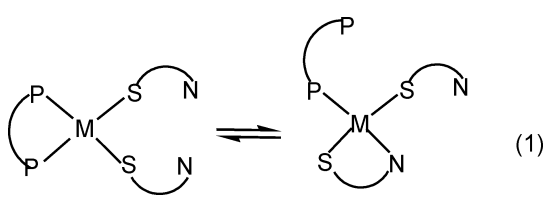
Both the pymS$^-$ ligands adopt η^1-S-bonding due to chelation by dppm. The trans P-Pt-S, 177.47(3)°, 175.27(3)° bond angles reveal that the geometry is less distorted than that of compound **2**. The P(1)-Pt-P(2) bite angle of 73.73(3)° is smaller than 85.19(8)° observed for a similar complex, [Pt(pyS)$_2$(dppe)] (**11**) [40]. All the four cis-angles around Pt vary from 84.84(2)°−95.68(2)°. The Pt-S(1A)-C(1A) and Pt-S(1B)-C(1B) bond angles of 113.41(11)°, 113.15(11)° are comparable with 116.9(4)° observed for **11** with η^1-S-bonded pyS$^-$ ligand [40]. The Pt-P and Pt-S distances, {2.2683(8), 2.2727(8) Å} and {2.3445(8) Å, 2.3479(8) Å}, respectively, are similar with the literature values [40].

Solution state behaviour

The deprotonation ofthe pyrimidine-2-thione ligand in the complexes is evident from the absence of NH proton signal ($\delta_{N\text{-}H}$, 13.4 ppm, free pyrimidine-2-thione) and it supports the bonding via S, or N, S-donor atoms in the complexes. The proton signals, H(4), H(5), and H(6), move downfield in the complexes as compared with the free ligand. This is due to the increased ring aromaticity of the complexes. The downfield shift of H(6) signal in complexes **1** and **2** is comparatively less as compared with that of complexes **3**−**6**.

In the ^{13}C NMR spectra, a significant low field shift occurs for C(2) and this shift is less marked for C(6), C(4) and C(5) carbons which shift upfield relative to the free ligand. This behaviour is quite similar to that observed for **7** and it clearly shows that Pt^{II} and Pd^{II} bonding in complexes is via S$^-$ and N, S- donor atoms. The signals for C(4) and C(6) carbon atoms are close and merge into a single signal. The ipso-, ortho-, meta- and para- carbon signals of Ph-P moiety in complexes exhibit low field shifts and appeared as separate bands.

The ^{31}P NMR spectra of complexes **1**, **2** and **4** showed one peak each and it revealed that there is only one species in the solution state, same as in the solid state (cf. experimental section). The order of coodination shifts ($\Delta\delta$) is: **1** > **2** > **4**. Each of complexes **3**, **5** and **6** showed two peaks with the coordination shifts higher than for compounds **1**, **2** and **4**. The shifts are similar with the literature trends for similar compounds with other N, S donor ligands [40]. The two peaks in complexes **3**, **5** and **6** reveal more than one species in the solution state as shown below (Eq. (1)).



(1)

Fo. 3

Conclusion

Pyrimidine-2-thione has formed Pd^{II}/Pt^{II} complexes which are devoid of halogens, and tertiary phosphines have induced different bonding behaviour of pyrimidine-2-thione in complexes. Pyrimidine-2-thiolate has shown both η^1-S and η^2-N, S- bonding modes (**1**, **2**) with PPh_3 as co-ligand, and only η^1-S bonding mode with chelating diphosphines (**3**−**6**). The square plane of the complexes **3** - **6** is less distorted than that of complexes **1** and **2**. Finally, complexes **3**, **5** and **6** exhibited dynamic exchange in the solution state.

Supplementary material: Supplementary data are available from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK(fax : + 44-1223-336033; email: deposit@ccdc.cam.ac.uk) on request quoting the deposition number CCDC 653708-11).

Acknowledgements. Financial support from Council of Scientific and Industrial Research, New Delhi, is gratefully acknowledged.

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