Chapter 3
Experimental

This chapter is divided into two parts, General experimental and Methods of preparation of complexes along with analytical and spectral data.

GENERAL EXPERIMENTAL

This chapter gives general details of various analytical, spectroscopic and structural techniques. In addition, methods of preparation of metal salts/ procurement of various materials are described.

Techniques Used
Elemental analysis. C, H and N elemental analysis were obtained with a Carlo-Ebra 1108 microanalyser from university of Santiago, Spain and a CHNS-O Analyser, Flash-EA-1112 series, department of Chemistry, Guru Nanak Dev University, Amritsar.

I.R. Infrared (IR) spectra were recorded using KBr pellets on a Pye Unicam SP-3-300 or FTIR NICOLET 320 fourier transform infrared spectrophotometer in the 4000-200 (or 400 cm\(^{-1}\)) range.

Melting point. The melting points were determined with a Gallen Kamp electrically heated apparatus.

NMR Spectroscopy. The \(^1\)H and \(^{13}\)C NMR spectra of the complexes were recorded on a AL - 300 FT JEOL spectrometer operating at a frequency at 300 MHz. The NMR spectra of pyrimidine-2-thione complexes were recorded in CDCl\(_3\), that of purine-6-thione in CDCl\(_3\)-dmsod\(_6\) with TMS as the internal reference. The \(^{31}\)P NMR spectra were recorded at 121.5 MHz with TMP\{((CH\(_3\)O)\(_3\))P\} as the external reference taken as zero position.
X-Ray Crystallography

The data for compounds 1 and 10 were collected at 293 K on a Siemens P4 diffractometer. The 0–2θ technique was used to measure the intensities up to a maximum of 20 – 50° with graphite monochromatised Mo-Kα radiator (λ = 0.71073 Å). Cell parameters were refined in the 0 range, 10-12.5° using XSCANS [199] 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 F². All hydrogen atoms were refined anisotropically, fixed geometrically, and were not refined. Scattering factors from the International Tables for X-ray crystallography were used [200]. Data reduction, structure solution, refinement and molecular graphics were performed using SHELXTL-PC [201] and WinGX [202].

A yellow prismatic crystal of 3 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-Kα radiation (λ = 0.71073 Å) was used throughout. The data were processed with SAINT [203] and corrected for absorption using SADABS (transmissions factors: 1.000 - 0.791) [204]. The structure was solved by direct methods using the program SHELXS-97 [205] and refined by full-matrix least-squares techniques against F² using SHELXL-97 [206]. 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" [207]. Molecular graphics from PLATON [208] and SCHAKAL [209].

The yellow block like crystal of 8 was attached to a thin glass fibre and mounted on a Brucker Smart CCD diffractometer employing graphite monochromated Mo-Kα radiator (λ = 0.71073 Å). Cell constants were obtained from a least square refinement. Data were collected at 100 (2) K. The data integration and reduction were undertaken with SAINT and XPREP [210]. An empirical absorption correction determined with SADABS [211] was applied to the data. The structure was solved by direct methods with SHELXS-97 [212] and extended and refined by SHELXL-97 [213].
A pale orange yellow, plate like crystal of compound 9, 17 and 25 was mounted on X Calibur, Ruby, Gemini diffractometer equipped with a graphite monochromator and Mo-K$_\alpha$ radiator ($\lambda = 0.71073$ Å). The unit cell dimensions and intensity data were measured at 123(2) 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 -97 [206]. The hydrogen atoms were calculated using structure factor calculations in their idealized positions.

A colourless crystal of compound 11 was mounted on an automatic Enraf Nonius CAD-4 diffractometer equipped with a graphite monochromator and Mo-K$_\alpha$ radiator ($\lambda = 0.71073$ 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 [206]. The hydrogen atoms were calculated using structure factor calculations in their idealized positions.

The colorless crystals of 18 were attached to a fine focus sealed tube and mounted on a diffractometer employing graphite monochromated Mo-K$_\alpha$ radiator ($\lambda = 0.71073$ Å). Cell constants were obtained from a least square refinement. Data were collected at 123 K. The structure was solved by direct methods with SHELXS-97 [212] and extended and refined by SHELXL-97 [212]. The non – hydrogen atoms were modeled with anisotropic displacement parameters and in general a riding model was used for H-atoms.

A brown prismatic crystal of compound 19 was mounted on a glass fiber and used for data collection. Cell constants and an orientation matrix for data collection were obtained by least square refinement of the diffraction data from 25 reflections in the range of $17.739< \theta < 23.967$ deg. on an Enraf Nonius CAD4 automatic diffractometer [213]. Data were collected at 223 K using Cu-K$_\alpha$ radiation ($\lambda = 1.54184$ Å) and the omega-scan technique, and corrected for Lorentz and polarization effects [214]. A semiempirical absorption correction (Psi-scans) was made [215]. The structure was solved by direct methods [216] and subsequent difference Fourier map, and refined on F$^2$ by a full matrix least-squares procedure using anisotropic displacement parameters [203]. All hydrogen atoms were included in geometrically idealized positions employing appropriate riding models. Atomic scattering factors from “International Tables for
Crystallography” [207]. Molecular Graphics from PLATON [208] and SCHAKAL [209].

A brown yellow triclinic crystal of compound 22 was mounted on an automatic Enraf Nonius CAD-4 diffractometer equipped with graphite monochromator and Mo-Kα 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 F². All nonhydrogen atoms were refined anisotropically using XCAD-49 (data reduction) and SHELXL [206]. The hydrogen atoms were calculated using structure factor calculations in their idealized positions [207-209].

An orange block like crystal of 24 or orange rod like crystal of 25 were attached to a thin glass fibre and mounted on a Brucker Smart CCD diffractometer employing graphite monochromated Mo-Kα radiation (λ = 0.71073 Å). Cell constants were obtained from a least square refinement. Data were collected at 150 K. The data integration and reduction were undertaken with SAINT and XPREP [210], and subsequent computations were carried out with WINGX [217] graphical user interface. An empirical absorption correction determined with SADABS [211] was applied to the data. The structure was solved by direct methods with SHELXS-97 [212] and extended and refined by SHELXL-97 [212]. The non–hydrogen atoms were modeled with anisotropic displacement parameters and in general a riding model was used for H-atoms. An ORTEP [218] depiction of molecule with 50% displacement ellipsoids are provided in the figures.

An orange prismatic crystal of 26 was mounted on a glass fiber and used for data collection. Cell constants and an orientation matrix for data collection were obtained by least square refinement of the diffraction data from 25 reflections in the range of 17.739<θ< 23.967 deg. on an Enraf Nonius CAD4 automatic diffractometer [213]. Data were collected at 223 K using Cu-Kα radiation (λ = 1.54184 Å) and the omega-scan technique, and corrected for Lorentz and polarization effects [214]. A semiempirical absorption correction (Psi-scans) was made [215]. The structure was solved by direct methods [216] and subsequent difference Fourier map, and refined on F² by a full matrix least-squares procedure using anisotropic displacement parameters [203]. All hydrogen atoms were included in geometrically idealized positions employing an appropriate riding model.

A colorless chunk crystal of compound 27 was mounted on X Calibur, Ruby, Gemini diffractometer equipped with a graphite monochromator and Mo-Kα radiation (λ = 0.71073 Å). The unit cell dimensions and intensity data were measured at 123 K. The structures were solved by direct methods and refined by full matrix least squares method based on F². The structure was solved by direct methods with SHELXS-97 [217] and extended and refined by SHELXL-97 [212]. The hydrogen atoms were calculated using structure factor calculations in their idealized positions.

A yellow block like crystal of 29 was attached to a thin glass fibre and mounted on a Brucker Smart CCD diffractometer employing graphite monochromated Mo-Kα radiation (λ = 0.71073 Å). Cell constants were obtained from a least square refinement. Data were collected at 100 K. The data integration and reduction were undertaken with SAINT and XPREP [210]. An empirical absorption correction determined with SADABS [211] was applied to the data. The structure was solved by direct methods with SHELXS-97 [212] and extended and refined by SHELXL-97 [212].

A colorless, prismatic crystal of 30 was mounted on a glass fibre. All measurements were made on a Rigaku/MSC Mercury CCD diffractometer with graphite monochromated Mo-Kα radiation (λ = 0.71073 Å). The data was collected at a temperature of 193 K. The structure was solved by heavy-atom Patterson methods [219] and expanded using Fourier techniques [220]. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included but not refined. The final cycle of full-matrix least-squares refinement [203] was based on 1185 observed reflections (I > 2σ(I)) and 86 variable parameters. All calculations were performed by using the teXsan crystallographic software package of molecular structure corporation [221]

Preparation/Procurement of ligands and other metal salts. Pyrimidine - 2- thione, purine -6- thione, ruthenium(III) chloride, palladium(II) chloride, platinum(II) chloride, platinum(IV) chloride, hexaplatinic acid, triphenylphosphine, 1,1-bis(diphenylphosphino)methane (dppm), 1,3-bis(diphenylphosphino)propane (dppp) were obtained from standard firms. 1,2-bis(diphenylphosphino)ethane (dppe), 1,4-
bis(diphenylphosphino)butane (dppb) were prepared by using standard methods as given later.

**Preparation of Copper(I) iodide.** CuSO₄.5H₂O (5g, 0.02 M) was dissolved in 50 mL of warm distilled water. To it was added KI (3.14g, 0.02 M) and stirred with a glass rod until clear solution was formed. Through this was passed SO₂ gas (SO₂ was produced by addition of conc. H₂SO₄ to Na₂SO₃), white precipitates were formed. Washed them three-four times with distilled water and then with two-three times with methanol, and dried in vacuo.

**Preparation of copper(I) bromide.** CuSO₄.5H₂O (5g, 0.02 M) was dissolved in 50 mL of warm distilled water. To it was added NaBr (2.04g, 0.02 M) and stirred with a glass rod until clear solution was formed. Through this was passed SO₂ gas (SO₂ was produced by addition of Conc. H₂SO₄ to Na₂SO₃), white precipitates were formed. Washed them three-four times with distilled water and then with two-three times with methanol, and dried in vacuo.

**Preparation of copper(I) chloride.** CuSO₄.5H₂O (5g, 0.02 M) was dissolved in 50 mL of warm distilled water. To it was added NaCl (1.17g, 0.02 M) and stirred with a glass rod until clear solution was formed. Through this was passed SO₂ gas (SO₂ was produced by addition of Conc. H₂SO₄ to Na₂SO₃), white precipitates were formed. Washed them three-four times with distilled water and then with two-three times with methanol, and dried in vacuo.

**Preparation of dichlorobis(triphenylphosphine)palladium(II) [194].** To dry acetonitrile (25mL) in 50 mL round bottom flask, was added palladium(II) chloride (0.050 g, 0.282 mM). The contents were stirred and triphenyl phosphine (0.148 g, 0.564 mM) was added to it. Stirring was done for 30 minutes. Yellow coloured complex formed was filtered and dried in vacuo.

\[
PdCl_2 + 2PPh_3 \xrightarrow{CH_3CN} PdCl_2(PPh_3)_2
\]
PtCl$_2$(PPh$_3$)$_2$ was prepared similarly. Complexes MCl$_2$(L-L) (M=Pd, Pt, L-L = dppm, dppe, dppp, dppb) were similarly prepared.

**Preparation of dichlorotris(triphenylphosphine)ruthenium(II) [196]**: A solution of RuCl$_3$.xH$_2$O (0.262 g, 1 mM) in dry ethanol (100 mL) was refluxed for about 10 minutes. To it was added solid PPh$_3$ (1.572 g, 6 mM) and refluxing was continued. After a few minutes, brown crystalline compound started separating at the bottom of the flask. The contents were filtered after half an hour (while the solution was still hot) and were washed with hot ethanol. This compound was dried in vacuo. Complex is soluble in dichloromethane, chloroform and benzene. (M.p = 132-134°C, yield 74%).

\[
\text{RuCl}_3\cdot x\text{H}_2\text{O} + 6\text{PPh}_3 \xrightarrow{\text{reflux}} \text{RuCl}_2(\text{PPh}_3)_3
\]

**Preparation of (dichlorobis(diphenylphosphino)methane)ruthenium(II) [197]**: A solution of RuCl$_3$.xH$_2$O (0.262 g, 1 mM) in dry ethanol (100 mL) was refluxed for about 10 minutes. To it was added solid dppm (0.0806 g, 2.1 mM) and refluxing was continued. After a few minutes, orange crystalline compound started separating at the bottom of the flask. The contents were filtered after half an hour (while the solution was still hot) and were washed with hot ethanol. This compound was dried in vacuo. Complex is soluble in dichloromethane, chloroform and benzene (M.p > 280 °C, yield 70%).

\[
\text{RuCl}_3\cdot x\text{H}_2\text{O} + 2\text{dppm} \xrightarrow{\text{reflux}} \text{RuCl}_2(\text{dppm})_2
\]

**Preparation of (dichlorobis(diphenylphosphino)propane)ruthenium(II) [197]**: A solution of RuCl$_3$.xH$_2$O (0.262 g, 1 mM) in dry ethanol (100 mL) was refluxed for about 10 minutes. To it was added solid dppp (0.0845 g, 2.1 mM) and refluxed under N$_2$ atmosphere. After a few minutes, yellow – orange crystalline compound started separating at the bottom of the flask. The contents were filtered after half an hour (while the solution was still hot) and were washed with hot ethanol. This compound was dried in
vacuo. Complex is soluble in dichloromethane, chloroform and benzene (M.p > 280 °C, yield 70%).

\[
\text{RuCl}_3\cdot x\text{H}_2\text{O} + 2\text{dppb} \xrightarrow{\text{reflux}} \text{RuCl}_2(\text{dppb})_2
\]

**Preparation of \([\text{tetrachlorotris(1,4-bis(diphenylphosphino) butane)} \text{ diruthenium(II)}] [197]\):** A solution of \(\text{RuCl}_3\cdot x\text{H}_2\text{O}\) (0.262 g, 1 mM) in dry ethanol (100mL) was refluxed for about 10 minutes. To it was added solid dppb (0.0845 g, 2.1 mM) and refluxing was continued. After half an hour, light green colored powder started separating at the bottom of the flask. The contents were refluxed for a further period of 0.5 hr, cooled, filtered, washed with hot ethanol and dried in vacuo. Complex is soluble in dichloromethane, chloroform and benzene (M.p = 186 °C, yield 70%).

\[
\text{RuCl}_3\cdot x\text{H}_2\text{O} + 2\text{dppb} \xrightarrow{\text{reflux}} \text{Ru}_2\text{Cl}_4(\text{dppb})_3
\]

**Preparation of 1,2-bis(diphenylphosphino)ethane (dppe)/butane(dppb) [221].** The ligand dppe was prepared by adding finely divided lithium metal (1.06 g, 0.35mM) to a solution of PPh\(_3\) (20 g, 0.076 mM) in 100 mL of dry THF. The reaction mixture was stirred for 2-3 hours until the colour of the solution become red and the temperature raised to 48°C. Cooled the mixture in ice bath and added 8 mL of 1,2-dichloroethane solution in 10 mL of dry THF in one hour. Now the mixture was refluxed on water bath for 2-3 hours until the colour of the solution becomes faint red. White precipitates of dppe were formed on adding ice cold methanol. It was filtered, dried and recrystallised from benzene-ethanol mixture.

1,2-bis(diphenylphosphino)butane (dppb) was prepared by a similar method (8 ml of 1,2-dichlorobutane solution was added instead of 1,2-dichloroethane).

\[
\text{Ph}_3\text{P} + 2\text{Li} \xrightarrow{\text{THF}} \text{Ph}_2\text{P}^+\text{Li}^+ + \text{PhLi}
\]

\[
2\text{Ph}_2\text{P}^+\text{Li}^+ + \text{Cl(CH}_2\text{)}_n\text{Cl} \xrightarrow{\text{}} \text{Ph}_3\text{P(}]\text{CH}_2\text{)}_n\text{PPh}_2 + 2\text{LiCl}
\]

Where \(n=2, \text{dppe} \quad n=4, \text{dppb}\)
**Drying of Benzene.** Benzene (LR) was stirred mechanically for 20-30 minutes with about 15% of its volume of conc. H₂SO₄. The mixture was allowed to settle down and the orange or yellow coloured acid layer was separated using a separating funnel. The process was repeated 3-4 times, until the acid layer is colorless. Benzene was then washed twice with water in order to remove most of the acid, once with 10% Na₂CO₃ or NaHCO₃ solution and once again with water. The benzene was dried overnight over anhydrous CaCl₂ and filtered. Pure benzene was then obtained by distillation and the fraction at 80°C was collected. To get perfectly dry benzene, sodium wire was introduced into it and stored in dark place. (Benzene was phased out in June 2004).

**Drying of absolute ethanol / methanol [222].** Ethanol was obtained by dehydration of rectified spirit (95% EtOH) by quick lime. For this, to about 2-2.5 L of rectified spirit in RBF of capacity 3-4 L was added CaO (800g). The mixture was then refluxed over a heating mantle for about 8 h. Reaction mixture was then distilled and fraction at 78°C was collected. Ethyl alcohol so obtained is hygroscopic. Extremely dry ethyl alcohol was obtained by treatment of ethyl alcohol (99.5%) with Mg powder (clean and dry) (5g) and I₂ crystals (0.2 g) and were heated gently in RBF fitted with reflux condenser equipped with a guard tube. Flask was gradually cooled to RT. CaO treated EtOH was poured into flask and refluxed until I₂ disappeared and refluxing was continued for 5-6 h until all Mg is converted to Mg ethanolate. Mg ethanolate on reaction with H₂O gives highly insoluble Mg(OH)₂ indicated by milkiness which appears at the bottom of the flask.

\[
\begin{align*}
\text{Mg} + 2\text{EtOH} & \rightarrow 2\text{H}^+ + \text{Mg(OEt)}_2 + \text{H}_2 \\
\text{Mg(OEt)}_2 + \text{H}_2\text{O} & \rightarrow \text{Mg(OH)}_2 + 2\text{EtOH}
\end{align*}
\]

Ethanol was then distilled at 78.4°C about 99.9% pure.

**Drying of Chloroform.** To chloroform in RBF, was added calcium chloride and kept overnight. After distillation, dry chloroform was obtained.
**Drying of acetonitrile.** To acetonitrile, was added phosphorus pentaoxide and was kept overnight. It was refluxed for 1 h, followed by distillation to get dry acetonitrile.

**Drying of Tetrahydrofuran.** Tetrahydrofuran was refluxed over Na metal and distilled. A fraction at 65-66°C was stored over sodium wire.

**Ligand data**

**$^1$H - NMR of pyrimidine-2-thione:**

$^1$H NMR (δ, ppm, J, Hz, CDCl$_3$): 8.59 [dd, 2H, $J_{HH}$ 4.8, H$_4$, H$_6$], 7.10 [t, 1H, $J_{HH}$ 5.1, H$_5$].

**$^1$H - NMR of purine-6-thione:**

$^1$H NMR (δ, ppm, J, Hz, dms-o-d$_6$): 7.75 [s, 1H, H$_2$], 7.1 [s, 1H, H$_8$].

**IR of pyrimidine-2-thione:**

Main IR peaks (KBr, cm$^{-1}$); $\nu$(N – H), 3300; $\nu$(C – H), 2910; $\nu$(C – C) + $\nu$(C – N), 1560, 1460; $\nu$ (C = S), 980.

**IR of purine-6-thione:**

Main IR peaks (KBr, cm$^{-1}$); $\nu$(N – H), 3431; $\nu$(C – H), 3095; $\nu$(C – C) + $\nu$(C – N), 1573, 1471; $\nu$ (C = S), 868.
METHOD OF PREPARATION

\[\text{[Pd(\eta^2-N,S- pymS)(\eta^1-S- pymS) (PPh_3)]} \ 1.\] To a solution of pyrimidine-2-thione (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 mL), which formed a clear light yellow solution. To this solution was added suspension of \(\text{PdCl}_2(\text{PPh}_3)_2\) (0.025 g, 0.035 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 crystallise at room temperature and dark yellow crystals were formed over a period of 5 d. Yield 60%, M.pt. 170-175\(^\circ\) C. Anal. Calcd C\(_{26}\)H\(_{21}\)N\(_4\)PPdS\(_2\) (590.96); C, 52.7; H, 3.96; H, 9.47; Found. C, 53.4; H, 3.76; N, 9.53. Main IR peaks (KBr, cm\(^{-1}\)); \(\nu(C-H)\), 3060; \(\nu(C-C) + \nu(C-N)\), 1575, 1480; \(\nu(C-S)\), 850w, 820w; \(\nu(P-C)\), 1070 \(^1\)H NMR (\(\delta,\) ppm, J, Hz, CDCl\(_3\)): 8.58 [d, 1H, \(J_{\text{HH}}\) 4.8, H\(_4\)], 8.14 [d, 1H, \(J_{\text{HH}}\) 5.1, H\(_6\)], 7.26 [t, 1H, \(J_{\text{HH}}\) 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: 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: 33.6. \(\Delta\delta (\delta_{\text{complex}} - \delta_{\text{ligand}}) = 38.3 \text{ ppm.}\)

Complexes 2 – 5 were prepared by a method similar to complex 1 using precursor \(\text{PdCl}_2(dppm), \text{PdCl}_2(dppe), \text{PdCl}_2(dppp), \text{PdCl}_2(dpbb)\) respectively.

\[\text{[Pd(\eta^1-S-pymS)(dppm)]} \ 2.\] Yellowish orange crystalline mass was formed in a period of 5 d. (70%, M.pt. 180-185\(^\circ\) C). Anal. Calcd C\(_{33}\)H\(_{26}\)N\(_4\)P\(_2\)PdS\(_2\) (713); C, 55.38; H, 3.81; N, 7.83; Found. C, 55.4; H, 3.76; N, 7.60. Main IR peaks (KBr, cm\(^{-1}\)); \(\nu(C-H)\), 3049; \(\nu(C-C) + \nu(C-N)\), 1562, 1481; \(\nu(C-S)\), 885m, 850w; \(\nu(P-C)\), 1064. \(^1\)H NMR (\(\delta,\) ppm, J, Hz, CDCl\(_3\)): 8.58 [d, 1H, \(J_{\text{HH}}\) 4.8, H\(^4\)], 8.18 [d, 1H, \(J_{\text{HH}}\) 4.8, H\(^6\)], 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, \(J_{\text{HH}}\) 11.4, CH\(_2\)]. \(^{13}\)C NMR: 188.71 [s,C\(_2\)],163.93 [s, C\(^4\),C\(_6\)],132.56 [s, i-C], 131.83 [s, o-C], 131.19 [d, m-C, Jcc 23], 128.65 [d, p-C, Jcc 59.23], 47.96 [s, -CH\(_2\)]. \(^{31}\)P NMR: 30.9, 25.7. \(\Delta\delta (\delta_{\text{complex}} - \delta_{\text{ligand}}) = 35.6, 30.4.\)
[Pd(η⁴-S-pyms)₂(dppe)] 3. Dark yellow crystals were formed in a period of 5 days. (70%, M.pt. 200-210⁰ C). Anal. Calcd. C₃₄H₅₀N₄P₂PdS₂ (727.08); C, 55.06; H, 4.115; N, 7.68; Foud. C, 55.01; H, 4.05; N, 7.35. Main IR peaks (KBr, cm⁻¹); ν(C – H), 3049; ν(C – C) + ν(C – N), 1562, 1485; ν (C = S), 879m, 819s; ν(P – C), 1043. ¹H NMR (δ, ppm, J, Hz, CDCl₃): 8.58 [dd, 2H, Jₘₙₘₙ 4.8, H¹, H⁶], 7.09 [t, 1H, H⁵], 7.88 [m, 6H, o-H]. 7.83 [m, 6H, m-H], 7.21 [m,3H, p-H], 4.65 [b, 4H, -CH₂-CH₂]. ¹³C NMR: 185.0 [s,C²], 155.65 [s, C⁴,C⁶], 131.73 [s, i-C], 114.55 [s, C⁵], 132.99 [d, Jcp 10.5, o-C], 130.74 [d, Jcc 9.28, p-C], 128.58 [t. Jcc 11.8,m-C]. ³¹P NMR: 33.2, 28.7 (δ(complex − δ(ligand)) = 37.9, 33.4. The complex is soluble in chloroform, dichloromethane and acetone.

[Pd(η⁴-S-pyms)₂(dppe)] 4. Yellow crystalline mass was formed within a period of 5 d. M.pt. 190-200⁰ C, Yield, 70%. Anal. Calcd. C₅₅H₇₂N₄P₂PdS₂ (741); C, 56.6; H, 4.311; N, 7.55; Found. C, 56.22; H, 4.30; N, 7.425. Main IR peaks (KBr, cm⁻¹); ν(C – H), 3049; ν(C – C) + ν(C – N), 1560, 1436; ν (C = S), 840m, 820s; ν(P – C), 997. ¹H NMR (δ, ppm, J, Hz, CDCl₃): 8.106 [dd, 2H, Jₘₙₘₙ 4.5, H¹, H⁶], 6.643 [t, 1H, Jₘₙₘₙ 5.1, H⁵], 7.924 [m, 6H, o-H], 7.490 [m, 6H, m-H], 7.383 [m,3H, p-H], 4.65 [b, 4H, -CH₂-CH₂]. ¹³C NMR: 195.9 [s,C²], 155.67 [s, C⁴], 150.7 [s, C⁵], 114.11 [s, i-C], 118.1 [s, C⁵], 132.95 [d, o-C], 130.69 [d, p-C], 128.63 [t. m-C]. ³¹P NMR: 33.0, 28.3 (δ(complex − δ(ligand)) = 37.7, 33.0.

[Pd(η¹-S-pyms)₂(dppe)] 5. Yellow crystalline mass was formed within a period of 5 d. M.pt. 170-175⁰ C, Yield, 70%. Anal. Calcd. C₃₆H₅₄N₄P₂PdS₂ (775); C, 57.2; H, 4.50; N, 7.41; Found. C, 56.95; H, 4.45; N, 7.35. Main IR peaks (KBr, cm⁻¹); ν(C – H), 3049; ν(C – C) + ν(C – N), 1558, 1434; ν (C = S), 841m, 810s; ν(P – C), 997. ¹H NMR (δ, ppm, J, Hz, CDCl₃): 8.16 [dd, 2H, Jₘₙₘₙ 0.9, H¹, H⁶], 6.7 [t, 1H, Jₘₙₚₚ 4.5, H⁵], 7.694 [m, 6H, o-H], 7.490 [m, 6H, m-H], 7.383 [m,3H, p-H], 4.65 [b, 4H, -CH₂-CH₂]. ¹³C NMR: 192.8 [s,C²], 153.7 [s, C⁴], 153.7 [s, C⁵], 116.4 [s, C⁵], 132.95 [d, o-C], 130.69 [d, p-C], 128.63 [t. m-C]. ³¹P NMR: 33.2, 2.8 (δ(complex − δ(ligand)) = 37.9, 7.5.

[Pd(η²-N,S-puS)(PPh₃)₂] 6. To a solution of purine-6-thione (puSH₂) (0.050 g, 0.0713 mmol) placed in round bottom flask was added a solution of sodium hydroxide (NaOH) (0.002 g) in distilled water (2 mL), which formed a clear light yellow solution. To this
solution was added suspension of \( \text{PdCl}_2(\text{PPh}_3)_2 \) (0.050 g, 0.0713 mmol) in ethanol, and the contents were stirred for 6 h. The colour of the reaction mixture became yellow and NaCl formed was filtered off. The filtrate was allowed to crystallise at room temperature and yellow crystals were formed over a period of five days. The crystals are solvent stored and become opaque when dry. M.pt. 240-250 °C, Yield, 60%. Anal. Calcd C\(_{41}\)H\(_{32}\)N\(_4\)P\(_2\)S\(_2\)Pd (780); C, 63.0; H, 4.10; N, 7.11; Found. C, 62.1; H, 4.00; N, 7.01. Main IR peaks (KBr, cm\(^{-1}\)): \( \nu(C – C) + \nu(C – N) \), 1555, 1440; \( \nu(C = S) \), 860 s; \( \nu(P – C) \), 1125. \(^1\)H NMR (\( \delta \), ppm, J, Hz, CDCl\(_3\) + dmso-d\(_6\)): 7.2 [s, 1H, H\(_2\)], 7.29 [m, 6H, o-H], 7.47 [m, 6H, m-H], 7.68 [m,3H, p-H]. \(^3\)P NMR: 26.5, -8.29. \( \Delta \delta (\delta_{\text{complex}} – \delta_{\text{ligand}}) = 31.2, -3.6 \) ppm.

Complexes 7 – 9 were prepared by the similar method as 6.

\[ \text{[Pd(\eta^2-N, S- puS)(dppm)]} \] 7. Yellow crystalline mass was formed in a period of 5 days. M.pt. 260-270 °C, Yield, 70%. Anal. Calcd C\(_{30}\)H\(_{24}\)N\(_4\)P\(_2\)S\(_2\) (640); C, 56.2; H, 3.75; N, 8.75; Found. C, 55.5; H, 3.68; N, 8.48. Main IR peaks (KBr, cm\(^{-1}\)): \( \nu(C – C) + \nu(C – N) \), 1545, 1450; \( \nu(C = S) \), 860w, 880m; \( \nu(P – C) \), 1180. \(^1\)H NMR (\( \delta \), ppm, J, Hz, CDCl\(_3\) + dmso-d\(_6\)): 8.96 [s, 1H, H\(_8\)], 8.54, 8.44 [s, 1H, H\(_2\)], 7.47 [m, 6H, o-H], 7.68 [m, 6H, m-H], 7.88 [m,3H, p-H]. \(^3\)P NMR: 27.8, 22.7. \( \Delta \delta (\delta_{\text{complex}} – \delta_{\text{ligand}}) = 32.4, 27.40 \) ppm.

\[ \text{[Pd(\eta^2-N, S- puS)(dppp)]} \] 8. Dark yellow crystals were formed in a period of 5 days. M.pt. 270-280 °C, Yield, 70%. Anal. Calcd C\(_{32}\)H\(_{28}\)N\(_4\)P\(_2\)S\(_2\) (668.9); C, 57.4; H, 4.18; N, 8.37; Found. C, 57.12; H, 4.08; N, 8.02. Main IR peaks (KBr, cm\(^{-1}\)): \( \nu(C – C) + \nu(C – N) \), 1537, 1481; \( \nu(C = S) \), 881w, 836m; \( \nu(P – C) \), 1166. \(^1\)H NMR (\( \delta \), ppm, J, Hz, CDCl\(_3\) + dmso-d\(_6\)): 8.45 [s, 1H, H\(_8\)], 6.61 [s, 1H, H\(_2\)], 7.34 [m, 6H, o-H], 7.59 [m, 6H, m-H], 7.72 [m,3H, p-H]. \(^3\)P NMR: 37.31, 34.45, 13.9. \( \Delta \delta (\delta_{\text{complex}} – \delta_{\text{ligand}}) = 42.0, 39.15, 18.6 \) ppm.

\[ \text{[Pd(\eta^2-N, S- puS)(dppb)]} \] 9. Dark yellow crystals were formed in a period of 5-6 days. M.pt. 280-290°C, Yield, 70%. Anal. Calcd C\(_{33}\)H\(_{30}\)N\(_4\)P\(_2\)S\(_2\) (682); C, 58.06; H, 4.39; N, 8.21; Found. C, 57.99; H, 4.35; N, 8.35. Main IR peaks (KBr, cm\(^{-1}\)): \( \nu(C – C) + \nu(C – N) \), 1550, 1440; \( \nu(C = S) \), 840w, 810s; \( \nu(P – C) \), 1135. \(^1\)H NMR (\( \delta \), ppm, J, Hz, CDCl\(_3\) +
dmsø-d₆): 9.01 [s, 1H, H⁸], 8.50, 8.46 [s, 1H, H²], 7.43 [m, 6H, o-H], 7.65 [m, 6H, m-H], 7.74 [m, 3H, p-H]. ³¹P NMR: 32.08, 29.35, 9.39. Δδ (δcomplex – δligand) = 36.68, 34.05, 14.09 ppm.

[Pt(η²-N,S-pymS)(η¹-S-pymS)(PPh₃)] 10. To the solid pyrimidine -2- thione (pymSH) (0.024 g, 0.11 mmol) suspended in dry benzene (5 mL) in a round bottom flask was added a solution of platinic acid, H²PtCl₆ (0.05 g, 0.116 mmol) in dry ethanol (15 mL) in the presence of Et₃N base (2 mL). The contents were stirred for 2 h until turbidity appeared and to this was added solid triphenylphosphine (PPh₃) (0.061 g, 0.116 mmol). The clear orange colour solution was stirred overnight and Et₃NH⁺Cl⁻ formed was filtered off, and the filtrate was allowed to crystalize at room temperature. The brown crystals were formed in a period of six days. Complex is soluble in chloroform, dichloromethane and acetone. M.pt. 180° C, Yield, 65%. Anal. Calcd C₂₆H₂₁N₄PPtS₂ (679.65); C, 44.8; H, 3.52; N, 8.75; Found. C, 44.19; H, 3.59; N, 9.05. Main IR peaks (KBr, cm⁻¹); ν(C – H), 3060; ν(C – C) + ν(C – N), 1537, 1481; ν (C = S), 923m, 860w; ν(P – C), 1070. ¹H NMR (δ, ppm, J, Hz, CDCl₃): 8.58 [d, 1H, JHH 4.8, H₄], 7.09 [t, 1H, JHH 4.8, H₆], 6.99 [t, 1H, JHH 1.8, H₆], 7.47 [m, 6H, o-H], 7.67 [m, 6H, m-H], 7.70 [m, 3H, p-H]. ¹³C NMR: 157.94 [s, C⁴,C⁶], 134.07 [s, i-C], 133.08 [s, o-C], 131.97 [dd, Jcc 5.95, p-C], 128.4 [d, Jcc 11.6, m-C], 45.79 [s, CH₂]. ³¹P NMR: 29.8. Δδ (δcomplex – δligand) = 34.5.

[Pt(η¹-S-pymS)₂(dppm)] 11. To the solid pyrimidine -2- thione (pymSH) (0.033 g, 0.148 mmol) suspended in dry benzene (5 mL) in a round bottom flask was added a solution of platinium(IV) chloride, PtCl₄ (0.050 g, 0.148 mmol) in dry ethanol (15 mL) in the presence of Et₃N base (2 mL). 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 was stirred overnight and Et₃NH⁺Cl⁻ formed was filtered off, and the filtrate was allowed to crystalize at room temperature. The yellow crystals were formed in a period of 6 d. The complex is soluble in chloroform, dichloromethane, acetone. M.pt. 190° C, Yield, 65%. Anal. Calcd C₃₃H₂₈N₄P₂PtS₂ (801.74); C, 49.2; H, 3.48; N, 6.97; Found. C, 48.8; H, 3.43; N, 7.05. Main IR peaks (KBr, cm⁻¹); ν(C – H), 3040; ν(C – C) + ν(C – N),
$^{1}$H NMR ($\delta$, ppm, J, Hz, CDCl$_3$): 8.58 [d, 2H, $J_{HH}$ 4.8, H$_4$], 7.08 [t, 1H, $J_{HH}$ 4.8, H$_6$], 6.70 [bb, 1H, H$_5$], 7.33 [m, 6H, o-H], 7.49 [m, 6H, m-H], 7.73 [m, 3H, p-H]. $^{13}$C NMR: 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: -6.4. $\Delta \delta$ ($\delta_{\text{complex}} - \delta_{\text{ligand}}$) = -1.7. With platinic acid similar product is formed.

Complexes 12-14 were prepared as the similar method as 11.

[Pt($\eta^1$-S- pymS)$_2$(dppe)] 12. Yellow crystalline mass was formed in a period of 4 d. The complex is soluble in chloroform, dichloromethane and acetone. M.pt. 190° C, Yield, 65%. Anal. Calcd C$_{34}$H$_{30}$N$_4$P$_2$PtS$_2$ (815); C, 50.00; H, 3.50; N, 5.86; Found. C, 49.89; H, 3.50; N, 6.75. Main IR peaks (KBr, cm$^{-1}$); ν(C – H), 3049; ν(C – C) + ν(C – N), 1550, 1480; ν(C = S), 880w, 820m; ν(P – C), 1100. $^{1}$H NMR ($\delta$, ppm, J, Hz, CDCl$_3$): 8.58 [dd, 2H, $J_{HH}$ 4.8, H$_4$], 7.09 [t, 1H, $J_{HH}$ 4.8, H$_6$], 7.86 [m, 6H, o-H], 7.73 [m, 6H, m-H], 7.67 [m, 3H, p-H]. $^{13}$C NMR: 184.97 [s, C$^2$], 157.94 [s, C$^4$, C$^6$], 132.13 [s, i-C], 118.23 [s, C$^5$], 130.77 [d, o, p-C], 128.84 [d, J$_{cc}$ 6.26, m-C]. $^{31}$P NMR: 33.9, 42.0. $\Delta \delta$ ($\delta_{\text{complex}} - \delta_{\text{ligand}}$) = 38.6, 46.7.

[Pt($\eta^1$-S- pymS)$_2$(dppp)] 13. Yellow crystalline mass was formed in a period of 4 d. The complex is soluble in chloroform, dichloromethane and acetone. M.pt. 185° C, Yield, 65%. Anal. Calcd C$_{35}$H$_{32}$N$_4$P$_2$PtS$_2$ (829); C, 50.46; H, 3.50; N, 5.86; Found. C, 49.88; H, 3.50; N, 6.70. Main IR peaks (KBr, cm$^{-1}$); ν(C – H), 3049; ν(C – C) + ν(C – N), 1550, 1480; ν(C = S), 880w, 820m; ν(P – C), 1100. $^{1}$H NMR ($\delta$, ppm, J, Hz, CDCl$_3$): 8.02 [d, 1H, $J_{HH}$ 4.8, H$_4$], 7.132 [d, 1H, $J_{HH}$ 4.8, H$_6$], 6.50 [s, 1H, H$^5$], 7.175 [m, 6H, o-H], 7.453 [m, 6H, m-H], 7.690 [m, 3H, p-H]. $^{13}$C NMR: 160.37 [s, C$^4$, C$^6$], 132.13 [s, i-C], 131.80 [s, o-C], 130.5 [s, p-C], 128.64 [s, m-C], 29.2, 30.9 [s, -CH$_2$], $^{31}$P NMR: 33.4, 28.4. $\Delta \delta$ ($\delta_{\text{complex}} - \delta_{\text{ligand}}$) = 37.1, 33.1.

[Pt($\eta^1$-S- pymS)$_2$(dppb)] 14. Yellow crystalline mass was formed in a period of 4 d. The complex is soluble in chloroform, dichloromethane and acetone. M.pt. 180° C, Yield, 65%. Anal. Calcd C$_{36}$H$_{34}$N$_4$P$_2$PtS$_2$ (843); C, 51.2; H, 4.03; N, 6.64; Found. C, 50.86; H,
4.00; N, 6.52. Main IR peaks (KBr, cm$^{-1}$); $\nu$(C – H), 3049; $\nu$(C – C) + $\nu$(C – N), 1560, 1436; $\nu$ (C = S), 845m, 820m; $\nu$(P – C), 1036. $^1$H NMR (δ, ppm, J, Hz, CDCl$_3$): 8.58 [d, 1H, $J_{HH}$ 4.5, H$^8$], 8.05 [t, 1H, $J_{HH}$ 5.1, H$^5$], 7.32 [m, 6H, o-H], 7.452 [m, 6H, m-H], 7.654 [m,3H, p-H]. $^{13}$C NMR: 157.93 [s, C$^4$, C$^6$], 133.03 [s, i-C], 118.22 [s, C$^5$], 132.95[d, o-C], 128.84 [d, m-C], 130.7 [s, p-C]. $^{31}$P NMR: 33.1, 2.8, $\Delta$δ (δ$_{\text{complex}}$ – δ$_{\text{ligand}}$) = 37.8, 7.5.

[Pt($\eta^2$-N, S-puS)(PPh$_3$)$_2$] 15. To the solid purine-6-thione (puSH$_2$) (0.039 g, 0.116 mmol) suspended in dry benzene (5 cm$^3$) in a round bottom flask was added a solution of platinic acid, H$_2$PtCl$_6$ (0.05 g, 0.116 mmol) in dry ethanol (15 cm$^3$) in the presence of Et$_3$N base (2 cm$^3$). The contents were stirred for 2 h until turbidity appeared and to this was added solid triphenylphosphine (PPh$_3$) (0.061g, 0.116mmol). The clear yellow colour solution was stirred overnight and Et$_3$NH$^+$Cl$^-$ formed was filtered off, and the filtrate was allowed to crystalize at room temperature. The yellow crystalline mass was formed in a period of 4 d. M.pt. 220–230ºC, Yield, 60%. Anal. Calcd C$_{41}$H$_{32}$N$_4$PPtS$_2$ (869); C, 55.4; H, 3.46; N, 6.53: Found. C, 55.21; H, 3.25; N, 6.22. Main IR peaks (KBr, cm$^{-1}$); $\nu$(C – C) + $\nu$(C – N), 1560, 1440; $\nu$ (C = S), 860w, 810s; $\nu$(P – C), 1150. $^1$H NMR (δ, ppm, J, Hz, CDCl$_3$ + dmso-d$_6$): 8.5 [s, 1H, H$^8$], 7.40 [s, 1H, H$^2$], 7.47 [m, 6H, o-H], 7.60 [m, 6H, m-H], 7.66 [m,3H, p-H]. $^{31}$P NMR: 33.1, 2.8, $\Delta$δ (δ$_{\text{complex}}$ – δ$_{\text{ligand}}$) = 37.8, 7.5.

Complexes 16 – 18 were prepared similarly as 15.

[Pt($\eta^2$-N, S-puS)(dppm)] 16. Yellowish orange crystalline mass was formed in a period of 5 days. M.pt. 230-240ºC, Yield, 70%. Anal. Calcd C$_{30}$H$_{24}$N$_4$P$_2$PtS$_2$ (729); C 48.8; H, 3.13; N, 7.60; Found. C, 48.76; H, 2.98; N, 7.29. Main IR peaks (KBr, cm$^{-1}$); $\nu$(C – C) + $\nu$(C – N), 1545, 1450; $\nu$ (C = S), 850w; $\nu$(P – C), 1180. $^1$H NMR (δ, ppm, J, Hz, CDCl$_3$ + dmso-d$_6$): 7.22 [s, 1H, H$^8$], 6.50 [s, 1H, H$^2$], 6.68 [m, 6H, o-H], 6.81 [m, 6H, m-H], 6.90 [m,3H, p-H]. $^{31}$P NMR: 32.46. $\Delta$δ (δ$_{\text{complex}}$ – δ$_{\text{ligand}}$) = 37.16 ppm.

[Pt($\eta^2$-N, S-puS)(dppp)] 17. Dark yellow crystals were formed in a period of 5 days. These become opaque when come in contact with air, so these are solvent stored. M.pt.
260-270°C, Yield, 70%. Anal. Calcd C_{32}H_{28}N_{4}P_{2}PtS_{2} (757); C 50.22; H, 3.30; N, 7.42; Found. C, 50.01; H, 3.17; N, 7.10. Main IR peaks (KBr, cm\(^{-1}\)): ν(C – C) + ν(C – N), 1550, 1445; ν(C = S), 850w; ν(P – C), 1110. \(^1\)H NMR (δ, ppm, J, Hz, CDCl\(_3\) + dmso-d\(_6\)): 8.50 [s, 1H, H^8], 6.50 [s, 1H, H^2], 7.35 [m, 6H, o-H], 7.51 [m, 6H, m-H], 7.70 [m,3H, p-H]. \(^{31}\)P NMR: 29.98. Δδ (δ\(_{\text{complex}}\) – δ\(_{\text{ligand}}\)) = 31.68 ppm.

\[\text{[Pt(η\(^2\)-N, S- pymS)(dppb)] 18.}\] Yellow crystals were formed in a period of 5 days. M.pt. 270-280°C, Yield, 70%. Anal. Calcd C\(_{33}\)H\(_{30}\)N\(_4\)P\(_2\)PtS\(_2\) (771.7); C 51.3; H, 3.89; N, 7.26; Found. C, 50.95; H, 3.35; N, 7.35. Main IR peaks (KBr, cm\(^{-1}\)): ν(C – C) + ν(C – N), 1550, 1445; ν(C = S), 850w; ν(P – C), 1110. \(^1\)H NMR (δ, ppm, J, Hz, CDCl\(_3\) + dmso-d\(_6\)): 8.50 [s, 1H, H^8], 6.64 [s, 1H, H^2], 7.37 [m, 6H, o-H], 7.62 [m, 6H, m-H], 7.66 [m,3H, p-H]. \(^{31}\)P NMR: 34.58. Δδ (δ\(_{\text{complex}}\) – δ\(_{\text{ligand}}\)) = 39.28 ppm.

\[\text{[Ru(η\(^2\)-N, S- pymS)(2PPh\(_3\))] 19.}\] To the brown solution of RuCl\(_2\)(PPh\(_3\))\(_3\) (0.050 g, 0.052 mmol) in degassed benzene (25 mL) was added a solution of pymSH (0.011 g, 0.104 mmol) in benzene (10 mL) along with Et\(_3\)N (2 mL). The mixture was refluxed under dry and oxygen free N\(_2\) for 24 h. The colour of the solution changes from dark brown to orange brown. The precipitated Et\(_3\)NH\(^+\)Cl\(^-\) was filtered off and the filtrate concentrated to one third of its initial volume. The filtrate was placed for crystallization at room temperature by adding n-hexane (20 mL) .Orange brown crystals were formed after 3 – 4 days. The complex is soluble in chloroform, dichloromethane and acetone. Yield 65%, M.pt. 250-260(d°C). Anal. Calcd C\(_{47}\)H\(_{39}\)N\(_4\)P\(_2\)RuS\(_2\) (886.95); C 63.0; H, 4.58; N, 6.26; Found. C, 63.13; H, 4.55; N, 6.24. Main IR peaks (cm\(^{-1}\)): ν(C–H), 3180; ν(C – C) + ν(C – N), 1560, 1480; ν (C = S), 850m; ν(P–C), 1090. \(^1\)H NMR (δ, ppm, J, Hz, CDCl\(_3\)): 7.9 [d, 1H, J\(_{HH}\) 4.56, H\(^4\)], 7.3 [q,1H, J\(_{HH}\) 3.2, H\(^6\)], 6.06 [t, 1H, J\(_{HH}\) 5.118, H\(^5\)], 7.06 [t, 6H, J\(_{HH}\) 7.464,o-H], 7.14 [d, 6H, J\(_{HH}\) 14.4, m-H], 7.26 [t, 3H, J\(_{HH}\) 0.69, p-H], \(^{13}\)C NMR: 188.056 [s,C\(^2\)], 155.188 [s,C\(^6\)], 153.449 [s, C\(^4\)], 135.66 [t, J\(_{cc}\) 19.5, i-C], 118.23 [s, C\(^5\)], 133.95 [t, J\(_{cc}\) 4.97,o,p-C], 127.22 [t, J\(_{cc}\) 4.30, m-C]. \(^{31}\)P NMR: 19.386. Δδ (δ\(_{\text{complex}}\) – δ\(_{\text{ligand}}\)) = 24.08.

Complexes 20, 22-23 were prepared by the method used for as 19, with precursors RuCl\(_2\)(dppm)\(_2\), RuCl\(_2\)(dppp)\(_2\) and Ru\(_2\)Cl\(_6\)(dppb)\(_3\) respectively.
[Ru(η²-N, S-pymS)₂(dppm)] 20. Orange crystalline mass was obtained after 3 – 4 days. The complex is soluble in chloroform, dichloromethane and acetone. Yield 70%, M.pt. 210-215(d)°C. Anal. Calcd. C₃₅H₃₈N₄P₂S₂Ru (707); C 56.01; H, 3.96; N, 7.92; Found. C 55.9; H, 3.89; N, 7.67. Main IR peaks (cm⁻¹): ν(C–H), 3049; ν(C – C) + ν(C – N), 1560, 1480; ν(C = S), 840w, 790w; ν(P–C), 1095. ¹H NMR (δ, ppm, J, Hz, CDCl₃): 8.425 [d, 1H, JHH 2.7, H¹], 8.197 [dd, 1H, JHH 4.9, H⁶], 6.461 [t, 1H, JHH 4.8, H⁵], 7.24 [m, 6H, o-H], 7.35 [m,6H,m-H], 7.50 [m, 3H, p-H]. ¹³C NMR: 184 [s,C²], 156.1 [s,C⁵], 155.6 [s, C⁴], 131.9 [s, i-C], 129.9 [m ,o-C], 127.9 [m, m-C], 128.3 [m ,p-C], 45.79 [s, CH₂]. ³¹P NMR: 9.72. Δδ (δcomplex – δligand) = 14.42.

[Ru(η²-N, S-pymS)₂(dppp)] 22. The orangish yellow crystals were grown in dry benzene in 4-5 days. Yield 65%, M.pt. 220-230(d)°C. The complex is soluble in chloroform, dichloromethane, acetone. Anal. Calcd. C₃₅H₃₂N₄P₂S₂Ru: (735.78); C 57.1; H, 4.35; N, 7.61; Found. C 56.34; H, 4.43; N, 7.30. Main IR peaks (cm⁻¹): ν(C–H), 3049; ν(C – C) + ν(C – N), 1560, 1480; ν(C = S), 856m, 800s; ν(P–C), 1095. ¹H NMR (δ, ppm, J, Hz, CDCl₃): 7.945 [d, 2H, JHH 2.4, H⁴,H⁶], 6.076 [t, 1H, JHH 5.1, H⁵], 7.223 [m, 6H, o-H], 7.301 [m,6H,m-H], 7.461 [m, 3H, p-H]. ¹³C NMR: 181.3 [s,C²], 154.9 [s,C⁵], 153.9 [s, C⁴], 132.2 [s, i-C], 115.2 [s, C⁵], 131.3 [m ,o-C], 127.9 [m, m-C], 128.8 [m ,p-C]. ³¹P NMR: 42. Δδ (δcomplex – δligand) = 46.7.

[Ru(η²-N, S-pymS)₂(dppb)] 23. The orangish yellow crystals were grown in dry CH₂Cl₂ and CH₃OH in 4-5 days. Yield 65%, M.pt. 210-220(d)°C. Anal. Calcd. C₃₆H₃₄N₄P₂S₂Ru: (749); C 57.6; H, 4.53; N, 7.47; Found. C 57.21; H, 4.48; N, 7.40. Main IR peaks (cm⁻¹): ν(C–H), 3049; ν(C – C) + ν(C – N), 1560, 1480; ν (C = S), 871m, 791m; ν(P–C), 1095. ¹H NMR (δ, ppm, J, Hz, CDCl₃): 7.951[d, 1H, JHH 2.4, H⁴], 7.642 [d, 1H, JHH 4.5, H⁶], 6.115 [t, 1H, JHH 5.1, H⁵], 7.082 [m, 6H, o-H], 7.260 [m, 6H, m-H], 7.544 [m, 3H, p-H]. ¹³C NMR: 188.254 [s,C²], 155.044 [s,C⁵], 154.04 [s, C⁴], 131.4 [s, i-C], 113.1 [s, C⁵], 129.2 [m ,o-C], 127.4 [m, m-C], 128.4 [m ,p-C]. ³¹P NMR: 48.8. Δδ (δcomplex – δligand) = 53.5.
[Ru(η²-N, S- pymS)₂(dppe)] 21. To the colorless solution of dppe (0.02077 g, 0.0502 mmol) in dry toluene (15 mL), added brown color complex of [Ru(pymS)₂(PPh₃)₂] in dry toluene (10 mL) along with Et₃N (2 mL). The mixture was refluxed under dry and oxygen free N₂ for 48 hours. The colour of solution changes from brown to yellow. The precipitated Et₃NH⁺Cl⁻ was filtered off and filtrate was concentrated to one third of its initial volume. The filtrate was placed for crystallization at room temperature by adding n-hexane (20 mL). Orange crystalline mass is obtained. Yield 70%, M.pt. 210-215(d)°C.

Anal. Calcd. C₃₄H₃₄N₄P₂S₂Ru (721); C 56.50; H, 4.16; N, 7.76; Found. C 56.31; H, 4.20; N, 7.64. Main IR peaks (cm⁻¹); ν(C–H), 3040; ν(C – C) + ν(C – N), 1560, 1480; ν( C = S), 850w, 800s; ν(P–C), 1090. ¹H NMR (δ, ppm, J, Hz, CDCl₃): 8.129 [d, 2H, JHH 7.2, H₄], 6.63 [t, 1H, JHH 4.8, H₅], 7.28 [m, 6H, o-H], 7.67 [m,6H,m-H], 7.79 [m, 3H, p-H], ¹³C NMR (ppm, J Hz CHCl₃ –d): 155.8 [s, C₆], 155.1 [s, C₄], 134.2 [s, i-C], 114.2 [s, p-H], 131.3 [m, o-C], 127.9 [m, m-C], 128.4 [m, p-C]. ³¹P NMR (CDCl₃, δ): 34.6, 30.46. ∆δ (δcomplex – δligand) = 39.3, 35.16.

[CuCl(η¹-S-pymSH)(PPh₃)₂] 24. To a solution of CuCl (0.020 g, 0.22 mmol) in dry acetonitrile (5 mL), was added a solution of pyrimidine-2-thione (pymSH) (0.025 g, 0.22 mmol) in dry acetonitrile (15 mL). The contents were stirred when red precipitates were formed, which were suspended in CHCl₃ (10 mL) and to it was added a solution of triphenylphosphine (0.058 g, 0.22 mmol) in CHCl₃ (15 mL). The mixture was stirred for 5–6 h and the bright orange solution on cooling at room temperature for 2 days formed an orange solid. The crystals were grown in dry CH₂Cl₂–MeOH mixture (2:1 v/v). Yield 65%. M.pt. 190-195°C. Anal. Calcd (%) for C₄₀H₃₄ClCuN₂P₂S: (735.68); C, 65.3; H, 4.62; N, 3.80; Found. C, 65.01; H, 4.70; N, 3.98. Main IR peaks (cm⁻¹); δ (N–H), 3460; ν(C–H), 3160; ν(C – C) + ν(C – N), 1570, 1490; ν (C = S), 850w; ν(P–C), 1100. ¹H NMR (δ, ppm, J, Hz, CDCl₃): 7.46 [br, 1H, H₄], 7.29 [m, 1H, H⁶], 6.60 [t, 1H, JHH 5.4, H⁵], 7.38 [m, 12H, o-H], 7.27 [m, 6H, p-H], 7.19 [m, 12H, m-H]. ¹³C NMR: 180.5 [s, C²], 109.9 [s, C⁵], 134.0(s, i-C), 133.8 [d, o-C], 128.2 [d, m-C], 129.3 [s, p-C]. ³¹P NMR: -2.9. ∆δ (δcomplex – δligand) = 1.8.

Complexes 25 and 26 are formed by the same method as the complex 24.
[CuBr(η^1-S-pymSH)(PPh_3)_2] 25. Yield 70%. M.pt. 190-195°C. The crystals were grown by the recrystallisation in dry CH_2Cl_2 / MeOH. Anal. Calcd. C_(40)H_(34)BrCuN_2P_2S: (780.14); C, 61.5; H, 4.35; N, 3.60; Found. C, 61.0; H, 4.34; N, 3.80. Main IR peaks (cm⁻¹); δ (N–H), 3480; ν(C–H), 3160; ν(C – C) + ν(C – N), 1570, 1470; ν (C = S), 820w; ν(P–C), 1100. ^1H NMR (δ, ppm, J, Hz, CDCl_3): 7.49 [br, 1H, H^4], 7.31 [d, 1H, J_HH 0.9, H^6], 6.57 [t, 1H, J_HH 5.4, H^5], 7.44 [m, 12H, o-H], 7.28 [s, 6H, p-H], 7.18 [m, 12H, m-H]. ^13C NMR: 179.9 [s, C^2], 109.8 [s, C^5], 134.1(s, i-C], 133.9 [t, o-C], 128.2 [d, m-C], 129.3 [s, p-C]. ^31P NMR: -3.6. Δδ (δ_{complex} – δ_{ligand}) = 1.1.

[Cu_2(μ-I)_2(PPh_3)_2(μ-N,S-pymSH)].CH_3CN 26. Red crystals were formed from the filtrate (15 mL) on slow evaporation after 24 h. Yield 60%. M.pt. 175-180°C. The crystals were grown by the recrystallisation in dry CH_2Cl_2 / MeOH. Anal. Calcd. C_(42)H_(37)Cu_2I_2N_2P_2S: (1058.63); C, 46.6; H, 3.35; N, 4.95; Found. C, 46.8; H, 3.42; N, 4.92. Main IR peaks (cm⁻¹); δ (N–H), 3460; ν(C–H), 3160; ν(C – C) + ν(C – N), 1580, 1450; ν (C = S), 790w; ν(P – C), 1120. ^1H NMR (δ, ppm, J, Hz, CDCl_3): 7.51 [t, br, 1H, H^4], 7.31 [t, 1H, J_HH 1.8, H^6], 6.93 [t, 1H, J_HH 5.3, H^5], 7.44[m, 6H, o-H], 7.45[m, 6H, o-H], 7.41 [m, 3H, p-H], 7.38 [m, 3H, p-H], 7.35[m, 6H, m-H], 7.33[m, 6H, m-H]. ^31P NMR: 29.1, -4.9. Δδ (δ_{complex} – δ_{ligand}) = 33.8, -0.2.

[Cu(η^2-N, S-puS)(PPh_3)_2]. CH_3OH 27. To a solution of CuCl (0.050g,0.50 mmol) in dry acetonitrile (5 mL), was added a suspension of purine-6-thione (puSH) (0.085 g, 0.50 mmol) in dry acetonitrile (15 mL). The contents were stirred when orange precipitates were formed, which were suspended in MeOH (10 mL) and to it was added a solution of triphenylphosphine (0.132 g, 1.01 mmol) in MeOH (15 mL). The mixture was stirred for 5–6 h and the yellow crystals were formed on cooling at room temperature after 2 days. The crystals are solvent stored, become opaque when come in contact with air. Yield 65%, M.pt. 150-160°C. Anal. Calcd. C_(42)H_(38)N_4OP_2SCu: (771.5); C, 65.3; H, 4.92; N, 7.25; Found. C, 64.4; H, 4.78; N, 7.22. Main IR peaks (cm⁻¹); ν(C–H), 3049; ν(C – C) + ν(C – N), 1596, 1481; ν (C = S), 858w,790s; ν(P–C), 1093. ^1H NMR (δ, ppm, J, Hz, CDCl_3): 7.49 [br, 1H, H^4], 7.31 [d, 1H, J_HH 0.9, H^6], 6.57 [t, 1H, J_HH 5.4, H^5], 7.44 [m, 12H, o-H], 7.28 [s, 6H, p-H], 7.18 [m, 12H, m-H]. ^13C NMR: 179.9 [s, C^2], 109.8 [s, C^5], 134.1(s, i-C], 133.9 [t, o-C], 128.2 [d, m-C], 129.3 [s, p-C]. ^31P NMR: -3.6. Δδ (δ_{complex} – δ_{ligand}) = 1.1.
CDCl₃ + dmsod₆): 8.02 [s, 1H, H₈], 7.22 [s, 1H, H²], 7.34 [m, 6H, o-H], 7.53 [m, 6H, m-H], 7.68 [m, 3H, p-H]. ³¹P NMR: 26.98. ∆δ (δcomplex − δligand) = 31.68 ppm.

The complexes 28 – 29 are prepared as the same method as 27.

[Cu(η¹-S-puSH)(PPh₃)₂].CH₃OH 28. A light yellow colour crystals were formed on cooling at room temperature in 4-5 days. The crystals become opaque when come in contact with air. Yield 65%, M.pt. 180-190°C. Anal. Calcd. C₄₂H₃₈N₄P₂SCu: (771.3); C, 65.3; H, 4.92; N, 7.25; Found. C, 65.0; H, 4.82; N, 7.12. Main IR peaks (cm⁻¹): ν(C–H), 3049; ν(C – C) + ν(C – N), 1550, 1481; ν (C = S), 848; ν(P–С), 1093. ¹H NMR (δ, ppm, J, Hz, CDCl₃ + dmsod₆): 8.14 [s, 1H, H₈], 7.23 [s, 1H, H²], 7.33 [m, 6H, o-H], 7.55 [m, 6H, m-H], 7.68 [m, 3H, p-H].

[CuI(η¹-S-puSH)(PPh₃)₂] 29. A light yellow colour crystals were formed on cooling at room temperature in 4-5 days. Yield 65%, M.pt. 240-250°C. Anal. Calcd. C₄₁H₃₄N₄P₂SCuI: (867); C, 56.74; H, 3.92; N, 6.45; Found. C 55.5; H, 4.08; N, 6.80. Main IR peaks (cm⁻¹): ν(C–H), 3049; ν(C – C) + ν(C – N), 1537, 1477; ν (C = S), 871w, 836s; ν(P–С), 1093. ¹H NMR (δ, ppm, J, Hz, CDCl₃ + dmsod₆): 7.25 [s, 1H, H₈], 7.14, 7.11 [s, 1H, H²], 6.36 [m, 6H, o-H], 6.672 [m, 6H, m-H], 6.82 [m, 3H, p-H]. ³¹P NMR: 31.804, 0.69. ∆δ (δcomplex − δligand) = 36.504, 5.39s ppm.

[Cu₆(μ₂-I)(μ₃-I)(μ₁-I)(m-toly13P)₄(CH₃CN)₂] 30. To the solution of tri-m-tolylphosphine (0.040 g, 0.13 mmol) in dry acetonitrile (20 mL) was added to the solution of copper(I) iodide (0.025 g, 0.13 mmol) dry acetonitrile (10 ml) and the mixture was stirred for 6 h and filtered. The colourless crystals were obtained by slow evaporation at room temperature in a few days. M.pt. 180 – 190°C. Anal. Calcd. C₈₈H₆₄Cu₆I₄N₂P₄: (2436.24); C 43.40; H, 3.48; N, 1.15; Found. C 43.16; H, 3.68; N, 0.90. Main IR peaks (cm⁻¹); ν(C–H), 3029. ³¹P NMR: 90.9. ∆δ (δcomplex − δligand) = 95.6.