Chapter 4
SYNTHESIS OF COMPLEXES

This chapter describes complexes of coinage metal ions (Cu\textsuperscript{I}, Cu\textsuperscript{II}, Ag\textsuperscript{I}) with a series of heterocyclic thioamides (Charts 1a and 1b). Complexes of different nuclearities, namely, mononuclear (Cu\textsuperscript{I}, Cu\textsuperscript{II}, Ag\textsuperscript{I}), dinuclear (Cu\textsuperscript{II}, Ag\textsuperscript{I}), trinuclear (Cu\textsuperscript{I}, Cu\textsuperscript{I, II} mixed-valent), tetranuclear (Cu\textsuperscript{II}) and polynuclear (Cu\textsuperscript{I, II}, Cu\textsuperscript{I, II} mixed-valent) have been obtained. Triphenylphosphine (PPh\textsubscript{3}) has been used as coligand in some cases. These complexes have been characterized by analytical data, spectroscopic techniques (IR, UV-Vis, fluorescence, NMR, Mass), and single crystal X-ray crystallography.

4.1 General Procedures

The complexes of coinage metals (Cu\textsuperscript{I}, Cu\textsuperscript{II}, Ag\textsuperscript{I}) with heterocyclic thioamides (Charts 1a and 1b) in the presence or absence of PPh\textsubscript{3} have been synthesized. Three main procedures were
adopted for preparing metal complexes (*details of complexes with numbering follows general procedure*).

**Method 1**

In this method, solution of copper(I) salts was slowly mixed with solution of thio-ligand in CH$_3$CN / DMSO / CH$_3$CN–CHCl$_3$ mixture at room temperature. The complexes 1–5, 10–30 were prepared by this method.

**Method 2**

In this method, metal salt dissolved or suspended in acetonitrile / acetonitrile-methanol mixture was reacted with thio-ligand under stirring followed by addition of PPh$_3$. The complexes 6–9, 31–41, and 58–68 were prepared by this method.

**Method 3**

In this method, metal salt was first reacted with coligand PPh$_3$ in acetonitrile under stirring. The solid obtained was reacted with thio-ligand in chloroform. The complexes 42–57 were prepared by this method.

### 4.2 Synthesis of complexes

\[\text{[Cu}_8(\mu_3-S-imdzSH)_4(\mu-S-imdzSH)_4(\eta^1-\text{Cl})_6]_n \] (1)

To a solution of copper(I) chloride (0.025 g, 0.24 mmol) in acetonitrile was added a solution of imidazolidine-2-thione (0.025 g, 0.24 mmol) in acetonitrile, and the solution was kept undisturbed. The slow evaporation of solution at room temperature formed pale olive green prismatic crystals of complex 1 (Yield 67%, M.p. 235-237°C). Anal. Calcd for C$_{12}$H$_{24}$Cl$_4$Cu$_4$N$_8$S$_4$ (%): C, 17.90; H, 3.00; N, 13.93; Found: C, 18.08; H, 3.43; N, 13.97. Main IR peaks (KBr, cm$^{-1}$): ν(N-H) 3290(br), 3137(br); ν(C-H) 3059–
2976(w); ν(C-N) + δ(C-H) 1529(s), 1475(s); ν(C=S) 1192(m), 989(m), 904(m). Electronic absorption spectra [dmso, λ_{max} (ε/L mol^{-1} cm^{-1})]: 10^{-4}M solution: 296 (4.000×10^{5}). Fluorescence spectra: 10^{-5}M, λ_{ex} = 290 nm, λ_{em} = 324 nm.

[Cu_{6}(μ_{3}-imidzSH)_{2}(μ-S-imdzSH)_{4}(μ-Cl)_{4}(η^{1}-Cl)_{2}]_n (2)

To a solution of copper(I) chloride (0.025 g, 0.24 mmol) in acetonitrile was added a solution of imidazolidine-2-thione (0.050 g, 0.48 mmol) in acetonitrile, and the solution was kept undisturbed. The reduction of volume to nearly half of its original volume by evaporation of the solution at room temperature formed pale olive green prismatic crystals of polymer [Cu_{8}(μ_{3}-imidzSH)_{4}(μ-imdzSH)_{4}(η^{1}-Cl)_{8}]_n, 1 (Yield 33%) and further evaporation of filtrate gave colorless prismatic crystals of polymer 2 (Yield 35%, M.p. 175-178°C). Anal. Calcd for C_{9}H_{18}Cu_{3}Cl_{3}N_{6}S_{3} (%): C, 17.90; H, 3.00; N, 13.93; Found: C, 18.12; H, 3.23; N, 14.06. Main IR peaks (KBr, cm^{-1}): ν(N-H) 3250(br), 3150(m); ν(C-H) 3059-2875(w), ν(C-N) + δ(C-H) 1490(s), 1450(s); ν(C=S) 1190(m), 984(m), 901(m).

[Cu_{6}(μ_{3}-imidzSH)_{2}(μ-S-imdzSH)_{4}(μ-Br)_{4}(η^{1}-Br)_{2}]_n (3)

To a solution of copper(I) bromide (0.025 g, 0.17 mmol) in acetonitrile was added a solution of imidazolidine-2-thione (0.018 g, 0.17 mmol) in acetonitrile, and the solution was kept undisturbed. The slow evaporation of solution at room temperature yielded colorless prismatic crystals of complex 3 (Yield 69%, M.p. 180-185°C). Anal. Calcd for C_{9}H_{18}Br_{5}Cu_{3}N_{6}S_{3} (%): C, 14.65; H, 2.44; N, 11.40; Found: C, 14.73; H, 2.40; N, 11.52. Main IR peaks (KBr, cm^{-1}): ν(N-H) 3288(m),
3245(m); ν(C-H) 2980–2886(w); ν(C-N) + δ(C-H) 1530(s), 1474(sh); ν(C=S) 1202(s), 987(m), 913(m).

\[\text{[Cu}_6(\mu_3-S\text{-imidzSH})_2(\mu-S\text{-imidzSH})_4(\mu-I)_4(\eta^1-I)_2]_n\ (4)\]

It was prepared by a similar method as complex 3. (Yield 68%, M.p. 192-195°C). Anal. Calcd for C_{9}H_{18}Cu_{3}I_{3}N_{6}S_{3} (%): C, 12.30; H, 2.05; N, 9.57; Found: C, 12.42; H, 2.23; N, 9.65. Main IR peaks (KBr, cm\(^{-1}\)):

ν(N-H) 3323(sh), 3259(m); ν(C/H) 2960-2881(w); ν(C/N) + δ(C/H) 1514(s), 1471(sh); ν(C=S) 1192(s), 983(m), 910(m).

\[\text{[Cu}\{\eta^2-N,N\text{-imidz}S\}\{\mu-O,OSO}_2\} (\eta^1-OH_2)]_n\ (5)\]

To a solution of copper(I) chloride (0.025 g, 0.24 mmol) in dimethyl sulfoxide was added a solution of imidazolidine-2-thione (0.025 g, 0.24 mmol) in dimethyl sulfoxide and the solution was kept undisturbed. After 3-4 weeks, prismatic blue crystals of polymer 5 were obtained (Yield 70%, M.p. 215-217°C). Anal. Calcd for C_{6}H_{12}N_{4}O_{5}S_{2}Cu (%): C, 20.70; H, 3.45; N, 16.10; S, 18.40; Found: C, 20.56; H, 3.40; N, 16.35; S 18.74. Electronic absorption spectra [dms, \(\lambda_{\text{max}}, \text{nm}; \varepsilon /\text{L mol}^{-1} \text{ cm}^{-1}\)]: 10\(^{-4}\)M solution: 266 (1.375×10\(^3\)); 10\(^{-3}\)M solution: very intense absorption in 266 nm region; 676 nm (132). Main IR peaks (KBr, cm\(^{-1}\)):

ν(NH + OH) 3300–3200(br); ν(C-H) 3020–2900(w); ν(SO\(_4\)) 1100w, 1020m (\(v_3\)); 995m (\(v_1\)) and 608s (\(v_4\)); ν(C-S) 1170(w), 950(m). Magnetic moment (BM): 1.975 per copper.

The complex 5 can also be synthesized in dimethylformamide. The similar reaction of copper(I) bromide with imdzSH also formed complex 5.
[CuCl(η¹-S-imzSH)(PPh₃)₂Cl]·[CuCl(PPh₃)₂]·CH₃OH (6)

To a solution of copper(I) chloride (0.025 g, 0.25 mmol) in acetonitrile was added imidazoline-2-thione (0.025 g, 0.25 mmol), followed by stirring for 1h at room temperature and to the white precipitates formed was added Ph₃P (0.132 g, 0.50 mmol) and stirred until a clear solution was obtained. The crystalline fibers formed were redissolved in MeOH–CHCl₃ mixture. The slow evaporation of solution at room temperature formed colorless crystals of complex 6 (Yield 56%, M.p. 135-138°C). Anal. Calcd for C₇₆H₆₈Cl₂Cu₂N₂OP₄S (%): C, 66.18; H, 4.93; N, 2.03; Found: C, 66.36; H, 4.90; N, 1.63. Main IR peaks (KBr, cm⁻¹): ν(OH + NH) 3363(br), 3138(w); ν(C/H) 3072–2862(w); ν(C-N) + δ(C-H) 1581(s), 1481(s); ν(C=S) 1217(s), 1066(m), 912(s); ν(P-C Ph) 1093(s).

¹H NMR data (CDCl₃, δ ppm): 7.23 t (2H, C₄,₅H), 7.37 m (o/H), 7.33 m (p/H), 7.25–7.27 m (m/H) [Species 6a], 7.67 m (o/H), 7.55 m (p/H), 7.46 m (m/H) [Species 6b].

³¹P NMR (CDCl₃, δ ppm): -3.42 (Species 6a), 30.74 ppm (Species 6b), ∆δ(δcomplex – δPPh₃) = 1.28 (Species 6a), 35.44 ppm (Species 6b). The complex is soluble in chloroform, dichloromethane and acetonitrile.

[CuBr(η¹-S-imzSH)(PPh₃)₂]·H₂O (7)

To a solution of copper(I) bromide (0.025 g, 0.17 mmol) in acetonitrile was added imidazoline-2-thione (0.017 g, 0.17 mmol), followed by stirring for 1h at room temperature and to the white precipitates formed was added Ph₃P (0.091 g, 0.34 mmol) and stirred until a clear solution was obtained. Chloroform was added to the reaction medium. The slow evaporation of solution at room temperature formed pale yellow crystals of complex 7 (Yield 73%, M.p. 155-157°C). Anal. Calcd for C₃₉H₃₆BrCuN₂OP₂S (%): C, 59.58; H, 4.58; N, 3.56; Found: C, 60.31; H, 4.41; N, 3.12. Main IR peaks (KBr, cm⁻¹): ν(OH + NH) 3396(b), 3138(br); ν(C-H) 3070–2904(w); ν(C-N) + δ(C-H) 1581(s), 1477(s); ν(C=S) 1216(s), 1065(m), 912(s); ν(P-C Ph) 1093(s).

¹H NMR data (CDCl₃, δ ppm): 10.9 bs (1H, NH), 6.74 t (2H, C₄,₅H), 7.41 m (o/H), 7.33 m (p/H), 7.27 m (m/H) [CuBr(PPh₃)₂].

³¹P NMR (CDCl₃, δ ppm): -4.3 ppm, ∆δ(δcomplex – δPPh₃) = 0.40 ppm (7). The complex is soluble in chloroform, dichloromethane and acetonitrile.
[CuI(η¹-S-imzSH)(PPh₃)₂] (8)

It was prepared by a similar method as complex 7. Color: yellow (Yield 71%, M.p. 205-207°C). Anal. Calcd for C₃₉H₃₄CuIN₂P₂S (%): C, 57.46; H, 4.17; N, 3.44; Found: C, 57.24; H, 4.15; N, 3.14. Main IR peaks (KBr, cm⁻¹): ν(N-H) 3145(w); ν(C/H) 3070–2958(w); ν(C-N) + δ(C-H) 1577(s), 1473(s); ν(C=S) 1205(s), 1066(m), 910(s); ν(P-CPh) 1092(s). ¹H NMR data (CDCl₃, δ ppm): 6.79 t (2H, C₄,5H), 7.47 m (o/H), 7.39 m (p/H), 7.27 m (m/H) (8), 7.68 m (o-H), 7.64 m (p-H), 7.54 m (m-H) [CuI(PPh₃)₂]. ³¹P NMR (CDCl₃, δ ppm): -5.1 ppm, Δδ(δcomplex – δPPh₃), -0.4 ppm (8). The complex is soluble in chloroform, dichloromethane and acetonitrile.

[CuBr(η¹-S-bzimzSH)(PPh₃)₂]·CH₃COCH₃ (9)

To a solution of copper(I) bromide (0.025 g, 0.17 mmol) in acetonitrile was added a solution of benzimidazoline-2-thione (0.026 g, 0.17 mmol) in acetone, followed by stirring for 2h at room temperature and to the white precipitates formed was added PPh₃ (0.091 g, 0.34 mmol) and the contents stirred until a clear solution was obtained. The slow evaporation of solution at room temperature formed colorless crystals of 9 (Yield 72%, M.p. 228-231°C). Anal. Calcd for C₄₆H₄₂BrCuN₂OP₂S (%): C, 63.05; H, 4.79; N, 3.20; Found: C, 62.97; H, 4.51; N, 2.90. Main IR peaks (KBr, cm⁻¹): ν(N-H) 3110(m); ν(C/H) 3041–2854(w); ν(C-N) + δ(C-H) 1604(w), 1483(w); ν(C=S) 1155(s); ν(P-CPh) 1091(m). ¹H NMR data (CDCl₃, δ ppm): 11.2 bs (1H, NH) 7.47 m (o/H), 7.35 m (p/H), 7.22 – 7.30 m (m-H, C₄/7H, bzimzSH) (9), 7.64 – 7.71 m (o-H, p-H), 7.55 m (m-H) [CuBr(PPh₃)₂]. ³¹P NMR (CDCl₃, δ ppm): -3.6 ppm (9), 30.84 ppm [CuI(PPh₃)₂]; Δδ(δcomplex – δPPh₃), 1.10 (9) ppm, 35.54 ppm [CuI(PPh₃)₂]. The complex is soluble in chloroform, acetonitrile and dichloromethane.
[Cu$_2$($\eta^2$-N,N-(mimz)$_2$S)$_2$(µ-Cl)$_2$Cl] (10) and CuSO$_4$·5H$_2$O (11)

To a solution of copper(I) chloride (0.025 g, 0.25 mmol) in acetonitrile was added a solution of 1-methylimidazole-2-thione (0.029 g, 0.25 mmol) in acetonitrile and the solution was kept undisturbed. After 2-3 days color of solution changed to green and prismatic green crystals of complex 10 were formed along with blue crystals of CuSO$_4$·5H$_2$O 11. (Yield of complex 10, 55%, M.p. 233-237°C). Anal. Calcd for C$_{16}$H$_{20}$N$_8$S$_2$Cu$_2$Cl$_4$ (%): C, 29.2; H, 3.0; N, 17.0; S, 9.73; Found: C, 28.96; H, 3.26; N, 16.9; S, 9.55. Electronic absorption spectra [dmso, $\lambda_{\text{max}}$, nm; $\varepsilon$ /L mol$^{-1}$ cm$^{-1}$]: 10$^{-4}$M solution: 261 (2.889×10$^3$); 10$^{-3}$M solution: very intense absorption in 261 nm region; 739 nm (117). Main IR peaks (KBr, cm$^{-1}$): $\nu$(C-H) 3026–2948(w); $\nu$(C/N) + $\delta$(C/H) 1525(s), 1481(s); $\nu$(C=S) 870(s); $\delta$(N/CH$_3$) 763(s). Magnetic moment (BM): 1.966 per copper. Analytical data for the formation of CuSO$_4$·5H$_2$O (%): H, 4.0; S, 12.8; Found: H, 4.1; S, 13.17.

Complex 10 can also be synthesized in dimethyl sulfoxide or CH$_3$CN–CHCl$_3$ mixture.

[Cu$_3$(µ-S-mimzSH)$_2$($\eta^1$-Br)$_3$]-CH$_3$CN (12)

To a solution of copper(I) bromide (0.025 g, 0.17 mmol) in acetonitrile was added a solution of 1-methylimidazole-2-thione (0.020 g, 0.17 mmol) in acetonitrile. The solution was kept undisturbed. Slow evaporation of solution at room temperature formed colorless prismatic crystals of complex 12 (Yield 65%, M.p. 178-180°C). Anal. Calcd for C$_{28}$H$_{42}$Br$_6$Cu$_6$N$_{14}$S$_6$ (%): C, 20.65; H, 2.58; N, 12.05; Found: C, 20.69; H, 2.77; N, 11.80. Main IR peaks (KBr, cm$^{-1}$): $\nu$(N-H) 3213(w), 3124(m); $\nu$(C-H) 3045–2948(w); $\nu$(C-N) + $\delta$(C-H) 1529(s), 1481(s); $\nu$(C=S) 923(s); $\delta$(N-CH$_3$) 777(s). Electronic absorption spectra [dmso, $\lambda_{\text{max}}$...
(ε/L mol⁻¹ cm⁻¹)): 10⁻⁴ M solution: 267 (1.106×10³). Fluorescence spectra: 10⁻⁵ M, λₑₓ = 258 nm, λₑₘ = 319 nm. The complex is very poorly soluble in acetonitrile and chloroform.

[Cu₄{η¹-N-(mimzBr)}₄(μ₄-O)(μ-Br)₆] (13)

To a solution of copper(I) bromide (0.025 g, 0.17 mmol) in acetonitrile was added a solution of 1-methyl-imidazoline-2-thione (0.020 g, 0.17 mmol) in chloroform. After 2-3 days color of solution changed from colorless to brownish green and black prismatic crystals of complex 13 were formed along with CuSO₄·5H₂O (Yield of complex 13, 54%, M.p. 182-185°C). Anal. Calcd for C₁₆H₂₀Br₁₀Cu₄N₈O (%): C, 13.78; H, 1.44; N, 8.04; Found: C, 14.05; H, 1.65; N, 8.22. Electronic absorption spectra [dmso, λₑₓ, nm; ε/L mol⁻¹ cm⁻¹]: 10⁻⁴M solution: 259 (1.269×10⁴). Fluorescence spectra: 10⁻⁵ M, λₑₓ = 270 nm, λₑₘ = 329 nm. Main IR peaks (KBr, cm⁻¹): ν(C-H) 3121–2960(m); ν(C/N) + δ(C/H) 1535(sh), 1475(s); δ(N/CH₃) 754(s). Magnetic moment (BM): 1.972 per copper. Mass spectra (m/z): 161.4 (expected, 160, N₂C₄H₅Br⁷⁹), 163.4 (162, N₂C₄H₅Br⁸¹); 223.3 (223, Cu⁶³Br⁷⁹Br⁸¹, 225.3 (225, Cu⁶³Br₂⁸¹), 227.3 (227, Cu⁶⁵Br₂⁸¹); 241.3 (241, Cu⁶⁵ON₂C₄H₅Br⁷⁹), 243.3 (243, Cu⁶⁵ON₂C₄H₅Br⁸¹); 268.3 (268, Cu⁶³⁰); 383.2 (383, Cu⁶³Br₂⁷⁹N₂C₄H₅Br⁸¹), 385.2 (385, Cu⁶³Br₂⁸¹N₂C₄H₅Br⁷⁹), 387.2 (387, Cu⁶³Br₂⁸¹N₂C₄H₅Br⁸¹), 389.2 (389, Cu⁶³Br₂⁸¹N₂C₄H₅Br⁸¹).

[Cu{η²-N,N-(mimz)₂S}(η²-O,OSO₂)(η¹-OH₂)] (14)

To a solution of copper(I) bromide (0.025 g, 0.17 mmol) in dimethyl sulfoxide was added a solution of 1-methyl-imidazoline-2-thione (0.020 g, 0.17 mmol) in dimethyl sulfoxide and the solution was kept undisturbed. After 3-4 weeks, prismatic blue crystals of complex 14 were obtained. (Yield 71%, M.p. 195-197°C). Anal. Calcd for C₈H₁₂N₄O₅S₂Cu (%): C, 25.8; H, 3.2; N, 15.07; S, 17.2; Found: C, 25.57; H, 3.1; N, 15.2; S 17.42. Electronic
absorption spectra [dmso, $\lambda_{\text{max}}$, nm; $\varepsilon$ /L mol$^{-1}$ cm$^{-1}$]: 10$^{-4}$M solution: 265 (1.372×10$^3$); 10$^{-3}$M solution: very intense absorption in 265 nm region; 675 nm (130). Main IR peaks (KBr, cm$^{-1}$): $\nu$(O-H) 3300(br); $\nu$(C-H) 3015–2910(w); $\nu$(SO$_4$) 1105w, 1022m ($\nu_3$); 990m ($\nu_1$) and 610s ($\nu_4$); $\nu$(C-S) 865(m); $\delta$(N-CH$_3$) 763(s). Magnetic moment (BM): 1.972 per copper.

Complex 14 was also prepared by the reaction of CuSCN with mimzSH in acetonitrile-dimethyl sulfoxide mixture.

$$[\text{Cu}_2(\mu-S\text{-mimzSH})_2(\mu-I)_2]_n\ (15)$$

It was prepared by a method similar to that for complex 12. Color: colorless (Yield 70%, M.p. 175-178°C). Anal. Calcd for C$_{4}$H$_{6}$CuIN$_{2}$S (%): C, 15.80; H, 1.97; N, 9.19; Found: C, 16.14; H, 1.98; N, 8.93. Main IR peaks (KBr, cm$^{-1}$): $\nu$(N-H) 3212(br), 3110(w); $\nu$(C-H) 3039–2937(w); $\nu$(C-N) + $\delta$(C/H) 1571(s), 1473(s); $\nu$(C=S) 920(s); $\delta$(N–CH$_3$) 736(s). Electronic absorption spectra [dmso, $\lambda_{\text{max}}$ ($\varepsilon$ /L mol$^{-1}$ cm$^{-1}$)]: 10$^{-3}$ M solution: 806 (56), 10$^{-4}$ M solution: 268 (1.276×10$^3$). Fluorescence spectra: 10$^{-6}$ M, $\lambda_{\text{ex}}$ = 272 nm, $\lambda_{\text{em}}$ = 322 nm. It is very poorly soluble in acetonitrile and chloroform.

$$[\text{Cu}\{\eta^2-N,N\text{-}(mimz)S\}_2(\eta^1-OH)_2](\text{BF}_4)_2\cdot2\text{H}_2\text{O} \ (16)$$

To a solution of 1-methyl-imidazoline-2-thione (0.036 g, 0.32 mmol) in acetonitrile was added a solution of [Cu(CH$_3$CN)$_4$](BF$_4$) (0.050 g, 0.16 mmol) in acetonitrile. The reaction mixture was kept undisturbed. Dark purple needles of complex 16 were formed on slow evaporation of solution at room temperature along with CuSO$_4$·5H$_2$O (Yield of complex 16, 57%, M.p. 220-223°C). Anal. Calcd for C$_{16}$H$_{28}$B$_2$CuF$_8$N$_8$O$_4$S$_2$ (%): C, 27.52; H, 4.01; N, 16.05; Found: C, 27.64; H, 4.12; N, 16.13. Main IR peaks (KBr, cm$^{-1}$): $\nu$(O–H) 3444(br); $\nu$(C–H) 3101–2947(m); $\nu$(C–N) + $\delta$(C-H) 1547(sh), 1458(s); $\nu$(C-S) 883(m); $\delta$(N–CH$_3$) 782(s).
[Cu{η²-N,N-(mimz)2S}2(η¹-OH)2](NO3)2 (17)

To a solution of copper(II) nitrate (0.025 g, 0.10 mmol) in methanol was added a solution of 1-methyl-imidazoline-2-thione (0.024 g, 0.20 mmol) in acetonitrile. The reaction mixture was kept undisturbed. Blue prismatic crystals of complex 17 were formed on slow evaporation of solution at room temperature along with CuSO₄·5H₂O (Yield 57%, M.p. 173-175°C). Anal. Calcd for C₁₆H₂₄CuN₁₀O₈S₂ (%): C, 31.37; H, 3.92; N, 22.87; Found: C, 31.51; H, 4.03; N, 23.01. Main IR peaks (KBr, cm⁻¹): ν(O−H) 3432(br); ν(C−H) 3107–2935(m); ν(C−N) + δ(C/H) 1570(m), 1483(s); ν(C=S) 1107(m), 1483(s); ν(C=S) 1107(s); δ(N–CH₃) 770(s).

[CuCl(η²-N,S-tztzdS)] (18)

To a solution of copper(I) chloride (0.025 g, 0.25 mmol) in acetonitrile was added a solution of thiazolidine-2-thione (0.030 g, 0.25 mmol) in acetonitrile. After 2-3 days color of solution turned greenish brown and red violet plates of complex 18 were formed along with CuSO₄·5H₂O (Yield of 18, 64%, M.p. 172-175°C). Anal. Calcd for C₆H₈ClCuN₂S₃ (%): C, 23.76; H, 2.64; N, 9.24; Found: C, 23.44; H, 2.55; N, 9.47. Main IR peaks (KBr, cm⁻¹): ν(C−H) 2922–2855(m); ν(C−N) + δ(C/H) 1587(s), 1450(sh); ν(C=S) 942(s).

[CuBr(η²-N,S-tztzdS)] (19)

It was prepared by a similar method as complex 18. Color: Violet (Yield 61%, M.p. 187-190°C). Anal. Calcd for C₆H₈BrCuN₂S₃ (%): C, 20.72; H, 2.30; N, 8.06; Found: C, 20.55; H, 2.42; N, 8.19. Main IR peaks (KBr, cm⁻¹): ν(C−H) 2995–2817(m); ν(C−N) + δ(C-H) 1584(s), 1450(sh); ν(C=S) 940(s).
[Cu$_2$(µ-I)$_2$(η$^1$-S-tzdSH)$_4$] (20)

It was prepared by a similar method as complex 18. Color: colorless (Yield 68%, M.p. 120-125°C). Anal. Calcd for C$_6$H$_{10}$CuIN$_2$S$_4$ (%): C, 16.80; H, 2.33; N, 6.53; Found: C, 16.94; H, 2.41; N, 6.62. Main IR peaks (KBr, cm$^{-1}$): ν(N–H) 3206(br); ν(C–H) 3018–2943(w); ν(C–N) + δ(C–H) 1522(s), 1456(s); ν(C=S) 994(s). $^1$H NMR data (dms-o-d$_6$, δ ppm): 10.0 bs (1H, NH), 3.54 septet (2H, C$_4$H), 4.02 t (2H, C$_5$H). $^{13}$C NMR data (dms-o-d$_6$, δ ppm): 32.3 (C$_4$), 50.9 (C$_5$), 199.8 (C$_2$).

[Cu(η$^2$-N,S-tztzdS)$_2$](BF$_4$) (21)

To a solution of thiazolidine-2-thione (0.038 g, 0.32 mmol) in acetonitrile was added [Cu(CH$_3$CN)$_4$](BF$_4$) (0.050 g, 0.16 mmol) in acetonitrile. The reaction mixture was kept undisturbed. Dark purple needles of complex 21 were obtained on slow evaporation of solution at room temperature along with CuSO$_4$·5H$_2$O (Yield of 21, 59%, M.p. 210-213°C). Anal. Calcd for C$_{12}$H$_{16}$BCuF$_4$N$_4$S$_6$ (%): C, 25.76; H, 2.86; N, 10.01; Found: C, 25.84; H, 3.00; N, 10.16. Main IR peaks (KBr, cm$^{-1}$): ν(C–H) 3077–2920(w); ν(C–N) + δ(C–H) 1532(s), 1497(sh); ν(C=S) 930(m).

{Cu$_4$(µ$_3$-I)$_2$(µ-I)$_2$(µ-S-imdzSH-Me)$_2$(η$^1$-S-imdzSH-Me)$_2$}$_n$ (22), [Cu$_2$Cu$_{11}$(η$^2$-N,S-imdzdzS-Me)(µ-S-imdzdzS-Me)(µ-I)$_2$(η$^1$-I)$_2$] (23)
To a solution of copper(I) iodide (0.025 g, 0.13 mmol) in acetonitrile was added a solution of 1-methyl-imidazolidine-2-thione (0.015 g, 0.13 mmol) in acetonitrile. After 2-3 days, colorless prismatic crystals of complex 22 were obtained (Yield 32%, M.p. 157-160°C). Anal. Calcd for C₄H₈CuIN₂S (%): C, 15.65; H, 2.61; N, 9.13; Found: C, 15.76; H, 2.70; N, 9.17. Main IR peaks (KBr, cm⁻¹): ν(N-H) 3272(m); ν(C-H) 2930–2878(w); ν(C-N) + δ(C-H) 1536(s), 1503(m); ν(C=S) 1190(m); δ(N-CH₃) 958(m). The color of filtrate changed to brownish green in next 2 days and black prismatic crystals of complex 23 were obtained along with CuSO₄·5H₂O (Yield of 23, 18%, M.p. 215-217°C). Anal. Calcd for C₁₆H₂₈Cu₃I₄N₈S₂ (%) C, 17.53; H, 2.56; N, 10.23; Found: C, 17.45; H, 2.44; N, 10.32. Main IR peaks (KBr, cm⁻¹): ν(C-H) 2919(w), 2871(w); ν(C-N) + δ(C-H) 1587–1528(s); ν(C=S) 1114(s); δ(N-CH₃) 971(m). Both compounds are very poorly soluble in acetonitrile and chloroform.

[CuI(eimdzSH)]ₙ (24), [Cu₃I₆(imdzdzS-Et)]·2CH₃CN (25)

To a solution of copper(I) iodide (0.025 g, 0.13 mmol) in acetonitrile was added a solution of 1-ethyl-imidazolidine-2-thione (0.017 g, 0.13 mmol) in acetonitrile. After 2 days colorless crystals of complex 24 were obtained (Yield 38%, M.p. 140-142°C). Anal. Calcd. for
C₅H₁₀CuIN₂S (%): C, 18.72; H, 3.12; N, 8.74; Found: C, 18.86; H, 3.04; N, 8.82. Main IR peaks (KBr, cm⁻¹): ν(N-H) 3285(s); ν(C-H) 2964(w), 2924(w); ν(C-N) + δ(C-H) 1534(m), 1509(sh); ν(C=S) 1190(m). The color of filtrate changed to brownish green in 4-5 days and black prismatic crystals of composition \([\text{Cu}_3\text{I}_8(\text{imdzdzS-Et})_2]\cdot 2\text{CH}_3\text{CN} \ 25\) were obtained along with CuSO₄·5H₂O (Yield of complex 25, 17%, M.p. 158-160°C). Anal. Calcd for C₂₄H₄₂Cu₃I₈N₁₀S₂ (%): C, 16.58; H, 2.42; N, 8.06; Found: C, 16.75; H, 2.53; N, 8.90. Main IR peaks (KBr, cm⁻¹): ν(C-H) 2961–2872(m); ν(C/N) + δ(C/H) 1583(s), 1513(m); ν(C=S) 1160(m).

Both compounds are very poorly soluble in acetonitrile and chloroform.

\([\text{Cu}(\mu-\text{S-imdzS-Pr}^n)\text{I}_2(\eta^-\text{I}_3)]_n \ 26\), \([\text{Cu}_3(\mu-\text{S-imdzS-Pr}^n)\text{I}_2(\eta^-\text{I}_3)]_2 \ 27\)

To a solution of copper(I) iodide (0.025 g, 0.13 mmol) in acetonitrile was added a solution of 1-propyl-imidazolidine-2-thione (0.019 g, 0.13 mmol) in acetonitrile. After 2 days, colorless needles of complex 26 were obtained (Yield 31%, M.p. 143-145°C). Anal. Calcd for C₆H₁₂CuIN₂S (%): C, 21.51; H, 3.58; N, 8.37; Found: C, 21.37; H, 3.35; N, 8.51. Main IR peaks (KBr, cm⁻¹): ν(N-H) 3278(s); ν(C-H) 2954–2870(m); ν(C-N) + δ(C-H) 1534(s)–1467(sh); ν(C=S) 1190(m). The color of filtrate changed to greenish yellow in 2-3 days and brown needles of \([\text{Cu}_3(\mu-\text{S-imdzdzS-Pr}^n)\text{I}_2(\eta^-\text{I}_3)]_2 \ 27\) were obtained along with CuSO₄·5H₂O (Yield of 27, 19%, M.p. 161-163°C). Anal. Calcd for C₂₄H₃₆Cu₃I₈N₈S₂ (%): C, 16.88; H, 2.11; N, 6.56; Found: C, 16.74; H, 2.02; N, 6.68. Main IR peaks (KBr, cm⁻¹): ν(C-H) 2956–2868(m); ν(C-N) + δ(C-H) 1586(s), 1514(s); ν(C=S) 1134(m). Both compounds are very poorly soluble in acetonitrile and chloroform.
[Cu(µ-N,S-imdzdz-S-Bu³)₂] · 2I₃ (28)

To a solution of copper(I) iodide (0.025 g, 0.13 mmol) in acetonitrile was added a solution of 1-butyl-imidazolidine-2-thione (0.021 g, 0.13 mmol) in acetonitrile. After 2-3 days color of solution changed to greenish brown and black prismatic crystals of complex 28 were obtained along with CuSO₄ · 5H₂O (Yield of 28, 53%, M.p. 155-157°C). Anal. Calcd for C₂₈H₆₆Cu₆N₈S₂ (%): C, 24.17; H, 3.74; N, 8.06; Found: C, 24.12; H, 3.66; N, 8.15. Main IR peaks (KBr, cm⁻¹): ν(C-H) 2956–2870(w); ν(C/N) + δ(C/H) 1587(s), 1509(sh); ν(C=S) 1113(m). It is very poorly soluble in acetonitrile and chloroform.

[Cu¹⁺Cu²⁺Br₅(µ-μ-S-imdzdzS-Me)]₄n (29) To a solution of copper(I) bromide (0.025 g, 0.17 mmol) in acetonitrile was added a solution of 1-methyl-imidazolidine-2-thione (0.020 g, 0.17 mmol) in acetonitrile. The solution was kept undisturbed. After two days, light greenish crystalline compound of composition [CuBr(imdzSH-Me)] · 0.25CHCl₃ was obtained (Yield 38%, M.p. 170-172°C). Anal. Calcd for C₄₂₅H₈₂₅BrCuCl₀.₇₅N₂S (%): C, 17.63; H, 2.85; N, 9.68; Found: C, 17.40; H, 2.29; N, 9.69. Main IR peaks (KBr, cm⁻¹): ν(N-H) 3235(w), ν(C/H) 2980–2894(w); ν(C-N) + δ(C-H) 1552(s), 1468(sh); ν(C=S) 1195(s); δ(N/CH₃) 959(w). From the filtrate, black crystalline product of complex 29 was obtained along with CuSO₄ · 5H₂O (Yield of 29, 18%, M.p. 165-167°C). Anal. Calcd for C₁₆H₂₆Br₅Cu₄N₈S₂ (%): C, 18.28; H, 2.66; N, 10.66; Found: C, 18.12; H, 2.56; N, 10.50. Main IR peaks (KBr, cm⁻¹): ν(C-H) 2925–2880(w); ν(C-N) + δ(C-H) 1602(s), 1549(s); ν(C=S) 1136(m); δ(N/CH₃) 960(w).

[CuBr(η¹-S-imdzSH-Me)] (30)

To a solution of copper(I) bromide (0.025 g, 0.17 mmol) in acetonitrile was added a solution of 1-methyl-imidazolidine-2-thione (0.040 g, 0.34 mmol) in acetonitrile. The solution was kept undisturbed. Slow evaporation of solution at room temperature formed colorless crystals of complex 30 (Yield 66%, M.p. 194-196°C). Anal. Calcd for C₈H₁₆BrCuN₄S₂ (%): C, 25.57; H, 4.26; N, 14.91; Found: C, 25.80; H, 4.62; N, 14.74. Main IR peaks (KBr, cm⁻¹): ν(N-H) 3251(m); ν(C-H)
2932(m), 2878(m); \nu(C-N) + \delta(C-H) 1539(s)–1438(sh); \nu(C=S) 1198(m); \delta(N-CH_3) 960(m).

$^1$H NMR data (CDCl$_3$, δ ppm): 8.29 bs (1H, NH), 3.71 m (4H, C$_4$,C$_5$H), 3.10 s (3H, CH$_3$).

$[\text{Cu}_2(\mu-\text{Cl})(\mu-\text{S},\text{S-dtucH})(\text{PPh}_3)_4]$ (31), $[\text{Cu}_2\text{Cl}_2(\text{dtucH}_2)(\text{PPh}_3)_4]$ (32), $[\text{CuCl}(\mu-\text{S},\text{S-dtucH}_2)(\text{PPh}_3)_n]$ (33)

To a solution of copper(I) chloride (0.025 g, 0.25 mmol) in acetonitrile (10 mL) was added a solution of 2,4-dithiouracil (0.036 g, 0.25 mmol) in methanol (5 mL) followed by stirring for 24 h at room temperature and to the orange precipitates formed was added solid Ph$_3$P (0.132 g, 0.50 mmol). The contents were stirred until a clear solution was obtained and slow evaporation of solution at room temperature formed light yellow crystals of $[\text{Cu}_2(\mu-\text{Cl})(\mu-\text{S},\text{S-dtucH})(\text{PPh}_3)_4]$ 31 (Yield 19%, M.p. 178-180°C). Anal. Caled for C$_{76}$H$_{63}$ClCu$_2$N$_2$P$_4$S$_2$ (%): C, 67.38; H, 4.65; N, 2.07; Found: C, 67.02; H, 4.56; N, 2.18. Main IR peaks (KBr, cm$^{-1}$): ν(N-H) 3049(m); ν(C-H) 2995–2927(w); ν(C-N) + δ(C-H) 1543–1478(s); ν(C=S) 1128(s); ν(P-C$_{Ph}$) 1093(m). $^{31}$P NMR (CDCl$_3$, δ ppm): -4.0 ppm, Δδ(δ$_{\text{complex}}$ - δ$_{\text{PPh}_3}$) = 1.45 ppm. From the filtrate orange color crystals of composition $[\text{Cu}_2\text{Cl}_2(\text{dtucH}_2)(\text{PPh}_3)_4]$ 32 were obtained which are stable in mother liquor (Yield 18%, M.p. 189-191°C). Anal. Caled for C$_{76}$H$_{64}$Cl$_2$Cu$_2$N$_2$P$_4$S$_2$ (%): C, 65.61; H, 4.60; N, 2.01; Found: C, 65.29; H, 4.45; N, 2.13. Main IR peaks (KBr, cm$^{-1}$): ν(N-H) 3053(m); ν(C-H) 2993–2934(w); ν(C-N) + δ(C-H) 1546-1477(m); ν(C=S) 1123(s); ν(P-C$_{Ph}$) 1093(m). Further, from the filtrate dark orange color crystals of complex 33 were obtained (Yield 23.5%, M.p. 280-283°C). Anal. Caled for C$_{22}$H$_{19}$ClCuN$_2$PS$_2$ (%): C, 52.26; H, 3.76; N, 5.54; Found: C, 52.44; H, 3.57; N, 5.31.
Main IR peaks (KBr, cm\(^{-1}\)):
\[ \nu(\text{N-H}) \ 3050(\text{m}); \]
\[ \nu(\text{C-H}) \ 3010-2910(\text{w}); \]
\[ \nu(\text{C-N}) + \delta(\text{C-H}) \ 1590-1510(\text{s}); \]
\[ \nu(\text{C=S}) \ 1090(\text{s}); \]
\[ \nu(\text{P-C}_\text{Ph}) \ 1075(\text{m}). \]

Complexes 34–36 were prepared by a similar method as complexes 31–33.

\[ [\text{Cu}_2(\mu\text{-Br})(\mu\text{-S,S-dtucH})(\text{PPh}_3)_4] \ (34), \quad [\text{Cu}_2\text{Br}_2(\text{dtucH}_2)(\text{PPh}_3)_4] \ (35), \quad [\text{CuBr}(\mu\text{-S,S-dtucH}_2)(\text{PPh}_3)_n] \ (36) \]

Slow evaporation of solution at room temperature formed pale yellow crystals of \([\text{Cu}_2(\mu\text{-Br})(\mu\text{-S,S-dtucH})(\text{PPh}_3)_4] \ (34)\) (Yield 20\%, M.p. 181-183°C). Anal. Calcd for C\(_{76}\)H\(_{63}\)BrCu\(_{2}\)N\(_2\)P\(_4\)S\(_2\) (%): C, 65.18; H, 4.50; N, 2.00; Found: C, 65.15; H, 4.21; N, 2.14. Main IR peaks (KBr, cm\(^{-1}\)):
\[ \nu(\text{N-H}) \ 3048(\text{m}); \]
\[ \nu(\text{C-H}) \ 2970-2853(\text{w}); \]
\[ \nu(\text{C/N}) + \delta(\text{C-H}) \ 1541-1479(\text{s}); \]
\[ \nu(\text{C=S}) \ 1126(\text{s}); \]
\[ \nu(\text{P/C}_\text{Ph}) \ 1093(\text{sh}). \]

\[ ^{31}\text{P} \text{NMR (CDCl}_3, \delta \text{ ppm):} \ -4.4 \text{ ppm, } \Delta \delta (\delta_{\text{complex}} - \delta_{\text{PPh}_3}) = 1.07 \text{ ppm.} \]

From the filtrate orange color crystals of composition \([\text{Cu}_2\text{Br}_2(\text{dtucH}_2)(\text{PPh}_3)_4] \ (35)\) were obtained which are stable in mother liquor (Yield 19\%, M.p. 183-185°C). Anal. Calcd for C\(_{76}\)H\(_{63}\)BrCu\(_{2}\)N\(_2\)P\(_4\)S\(_2\) (%): C, 61.66; H, 4.32; N, 1.89; Found: C, 61.26; H, 4.14; N, 1.00. Main IR peaks (KBr, cm\(^{-1}\)):
\[ \nu(\text{N-H}) \ 3049(\text{m}); \]
\[ \nu(\text{C-H}) \ 2958-2853(\text{w}); \]
\[ \nu(\text{C-N}) + \delta(\text{C-H}) \ 1548(\text{s}), 1479(\text{m}); \]
\[ \nu(\text{C=S}) \ 1119(\text{s}); \]
\[ \nu(\text{P-C}_\text{Ph}) \ 1093(\text{sh}). \]

\[ ^{31}\text{P} \text{NMR (CDCl}_3, \delta \text{ ppm):} \ -4.2, 29.32 \text{ ppm, } \Delta \delta (\delta_{\text{complex}} - \delta_{\text{PPh}_3}) = 1.25, 34.77 \text{ ppm.} \]

Further, from the filtrate dark orange color crystals of complex 36 were obtained (Yield 22\%, M.p. 290-294°C). Anal. Calcd for C\(_{22}\)H\(_{19}\)BrCuN\(_2\)PS\(_2\) (%): C, 48.03; H, 3.46; N, 5.09; Found: C,
48.32; H, 3.72; N, 4.90. Main IR peaks (KBr, cm\(^{-1}\)): \(\nu\) (N-H) 3010(m); \(\nu\) (C-H) 2830–2925(w); 
\(\nu\) (C-N) + \(\delta\) (C-H) 1590–1525(m); \(\nu\) (C=S) 1105(s); \(\nu\) (P-C\(_{Ph}\)) 1085(sh).

\[\text{[Cu}_{2}\text{I(dtucH)}(\text{PPh}_3)_4]\] (37), \[\text{[CuI(\mu-S,S-dtucH)_2(PPh}_3)\text{]}_n\cdot n\text{CHCl}_3\] (38)

To a solution of copper(I) iodide (0.025 g, 0.13 mmol) in acetonitrile (10 mL) was added a solution of 2,4-dithiouracil (0.019 g, 0.13 mmol) in methanol (5 mL) followed by stirring for 24 h at room temperature and to the orange precipitates formed was added solid Ph\(_3\)P (0.069 g, 0.50 mmol). The contents were stirred until a clear solution was obtained and slow evaporation of solution at room temperature formed light yellow crystals of \[\text{[Cu}_{2}\text{I(dtucH)}(\text{PPh}_3)_4]\] (Yield 68%, M.p. 117-120°C). Anal. Calcd for C\(_{76}\)H\(_{63}\)ICu\(_2\)N\(_2\)P\(_4\)S\(_2\) (%): C, 63.11; H, 4.36; N, 1.94; Found: C, 63.32; H, 4.25; N, 1.85. Main IR peaks (KBr, cm\(^{-1}\)): \(\nu\) (N-H) 3048(m); \(\nu\) (C-H) 2925–2860(w); \(\nu\) (C-N) + \(\delta\) (C-H) 1537–1478(s); \(\nu\) (C=S) 1122(s); \(\nu\) (P-C\(_{Ph}\)) 1092(m). \(^{31}\)P NMR (CDCl\(_3\), \(\delta\) ppm): -5.0 ppm, \(\Delta\delta\) (\(\delta\)\(_{\text{complex}}\) – \(\delta\)\(_{\text{PPh}_3}\)) = 0.45 ppm. The above reaction in CH\(_3\)CN–MeOH-CHCl\(_3\) yielded dark orange crystals of complex 38 (Yield 63%, M.p. 278-280°C). Anal. Calcd for C\(_{23}\)H\(_{20}\)Cl\(_2\)CuIN\(_2\)PS\(_2\) (%): C, 38.53; H, 2.79; N, 3.91; Found: C, 38.65; H, 2.91; N, 3.78. Main IR peaks (KBr, cm\(^{-1}\)): \(\nu\) (N-H) 3110(w), 3040(w); \(\nu\) (C-N) + \(\delta\) (C-H) 1555–1510(m); \(\nu\) (C=S) 1125(s); \(\nu\) (P-C\(_{Ph}\)) 1110(sh).

\[\text{[CuCl(\eta}^1\text{-S-tucH}_2)(\text{PPh}_3)_2]\] (39)

To a solution of copper(I) chloride (0.025 g, 0.25 mmol) in acetonitrile was added a solution of 2-thiouracil (0.030 g, 0.25 mmol) in methanol, followed by stirring for 1h at room temperature and to the precipitates formed was added Ph\(_3\)P (0.132 g, 0.50 mmol) and stirred until a clear solution was obtained. The slow evaporation of solution at room
temperature formed pale yellow crystals of complex 39 (Yield 63%, M.p. 180-182°C). Anal. Calcd for C_{40}H_{34}ClCuN_{2}OP_{2}S (%): C, 63.91; H, 4.53; N, 3.73; Found: C, 63.85; H, 4.34; N, 3.56. Main IR peaks (KBr, cm⁻¹): ν(N-H) 3048(m); ν(C-H) 3010–2960(w); ν(C-N) + δ(C-H) 1584(m), 1480(s); ν(C=S) 1172(s); ν(P-C_Ph) 1091(s). \(^1\)H NMR data (CDCl₃, δ ppm): 13.58 bs (1H, NH), 5.82 d (1H, C₅H), 7.02 d (1H, C₆H), 7.19 – 7.42 m (15H + 1H, Ph₃P, CHCl₃). \(^31\)P NMR (CDCl₃, δ ppm): 0.0 ppm, ∆δ(δ_{complex} – δ_{PPh₃}) = 1.48, 34.81 ppm.

**[Cu₃Cl₂(H₂tmt)(PPh₃)₆]** (40)

To a solution of copper(I) chloride (0.025 g, 0.25 mmol) in acetonitrile (10 mL) was added a solution of 2,4,6-trimercaptotriazine (0.045 g, 0.25 mmol) in methanol (5 mL) followed by stirring for 24 h at room temperature and to the orange precipitates formed was added solid Ph₃P (0.132 g, 0.50 mmol). The contents were stirred until a clear solution was obtained and slow evaporation of solution at room temperature formed yellow crystals of 40, which are stable in mother liquor (Yield 67%, M.p. 190-193°C). Anal. Calcd for C₁₁₁H₉₂Cl₂Cu₃N₃P₆S₃ (%): C, 66.21; H, 4.57; N, 2.09; Found: C, 66.15; H, 4.42; N, 1.14. Main IR peaks (KBr, cm⁻¹): ν(N-H) 3050(m); ν(C-H) 2926–2853(w); ν(C/N) + δ(C-H) 1532(s), 1477(s); ν(C=S) 1110(s); ν(P-C_Ph) 1093(m). \(^31\)P NMR (CDCl₃, δ ppm): -3.97, 29.36 ppm, ∆δ(δ_{complex} – δ_{PPh₃}) = 2.47 ppm.

Complex 41 was prepared by a similar method as complex 40.

**[Cu₃Br₂(µ-S-H₂tmt)(PPh₃)₆]** (41)

Color: yellow (Yield 68%, M.p. 200-203°C). Anal. Calcd for C₁₁₁H₉₂Br₂Cu₃N₃P₆S₃ (%): C, 63.42; H, 4.38; N, 2.00; Found: C, 63.47; H, 4.51; N, 1.27. Main IR peaks (KBr, cm⁻¹): ν(N-H) 3140(w), 3048(m); ν(C-H) 3010–2855(w); ν(C-N) + δ(C-H) 1524(s), 1460(s); ν(C=S) 1105(s); ν(P-C_Ph) 1093(m). \(^31\)P NMR (CDCl₃, δ ppm): -7.92, 24.55 ppm, ∆δ(δ_{complex} – δ_{PPh₃}) = -2.45, 30.02 ppm.
To silver(I) chloride (0.025 g, 0.17 mmol) suspended in acetonitrile was added solid PPh₃ (0.045 g, 0.17 mmol) and the contents were stirred for 24 h. The white solid formed was filtered and dried in vacuo. To this solid suspended in chloroform was added solid imdazolidine-2-thione (0.018 g, 0.17 mmol) and the contents were stirred until a clear solution was obtained, which was allowed to evaporate at room temperature. The solid obtained was dissolved in dichloromethane and acetonitrile mixture. Slow evaporation of the solution resulted in colorless crystals of complex 42 (Yield 70%, M.p. 163-165°C). Anal. Calcd for C₂₁H₂₁AgClN₂PS (%): C, 49.70; H, 4.14; N, 5.52; Found: C, 49.54; H, 4.16; N, 6.07. Main IR peaks (KBr, cm⁻¹): ν(N–H) 3150(m); ν(C–H) 3040–2865(w); ν(C–N) + δ(C/H) 1509(s), 1439(sh); ν(C=S) 1186(s), 986(m), 915(m); ν(P–Ph₃) 1108(w). ¹H NMR data (CDCl₃, δ ppm): 7.79 bs (1H, NH), 3.73 s (4H, C₄,5), 7.26 – 7.44 m (15H + 1H, PPh₃, CHCl₃). ³¹P NMR (CDCl₃, δ ppm): 13.62 ppm, Δδ(δ_complex – δPPh₃) = 19.1 ppm.

To silver(I) chloride (0.025 g, 0.17 mmol) suspended in acetonitrile was added solid PPh₃ (0.091 g, 0.34 mmol) and the contents were stirred for 24 h. The white solid formed was filtered and dried in vacuo. To this solid suspended in chloroform was added solid imdazolidine-2-thione (0.018 g, 0.17 mmol) and the contents were stirred until a clear solution was obtained, which was allowed to evaporate at room temperature. The solid obtained was dissolved in dichloromethane and acetonitrile mixture. Slow evaporation of the solution resulted in colorless crystals of complex 43 (Yield 72%, M.p. 169-172°C). Anal. Calcd for C₃₉H₃₇₃₀AgClN₂O₀.₆₅P₂S (%): C, 59.93; H, 4.77; N, 4.00; Found: C, 60.09; H, 5.05; N, 3.56. Main IR peaks (KBr, cm⁻¹): ν(O–H) 3390(br); ν(N–H) 3209(m), 3167(m); ν(C–H) 3069–2893(m); ν(C–N) + δ(C–H) 1537(s), 1433(s); ν(C=S) 1180(m), 997(m), 916(m); ν(P–Ph₃) 1093(m). ¹H NMR data (CDCl₃, δ ppm): 3.79 s (4H, C₄,5), 7.26 – 7.44 m (15H + 1H, PPh₃, CHCl₃). ¹³C NMR data (CDCl₃, δ ppm): 45.5 (C₄, C₅, imdzSH),
134.3 (o-C, J = 17.32 Hz, P-Ph), 134.2 (i-C, J = 9.07 Hz, P-Ph), 130.1 (p/C, P-Ph), 129.1 (m/C, J = 8.62 Hz, P-Ph). $^{31}$P NMR (CDCl$_3$, $\delta$ ppm): 4.5 ppm, $\Delta\delta(\delta_{\text{complex}} - \delta_{\text{PPh}_3}) = 9.2$ ppm.

$[^{1}\text{AgBr(imdzSH)(PPh}_3)]_2$ (44)

To silver(I) bromide (0.025 g, 0.13 mmol) suspended in acetonitrile was added solid PPh$_3$ (0.070 g, 0.26 mmol) and the contents were stirred for 24 h. The white solid formed was filtered and dried in vacuo. To this solid suspended in chloroform was added solid imidazolidine-2-thione (0.014 g, 0.13 mmol) and the contents were stirred until a clear solution was obtained, which was allowed to evaporate at room temperature. The solid obtained was dissolved in dichloromethane and acetonitrile mixture. A slow evaporation of the solution resulted in colorless crystals of 44 (Yield 68%, M.p. 148-150°C). Anal. Calcd for C$_{21}$H$_{21}$AgBrN$_2$PS (%): C, 45.68; H, 3.81; N, 5.07. Found: C, 45.90; H, 3.65; N, 5.30. Main IR peaks (KBr, cm$^{-1}$): $\nu$(N=H) 3307(br), $\nu$(C−H) 3053–2920(m), $\nu$(C−N) + $\delta$(C/H) 1527(s), 1433(s), $\nu$(C=S) 1193m, 995m, 913(s), $\nu$(P-Ph$_3$) 1095(s). $^1$H NMR data (CDCl$_3$, $\delta$ ppm): 7.13 bs (1H, NH), 3.75 d (4H, C$_4$,5 H), 7.26 – 7.41 (15H + 1H, PPh$_3$, CHCl$_3$). $^{31}$P NMR (CDCl$_3$, $\delta$ ppm): 4.62 ppm, $\Delta\delta(\delta_{\text{complex}} - \delta_{\text{PPh}_3}) = 10.1$ ppm.

$[^{1}\text{AgCl(η}^1\text{-imdzSH-Me)(PPh}_3)]_2$ (45)

It was prepared by a similar method as complex 43 (Yield 68%, M.p. 165-167°C). Anal. Calcd for C$_{40}$H$_{38}$AgClN$_2$P$_2$S (%): C, 61.26; H, 4.85; N, 3.57; Found: C, 61.40; H, 4.95; N, 3.62. Main IR peaks (KBr, cm$^{-1}$): $\nu$(N=H) 3212(br), $\nu$(C−H) 3066–2799(m), $\nu$(C−N) + $\delta$(C−H) 1515(s), 1479(s), $\nu$(C=S) 1180(m); $\nu$(P-Ph$_3$) 1093(m); $\delta$(N-CH$_3$) 996(w). $^1$H NMR data (CDCl$_3$, $\delta$ ppm): 8.64 bs (1H, NH), 3.61 m (4H, C$_{4}$,5 H), 3.08 m (3H, CH$_3$), 7.26 – 7.42 m (15H + 1H, PPh$_3$, CHCl$_3$). $^{31}$P NMR (CDCl$_3$, $\delta$ ppm): 3.78 ppm, $\Delta\delta(\delta_{\text{complex}} - \delta_{\text{PPh}_3}) = 9.25$ ppm.
[Ag(μ-Br)(η^1-S-imdzSH-Me)(PPh₃)]₂ (46)

It was prepared by a similar method as complex 42 (Yield 69%, M.p. 170-173°C). Anal. Calcd for C₂₁H₂₁AgBrN₂PS (%): C, 46.64; H, 4.06; N, 4.95. Found: C, 46.77; H, 3.94; N, 5.10. Main IR peaks (KBr, cm⁻¹): ν(N–H) 3243(m); ν(C–H) 3051–2883(m); ν(C–N) + δ(C-H) 1514(s), 1479(sh); ν(C=S) 1186(m), ν(P-Cₚ₃) 1114(s), δ(N-CH₃) 945(w). ¹H NMR data (CDCl₃, δ ppm): 8.16 bs (1H, NH), 3.69 m (4H, C₄,₅ H), 3.10 s (3H, CH₃), 7.32 – 7.49 m (15H, PPh₃). ³¹P NMR (CDCl₃, δ ppm): 6.40, 28.59 ppm, Δδ(δ(complex) – δ(PPh₃)) = 11.87, 34.0 ppm.

[AgCl(imdzSH-Et)(PPh₃)]₂ (47)

It was prepared by a similar method as complex 43 (Yield 66%, M.p. 151-154°C). Anal. Calcd for C₄₁H₄₀AgClN₂P₂S (%): C, 61.71; H, 5.01; N, 3.51; Found: C, 61.55; H, 4.95; N, 3.62. Main IR peaks (KBr, cm⁻¹): ν(N–H) 3202(m); ν(C–H) 3050–2885(m); ν(C–N) + δ(C-H) 1517(s), 1478(m); ν(C=S) 1193(m), ν(P/Cₚ₃) 1094(s). ¹H NMR data (CDCl₃, δ ppm): 8.60 bs (1H, NH), 3.58 m (6H, C₄,₅ H, N/CH₂), 1.17 m (3H, CH₃), 7.26 – 7.70 m (15H + 1H, PPh₃, CHCl₃). ³¹P NMR (CDCl₃, δ ppm): 10.22 ppm, Δδ(δ(complex) – δ(PPh₃)) = 15.69 ppm.

[Ag₂(μ-Cl)₂(η^1-S-imdzSH-Et)₂(PPh₃)]₂ (48)

It was prepared by a similar method as complex 42. Yield 66%, M.p. 165-167°C. Anal. Calcd for C₄₆H₅₀Ag₂Cl₂N₄P₂S₂ (%): C, 51.51; H, 4.66; N, 5.22; Found: C, 51.35; H, 4.61; N, 5.14. Main IR peaks (KBr, cm⁻¹): ν(N–H) 3202(m), ν(C–H) 3051-2885(w), ν(C–N) + δ(C-H) 1516(s), 1478(sh), ν(C=S) 1187(m), ν(P-Cₚ₃) 1094(s). ¹H NMR data (CDCl₃, δ ppm): 3.63 m (6H, C₄,₅ H, N-CH₂), 1.20 t (3H, CH₃), 7.39 – 7.50 m (15H, PPh₃). ³¹P NMR (CDCl₃, δ ppm): 3.40, 29.63 ppm, Δδ(δ(complex) – δ(PPh₃)) = 8.85, 35.08 ppm.
It was prepared by a similar method as complex 42. (Yield 71%, M.p. 158-160°C). Anal. Calcd for C_{46}H_{52}Ag_{2}Br_{2}N_{4}P_{2}S_{2} (%): C, 47.48; H, 4.47; N, 4.82; Found: C, 47.54; H, 4.41; N, 4.82. Main IR peaks (KBr, cm⁻¹): ν(N–H) 3237(m), ν(C–H) 3050–2883(w), ν(C–N) + δ(C-H) 1514(s), 1477(sh), ν(C=S) 1187(m), ν(P-C_{Ph}) 1093(m). $^{1}$H NMR data (CDCl$_3$, δ ppm): 8.45 bs (1H, NH), 3.61 m (6H, C$_{4,5}$H, N/CH$_2$), 1.19 m (3H, CH$_3$), 7.24 – 7.50 m (15H + 1H, PPh$_3$, CHCl$_3$).

[AgCl($\eta^1$-S-imdzSH-Pr$^n$)(PPh$_3$)$_2$] (50)

It was prepared by a similar method as complex 43. (Yield 67%, M.p. 150-153°C). Anal. Calcd for C$_{42}$H$_{42}$AgClN$_2$P$_2$S (%): C, 62.11; H, 5.17; N, 3.45; Found: C, 61.95; H, 5.10; N, 3.48. Main IR peaks (KBr, cm⁻¹): ν(N–H) 3092(w); ν(C–H) 3051–2871(m); ν(C–N) + δ(C-H) 1511(s), 1479(sh); ν(C=S) 1186(m); ν(P-C_{Ph}) 1094(m). $^{1}$H NMR data (CDCl$_3$, δ ppm): 3.61 m (4H, C$_{4}$H, N/CH$_2$), 3.49 t (2H, C$_{5}$H), 1.60 m (2H, CH), 0.92 t (3H, CH$_3$), 7.26 – 7.43 m (15H + 1H, PPh$_3$, CHCl$_3$). $^{31}$P NMR (CDCl$_3$, δ ppm): 4.54 ppm, Δδ(δ$_{\text{complex}}$ − δ$_{\text{PPh$_3$}}$) = 10.0 ppm.

[Ag$_2$(µ-Br)$_2$(η$^1$-S-imzdSH-Pr$^n$)$_2$(PPh$_3$)$_2$] (51)

It was prepared by a similar method as 42. (Yield 69%, M.p. 140-142°C). Anal. Calcd for C$_{48}$H$_{54}$Ag$_2$Br$_2$N$_4$P$_2$S$_2$ (%): C, 48.46; H, 4.54; N, 4.71; Found: C, 48.53; H, 4.50; N, 4.62. Main IR peaks (KBr, cm⁻¹): ν(N–H) 3235(m), ν(C–H) 3053–2882(w), ν(C–N) + δ(C-H) 1513(s), 1477(sh), ν(C=S) 1184(m), ν(P-C_{Ph}) 1093(m). $^{1}$H NMR data (CDCl$_3$, δ ppm): 8.50 bs (1H, NH), 3.67 m (4H, C$_{4}$H, N/CH$_2$), 3.47 t (2H, C$_{5}$H), 1.60 m (2H, CH), 0.92 t (3H, CH$_3$), 7.29 – 7.51 m (15H, PPh$_3$). $^{31}$P NMR (CDCl$_3$, δ ppm): 7.13 ppm, Δδ(δ$_{\text{complex}}$ − δ$_{\text{PPh$_3$}}$) = 12.6 ppm.
**[AgCl(imdzSH-Bu\(^n\))(PPh\(_3\)](52)**

To silver(I) chloride (0.025 g, 0.17 mmol) suspended in acetonitrile was added solid PPh\(_3\) (0.091 g, 0.34 mmol) and the contents were stirred for 24 h. The white solid formed was filtered and dried in vacuo. To this solid suspended in chloroform was added solid 1-butyl-imidazolidine-2-thione (0.028 g, 0.17 mmol) and the contents were stirred until a clear solution was obtained, which was allowed to evaporate at room temperature. The solid obtained was dissolved in dichloromethane and acetonitrile mixture. A slow evaporation of the solution resulted in colorless crystals of 52, which are stable in mother liquor (Yield 72%, M.p. 145-147\(^\circ\)C). Anal. Calcd for C\(_{43}\)H\(_{44}\)AgClN\(_2\)P\(_2\)S (%): C, 62.54; H, 5.33; N, 3.39; Found: C, 62.32; H, 5.18; N, 3.52. Main IR peaks (KBr, cm\(^{-1}\)): \(\nu\)(N−H) 3169(m); \(\nu\)(C−H) 3045–2869(m); \(\nu\)(C−N) + \(\delta\)(C/H) 1509(s), 1478(sh); \(\nu\)(C=S) 1183(m); \(\nu\)(P/C\(_{\text{Ph}}\)) 1094(s).

**[\(1^H\) NMR data (CDCl\(_3\), \(\delta\) ppm):](398x114) 8.10 bs (1H, NH), 3.58 m (6H, C\(_{4,5}\)H, N/CH\(_2\)), 1.36 m (2H, /CH\(_2\)), 1.56 m (2H, /CH\(_2\)), 0.96 m (3H, CH\(_3\)), 7.29 − 7.47 m (15H, PPh\(_3\)).**

**[\(31^P\) NMR (CDCl\(_3\), \(\delta\) ppm):](251x100) 10.21 ppm, \(\Delta\delta(\delta_{\text{complex}} - \delta_{\text{PPh3}}) = 15.68\) ppm.**

**[AgBr(imdzSH-Bu\(^n\))(PPh\(_3\)](53)**

To silver(I) bromide (0.025 g, 0.13 mmol) suspended in acetonitrile was added solid PPh\(_3\) (0.070 g, 0.26 mmol) and the contents were stirred for 24 h. The white solid formed was filtered and dried in vacuo. To this solid suspended in chloroform was added solid 1-butyl-imidazolidine-2-thione (0.021 g, 0.13 mmol) and the contents were stirred until a clear solution was obtained, which was allowed to evaporate at room temperature. The solid obtained was dissolved in dichloromethane and acetonitrile mixture. A slow evaporation of this solution resulted in colorless prismatic crystals of 55, which are stable in mother liquor (Yield 71%, M.p. 148-150\(^\circ\)C). Anal. Calcd for C\(_{43}\)H\(_{44}\)AgBrN\(_2\)P\(_2\)S (%): C, 59.31; H, 5.06; N, 3.22; Found: C, 59.06; H, 5.00; N, 3.48. Main IR peaks (KBr, cm\(^{-1}\)): \(\nu\)(N−H) 3159(m); \(\nu\)(C−H) 3047–2866(m); \(\nu\)(C−N) + \(\delta\)(C/H) 1513(s), 1478(sh); \(\nu\)(C=S) 1184(s); \(\nu\)(P-C\(_{\text{Ph}}\)) 1094(s).

**[\(1^H\) NMR data (CDCl\(_3\), \(\delta\) ppm):](398x114) 7.93 bs (1H, NH), 3.55 m (6H, C\(_{4,5}\)H, N-CH\(_2\)), 1.36 m (2H, -CH\(_2\)), 1.56 m (2H, -CH\(_2\)), 0.96 t (3H, CH\(_3\)), 7.26 − 7.40 PPh\(_3\).**
m (15H + 1H, PPh₃, CHCl₃). ³¹P NMR (CDCl₃, δ ppm): 3.66, 29.31 ppm, Δδ(δcomplex - δPPh₃) = 9.13, 34.78 ppm.

[AgCl(η¹-S-mimzSH)(PPh₃)₂] (54)

To a solution of silver(I) acetate (0.025 g, 0.15 mmol) in acetone was added solution of 1-methyl-imidazoline-2-thione (0.034 g, 0.30 mmol) in acetonitrile followed by stirring for 2h at room temperature. To the precipitates formed was added PPh₃ (0.078 g, 0.30 mmol). Slow evaporation of solution at room temperature formed colorless prismatic crystals of 54 (Yield, 0.094 g, 69%, M.p. 184-190°C). Anal. Calcd for C₄₀H₃₆AgClN₂P₂S (%): C, 61.42; H, 4.60; N, 3.58. Found: C, 61.32; H, 4.65; N, 3.81. Main IR peaks (KBr, cm⁻¹): ν(N−H) 3123(br), ν(C−H) 3045–2894(w), ν(C−N) + δ(C/H) 1570(s), 1480(s), ν(C=S) 910(s), ν(P-Cₚ₈) 1094(m), δ(N-CH₃) 744(s). ¹H NMR data (CDCl₃, δ ppm): 13.07 bs (1H, NH), 6.79 t (1H, C⁴H), 6.67 t (1H, C⁵H), 3.58 s (3H, N/CH₃), 7.25 – 7.46 (15H + 1H, PPh₃, CHCl₃). ³¹P NMR (CDCl₃, δ ppm): 5.46, 30.17 ppm, Δδ(δcomplex - δPPh₃) = 10.11, 34.87 ppm.

[Ag₂(µ-Br)₂(η¹-S-mimzSH)₂(PPh₃)₂] (55)

To silver(I) bromide (0.025 g, 0.13 mmol) suspended in acetonitrile was added solid PPh₃ (0.078 g, 0.26 mmol) and the contents were stirred for 24 h. The white solid formed was filtered and dried in vacuo. To this solid suspended in chloroform was added solid 1-methyl-imidazoline-2-thione (0.015 g, 0.13 mmol) and the contents were stirred until a clear solution was obtained, which was allowed to evaporate at room temperature. The solid obtained was dissolved in dichloromethane and acetonitrile mixture. A slow evaporation of this solution resulted in colorless prismatic crystals of 55 (Yield 67%, M.p. 163-165°C). Anal. Calcd for C₃₉H₃₅AgClN₄P₂S₂ (%): C, 46.80; H, 3.72; N, 4.96; Found: C, 47.65; H, 3.81; N, 5.14. Main IR peaks (KBr, cm⁻¹): ν(N−H) 3243(m); ν(C−H) 3052–2883(w); ν(C−N) + δ(C-H) 1514(s), 1479(s); ν(C=S) 920(m); ν(P-Cₚ₈) 1093(w); δ(N-CH₃) 748(s). ¹H NMR data (CDCl₃, δ ppm):
6.75 t (1H, C\textsuperscript{4}H), 6.64 t (1H, C\textsuperscript{5}H), 3.54 s (3H, N-CH\textsubscript{3}), 7.39 – 7.52 (15H, PPh\textsubscript{3}). \textsuperscript{31}P NMR (CDCl\textsubscript{3}, δ ppm): 10.58 ppm, Δδ(δ\textsubscript{complex} - δ\textsubscript{PPh\textsubscript{3}}) = 15.28 ppm.

[AgCl(\eta\textsuperscript{1}-tzdSH)(PPh\textsubscript{3})\textsubscript{2}] (56)

![Complex 56](image)

To silver(I) chloride (0.025 g, 0.17 mmol) suspended in acetonitrile was added solid PPh\textsubscript{3} (0.091 g, 0.34 mmol) and the contents were stirred for 24 h. The white solid formed was filtered and dried in vacuo. To this solid suspended in chloroform was added solid thiazolidine-2-thione (0.018 g, 0.17 mmol) and the contents were stirred until a clear solution was obtained, which was allowed to evaporate at room temperature. The solid obtained was dissolved in dichloromethane and acetonitrile mixture. A slow evaporation of the solution resulted in yellow prismatic crystals of 56 (Yield 71%, M.p. 190-193°C). Anal. Calcd for C\textsubscript{39}H\textsubscript{35}AgClNP\textsubscript{2}S\textsubscript{2} (%): C, 59.46; H, 4.44; N, 1.77; Found: C, 60.02; H, 4.12; N, 1.62. Main IR peaks (KBr, cm\textsuperscript{-1}): ν(N=H) 3100(br); ν(C−H) 3008–2950(br); ν(C−N) + δ(C-H) 1525(s), 1450(sh); ν(P/C Ph) 1102(m); ν(C=S) 993(s). \textsuperscript{1}H NMR data (CDCl\textsubscript{3}, δ ppm): 10.54 bs (1H, NH), 3.36 t (2H, J = 7.8, 8.1 Hz, C\textsuperscript{4}H), 3.96 t (2H, J = 7.5, 8.4 Hz, C\textsuperscript{5}H), 7.23 – 7.42 m (15H + 1H, PPh\textsubscript{3}, CHCl\textsubscript{3}). \textsuperscript{13}C NMR data (CDCl\textsubscript{3}, δ ppm): 200.0 (C\textsuperscript{2}, tzdSH), 51.8 (C\textsuperscript{5}, tzdSH), 33.3 (C\textsuperscript{4}, tzdSH), 133.9 (o-C, J = 16.05 Hz, P-Ph), 133.3 (i-C, J = 19.72 Hz, P-Ph), 129.7 (p-C, P-Ph), 128.6 (m-C, J = 8.62 Hz, P-Ph). \textsuperscript{31}P NMR (CDCl\textsubscript{3}, δ ppm): 1.68 ppm, Δδ(δ\textsubscript{complex} - δ\textsubscript{PPh\textsubscript{3}}) = 6.38 ppm.

[AgBr(\eta\textsuperscript{1}-S-tzdSH)(PPh\textsubscript{3})\textsubscript{2}] (57)

![Complex 57](image)

It was prepared by a similar method as complex 57. (Yield 72%, M.p. 170-173°C). Anal. Calcd for C\textsubscript{39}H\textsubscript{35}AgBrNP\textsubscript{2}S\textsubscript{2} (%): C, 56.31; H, 4.21; N, 1.68; Found: C, 56.54; H, 4.05; N, 1.62. Main IR peaks (KBr, cm\textsuperscript{-1}): ν(N=H) 3052(m); ν(C−H) 3008–2811(m); ν(C−N) + δ(C-H) 1527(s), 1479(s); ν(P/C Ph) 1093(m); ν(C=S) 996(m). \textsuperscript{1}H NMR data (CDCl\textsubscript{3}, δ ppm): 9.72 bs (1H, NH), 3.47 t (2H, J = 7.5, 8.1 Hz, C\textsuperscript{4}H), 3.94 t (2H, J = 7.8, 8.1 Hz, C\textsuperscript{5}H), 7.26 – 7.43 m (15H + 1H, PPh\textsubscript{3}, CHCl\textsubscript{3}). \textsuperscript{13}C
NMR data (CDCl$_3$, δ ppm): 200.5 (C$^2$, tzdSH), 51.5 (C$^5$, tzdSH), 33.3 (C$^4$, tzdSH), 133.9 (o-C, J = 16.72 Hz, P-Ph), 133.2 (i-C, J = 19.72 Hz, P-Ph), 129.7 (p-C, P-Ph), 128.6 (m-C, J = 9.3 Hz, P-Ph). $^{31}$P NMR (CDCl$_3$, δ ppm): 2.42 ppm, ∆δ(δ$_{\text{complex}}$ - δ$_{\text{PPh}_3}$) = 7.1 ppm.

$[\text{Ag}_2(\mu-N,S-$dtucH$)(\mu-\text{Cl})(\text{PPh}_3)_4]$ (58)

To silver(I) chloride (0.025 g, 0.17 mmol) suspended in acetonitrile was added solution of 2,4-dithiouracil in methanol (0.025 g, 0.17 mmol) and the contents were stirred for 48 h. To the yellow precipitates formed was added solid PPh$_3$ (0.091 g, 0.17 mmol) and the contents were stirred until a clear solution was obtained. The slow evaporation of the solution resulted in yellow prismatic crystals of complex 58 (Yield 68%, M.p. 170-172°C). Anal. Calcd for C$_{76}$H$_{63}$Ag$_2$ClN$_2$P$_4$S$_2$ (%): C, 63.18; H, 4.36; N, 1.94; Found: C, 63.42; H, 4.22; N, 2.05. Main IR peaks (KBr, cm$^{-1}$): ν(N–H) 3046(m), ν(C–H) 3005–2928(w), ν(C–N) + δ(C/H) 1542–1478(s), ν(C=S) 1125(s), ν(P/C$_{\text{Ph}}$) 1094(m).

$[\text{Ag}_2(\mu-N,S-$dtucH$)(\mu-\text{Br})(\text{PPh}_3)_4]$ (59)

It was prepared by a similar method as complex 58. (Yield 70%, M.p. 155-157°C). Anal. Calcd for C$_{76}$H$_{63}$Ag$_2$BrN$_2$P$_4$S$_2$ (%): C, 61.29; H, 4.23; N, 1.88; Found: C, 61.37; H, 4.20; N, 1.94. Main IR peaks (KBr, cm$^{-1}$): ν(N–H) 3046(m), ν(C–H) 3010–2926(w), ν(C–N) + δ(C/H) 1545–1479(s), ν(C=S) 1123(s), ν(P-C$_{\text{Ph}}$) 1095(m). $^{31}$P NMR (dmoso-d$_6$, δ ppm): 2.70, 29.33 ppm, ∆δ(δ$_{\text{complex}}$ - δ$_{\text{ligand}}$) = 8.2, 34.8 ppm.

$[\text{Ag}_2(\mu-S-$tzdSH$)(\eta^1-S-$tzdSH$_2)(\text{PPh}_3)_2](\text{NO}_3)_2$ (60)

To a solution of AgNO$_3$ (0.025 g, 0.15 mmol) in acetonitrile was added a solution of thiazolidine-2-thione (0.035 g, 0.30 mmol) in acetonitrile.
acetonitrile followed by stirring for 1h at room temperature. To the precipitates formed was added PPh₃ (0.038 g, 0.15 mmol) and slow evaporation of solution at room temperature formed yellow prismatic crystals of 60 (Yield 67%, M.p. 163-165°C). Anal. Calcd for C₂₄H₂₂AgN₃O₃PS₄ (%): C, 42.94; H, 3.73; N, 6.26; Found: C, 43.06; H, 4.08; N, 6.41. Main IR peaks (KBr, cm⁻¹): ν(N−H) 3080(br); ν(C−H) 3010–2940(br); ν(C−N) + δ(C/H) 1535–1438(s); ν(P/C₆H₅) 1105(m); ν(C=S) 992(s).

1H NMR data (CDCl₃, δ ppm): 10.66 bs (1H, NH), 3.46 t (2H, J = 7.8, 8.1 Hz, C₄H), 3.96 t (2H, J = 7.8, 8.4 Hz, C₅H), 7.22 – 7.48 m (15H + 1H, PPh₃, CHCl₃).

13C NMR data (CDCl₃, δ ppm): 199.9 (C₂, tzdSH), 52.4 (C₅, tzdSH), 33.5 (C₄, tzdSH), 133.5 (o/C, J = 16.12 Hz, P/Ph), 131.4 (i/C, J = 27.15 Hz, P/Ph), 130.2 (p/C, P/Ph), 128.8 (m/C, J = 9.90 Hz, P/Ph).

31P NMR (CDCl₃, δ ppm): 6.64 ppm, ∆δ(δ_complex/δ_PPh₃) = 11.34 ppm.

To a solution of AgNO₃ (0.025 g, 0.15 mmol) in acetonitrile was added a solution of imidazolidine-2-thione (0.030 g, 0.30 mmol) in acetonitrile followed by stirring for 1h at room temperature. To the precipitates formed was added PPh₃ (0.076 g, 0.30 mmol) and MeOH. The slow evaporation of solution at room temperature formed colorless prismatic crystals of 61 (Yield 63%, M.p. 188-190°C). Anal. Calcd for C₅₀H₅₄Ag₂N₁₀O₄P₂S₄ (%): C, 45.14; H, 4.06; N, 10.53. Found: C, 45.26; H, 4.14; N, 10.67. Main IR peaks (KBr, cm⁻¹): ν(O−H) 3410(br); ν(N−H) 3247(br); ν(C−H) 3049–2892(m); ν(C−N) + δ(C/H) 1529(s), 1434(sh); ν(C=S) 1197(s), 995(m), 914(s); ν(P/Ph) 1094(m). 31P NMR (dmso-d₆, δ ppm): 7.81 ppm, ∆δ(δ_complex/δ_PPh₃) = 13.28 ppm.

To a solution of AgNO₃ (0.025 g, 0.15 mmol) in acetonitrile was added a solution of imidazoline-2-thione (0.014 g, 0.30 mmol) in acetonitrile followed by stirring for 1h at room temperature. To the precipitates formed was added PPh₃ (0.076 g, 0.30 mmol) and MeOH. The slow evaporation of solution at room temperature formed colorless prismatic crystals of 62.
methanol followed by stirring for 1h at room temperature. To the precipitates formed was added PPh₃ (0.076 g, 0.30 mmol). The slow evaporation of solution at room temperature formed pale yellow prismatic crystals of 62 (Yield 63%, M.p. 145-147°C). Anal. Calcd for C₂₅H₂₇AgN₅O₄PS₂ (%) : C, 45.15; H, 4.06; N, 10.53; Found: C, 45.06; H, 4.13; N, 10.45. ³¹P NMR (dmsod₆, δ ppm): δ = 7.90 ppm, Δδ(δ_complex - δ_PPh₃) = 13.35 ppm.

[Ag(q¹-S-mimzSH)₂(PPh₃)](NO₃) (63)

To a solution of AgNO₃ (0.025 g, 0.15 mmol) in acetonitrile was added a solution of 1-methyl-imidazoline-2-thione (0.033 g, 0.30 mmol) in acetonitrile followed by stirring for 1h at room temperature. To the precipitates formed was added PPh₃ (0.076 g, 0.30 mmol). The slow evaporation of solution at room temperature formed colorless crystals of 63 (Yield 38%, M.p. 147-150°C). Anal. Calcd for C₅₂H₅₄Ag₂N₁₀O₆P₂S₄ (%) : C, 47.27; H, 4.09; N, 10.61; Found: C, 43.06; H, 4.08; N, 6.41. Main IR peaks (KBr, cm⁻¹): ν(N–H) 3131(m); ν(C–H) 3013–2903(m); ν(C–N) + δ(C–H) 1575(s), 1477(s); ν(P–C₆H₅) 1092(s); δ(N–CH₃) 750(m). ³¹P NMR (dmsod₆, δ ppm): 8.90, 28.08 ppm, Δδ(δ_complex - δ_PPh₃) = 14.37, 33.55 ppm.

[Ag(η¹-S-imdzSH-Me)₂(PPh₃)](NO₃) (64)

To a solution of AgNO₃ (0.025 g, 0.15 mmol) in acetonitrile was added a solution of 1-methyl-imidazolidine-2-thione (0.034 g, 0.30 mmol) in acetonitrile followed by stirring for 1h at room temperature. To the precipitates formed was added PPh₃ (0.076 g, 0.30 mmol) and slow evaporation of solution at room temperature formed colorless crystals of 64 (Yield 66%, M.p. 158-160°C). Anal. Calcd for C₂₆H₃₁AgN₅O₃PS₂ (%) : C, 46.99; H, 4.67; N, 10.54; Found: C, 46.91; H, 4.82; N, 10.28. Main IR peaks (KBr, cm⁻¹): ν(N–H) 3213(br); ν(C–H) 3048-2896(w); ν(C–N) + δ(C–H) 1510(s), 1476(sh); ν(C=S) 1182(m); ν(P–C₆H₅) 1092(s); δ(N–CH₃) 995(w). ¹H NMR data (CDCl₃, δ ppm): 8.44 bs (1H, NH), 3.61 m (4H, C₄,5H), 3.09 s (3H, CH₃), 7.32 - 7.45 m (15H, PPh₃). ³¹P NMR (CDCl₃, δ ppm): 7.97 ppm, Δδ(δ_complex - δ_PPh₃) = 13.4 ppm.
[Ag(bzimzSH)(PPh$_3$)$_2$](NO$_3$) (65)

To a solution of AgNO$_3$ (0.025 g, 0.15 mmol) in acetonitrile was added benzimidazoline-2-thione (0.044 g, 0.30 mmol) followed by stirring for 2h at room temperature. To the precipitates formed was added PPh$_3$ (0.076 g, 0.30 mmol) and slow evaporation of solution at room temperature formed peach color crystals of 65 (Yield 68%, M.p. 195-197°C). Anal. Calcd for C$_{43}$H$_{36}$AgN$_3$O$_3$P$_2$S (%): C, 61.14; H, 4.27; N, 5.00; Found: C, 61.68; H, 4.42; N, 5.30. Main IR peaks (KBr, cm$^{-1}$): $\nu$(N−H) 3160(w); $\nu$(C−H) 3052–2856(w); $\nu$(C−N) + $\delta$(C/H) 1511(s), 1460(s); $\nu$(C=S) 1170(s). $^{31}$P NMR (CDCl$_3$, δ ppm): 7.70 ppm, $\Delta$δ(δ$_{\text{complex}}$ - δ$_{\text{PPh}_3}$) = 13.15 ppm.

[Ag(η$^1$-S-tzdSH)(η$^1$-S-tzdS)(PPh$_3$)$_2$] (66)

To a solution of silver(I) acetate (0.025 g, 0.15 mmol) in acetone was added a solution of thiazolidine-2-thione (0.035 g, 0.30 mmol) in acetonitrile followed by stirring for 1h at room temperature. To the precipitates formed was added PPh$_3$ (0.078 g, 0.30 mmol). Slow evaporation of solution at room temperature formed chunk pale yellow crystals of 66 (Yield 65%, M.p. 140-145°C). Anal. Calcd for C$_{42}$H$_{39}$AgN$_2$P$_2$S$_4$ (%): C, 57.94; H, 4.48; N, 3.22; Found: C, 57.82; H, 4.42; N, 3.18. Main IR peaks (KBr, cm$^{-1}$): $\nu$(N−H) 3070(w), $\nu$(C−H) 3046–2940(w), $\nu$(C−N) + $\delta$(C-H) 1538(s), 1478(sh), $\nu$(P-C$_{\text{ph}}$) 1092(m), $\nu$(C=S) 997(s). $^1$H NMR data (CDCl$_3$, δ ppm): 3.43 t (2H, J = 7.5, 8.1 Hz, C$_4$H), 3.92 t (2H, J = 7.5, 8.1 Hz, C$_5$H), 7.25 – 7.46 m (15H + 1H, PPh$_3$, CHCl$_3$). $^{31}$P NMR (CDCl$_3$, δ ppm): -2.42 ppm, $\Delta$δ(δ$_{\text{complex}}$ - δ$_{\text{ligand}}$) = 2.28 ppm.
To a solution of silver(I) acetate (0.025 g, 0.15 mmol) in acetone was added a suspension of benzimidazoline-2-thione (0.045 g, 0.30 mmol) in acetonitrile followed by stirring for 2h at room temperature. To the precipitates formed was added PPh₃ (0.078 g, 0.30 mmol). Slow evaporation of solution at room temperature formed colorless crystals of complex 67 (Yield 67%, M.p. 135-137°C). Anal. Calcd for C₅₂H₄₇AgN₄O₃P₂S₂ (%): C, 61.79; H, 4.65; N, 5.54; Found: C, 61.73; H, 4.52; N, 5.31. Main IR peaks (KBr, cm⁻¹): υ(O–H) 3432(br); υ(N–H) 3141(w); υ(C–H) 3065–2848(w); υ(C–N) + δ(C/H) 1547(m), 1462(s); υ(C=S) 1167(s); υ(P/CPh) 1095(s). ¹H NMR data (CDCl₃, δ ppm): 7.59 – 7.68 m (o/H), 7.45 – 7.57 m (p/H), 7.07 – 7.37 m (m/H, C₄/7H, bzimzSH).

To a solution of silver(I) acetate (0.025 g, 0.15 mmol) in acetone was added a solution of 1-methyl-imidazolidine-2-thione (0.034 g, 0.30 mmol) in acetonitrile followed by stirring for 1h at room temperature. To the precipitates formed was added PPh₃ (0.039 g, 0.15 mmol). Slow evaporation of solution at room temperature formed colorless crystals of complex 68 (Yield 67%, M.p. 161-164°C). Anal. Calcd for C₄₅H₄₈Ag₂Cl₂N₄P₂S₂ (%): C, 51.06; H, 4.54; N, 5.29; Found: C, 51.18; H, 4.52; N, 5.38. Main IR peaks (KBr, cm⁻¹): υ(N–H) 3178(m), υ(C–H) 3065-2880(w), υ(C–N) + δ(C-H) 1513(s), 1478(sh), υ(C=S) 1192(m), υ(P-CPh) 1093(s), δ(N-CH₃) 958(w). ¹H NMR data (CDCl₃, δ ppm): 9.14 bs (1H, NH), 3.70 d (4H, C⁴⁻⁵H), 3.10 s (3H, CH₃), 7.33 – 7.50 m (15H, PPh₃). ³¹P NMR (CDCl₃, δ ppm): -3.38, 26.58 ppm, Δδ(δ-complex – δ-PPh₃) = 2.07, 32.03 ppm.
Chapter 5 describes IR spectroscopy, X-ray crystallography and solution phase studies; Chapter 6 gives analysis of results i.e. offers general comments on the formation of complexes, and Chapter 7 gives summary and conclusions of the work done.