Synthesis, structure and reactivity with phosphines of Hg(II) *ortho*-cyano-aminothiophenolate complexes formed via C-S bond cleavage and dehydrogenation of 2-aminobenzothiazoles

Electronic supplementary information

Experimental section

General

^{1}H and ^{31}P{^{1}H} NMR spectra were recorded on a Varian Unity spectrometer. IR spectra were recorded on either a Shimadzu FT-IR 8400 spectrophotometer in the 400-4000 cm^{-1} range as KBr discs and in the 200-600 cm^{-1} as CsI discs or on Bruker Tensor 28 spectrometer with a platinum ATR unit in Martin-Luther Universität Halle-Wittenberg- Germany. Elemental analyses were carried out at Al Al-Bayt University, Jorden using a Euro vector EURO EA300 elemental analyzer. Melting points measured on a Gallenkamp melting point apparatus and are uncorrected. All commercially pure chemicals were used as received from distributor.

Synthesis of $[Hg\{SC_6H_3XN(C\equiv N)\}]_n$ (1a-e) (X = H, Me, Cl, Br, NO_2) ***(1a-e)***

A solution of 2-aminobenzothiazole (abt) (0.200 g, 1.330 mmol) in ethanol (10 ml) was added to a boiling solution of $Hg(OAc)_2$ (0.420 g, 1.330 mmol) in ethanol (10 ml). The mixture was heated at reflux for 2 h affording a pale-yellow precipitate. Upon cooling to room temperature this was collected by filtration, washed with ethanol and dried under vacuum to afford **1a**. Alternatively, sodium acetate (0.028 g, 0.349 mmol) in distilled water (10 ml) was added to a suspension of $[Hg(abt)Cl_2]_n$ (0.050 g, 0.087 mmol) in distilled water (10 ml). The mixture was heated under reflux for 2 h to afford a pale-yellow precipitate, which was filtered off, washed with ethanol and dried under vacuum. **1b-e** were prepared and isolated using similar methods.

1a: Yellow, yield: 0.398g (86%). Anal. Calc. for $C_7H_4HgN_2S$: C, 24.11; H, 1.16; N, 8.03. Found: C, 24.17; H, 1.22; N, 7.84%. IR (KBr): 3066m, 2119vs, 1577m, 1471s, 1433m, 746m, 665m cm^{-1}. ^{1}H NMR (DMSO-d^{6}): δ 6.72 (t, 1H, *J* 7.6 Hz); 7.07 (d, 1H, *J* 7.6 Hz); 7.13 (t, 1H, *J* 7.6 Hz); 7.55 (d, 1H, *J* 7.6 Hz) ^{13}C{^{1}H} NMR (DMSO-d^{6}): 111.3, 117.5, 121.4, 125.1, 127.7, 132.7, 144.5 ppm. Melting point: 228^{o}C (decomposes).

1b: Yellow, yield: 1.616 g (73%). Anal. Calc. for $C_8H_6HgN_2S$: C, 26.49; H, 1.67; N, 7.72. Found: C, 26.57; H, 1.72; N, 7.78%. IR: 3024w, 2974w, 2139vs, 1521s, 314m, 273m, cm^{-1}.^{1}H NMR (DMSO-d^6): δ 2.29 (s, 3H, CH_3); 6.89-6.96 (m, 2H); 7.37 (d, 1H, *J* 8.0 Hz). Melting point: 200°C (decomposes).

1c: Yellow, yield: 1.710 g (73%). Anal. Calc. for $C_7H_3ClHgN_2S$: C, 21.94; H, 0.79; N, 7.31. Found: C, 21.66; H, 0.72; N, 7.24%. IR: 3049w, 2136vs, 1519s, 293m, 258m cm^{-1}.^{1}H NMR (DMSO-d^6): δ 7.05 (d, 1H, *J* 7.9 Hz); 7.15 (d, 1H, *J* 7.9 Hz); 7.56 (s, 1H). Melting point: 207-210°C (decomposes).

1d: Olive, yield: 0.709 g (95%). Anal. Calc. for $C_7H_3BrHgN_2S$: C, 19.66; H, 0.71; N, 6.55. Found: C, 19.39; H, 1.01; N, 6.38 %. IR (KBr): 3029w, 2119vs, 1624s, 1461m, 746m, 675m cm^{-1}. ^{1}H NMR (DMSO-d^6): δ 6.34 (d, 1H, *J* 7.5 Hz); 6.9 (dd, 1H, *J* 7.5, 1.9 Hz); 7.15 (d, 1H, *J* 7.5 Hz) ppm. $^{13}C\{^1H\}$ NMR (DMSO-d^6): 110.73, 115.6, 117.5, 125.7, 130.3, 131.9, 141.7 ppm. Melting point: 247-249^{o}C (decomposes).

1e: Burnt yellow, yield: 2.185 g (91%). Anal. Calc. for $C_7H_3HgN_3O_2S$: C, 21.35; H, 0.77; N, 10.67. Found: C, 21.39; H, 0.91; N, 10.38 %. IR (KBr): 3029w, 2119vs, 1624s, 1461m, 746m, 675m cm^{-1}. ^{1}H NMR (DMSO-d^6): δ 7.15 (d, 1H, *J* 8.0 Hz); 7.41 (d,1H, *J* 8.0 Hz); 7.98 (s, 1H) ppm. Melting point: 222-224^{o}C (decomposes).

*Synthesis of $[Hg(\mu\text{-}abt\text{-}H)(\kappa^2\text{-}OAc)(EtOH)]_2$ (**3**)*

A suspension of $Hg(OAc)_2$ (1.061 g, 3.320 mmol) in ethanol (10 ml) was added to a solution of 2-aminobenzothiazole (0.50 g, 3.320 mmol) in ethanol (10 ml). The mixture was stirred for 2 h in an ice bath. The pale-yellow solution formed was set aside for a day. Yellow crystals formed which were isolated and dried under vacuum.

3: Yield: 1.134g (75%). Anal. Calc. for $C_{22}H_{30}Hg_2N_4O_6S_2$: C, 29.98; H, 3.32; N, 6.14. Found: C, 28.91; H, 3.03; N, 6.00 %. IR (KBr): 3427m, 3371m, 3027w, 2972w, 2121vw, 1595m, 1554m, 1525vs, 1461m, 1413m, 740m, 669m cm^{-1}. ^{1}H NMR (DMSO-d^6): δ 1.13 (s, 3H, CH_3); 3.57 (s, 2H, CH_2); 3.6 (s, 1H, NH); 6.99 (dt, 1H, *J* 7.5, 1.3 Hz); 7.19 (dt, 1H, *J* 7.5 1.3 Hz); 7.32 (dd, 1H, *J* 7.8, 1.2 Hz); 7.52 (dd, 1H, *J* 7.6, 1.2 Hz) ppm. Melting point: 225-227^{o}C (decomposes).

*Preparation of $[Hg\{SC_6H_3XN(C{\equiv}N)\}(PPh_3)]_2$ (**4a-e**)*

A solution of PPh_3 (0.300 g, 1.143 mmol) in $CHCl_3$ (10 ml) was added to a suspension of **1a** (0.199 g, 0.571 mmol) in $CHCl_3$ (10 ml). The mixture was stirred at room temperature for 2 h and the green-yellow solution formed was refluxed for another 2 h. A green-yellow precipitate formed which was filtered off, dried under vacuum, and then recrystallized from $CHCl_3$, to give yellow needle-like crystals of **4a**. Complexes **4b-e** were prepared and isolated using similar methods.

4a: Yellow, yield: 0.607g (83%). Anal. Calc. for $C_{25}H_{19}HgN_2PS.CHCl_3$: C, 42.75; H, 2.76; N, 3.84: C, 42.66; H, 2.85; N, 3.89 %. IR (KBr): 3053w, 2140vs, 1465s, 1433s, 744s, 692s cm^{-1}. ^1H NMR ($CDCl_3$): δ 6.35 (dt, 1H, *J* 7.4, 1.4 Hz); 6.55 (dd, 1H, *J* 7.1, 1.4 Hz); 6.92 (dt, 1H, *J* 7.1, 1.6 Hz); 7.38-7.63 (m, 16H, Ph and H) ppm. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 36.5 (brs) ppm. Melting point: 210-213°C.

4b: Dark yellow, yield: 0.189 g (78%). Anal. Calc. for $C_{26}H_{21}HgN_2PS$: C, 49.96; H, 3.39, N, 4.48. Found: C, 49.76; H, 3.29; N, 4.44 %. IR: 3064w, 2903w, 2142vs, 1562s, 1433s, 495s cm^{-1}. ^1H NMR ($CDCl_3$): δ 2.13 (s, 3H, CH_3); 6.64 (dd, 1H, *J* 8.0, 1.8 Hz); 6.93 (d, 1H, *J* 8.0 Hz); 7.12 (s, 1H); 7.48-7.62 (m, 15H, Ph) ppm. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 25.4 (brs) ppm. Melting point: 227-230°C.

4c: Yellow, yield: 0.142 g (60%). Anal. Calc. for $C_{25}H_{18}ClHgN_2PS.2CHCl_3$: C, 46.52; H, 2.81, N, 4.34. Found: C, 46.72; H, 3.01; N, 4.59 %. IR (KBr): 3058w, 2142vs, 1549s, 1433s, 493s cm^{-1}. ^1H NMR ($CDCl_3$): δ 6.56 (dd, 1H, *J* 8.0, 1.4 Hz); 6.82 (dd, 1H, *J* = 8.0, 1.4 Hz); 7.21 (s, 1H); 7.36-7.47 (m, 15H, Ph) ppm. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 29.0 (brs) ppm. Melting point: 212-213°C.

IR (KBr): 3072w, 2163vs, 2142vs, 1460vs, 1434vs, 1317s, 1099s, 746s, 688s cm^{-1}. ^1H NMR ($CDCl_3$): δ 6.75 (s, 1H); 6.94 (dd, 1H, *J* 8.5, 2.1 Hz); 7.13 (d, 1H, *J* 8.8 Hz); 7.3-7.70 (m, 15H, Ph) ppm. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 25.5 (brs) ppm. Melting point: 177-180°C.

4e: Brown-yellow, yield: 0.182 g (68%). Anal. Calc. for $C_{25}H_{18}HgN_3PO_2S.CHCl_3$: C, 40.27; H, 2.47; N, 5.42. Found: C, 40.17; H, 2.49; N, 5.51%. IR (KBr): 3055w, 2136vs, 1460vs, 1434vs, 1301vs (NO_2), 501s cm^{-1}. ^1H NMR ($CDCl_3$): δ 7.19-7.74 (m, 18H, Ph and H) ppm. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 35.6 (brs) ppm. Melting point: 181-184°C.

*Preparation of [Hg{$SC_6H_4N(C\equiv N)$}$(PPh_3)_2$] (**5**)*

A solution of PPh_3 (0.100 g, 0.380 mmol) in $CHCl_3$ (10 ml) was added to a suspension of **1a** (0.063 g, 0.190 mmol) in $CHCl_3$ (10 ml). The mixture was stirred at room temperature for 20

mins and reflux on water bath for 2 h, the mixture was left to evaporate the solvent and the yellow precipitate formed was filtered off and dried under vacuum. (Yield: 0.058 g, 35%).

5: Yellow, yield: 0.058 g (35%). Anal. Calc. for $C_{43}H_{34}HgP_2N_2S$: C, 59.14; H, 3.92; N, 3.21. Found: C, 58.89; H, 4.21; N, 3.28%. IR (KBr): 3053w, 2140vs, 1465s, 1434s, 1313m, 1101m, 748vs, 688m cm^{-1}. ^1H NMR ($CDCl_3$): δ 6.33 (t, 1H, *J* 6.8 Hz); 6.51 (d, 1H, *J* 7.5 Hz); 6.91 (dt, 1H, *J* 7.5, 1.6 Hz); 7.37-7.64 (m, 31H, Ph and H) ppm. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 29.2 ppm. Melting point: 212-215°C.

*Synthesis of [Hg{$SC_6H_3XN(C{\equiv}N)$}(κ^1-dppm)]$_2$ (**6a-d**)*

A solution of dppm (0.024 g, 0.062 mmol) in ethanol (10 ml) was added to a suspension of **1a** (0.021 g, 0.062 mmol) in ethanol (10 ml) and stirred at room temperature for 2 h. The green-yellow precipitate formed was filtered off, dried under vacuum, and recrystallized from $CHCl_3$ to give yellow crystals. Complexes **6b-d** were prepared using a similar method.

6a: Yellow, yield: 0.032 g (71%). Anal. Calc. for $C_{32}H_{21}HgN_2P_2S$: C, 52.79; H, 2.91; N, 3.85. Found: C, 52.71; H, 3.07; N, 3.87%. IR (KBr): 3051w, 2933w, 2155vs, 1463s, 1433s, 1301s, 1101m, 742vs, 690s cm^{-1}. ^1H NMR ($CDCl_3$): δ 4.0 (bs, 2H, CH_2); 6.55 (t, 1H, *J* 7.5 Hz); 6.84 (t, 1H, *J* 7.5 Hz); 7.06 (d, 1H, *J* 7.5 Hz); 7.28 (d, 1H, *J* 7.5 Hz); 7.31-7.64 (m, 20H, Ph) ppm. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ -2.6 (d, J 29 Hz), 9.9 (d, J 29 Hz) ppm. Melting point: 169-172°C.

6b: Yellow, yield: 0.456 g (78%). Anal. Calc. for $C_{33}H_{28}HgN_2P_2S$: C, 53.05; H, 3.78; N, 3.75. Found: C, 52.86; H, 3.53; N, 3.51%. IR: 3029w, 2923w, 2140vs, 1539s, 1434s, 503s, 351m, 254w cm^{-1}. ^1H NMR ($CDCl_3$): δ 2.36 (s, 3H, CH_3); 4.23 (brs, 2H, CH_2); 7.11-8.00 (m, 23H, Ph and H). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ -2.6 (d, *J* 29 Hz), 10.1 (d, J 29 Hz) ppm. Melting point: 102-103°C.

6c: Yellow, yield: 0.384 g (64%). Anal. Calc. for $C_{32}H_{25}ClHgN_2P_2S$: C, 50.07; H, 3.28; N, 3.65. Found: C, 49.98; H, 3.13; N, 3.52%. IR: 3083w, 2893w, 2138vs, 1539s, 1434s, 503s, 349m, 312m, 258w cm^{-1}. ^1H NMR ($CDCl_3$): δ 4.45 (brs, 2H, CH_2) ; 6.87-7.93 (m, 23H, Ph). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ -1.6 (d, *J* 31 Hz), 15.8 (d, *J* 31 Hz) ppm. Melting point: 114-117°C.

6d: Red-yellow, yield: 0.192 g (84%). Anal. Calc. for $C_{32}H_{25}HgN_3O_2P_2S$: C, 49.39; H, 3.24; N, 5.40. Found: C, 49.58; H, 3.51; N, 5.71 %. IR: 3055w, 2950w, 2136vs, 1460s, 1434s, 1301vs (NO_2), 503s, 351m cm^{-1}. ^1H NMR ($CDCl_3$): δ 3.73 (brs, 2H, CH_2); 7.15 (d, 1H, *J* 8.0 Hz); 7.28-7.43 (m, 20H, Ph); 7.73 (d, 1H, *J* 8.0 Hz); 7.83 (s, 1H). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ -6.0 (d, *J* 23 Hz), 13.1 (d, *J* 23 Hz) ppm. Melting point: 298-301°C.

Synthesis of [Hg_2(μ-Cl)(μ-dppm)$_2Cl_2$]Cl

Boiling **6a** in $CHCl_3$ for 8 h produced green-yellow crystals. X-ray diffraction showed that the product was [Hg_2(μ-Cl)(μ-dppm)$_2Cl_2$]Cl. This complex has previously been prepared *via* a quite different method [**1**].

*Synthesis of [Hg{$SC_6H_3XN(C{\equiv}N)$}(κ^1,κ^1-dppe)]$_n$ (**7a-d**)*

A solution of dppe (0.300 g, 1.143 mmol) in $CHCl_3$ (10 ml) was added to a suspension of **1a** (0.199 g, 0.571 mmol) in $CHCl_3$ (10 ml). The mixture was stirred at room temperature for 2 h. The green-yellow solution formed was further refluxed for 2 h. A green-yellow precipitate formed which was filtered off, dried under vacuum and recrystallized from $CHCl_3$ to give yellow needle-like crystals.

7a: Yield: 0.342 g (80%). Anal. Calc. for $C_{33}H_{28}HgN_2P_2S$: C, 53.05; H, 3.78, N, 3.75. Found: C, 53.11; H, 3.83; N, 3.59%. IR (KBr): 3051w, 2904, 2142vs, 1461s, 1434vs, 1294m, 1103m, 744s, 692m cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 2.67 (bs, 4H, 2CH_2); 7.12 (dt, 1H, *J* 7.8, 1.2 Hz); 7.58 (dd, 1H, *J* 7.8, 0.9 Hz); 7.28-7.56 (m, 22H, Ph and H) ppm. ^{31}P{^{1}H} NMR ($CDCl_3$): δ 23.7 (s) ppm. Melting point: 210-213^{o}C.

For **7b-d** similar methods were followed but the products were recrystallised from dmf to give analytically dmf adducts.

7b: Yellow, yield: 0.115 (79%). Anal. Calc. for $C_{48}H_{48}Hg_2N_6O_2P_2S_2$: C, 45.46; H, 3.81; N, 6.63. Found: C, 45.68; H, 3.93; N, 6.72%. IR: 3055w, 2914w, 2135vs, 1527s, 1436s, 509s, 337m, 300m, 243w cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 2.11 (s, 3H, CH_3); 2.63 (s, 4H, CH_2); 6.86 (dd, 1H, *J* 7.9, 1.6 Hz); 7.14 (d, 1H, *J* 8.0 Hz); 7.41 (s, 1H); 7.34-7.43 (m, 20H, Ph). ^{31}P{^{1}H} NMR ($CDCl_3$): δ 53.5 (d, *J* 29 Hz), 60.0 (d, *J* 29 Hz) ppm. Melting point: 182-185°C.

7c: Yellow, yield: 0.105 (70%). Anal. Calc. for $C_{46}H_{42}Cl_2Hg_2N_6O_2P_2S_2$: C, 42.21; H, 3.23; N, 6.42. Found: C, 42.36; H, 3.43; N, 6.76%. IR: 3055w, 2958w, 2133vs, 1564s, 1433s, 505s, 370m, 333m, 266w cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 2.86 (s, 4H, CH_2); 6.81 (dd, 1H, *J* 7.9, 1.6 Hz); 7.14 (d, 1H, *J* 7.9 Hz); 7.36-7.50 (m, 21H, Ph and H). ^{31}P{^{1}H} NMR (DMSO-d^6): δ 17.7 (d, *J* 35 Hz), 39.0 (d, *J* 35 Hz) ppm. Melting point: 181-182°C.

7d: Yellow, yield: 0.11g (67%). Anal. Calc. for $C_{33}H_{27}HgN_3O_2P_2S$: C, 50.03; H, 3.44; N, 5.30. Found C, 50.28; H, 3.51; N, 5.42: %. IR (KBr): 3058w, 2968w, 2142vs (CN), 1460s, 1434s, 1292vs (NO_2), 508s cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 2.23 (s, 4H, CH_2); 7.21-7.98 (m, 23H, Ph and

H). $^{31}P\{^{1}H\}$ NMR ($CDCl_3$): δ 36.5 (d, *J* 34 Hz), 45.5 (d, *J* 34 Hz) ppm . Melting point: >300°C (decomposes).

Synthesis of [Hg{$SC_6H_3XN(C{\equiv}N)$}(μ-dppp)]$_2$ ***(8a-d)***

A solution of dppp (0.106 g, 0.242 mmol) in ethanol (10 ml) was added to a suspension of **1a** (0.084 g, 0.242 mmol) in ethanol (10 ml). The mixture was stirred at room temperature for 2 h and the resulting green-yellow solution left to slowly evaporation at room temperature to give pale yellow solid which was filtered off and dried under vacuum.

8a: Yield: 0.150 g (80%). Anal. Calc. for $C_{34}H_{30}HgN_2P_2S$: C, 53.65; H, 3.97, N, 3.68. Found: C, 53.85; H, 3.93; N, 3.57%. IR (KBr): 3051w, 2921w, 2121vs, 1465s, 1433s, 1303s, 1101m, 744s, 694m cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 1.26 (t, 4H, *J* 7.0 Hz, $2CH_2$); 3.73 (m, 2H, CH_2); 6.53 (t, 1H, *J* 7.4 Hz); 6.78 (t, 1H, *J* 7.4 Hz); 7.12 (d, 1H, *J* 7.4 Hz); 7.24 (d, 1H, *J* 7.4 Hz); 7.33-7.47 (m, 20H, Ph) ppm. $^{31}P\{^{1}H\}$ NMR: δ 15.0 (bs) ppm. Melting point: 162-164^{o}C.

8b: Yellow, yield: 0.214 (78%). Anal. Calc. for $C_{43}H_{38}Hg_2N_4P_2S_2$: C, 45.38; H, 3.37; N, 4.92. Found: C, 45.46; H, 3.66; N, 5.08%. IR: 3053w, 2908w, 2121vs, 1562s, 1434s, 513s, 349m, 310m, 268w cm^{1}. ^{1}H NMR ($CDCl_3$): δ 1.80 (bs, 2H, CH_2); 2.89 (s, 3H, CH_3); 3.19 (bs, 4H, $2CH_2$); 6.92 (d, 1H, *J* 7. 8 Hz); 7.13 (d, 1H, *J* 7.8 Hz); 7.22 (s, 1H); 7.51-7.78 (m, 20H, Ph). $^{31}P\{^{1}H\}$ NMR ($CDCl_3$): δ 27.5 (d, *J* 36 Hz), 36.5 (d, *J* 36 Hz) ppm. Melting point: 108-111°C.

8c: Light yellow, yield: 0.202 (71%). Anal. Calc. for $C_{41}H_{32}Cl_2Hg_2N_4P_2S_2$: C, 41.77; H, 2.74; N, 4.75. Found: C, 41.46; H, 2.66; N, 4.48%. IR: 3053w, 2898w, 2115vs, 1545m, 1433s, 511s, cm^{1}. ^{1}H NMR ($CDCl_3$): δ 1.90 (bs, 2H, CH_2); 3.09 (bs, 4H, $2CH_2$); 6.72 (dd, 1H, *J* 8.0, 1.5 Hz); 6.82 (d, 1H, *J* 8.0 Hz); 7.22 (s, 1H); 7.51-7.78 (m, 20H, Ph). $^{31}P\{^{1}H\}$ NMR ($CDCl_3$): δ 21.5 (d, *J* 41 Hz), 36.5 (d, *J* 41 Hz) ppm. Melting point: 219-220°C.

8d: Brown, yield: 0.218 (75%). Anal. Calc. for $C_{41}H_{32}Hg_2N_6O_4P_2S_2$: C, 41.04; H, 2.69; N, 7.00. Found: C, 41.23; H, 2.81; N, 7.13%. IR: 3082w, 2911w, 2120vs, 1544m, 1436s, 505s, cm^{1}. ^{1}H NMR ($CDCl_3$): δ 1.81 (bs, 2H, CH_2); 2.76 (bs, 4H, $2CH_2$); 6.72-7.78 (m, 23H, Ph and H). $^{31}P\{^{1}H\}$ NMR ($CDCl_3$): δ 42.0 (bs) ppm. Melting point: 197-198°C.

Preparation of [Hg{$SC_6H_3XN(C{\equiv}N)$}(μ-κ^1,κ^1-dppb)] ***(9a-d)***

Prepared in a similar manner to that described above for dppp

9a: Cream, yield: 0.44g (65%). Anal. Calc. for $C_{35}H_{32}HgN_2P_2S$: C, 54.23; H, 4.16; N, 3.61. Found: C, 54.39; H, 4.14; N, 3.55%. IR (KBr): 3053w, 2918w, 2144vs, 1465s, 1433m, 1301m,

1105m, 746m, 688w cm^{-1}. ^1H NMR ($CDCl_3$): δ 1.80 (bs, 4H, $2CH_2$); 3.12 (bs, 4H, $2CH_2$); 6.58 (t, 1H, *J* 7.8 Hz); 6.86 (t, 1H, *J* 7.5 Hz); 7.07 (d, 1H, *J* 7.5 Hz); 7.31 (d, 1H, *J* 7.8 Hz); 7.59-7.88 (m, 20H, Ph) ppm. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 43.3 (bs) ppm. Melting point: 244-246°C.

9b: Yellow, yield: 0.436 g (81%). Anal. Calc. for $C_{36}H_{34}HgN_2P_2S$: C, 54.78; H, 4.34; N, 3.55 Found: C, 54.99; H, 4.14; N, 3.71%. IR: 3053w, 2929w, 2144vs, 1539s, 1434s, 509s, cm^{-1}. ^1H NMR ($CDCl_3$): δ 1.84 (bs, 4H, $2CH_2$); 2.56 (bs, 4H, $2CH_2$); 2.56 (s, 3H, CH_3); 7.00 (d, 1H, *J* 8.0 Hz); 7.13 (d, 1H, *J* 8.0 Hz); 7.39 (s, 1H); 7.40-7.78 (m, 20H, Ph) ppm. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 0.2 (d, *J* 30 Hz), 15.8 (d, *J* 30 Hz) ppm. Melting point: 215-218°C.

9c: Light yellow, yield: 0.436 g (79%). Anal. Calc. for $C_{35}H_{31}ClHgN_2P_2S$: C, 51.92; H, 3.86; N, 3.46. Found: C, 52.03; H, 3.81; N, 4.62%. IR: 3051w, 2929w, 2135vs, 1562s, 1433s, 511s, cm^{-1}. ^1H NMR ($CDCl_3$): δ 1.81 (bs, 4H, $2CH_2$); 2.38 (bs, 4H, $2CH_2$); 6.84 (dd,1H, *J* 8.0 1.4 Hz); 6.98 (d, 1H, *J* 8.0 Hz); 7.27 (s, 1H); 7.45-7.81 (m, 20H, Ph) ppm. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 23.4 (d, *J* 30 Hz), 29.6 (d, *J* 30 Hz) ppm. Melting point: 226-228°C.

9d: Brown-yellow, yield: 0.120 g (72%). Anal. Calc. for $C_{35}H_{31}HgN_3O_2P_2S$: C, 51.25; H, 3.81; N, 5.12. Found: C, 51.11; H, 3.77; N, 5.22%. IR: 3050w, 2899w, 2141vs, 1476s, 1434s, 506s, cm^{-1}. ^1H NMR ($CDCl_3$): δ 1.92 (bs, 4H, $2CH_2$); 2.62 (bs, 4H, $2CH_2$); 6.87-7.81 (m, 23H, Ph and H) ppm. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 3.7 (d, *J* 30 Hz), 24.3 (d, *J* 30 Hz) ppm. Melting point: 256-260°C.

*Preparation of [Hg{$SC_6H_3XN(C{\equiv}N)$}(dppf)] (**10a, 10e**)*

A solution of dppf (0.318 g, 0.573 mmol) in ethanol (10 ml) was added to a suspension of **1a** (0.200 g, 0.573 mmol) in ethanol (10 ml). The mixture was stirred at room temperature for 2 h and the resulting brownish-yellow solution left to slowly evaporation at room temperature to give brown- yellow solid which was filtered off and dried under vacuum. Complex **10e** was prepared and isolated using a similar method.

10a: Brown-yellow, yield: 0.368 g (71%). Anal. Calc. for $C_{41}H_{32}FeHgN_2P_2S$: C, 54.53; H, 3.57; N, 3.10. Found: C, 54.64; H, 3.75; N, 3.04%. IR (KBr): 3055w, 2144s, 1463s, 1433s, 1299m, 1099m, 746vs, 694s cm^{-1}. ^1H NMR ($CDCl_3$): δ 4.35 (brs, 4H, Cp); 4.41 (brs, 4H, Cp); 6.56 (t, 1H, *J* 7.3 Hz); 6.78 (t, 1H, *J* 7.3 Hz); 7.06 (d, 1H, *J* 7.3 Hz); 7.25 (d, 1H, *J* 7.3 Hz); 7.37-7.57 (m, 20H, Ph) ppm. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 26.1 (bs) ppm. Melting point: 160-176°C

10e: Brown-yellow, yield: 0.11 g (74%). Anal. Calc. for $C_{41}H_{31}FeHgN_3O_2P_2S$: C, 51.94; H, 3.30; N, 4.43. Found: C, 51.64; H, 3.25; N, 4.34%. IR (KBr): 3058w, 2142s, 1462s, 1436s, 1301vs (NO_2), 486m cm^{-1}. ^1H NMR ($CDCl_3$): δ 4.44 (brs, 4H, Cp); 4.51 (brs, 4H, Cp); 6.88-7.82 (m, 23H, Ph and H) ppm. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 43.4 (s) ppm. Melting point: >300 °C decomposes.

Crystallography

Crystals of **3**, **4a** and **4d** were mounted on glass fibers and all geometric and intensity data were taken from these samples using a Bruker SMART APEX CCD diffractometer with graphite-monochromater Mo-Kα radiation (ν = 0.71073 Å) at 150 ± 2 K. Data collection, indexing and initial cell refinements were done using SMART software. Data reduction was carried out with SAINT PLUS and absorption corrections applied using the programme, SADABS [**2**] [For **3**: R_{int} (before abs. correction) = 0.1329, R_{int} (after SADABS) = 0.0554, for **4a** R_{int} (before abs. correction) = 0.1211, R_{int} (after SADABS) = 0.0430, for **4d** R_{int} (before abs. correction) = 0.1849, R_{int} (after SADABS) = 0.0579]. Structures were solved by direct methods and developed using alternating cycles of least-squares refinement and difference-Fourier synthesis. All non-hydrogen atoms were refined anisotropically. Hydrogens were placed in calculated positions (riding model). Structure solution used SHELXTL PLUS V6.10 program package [**3**]. For **3**, a short intermolecular interaction (1.93 Å) is seen between H(3A) and H(9A) which results from use of the riding model to place these hydrogen atoms thus leading to an artificial short contact.

Crystals of **4b, 7b, 8b, 8c** and **9b** were mounted on a glass fiber and all geometric and intensity data were taken from this sample using a STOE-IPDS diffractometer with Mo-Kα radiation (λ = 0.7103 Å, graphite monochromator) at 213 ± 2 K or 200 ± 2 K. Absorption corrections were made using the IPDS software package [**4**]. All structures were solved by direct methods and refined using full-matrix least-square routines against F^2 with SHELXL-97 [**5**]. Non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were included in the models by calculating the positions (riding model) and refined with calculated isotropic displacement parameters. Illustrations were generated using DIAMOND 3.0 [**6**].

Crystallographic data and structure refinement details are given below. For a number of the structures there are relatively large min/max peaks remaining following refinement, which are

not unremarkable for structures with heavy atoms. The structures of **4a, 4d** and **9b** have previously be published as part of a communication [**7**]. Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre, Copies of this information may be obtained free of charge from the Director, CCDC, 12 Union Road, Cambridge, CB2 1 EZ, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.ac.uk).

The structure of **6a**.0.5 $CHCl_3$ was of poor quality but clearly shows the connectivity of the molecule which is in full accord with the NMR spectra. We thus include below a ball and stick model of this structure with some preliminary bond lengths and angles.

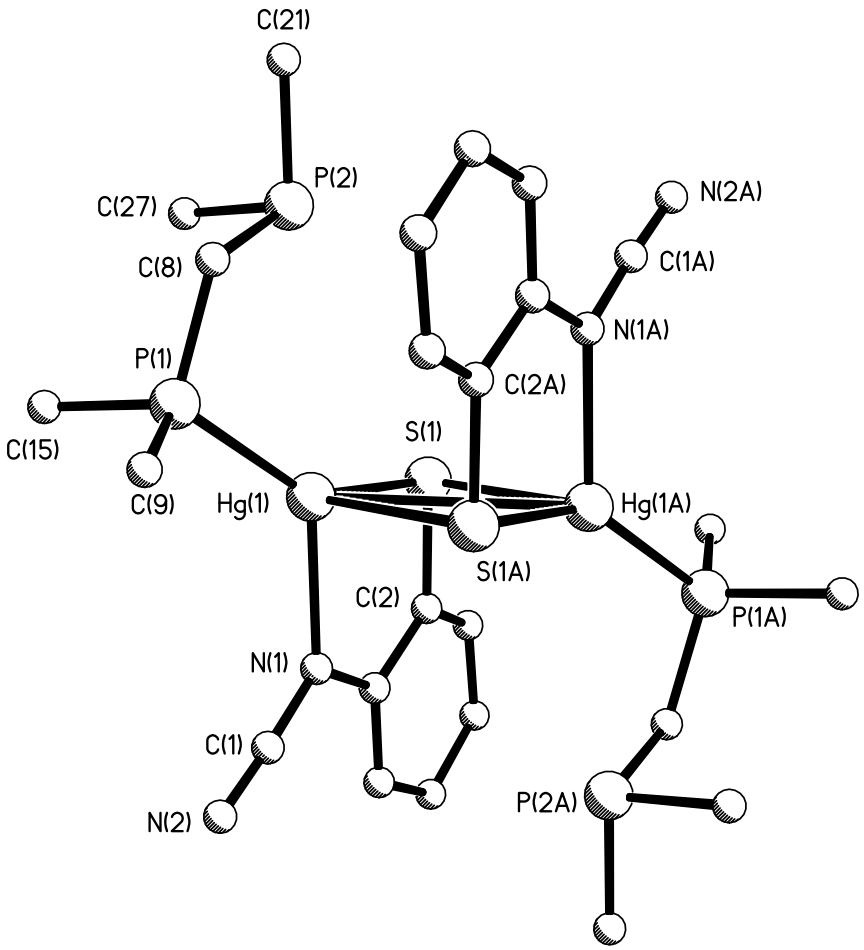

Figure ESI1. Molecular structure of [Hg{$SC_6H_4N(C{\equiv}N)$}(κ^1-dppm)]$_2$ (**6a**). Selected bond lengths (Å) and bond angles (°): Hg1-N1 2.238(10), Hg1-S1 2.414(3), Hg1-S1A 2.895(3), Hg1-P1 2.360(4), Hg1….Hg1A 3.4229(15), N1-C1 1.303(16), N2-C1 1.217(15); Hg1-S1-Hg1A

79.74(9), S1-Hg1-S1A 100.26(9), S1-Hg1-N1 81.6(3), P1-Hg-S1 145.21(13), P1-Hg1-N1 128.7(3), N1-C1-N2 177.1(17).

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	3	**4a [ref 7]**	**4b [ref 7]**
Identification code	CCDC 2112641	CCDC 934324	CCDC 2097813
Empirical formula	C_{11} H_{14} Hg N_2 O_3 S_1	C_{25} H_{19} Hg N_2 P S	C_{26} H_{21} Hg N_2 P S
Formula weight	454.89	611.04	625.07
Temperature	150(2) K	150(2) K	213(2) K
Wavelength	0.71073 Å	0.71073 Å	0.71073 Å
Crystal system, space group	monoclinic, $P2_1/c$	triclinic, P-1	triclinic, P-1
Unit cell dimensions	a = 11.161(4) Å, α = 90 deg.	a = 8.955(3) Å, α = 103.936(5) deg.	a = 9.5001(5) Å, α = 111.211(4) deg
	b = 8.363(3) Å, β = 92.388(6) deg.	b = 10.643(4) Å, β = 102.011(5) deg.	b = 11.3813(6) Å, β = 92.649(4) deg
	c = 13.481(5) Å, γ = 90 deg.	c = 12.059(4) Å, γ = 101.091(5) deg.	c = 12.3018(6) Å, γ = 104.909(4) deg.
Volume	1257.2(8) $Å^3$	1054.8(6) $Å^3$	1183.85(11) $Å^3$
Z, Calculated density	4, 2.403 Mg/m^3	2, 1.924 Mg/m^3	2, 1.754 Mg/m^3
Absorption coefficient	12.410 mm^{-1}	7.496 mm^{-1}	6.672 mm^{-1}
F(000)	856	588	604
Crystal size	0.10 x 0.09 x 0.05 mm	0.12 x 0.07 x 0.04 mm	0.26 x 0.21 x 0.10 mm
Theta range for data collection	3.04 to 28.48 deg	2.73 to 28.48 deg.	1.80 to 25.00 deg.
Limiting indices	-14<=h<=14, -11<=k<=10, -17<=l<=18	-11<=h<=11, -13<=k<=14, -15<=l<=15	-11<=h<=11, -13<=k<=13, -14<=l<=14
Reflections collected / unique	9967 / 2915 [R(int) = 0.0678]	8623 / 4657 [R(int) = 0.0392]	9054 / 4117 [R(int) = 0.0424]
Completeness to theta = 26.00	99.2 %	96.3 %	98.8 %
Max. and min. transmission	0.5380 and 0.3700	0.7539 and 0.4670	0.5225 and 0.2046
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data / restraints / parameters	2915 / 3 / 151	4657 / 0 / 271	4117 / 0 / 280
Goodness-of-fit on F^2	0.932	0.919	1.019
Final R indices [I>2sigma(I)]	R_1 = 0.0429, wR_2 = 0.0922	R_1 = 0.0377, wR_2 = 0.0647	R_1 = 0.0222, wR_2 = 0.0518
R indices (all data)	R_1 = 0.0734, wR_2 = 0.1123	R_1 = 0.0480, wR_2 = 0.0660	R_1 = 0.0268, wR_2 = 0.0552
Largest diff. peak and hole	2.42 and -2.37 e. $Å^{-3}$	1.73 and -1.73 e. $Å^{-3}$	1.02 and -0.58 e. $Å^{-3}$

	4d	**7b**	**8b**
Identification code	CCDC 934323	CCDC 2097812	CCDC 2097815
Empirical formula	C_{27} H_{20} Cl_6 Hg N_2 P S Br	C_{48} H_{48} Hg_2 N_6 O_2 P_2 S_2	C_{43} H_{38} Hg_2 N_4 P_2 S_2
Formula weight	928.68	1268.16	1138.01
Temperature	150(2) K	213(2) K	213(2) K
Wavelength	0.71073 Å	0.71073 Å	0.71073 Å
Crystal system, space group	triclinic, P-1	triclinic, P -1	triclinic, P-1
Unit cell dimensions	a = 9.444(3) Å, α = 86.793(4) deg	a = 10.1886(6) Å, α = 76.019(4) deg.	a = 12.5564(7) Å, α = 71.447(4) deg.
	b = 12.224(3) Å, β = 79.034(4) deg.	b = 10.8397(6) Å, β = 71.357(4) deg.	b = 13.6816(7) Å, β = 83.165(5) deg.
	c = 13.807(4) Å, γ = 87.326(5) deg.	c = 12.3566(6) Å, γ = 72.842(4) deg.	c = 13.8244(8) Å, γ = 64.836(4) deg.
Volume	1561.4(7) $Å^3$	1219.06(11) $Å^3$	2037.45(19) $Å^3$
Z, Calculated density	2, 1.975 Mg/m^3	1, 1.730Mg/m^3	2, 1.855 Mg/m^3
Absorption coefficient	6.862 mm^{-1}	6.484 mm^{-1}	7.743 mm^{-1}
F(000)	888	616	1092
Crystal size	0.23 x 0.18 x 0.16 mm	0.20 x 0.10 x 0.08 mm	0.26 x 0.16 x 0.11 mm
Theta range for data collection	2.42 to 28.45 deg	1.76 to 26.00 deg	1.55 to 26.00 deg.
Limiting indices	-12<=h<=12, -15<=k<=16, -17<=l<=17	-12<=h<=12, -13<=k<=13, -15<=l<=15	-15<=h<=15, -16<=k<=16, -17<=l<=17
Reflections collected / unique	12571 / 6784 [R(int) = 0.0489]	9597 / 4766 [R(int) = 0.0344]	15331 / 7898 [R(int) = 0.0700]
Completeness to theta = 26.00	96.6 %	99.2 %	98.5 %
Max. and min. transmission	0.4065 and 0.1607	0.6250 and 0.3571	0.4830 and 0.2380
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data / restraints / parameters	6784 / 0 / 352	4766 / 76 / 300	7898 / 0 / 478
Goodness-of-fit on F^2	0.942	1.003	1.011
Final R indices [I>2sigma(I)]	R_1 = 0.0449, wR_2 = 0.0945	R_1 = 0.0241, wR_2 = 0.0558	R_1 = 0.0410, wR_2 = 0.0981
R indices (all data)	R_1 = 0.0581, wR_2 = 0.0966	R_1 = 0.0298, wR_2 = 0.0578	R_1 = 0.0613, wR_2 = 0.1099
Largest diff. peak and hole	2.47 and -2.65 e. $Å^{-3}$	1.32 and -0.62 e. $Å^{-3}$	2.03 and -1.99 e. $Å^{-3}$

	8c	**9b [ref 7]**
Identification code	CCDC 2097814	CCDC 934322
Empirical formula	C_{41} H_{32} Cl_2 Hg_2 N_4 P_2 S_2	C_{36} H_{34} Hg N_2 P_2 S
Formula weight	1178.85	789.24
Temperature	213(2) K	200(2) K
Wavelength	0.71073 Å	0.71073 Å
Crystal system, space group	triclinic, P-1	triclinic, P-1
Unit cell dimensions	a = 12.4945(7) Å, α = 72.695(4) deg	a = 10.7428(7) Å, α = 72.356(5) deg.
	b = 13.6153(7) Å, β = 83.393(4) deg.	b = 11.9618(7) Å, β = 72.063(5) deg.
	c = 13.7342(7) Å, γ = 65.524(4) deg.	c = 14.0140(9) Å, γ = 88.360(5) deg.
Volume	2030.11(19) $Å^3$	1628.55(18) $Å^3$
Z, Calculated density	2, 1.928 Mg/m^3	2, 1.609 Mg/m^3
Absorption coefficient	7.902 mm^{-1}	4.916 mm^{-1}
F(000)	1124	780
Crystal size	0.23 x 0.12 x 0.04 mm	0.12 x 0.11 x 0.09 mm
Theta range for data collection	1.55 to 25.00 deg	3.98 to 29.19 deg.
Limiting indices	-14<=h<=14, -12<=k<=16, -16<=l<=16	-14<=h<=14, -16<=k<=16, -19<=l<=19
Reflections collected / unique	13879 / 7060 [R(int) = 0.0632]	22909 / 8763 [R(int) = 0.0789]
Completeness to theta = 26.00	98.7 %	99.3 %
Max. and min. transmission	0.7428 and 0.2637	0.6660 and 0.5900
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data / restraints / parameters	7060 / 0 / 478	8763 / 0 / 379
Goodness-of-fit on F^2	0.994	0.695
Final R indices [I>2sigma(I)]	R_1 = 0.0452, wR_2 = 0.1083	R_1 = 0.0330, wR_2 = 0.0517
R indices (all data)	R_1 = 0.0649, wR_2 = 0.1204	R_1 = 0.0852, wR_2 = 0.0602
Largest diff. peak and hole	2.52 and -1.68 e. $Å^{-3}$	1.78 and -2.64 e. $Å^{-3}$