Supplementary data

Syntheses and ligand interconversions of copper(II) derivatives of the metalloligand $[Pt_2(\mu\text{-}S)_2(PPh_3)_4]$

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Synthesis of $[Pt_2(\mu\text{-}S)_2(PPh_3)_4Cu(bipy)](BPh_4)_2$ 1a

A suspension of $[Pt_2(\mu\text{-}S)_2(PPh_3)_4]$ (208 mg, 0.138 mmol) with $[CuCl_2(bipy)]$ (45 mg, 0.155 mmol) in methanol (24 mL) was stirred for 24 hours giving a dark brown solution. The solution was filtered, and $NaBPh_4$ (91 mg, 0.266 mmol) added to the filtrate, giving a brown precipitate. After 2 hours stirring, the precipitate was filtered off, washed with methanol (5 mL) and diethyl ether (5 mL) and dried under vacuum to give **1a** as a dark brown powder (139 mg, 42%). M.p. 160-170 °C. A sample for elemental analysis was recrystallised as dark brown needles by vapour diffusion of diethyl ether into a dichloromethane solution of the complex. Found: C, 65.8; H, 4.5; N, 1.4.

$C_{130}H_{108}N_2B_2CuP_4Pt_2S_2$ requires C, 66.1; H, 4.6; N, 1.2%. ESI MS: $[M]^{2+}$ (*m/z* 861, 100%), $[M + BPh_4]^+$ (*m/z* 2042, 5%).

Synthesis of $[Pt_2(\mu\text{-}S)_2(PPh_3)_4Cu(NH_2CH_2CH_2NH_2)](PF_6)_2$ 4

A mixture of $[Pt_2(\mu\text{-}S)_2(PPh_3)_4]$ (200 mg, 0.133 mmol) with $CuCl_2.2H_2O$ (40 mg, 0.235 mmol) in methanol (30 mL) was stirred for 10 min. giving a clear deep brown solution. Ethylene-1,2-diamine (10 drops, excess) was added giving a greenish brown solution which was stirred for 10 min. The solution was filtered, and to the filtrate added NH_4PF_6 (100 mg, 0.61 mmol). After stirring for 30 min., the resulting greenish precipitate was filtered off, washed with water (2 x 10 mL) and diethyl ether (2 x 10 mL) and dried under vacuum to give **4** (80 mg, 31%). Found: C, 46.0; H, 3.4; N, 1.4. $C_{74}H_{68}N_2CuF_{12}P_6Pt_2S_2$ requires C, 46.4; H, 3.6; N, 1.5%. ESI MS: cone voltage 20 V, $[M]^{2+}$ (*m/z* 813, 100%) and $[M + PF_6]^+$ (*m/z* 1771, 10%). Recrystallisation from dichloromethane-diethyl ether gave black microcrystals which showed the ions $[Pt_2(\mu\text{-}S)_2(PPh_3)_4Cu(en)]^{2+}$ and $[Pt_2(\mu\text{-}S)_2(PPh_3)_4Cu]^{2+}$ in the positive-ion ESI MS spectrum (20 V).

Synthesis of $[Pt_2(\mu\text{-}S)_2(PPh_3)_4Cu\{NH_2CH_2CH(CH_3)NH_2\}](PF_6)_2$ 5

Following the method for **4**, $[Pt_2(\mu\text{-}S)_2(PPh_3)_4]$ (200 mg, 0.133 mmol) with $CuCl_2.2H_2O$ (50 mg, 0.293 mmol) and 1,2-diaminopropane (10 drops, excess) in methanol (30 mL) gave a brownish solution. Filtration followed by addition of NH_4PF_6 (200 mg, 1.23 mmol) gave **5** as a brown powder (60 mg, 23%). ESI MS: cone voltage 5 V, $[M]^{2+}$ (*m/z* 820, 100%) and $[M + PF_6]^+$ (*m/z* 1785, 30%). Found: C, 46.4; H, 3.6; N, 1.05. $C_{75}H_{70}N_2CuF_{12}P_6Pt_2S_2$ requires C, 46.65; H, 3.65; N, 1.45%.

Synthesis of $[Pt_2(\mu\text{-}S)_2(PPh_3)_4Cu\{1,2\text{-diaminocyclohexane}\}](PF_6)_2$ 6

Following the method for **4**, $[Pt_2(\mu\text{-}S)_2(PPh_3)_4]$ (200 mg, 0.133 mmol) with $CuCl_2.2H_2O$ (40 mg, 0.235 mmol) and 1,2-diaminocyclohexane (20 drops) in methanol (30 mL) gave a brownish solution. ESI MS showed the $[Pt_2(\mu\text{-}S)_2(PPh_3)_4Cu\{\text{diaminocyclohexane}\}]^{2+}$ cation (*m/z* 840). Filtration followed by addition of NH_4PF_6 (200 mg, 1.23 mmol) gave **6** as a greenish-brown powder which was dried under vacuum (130 mg, 50%). ESI MS: $[M]^{2+}$ (*m/z* 840, 100%), $[M + PF_6]^+$ (*m/z* 1825, 25%). Found: C, 47.2; H, 3.6; N, 1.1. $C_{78}H_{74}N_2CuF_{12}P_6Pt_2S_2$ requires C, 47.5; H, 3.8; N, 1.4%.

Reaction of $[Pt_2(\mu\text{-}S)_2(PPh_3)_4]$ with $CuCl_2$/pyridine

A mixture of $[Pt_2(\mu\text{-}S)_2(PPh_3)_4]$ (200 mg, 0.133 mmol) with $CuCl_2.2H_2O$ (50 mg, 0.293 mmol) in methanol (20 mL) was stirred for 5 min., giving a red-brown solution. Pyridine (10 drops, excess) was added, and the mixture stirred for 10 min. giving a green-brown solution. The solution was filtered, and to the stirred filtrate NH_4PF_6 (200 mg, 1.23 mmol) was added giving a greenish-brown solid which was filtered off, washed with water (2 x 10 mL), methanol (2 mL) and petroleum spirits (10 mL) and dried under vacuum to give **7**. ESI MS (cone voltage 5 V) showed predominantly $[Pt_2(\mu\text{-}S)_2(PPh_3)_4Cu(py)]^{2+}$ (*m/z* 822.5) and $[Pt_2(\mu\text{-}S)_2(PPh_3)_4Cu(py)_2]^{2+}$ (*m/z* 862). Recrystallisation by vapour diffusion of diethyl ether into a dichloromethane solution gave black microcrystals. No attempt was made to obtain elemental analytical data on this material.

Reaction of $[Pt_2(\mu\text{-}S)_2(PPh_3)_4]$ with $CuCl_2$/imidazole

As for the reaction with pyridine, $[Pt_2(\mu\text{-}S)_2(PPh_3)_4]$ (300 mg, 0.199 mmol) with $CuCl_2.2H_2O$ (50 mg, 0.293 mmol) and imidazole (100 mg, mmol), followed by precipitation with NH_4PF_6 (200 mg, 1.23) gave a greenish solid **8** (185 mg). ESI MS (cone voltage 5 V) showed $[Pt_2(\mu\text{-}S)_2(PPh_3)_4Cu(imid)]^{2+}$ (*m/z* 817) and $[Pt_2(\mu\text{-}S)_2(PPh_3)_4Cu(imid)_2]^{2+}$ (*m/z* 851). No attempt was made to obtain elemental analytical data on this material.

$[Pt_2(\mu\text{-}S)_2(PPh_3)_4Cu(CF_3COCHCOCF_3)](PF_6)$ 10b

Following the method for complex **10a**, $[Pt_2(\mu\text{-}S)_2(PPh_3)_4]$ (299 mg, 0.199 mmol) with $[Cu(CF_3COCHCOCF_3)_2]$ (204 mg, 0.427 mmol) in methanol (30 mL) gave a dark brown solution. Filtration, followed by addition of excess NH_4PF_6 and isolation as for **10a** gave the product as a brown powder (181 mg, 47%). Found: C, 46.5; H, 3.0. $C_{77}H_{61}CuF_{12}O_2P_5Pt_2S_2$ requires C, 48.2; H, 3.2%.

$[Pt_2(\mu\text{-}S)_2(PPh_3)_4Cu(CH_3COCHCOCF_3)](PF_6)$ 10c

Following the method for complex **10a**, $[Pt_2(\mu\text{-}S)_2(PPh_3)_4]$ (301 mg, 0.200 mmol) with $[Cu(CH_3COCHCOCF_3)_2]$ (202 mg, 0.547 mmol) in methanol (30 mL) gave a dark brown solution. Filtration, followed by addition of excess NH_4PF_6 and isolation as for **10a** gave the product as a brown powder (229 mg, 61%). Found: C, 48.7; H, 3.4. $C_{77}H_{64}CuF_9O_2P_5Pt_2S_2$ requires C, 49.6; H, 3.5%.

$[Pt_2(\mu\text{-}S)_2(PPh_3)_4Cu(PhCOCHCOPh)](PF_6)$ 10e

A suspension of $[Pt_2(\mu\text{-}S)_2(PPh_3)_4]$ (200 mg, 0.133 mmol) with $Cu(PhCOCHCOPh)_2$ (100 mg, 0.196 mmol) in methanol (30 mL) was stirred for 2.5 h, to give a deep red-brown, slightly cloudy solution. The mixture was filtered, and solid NH_4PF_6 (200 mg, 1.23 mmol) added to the filtrate. After stirring for 1 h the product was filtered off, washed with water (10 mL), methanol (10 mL) and diethyl ether (10 mL) and dried under vacuum to give **10e** (120 mg, 47%) as a red-brown microcrystalline solid. ESI MS: $[M]^+$ (*m/z* 1791, 100%), $[Pt_2(\mu\text{-}S)_2(PPh_3)_4Cu]^{2+}$ (*m/z* 783, 25%). Recrystallisation by vapour diffusion of diethyl ether into a dichloromethane solution of the complex gave black microcrystals. Found: C, 53.6; H, 3.7. $C_{87}H_{71}CuF_6O_2P_5Pt_2S_2$ requires C, 54.0; H, 3.7%. UV-vis λ_{max} 440 nm.

$[Pt_2(\mu\text{-}S)_2(PPh_3)_4Cu(^tBuCOCHCO^tBu)](PF_6)$ 10f

Following the method for complex **10a**, $[Pt_2(\mu\text{-}S)_2(PPh_3)_4]$ (299 mg, 0.199 mmol) with $[Cu(^tBuCOCHCO^tBu)_2]$ (197 mg, 0.458 mmol) in methanol (30 mL) gave a dark brown solution after stirring for 20 min. Filtration, followed by addition of excess NH_4PF_6 and isolation as for **10a** gave the product as a brown powder (201 mg, 53%). Found: C, 51.7; H, 4.0. $C_{83}H_{79}CuF_6O_2P_5Pt_2S_2$ requires C, 52.6; H, 4.2%.