Electronic Supplementary Material (ESI) for Dalton Transactions

Aurophilicity in Gold(I) Thiosemicarbazone Clusters

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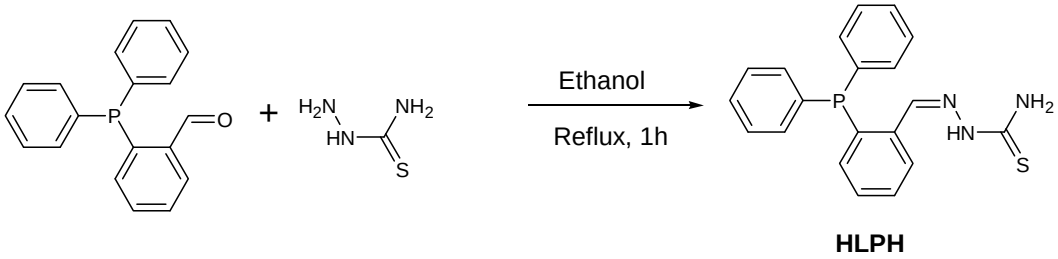
Suplemmentary information

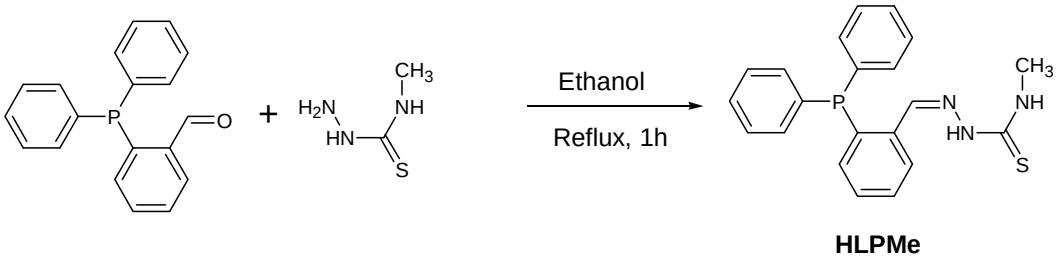


Scheme S1: Synthesis of the ligand HLPH

Synthesis of the ligand HLPH

Over a 50 mL ethanolic solution of 2-diphenylphosphinobenzaldehyde (0.5 g, 1.7 mmol), thiosemicarbazide (0.16 g, 1.7 mmol) was added. The resulting yellow solution was heated under reflux over a 1 h period, then concentrated to ca. 30 cm^3 and cooled to RT. The white precipitate was filtered off, washed with diethyl ether (3 × 5 mL) and dried under *vacuo*.

HLPH. Yield 0.53 g, 85 %; m.p. = 227 ºC; EA: (Found: C, 66.0; H, 5.1; N, 11.4; S, 8.8; $C_{20}H_{18}N_3P_1S_1$ required: C, 66.1; H, 5.0; N, 11.6; S, 8.8); ESI (+) 363.8 $[HLPH+H]^+$; ^1H NMR (DMSO-d_6, ppm): δ 6.76-8.64 (m, 14H), 6.75 (s, 1H), 8.16 (bs, 2H), 8.62 (d, 1H), 11.57 (s, 1H); ^{13}C NMR (DMSO-d_6, ppm): δ 177.7 (C=S), 140.53 (C=N), 137.6-128.8 (C_{ar}); ^{31}P NMR (DMSO-d_6, ppm): -13.22; IR (KBr, cm^{-1}): ν (NH) 3309, 3160, ν (C=N) + ν (C-N) 1582, 1534, 1457, ν (C=S) 748, ν (N-N) 1094. UV / Vis (nm): 232, 272, 320.



HLPMe

Scheme S1: Synthesis of the ligand HLPMe

Synthesis of the ligand HLPMe

Over a solution of 2-diphenylphosphinobenzaldehyde (0.5 g, 1.7 mmol) in ethanol 4-methyl-3-thiosemicarbazide (0.18 g, 1.7 mmol) was added. The pale yellow solution was heated under reflux over a 2 h period, then concentrated to dryness. The resulting yellow oil was treated with diethyl ether (10 mL). The pale yellow precipitate was filtered off, washed with diethyl ether (5 mL) and dried under *vacuo*.

HLPMe. Yield 0.62 g, 95 %; m.p. = 236 ºC; EA: (Found: C, 66.9; H, 5.3; N, 11.2; S, 8.3; $C_{21}H_{20}N_3P_1S_1$ required: C, 66.8; H, 5.3; N, 11.1; S, 8.5); ESI(+) 379.2 $[HLPMe+H]^+$; ^{1}H NMR (DMSO-d_6, ppm): δ 2.94 (d, 3H), 6.76-8.18 (m, 14H), 8.66 (d, 1H), 11.61 (s, 1H); ^{13}C NMR (DMSO-d_6, ppm): δ 178.1 (C=S), 140.7 (C=N), 138.3-127.4 (C_{ar}), 31.2 (C_{Me}); ^{31}P NMR (DMSO-d_6, ppm): -11.21; IR (KBr, cm^{-1}): ν (NH) 3332, 3140, ν (C=N) + ν (C-N) 1583, 1518, 1462, ν (C=S) 786, ν (N-N) 1088. UV / Vis (nm): 232, 272, 320.

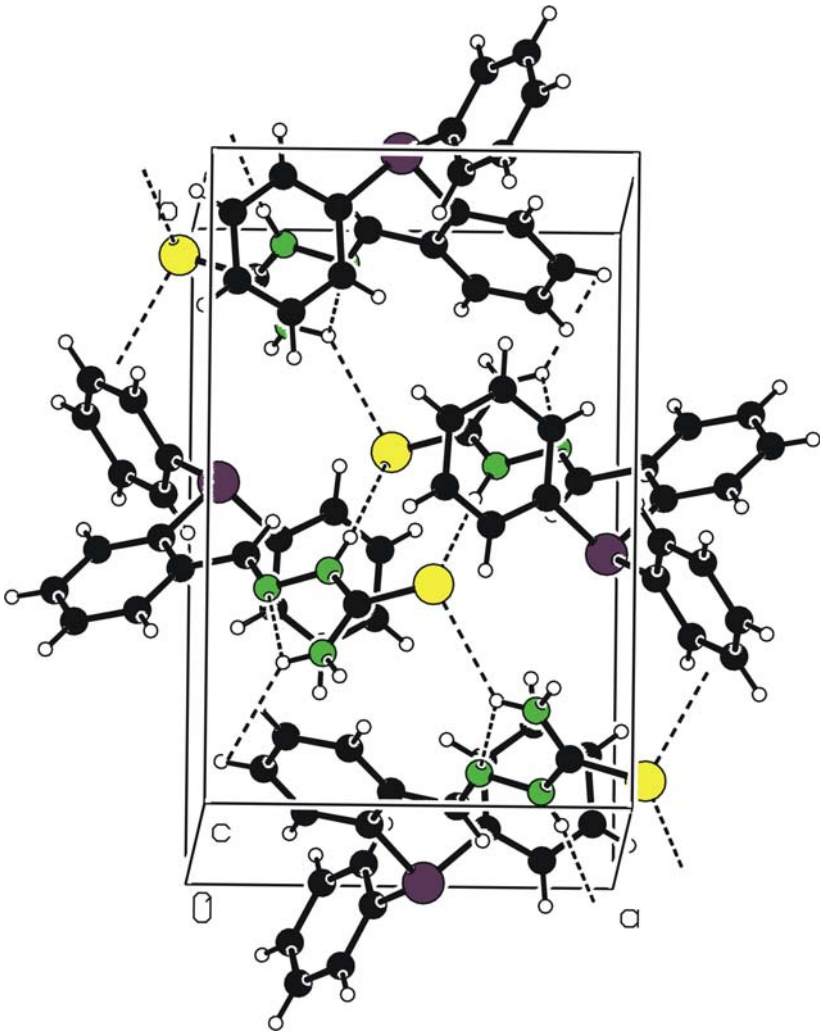


Figure S1. Packing diagram of the ligand HLPH. The dotted lines indicate hydrogen-bonds.

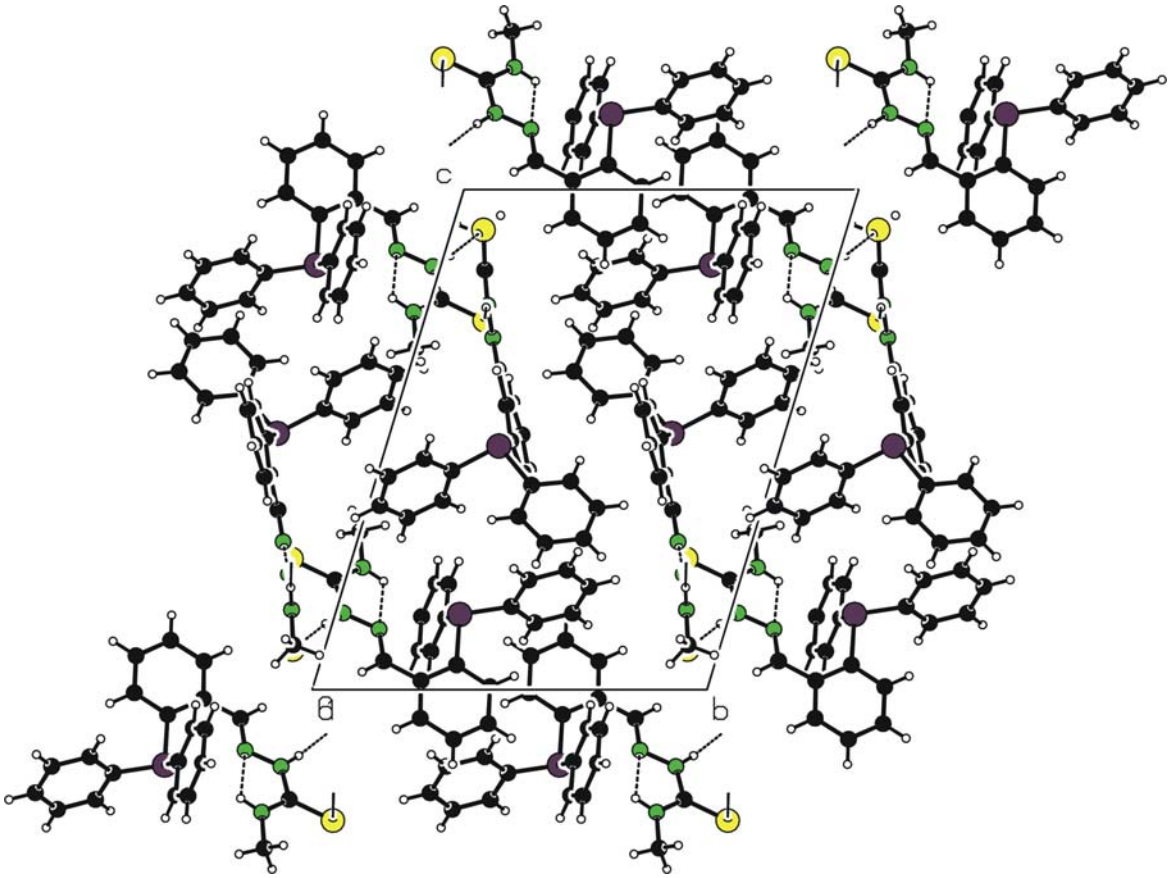


Figure S2. Unit cell of HLPMe showing hydrogen bond interactions.

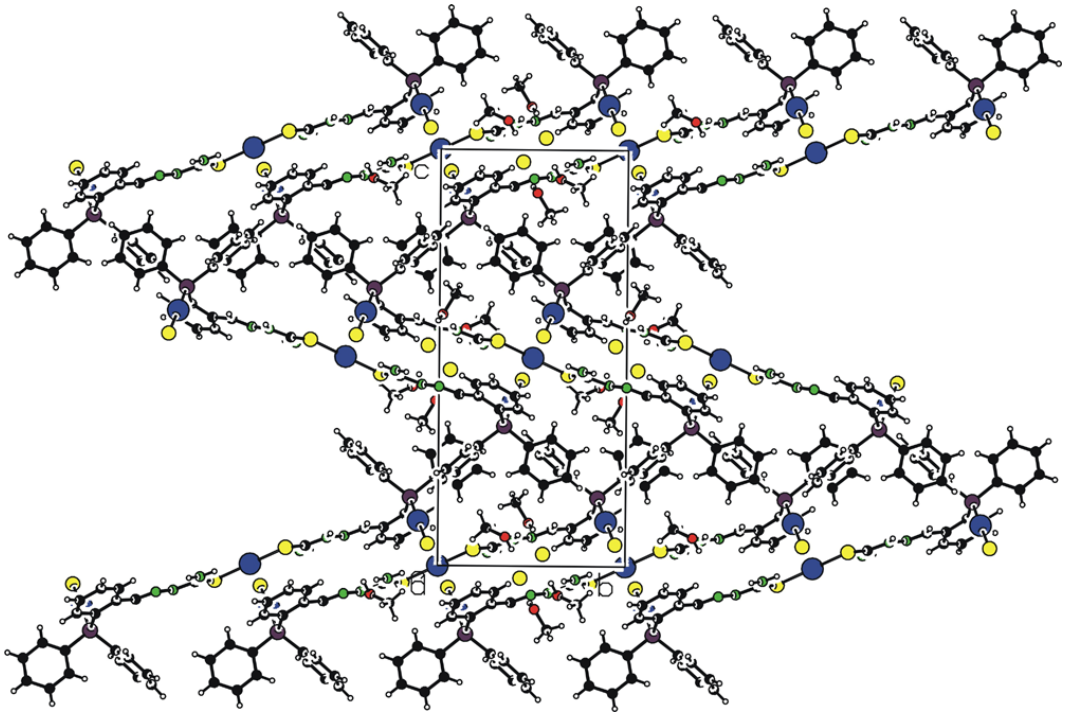


Figure S3. Zig-zag packing of **1**·4MeOH along the a-axis.

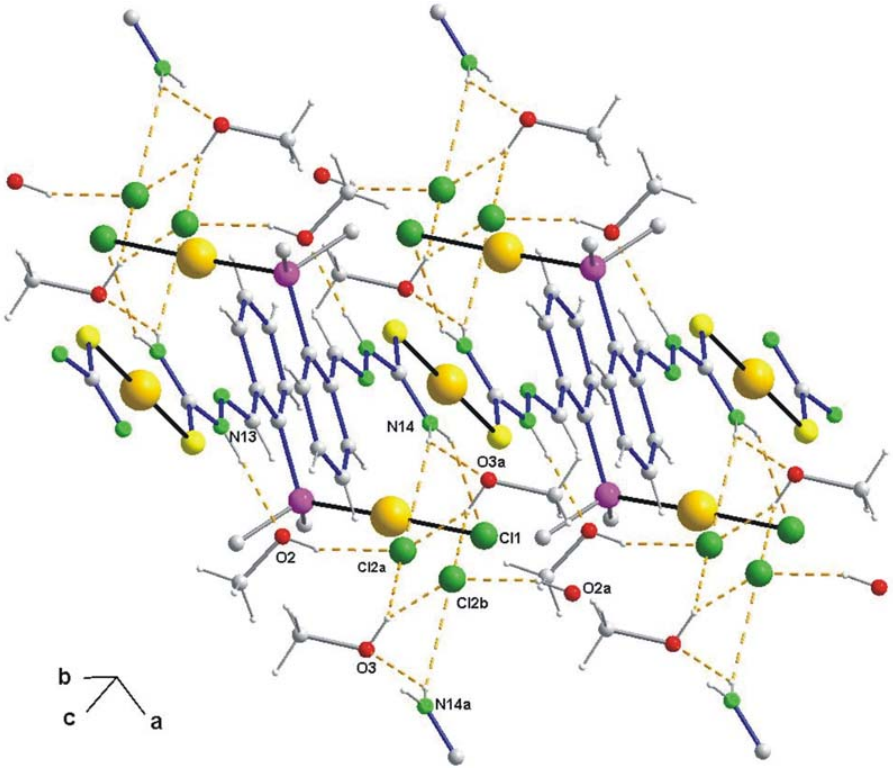


Figure S4. Fragment of the unit cell in **1**·4MeOH. Symmetry codes are given in Table 4. Thiosemicarbazone moieties are emphasized by blue bonds.

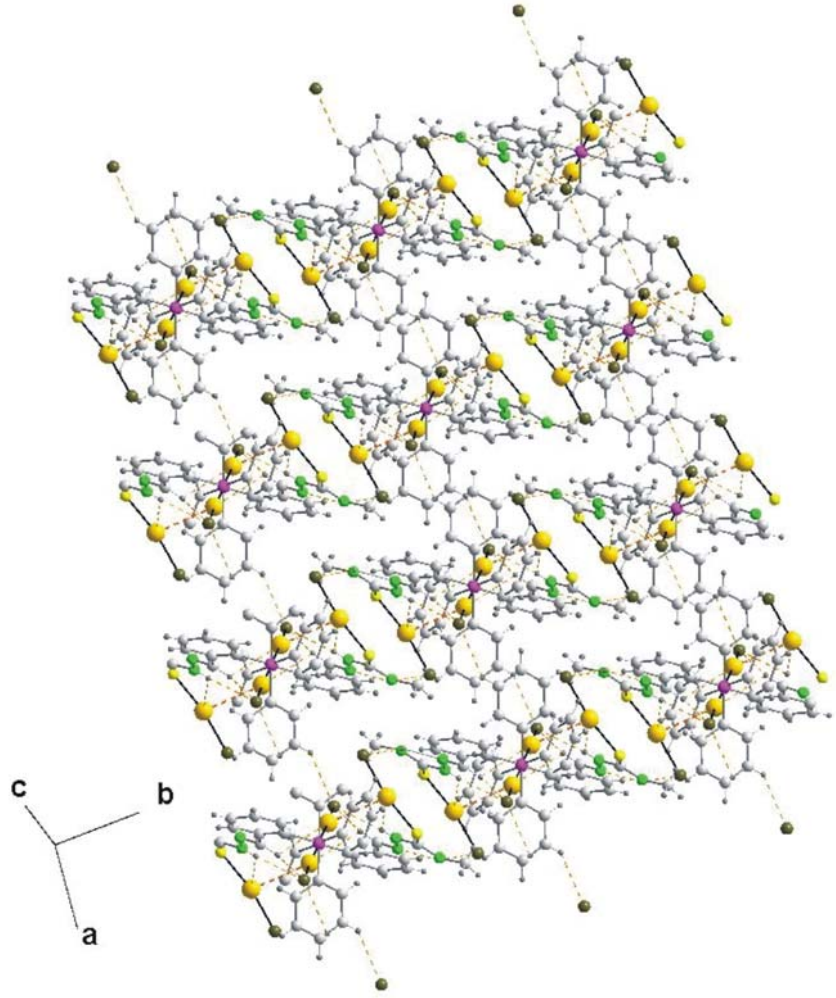


Figure S5. Crystal packing of complex **2** showing the H-bond structure.

Table S1. Hydrogen bond parameters [Å, º] for HLPH and HLPMe.

Compound	D-H···A	D-H	H···A	D···A	∠DHA
HLPH	N(13)-H(13A)···S(1)[1]	0.88	2.57	3.419 (4)	162.3
	N(14)-H(14A)···S(2)[2]	0.88	2.67	3.282(4)	127.1
	N(23)-H(23A)···S(2)[3]	0.88	2.59	3.443(4)	163.2
	N(24)-H(24B)···S(1)	0.88	2.70	3.305(4)	126.6
	N(14)-H(14A)···N(12)	0.88	2.32	2.671(6)	103.9
	N(24)-H(24B)···N(22)	0.88	2.29	2.649(6)	104.2
	C(17)-H(17)···P(1)	0.95	2.66	3.098(5)	108.7
	C(27)-H(27)···P(2)	0.95	2.67	3.103(5)	108.7
	Symmetry transformation,1: *-x+1, -y+1, -z+1*; 2: *x-1, y, z*; 3: *-x+2, -y, -z+1*				
HLPMe	N(13)-H(13A)···S(2)[1]	0.88	2.46	3.309(3)	160.9
	N(14)-H(14A)···N(12)	0.88	2.23	2.623(5)	106.9
	N(23)-H(23A)···S(1)[1]	0.88	2.53	3.408(3)	174.0
	N(24)-H(24A)···N(22)	0.88	2.25	2.639(4)	106.7
	N(24)-H(24A)···S(1)[2]	0.88	2.85	3.560(3)	139.2
	C(27)-H(27)···P(2)	0.95	2.72	3.131(4)	107.2
	Symmetry transformation, 1: *-x+2,-y,-z+1*; 2: *-x+1,-y,-z+1*				