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Journal of Organometallic Chemistry 643–644 (2002) 313–323

Journal of Organometallic Chemistry

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Hydrogen-bonded networks: (phosphine)gold(I) 4-amino-2-pyrimidine-thiolates

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Received 13 July 2001; accepted 20 September 2001

Abstract

Treatment of the gold(I) halide complexes LAuCl (where L = PMe_3, PEt_3, PPh_3, PPh_2Py) and $PP(AuCl)_2$ [where PP = bis(-diphenylphosphino)methane; 1,1′-bis(diphenylphosphino)ferrocene] with 4-amino-2-pyrimidine-thiol (2-SPym-4-NH_2) (one or two equivalents as required) in the presence of sodium methoxide provides the corresponding (phosphine)gold(I) thiolate complexes LAu(2-SPym-4-NH_2) and PP[Au(2-SPym-4-NH_2)]$_2$, respectively. A polyaurated product [$(Ph_3PAu)_2$(2-SPym-4-NH_2)]BF_4 is obtained on treating the thiol with the oxonium complex [$(Ph_3PAu)_3O$]BF_4. The compounds LAu(2-SPym-4-NH_2) (L = PPh_3, PPh_2Py, PEt_3) and [(dppm)Au_2(2-SPym-4-NH_2)$_2$] have been investigated crystallographically. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Gold(I) complexes; 4-Amino-2-pyrimidine-thiol; Hydrogen bonding; Aurophilicity; Tertiary phosphine complexes; Thiolate complexes

1. Introduction

Thiolate complexes have to be accorded a special place among the compounds of gold [1]. They have found use in a wide range of applications ranging from anti-arthritis [2] drugs to 'liquid gold' pastes in the ceramics and glass industry [3]. Furthermore, much of gold thin film technology and chemistry of self-assembly monolayers depend on the special properties of gold(I)–sulfur systems [4]. Academic interest in the coordination properties of thiols to gold(I) species is well established and has been heightened by the recent observation that many of these complexes display novel luminescence properties [5].

Our recent interest in polydentate, nitrogen-containing thiol ligands has led to the observation that this class of compounds is capable of displaying a rich and unusual chemistry [6]. The primary bonding sites are the thiol groups, however the nitrogen donors can also be expected to play an important role, especially in the solid state. The combination of hydrogen-bonding and aurophilic contacts (being interactions of comparable energies in the range 6–12 kcal mol^{-1}) has been discussed in a number of recent publications [7–11], in particular, it offers the possibility of using these 'weak' interactions to construct supramolecular networks in a controlled manner.

4-Amino-2-pyrimidine-thiol was chosen as the subject of this study as a ligand with four sites available for metal coordination and/or hydrogen bonding interactions. As expected, the first site of attack for gold was at the thiol sulfur atom to give thiolate complexes of the general formula [R_3PAu(2-SPym-4-NH_2)] (PR_3 = PMe_3, PEt_3, PPh_3, PPh_2Py) in reactions carried out with R_3PAuCl and base. The structures of single crystals of three complexes (PR_3 = PEt_3, PPh_3, PPh_2Py) were determined in order to investigate the solid state interactions between the molecules. As a useful comparison, the isocyanide analogue [2,6-$(CH_3)_2C_6H_3NCAu$(2-SPym-4-NH_2)] was also prepared by the reaction between 2-SPym-4-NH_2 and [$ClAuCNC_6H_3(CH_3)_2$-2,6] in the presence of sodium methoxide. Unfortunately, this complex did not yield crystals suitable for a structural investigation.

Two digold species were prepared through the use of the bis(phosphine)gold complexes $(dppm)(AuCl)_2$ and

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PII: S0022-328X(01)01284-0

$(dppf)(AuCl)_2$ which reacted readily with two molar equivalents of 4-amino-2-pyrimidine-thiol and 2.2 moles of NaOMe to provide the compounds $(dppm)[Au(2\text{-}SPym\text{-}4\text{-}NH_2)]_2$ and $(dppf)[Au(2\text{-}SPym\text{-}4\text{-}NH_2)]_2$, respectively. The former of these yielded suitable crystals for a diffraction study on crystallization from dimethylformamide. A further dinuclear species $[(Ph_3PAu)_2(2\text{-}SPym\text{-}4\text{-}NH_2)]BF_4$ was obtained through the action of the oxonium species $[(Ph_3PAu)_3O]BF_4$ on 4-amino-2-pyrimidine-thiol.

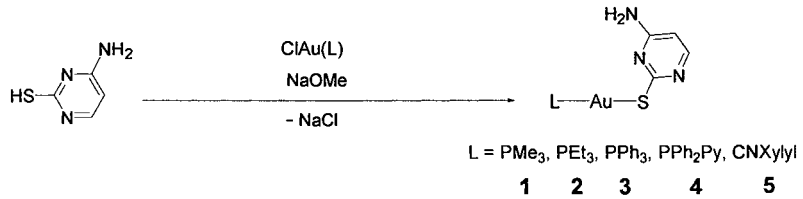
2. Experimental

2.1. General information

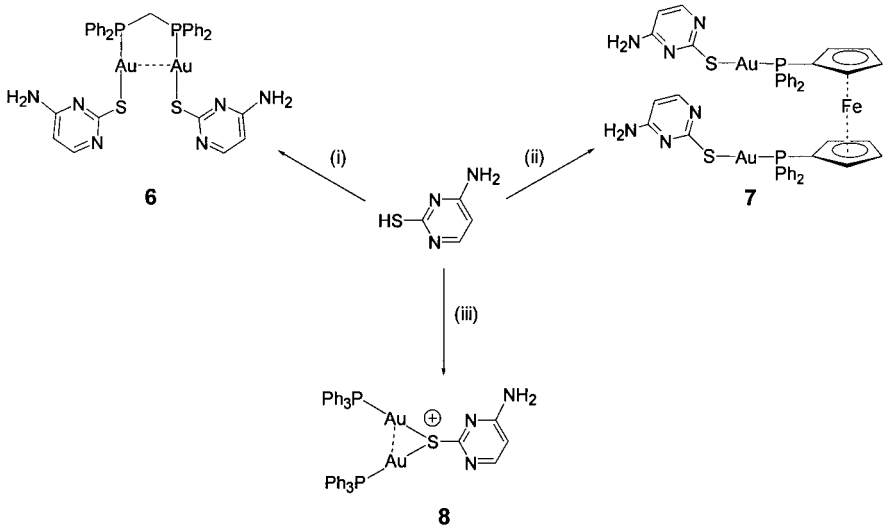
The experiments were carried out routinely in air. NMR: JEOL GX 400 spectrometer using deuterated solvents with the usual standards at 25 °C. MS: Varian MAT311A instrument (FAB, *p*-nitrobenzyl alcohol). IR: Perkin–Elmer 1600 FTIR. The ligand 4-amino-2-pyrimidine-thiol (4-HSPym-2-NH_2) was obtained commercially. The complexes $[R_3PAuCl]$ (R = Me [12], Et [13], Ph [12]; $R_3P = Ph_2PPy$ [14]), $[(dppm)(AuCl)_2]$ [15], $[(dppf)(AuCl)_2]$ [16], $[(2,6\text{-}Me_2C_6H_3NC)AuCl]$ [17] and $[(Ph_3PAu)_3O]BF_4$ [18] were prepared following literature procedures. The preparation of the mononuclear complexes **1**–**5** and the bimetallic compounds **6**–**8** are shown in Schemes 1 and 2, respectively.

2.2. $[Me_3PAu(2\text{-}SPym\text{-}4\text{-}NH_2)]$ (1)

An MeOH suspension (5 ml) of 4-amino-2-pyrimidine-thiol (20 mg, 0.16 mmol) and sodium methoxide (10 mg, 0.19 mmol) was added dropwise to a stirred solution of $[Me_3PAuCl]$ (50 mg, 0.16 mmol) in CH_2Cl_2 (15 ml). After stirring for 2 h, all solvent was removed and the crude product dissolved in CH_2Cl_2 (30 ml) and filtered through diatomaceous earth to remove NaCl. After concentration of the solution to ca. 10 ml, pentane (20 ml) was carefully added to precipitate a colorless solid. This was washed with pentane (20 ml) and dried. Yield: 51% (33 mg). MS (FAB) $m/z = 400$, 23% $[M]^+$, 307, 25% $[M - PMe_3 - NH_2]^+$, 273, 16% $[M - SR]^+$. $^{31}P\{^1H\}$-NMR (CD_2Cl_2, ppm): δ −1.5. ^1H-NMR (CD_2Cl_2, ppm): δ 1.59 (d, 9H, CH_3, $J_{HP} = 10.3$ Hz), 4.66 (s, 2 H, NH_2), 6.03 (d, 1H, H^5, $J_{HH} = 5.7$ Hz) 7.83 (d, 1H, H^6, $J_{HH} = 5.7$ Hz). Anal. Calc. for $C_7H_{13}AuN_3S$: C, 21.06; H, 3.28; N, 10.53. Found: C, 21.52; H, 3.44; N, 10.86%.



Scheme 1. Preparation of the mononuclear complexes **1**–**5**.



Scheme 2. Preparation of the bimetallic compounds **6**–**8**. (i) $dppm(AuCl)_2$, 2NaOMe; (ii) $dppf(AuCl)_2$, 2NaOMe; (iii) $[(Ph_3PAu)_3O]BF_4$, $NaBF_4$.

Table 1
Crystal data and structure refinement parameters for compounds **2**–**4** and **6**

	2	**3**·0.5CH_2Cl_2	**4**·CH_2Cl_2	**6**·DMF
Empirical formula	$C_{10}H_{19}AuN_3PS$	$C_{22.5}H_{20}AuClN_3PS$	$C_{22}H_{20}AuCl_2N_4PS$	$C_{36}H_{37}Au_2N_7OP_2S_2$
Formula weight	441.28	627.86	671.32	1103.72
Temperature (°C)	−130	−130	−130	−130
Crystal system	Orthorhombic	Triclinic	Triclinic	Monoclinic
Space group	$Pna2_1$	$P\bar{1}$	$P\bar{1}$	$P2_1$
Unit cell dimensions				
a (Å)	15.8231(2)	8.7123(1)	10.5634(1)	12.1200(2)
b (Å)	14.7751(2)	18.3437(2)	13.6415(1)	11.8640(2)
c (Å)	25.0687(4)	29.6895(3)	17.5285(2)	13.9670(2)
α (°)	90	74.934(1)	105.828(1)	90
β (°)	90	87.333(1)	101.72(1)	111.486(1)
γ (°)	90	77.902(1)	91.30(1)	90
V (Å^3)	5860.8(1)	4479.8(1)	2371.2(1)	1868.8(1)
Z	16	8	4	2
D_{calc} (g cm^{-3})	2.000	1.862	1.880	1.961
μ (Mo–K_α) (cm^{-1})	102.7	68.66	66.03	80.08
$F(000)$	3360	2424	1296	1060
Measured reflections	136 725	87 211	39 356	79 520
Unique reflections	6591 [$R_{int} = 0.065$]	17 040 [$R_{int} = 0.034$]	10 044 [$R_{int} = 0.029$]	10 003 [$R_{int} = 0.0474$]
Absorption correction	DELABS	DELABS	DELABS	DELABS
T_{min}/T_{max}	0.316/0.750	0.45/0.89	0.61/0.88	0.224/0.688
Refined parameters	578	1095	559	467
Final R values [$I \geq 2\sigma(I)$]	$R_1 = 0.0302$, wR_2 [a] = 0.0742	$R_1 = 0.0298$, wR_2 [a] = 0.0740	$R_1 = 0.0237$, wR_2 [a] = 0.0544	$R_1 = 0.0248$, wR_2 [a] = 0.0673
Absolute structure parameter	Twin refinement, BASF = 0.4988	–	–	0.001(3)
a, b	0.0381, 26.65	0.0348, 13.59	0.00, 4.60	0.00, 0.00
ρ_{fin}(max/min) (e Å^{-3})	2.65/−2.07	1.71/−1.60	1.28/−0.79	1.93/−1.90

[a] $wR_2 = \{[w(F_o^2 - F_c^2)^2]/[w(F_o^2)^2]\}^{1/2}$; $w = 1/[\sigma^2(F_o^2) + (ap)^2 + bp]$; $p = (F_o^2 + 2F_c^2)/3$.

2.3. [$Et_3PAu(2\text{-}SPym\text{-}4\text{-}NH_2)$] (**2**)

An MeOH suspension (5 ml) of 4-amino-2-pyrimidine-thiol (51 mg, 0.40 mmol) and sodium methoxide (24 mg, 0.44 mmol) was added dropwise to a stirred solution of [Et_3PAuCl] (140 mg, 0.40 mmol) in CH_2Cl_2 (15 ml). After stirring for 2 h, all solvent was removed and the crude product dissolved in CH_2Cl_2 (30 ml) and filtered through diatomaceous earth to remove NaCl. After concentration of the solution to ca. 10 ml, pentane (20 ml) was carefully added to precipitate a colorless solid. This was washed with pentane (20 ml) and dried. Yield: 68% (120 mg). MS (FAB) $m/z =$ 756, 43% $[2M - SR]^+$, 442, 100% $[M]^+$, 315, 68% $[M - SR]^+$. $^{31}P\{^1H\}$-NMR (CD_2Cl_2, ppm): δ 37.5. $^{13}C\{^1H\}$-NMR (CD_2Cl_2, ppm): δ 8.8 (s, CH_3), 18.1 (d, CH_2, $J_{CP} = 33.2$ Hz), 99.6 (s, C^5), 155.4 (s, C^6), 161.9 (s, C^4), 179.6 (s, C^2). ^1H-NMR (CD_2Cl_2, ppm): δ 1.23 (dt, 9H, CH_3, $J_{HP} = 18.3$ Hz, $J_{HH} = 7.7$ Hz), 1.87 (dq, 6H, CH_2, $J_{HP} = 9.65$ Hz, $J_{HH} = 7.7$ Hz), 4.71 (s, 2H, NH_2), 6.03 (d, 1H, H^5, $J_{HH} = 5.7$ Hz) 7.82 (d, 1H, H^6, $J_{HH} = 5.7$ Hz). Anal. Calc. for $C_{10}H_{19}AuN_3PS$: C, 27.22; H, 4.34; N, 9.52. Found: C, 27.15; H, 4.22; N, 9.53%.

2.4. [$Ph_3PAu(2\text{-}SPym\text{-}4\text{-}NH_2)$] (**3**)

An MeOH suspension (5 ml) of 4-amino-2-pyrimidine-thiol (26 mg, 0.20 mmol) and sodium methoxide

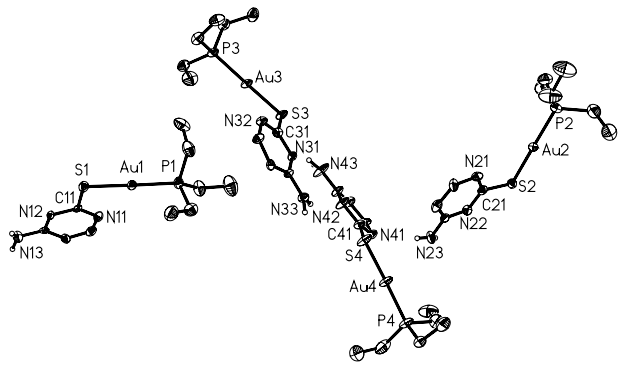


Fig. 1. Molecular structures of the four independent molecules in the asymmetric unit of crystals of compound **2**. (ORTEP, 50% probability ellipsoids; only the hydrogen atoms of the amino group are shown with arbitrary radii.) Selected bond lengths (Å) and angles (°): Au1–P1, 2.250(3); Au1–S1, 2.291(3); P1–Au1–S1, 173.6(1); Au1–S1–C11, 106.5(3); Au2–P2, 2.250(3); Au2–S2, 2.295(3); P2–Au2–S2, 171.6(1); Au2–S2–C21, 106.8(3); Au3–P3, 2.260(3); Au3–S3 2.307(2); P3–Au3–S3, 175.6(1); Au3–S3–C31, 103.8(3); Au4–P4 2.252(3); Au4–S4, 2.300(3); P4–Au4–S4, 174.7(1).

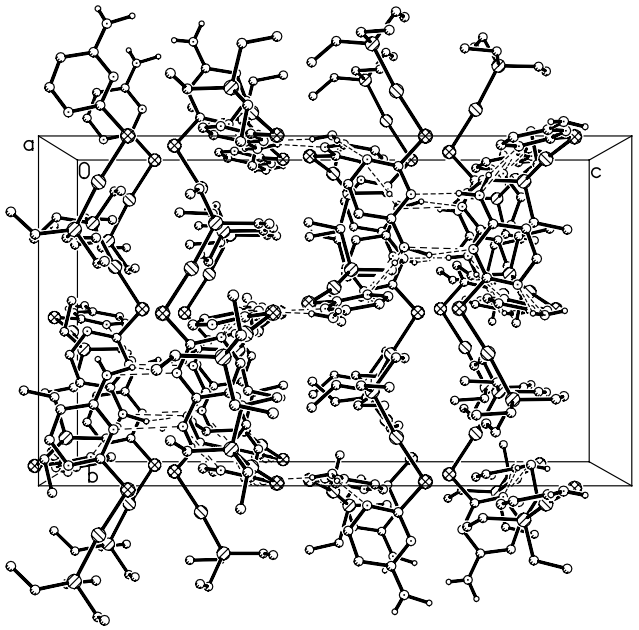


Fig. 2. Illustration of the connectivity of the individual monomers via hydrogen bonding projected down the *b* axis of the unit cell.

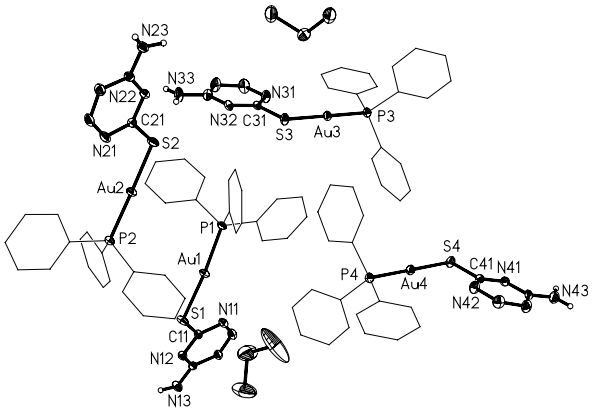


Fig. 3. Molecular structures of the four independent molecules in the asymmetric unit of crystals of compound **3**. (ORTEP, 50% probability ellipsoids; only the hydrogen atoms of the amino groups are shown with arbitrary radii.) Selected bond lengths (Å) and angles (°): Au1–P1, 2.262(1); Au1–S1, 2.308(1); P1–Au1–S1, 175.31(4), Au1–S1–C11, 102.6(1); Au2–P2, 2.249(1); Au2–S2, 2.307(1); P2–Au2–S2, 178.96(4); Au2–S2–C21, 99.3(1); Au3–P3, 2.260(1); Au3–S3, 2.306(1); P3–Au3–S3, 179.04(4); Au3–S3–C31, 101.9(1); Au4–P4, 2.256(1); Au4–S4, 2.303(1); P4–Au4–S4, 179.85(4); Au4–S4–C41, 100.4(1). The asymmetric unit contains two dichloromethane solvent molecules.

(12 mg, 0.22 mmol) was added dropwise to a stirred solution of $[Ph_3PAuCl]$ (100 mg, 0.20 mmol) in CH_2Cl_2 (15 ml). After stirring for 2 h, all solvent was removed and the crude product dissolved in dichloromethane (20 ml) and filtered through diatomaceous earth to remove NaCl. After concentration of the solution to ca. 10 ml, Et_2O (20 ml) was carefully added to precipitate a colorless solid. This was washed with Et_2O (20 ml) and dried. Yield: 68% (81 mg). MS (FAB) $m/z = 586$, 67% $[M]^+$, 460, 37% $[M - SR]^+$. $^{31}P\{^1H\}$-NMR (CD_2Cl_2, ppm): δ 38.1. $^{13}C\{^1H\}$-NMR (CD_2Cl_2, ppm): δ 99.9 (s, C^5), 129.1 (d, o/m-C_6H_5, $J_{CP} = 12.7$ Hz), 129.8 (d, *ipso*-C_6H_5, $J_{CP} = 56.9$ Hz), 131.6 (d, p-C_6H_5, $J_{CP} = 2.3$ Hz), 134.2 (d, o/m-C_6H_5, $J_{CP} = 12.7$ Hz), 155.4 (s, C^6), 162.1 (s, C^4), 179.3 (s, C^2). ^1H-NMR (CD_2Cl_2, ppm): δ 4.62 (s, 2H, NH_2), 6.03 (d, 1H, H^5, $J_{HH} = 5.7$ Hz) 7.45–7.64 (m, 15H, C_6H_5) 7.86 (d, 1H, H^6, $J_{HH} = 5.7$ Hz). Anal. Calc. for $C_{22}H_{19}AuN_3PS{\cdot}0.5CH_2Cl_2$: C, 43.04; H, 3.21; N, 6.69. Found: C, 42.68; H, 3.00; N, 6.23%.

2.5. *[$Ph_2PyPAu(2\text{-}SPym\text{-}4\text{-}NH_2)$]* (**4**)

An MeOH suspension (5 ml) of 4-amino-2-pyrimidine-thiol (26 mg, 0.20 mmol) and sodium methoxide (12 mg, 0.22 mmol) was added dropwise to a stirred solution of $[Ph_2PyPAuCl]$ (100 mg, 0.20 mmol) in CH_2Cl_2 (15 ml). After stirring for 2 h, all solvent was removed and the crude product dissolved in CH_2Cl_2 (20 ml) and filtered through diatomaceous earth to remove NaCl. After concentration of the solution to ca. 10 ml, pentane (20 ml) was carefully added to precipitate a colorless solid. This was washed with pentane (20 ml) and dried. Yield: 76% (90 mg). MS (FAB) $m/z = 587$, 100% $[M]^+$, 460, 40% $[M - SR]^+$, 324, 4% $[AuSR]^+$. $^{31}P\{^1H\}$-NMR (CD_2Cl_2, ppm): δ 37.1. ^1H-NMR (CD_2Cl_2, ppm): δ 4.77 (s, 2H, NH_2), 6.06 (d, 1H, H^5, $J_{HH} = 5.8$ Hz) 7.5, 7.8 (m × 2, 12H, $C_6H_5 + C_5H_4N$), 7.89 (d, 1H, H^6, $J_{HH} = 5.8$ Hz), 8.07 (t, 1H, $H^{4/5}$Py, $J_{HH} = 7.7$ Hz), 8.79 (d, 1H, $H^{3/6}$Py, $J_{HH} = 7.7$ Hz). Anal. Calc. for $C_{21}H_{18}AuN_4PS{\cdot}0.75CH_2Cl_2$: C, 40.18; H, 3.02; N, 8.62. Found: C, 40.23; H, 3.23; N, 8.31%.

2.6. *[$(2,6\text{-}Me_2C_6H_3NC)Au(2\text{-}SPym\text{-}4\text{-}NH_2)$]* (**5**)

An MeOH solution (5 ml) of 4-amino-2-pyrimidine-thiol (35 mg, 0.28 mmol) and sodium methoxide (16 mg, 0.30 mmol) was added dropwise to a stirred solution of $[(2,6\text{-}Me_2C_6H_3NC)AuCl]$ (100 mg, 0.28 mmol) in CH_2Cl_2 (15 ml). A yellow coloration appeared which dispersed after stirring for 1 h. All solvent was removed and the crude product dissolved in CH_2Cl_2 (20 ml) and filtered through diatomaceous earth to remove NaCl. After concentration of the solution to ca. 10 ml, pentane (20 ml) was carefully added to precipitate a colorless solid. This was washed with pentane (20 ml) and dried. Yield: 66% (63 mg). IR (Nujol/KBr, cm^{-1}): ν(CN) = 2201. MS (FAB) $m/z = 782$, 11% $[2M - SR]^+$, 456, 100% $[M]^+$, 324, 26% $[M - CNX]^+$. ^1H-NMR (CD_2Cl_2, ppm): δ 2.40 (s, 6H, CH_3), 4.75 (s, 2H, NH_2), 6.11 (d, 1H, H^5, $J_{HH} = 6.2$ Hz), 7.11 (d, 2H, $H^{3,5}C_6H_3$, $J_{HH} = 7.7$ Hz), 7.27 (t, 1H, $H^4C_6H_3$, $J_{HH} = 7.7$ Hz), 7.80 (d, 1H, H^6, $J_{HH} = 6.2$ Hz). Anal. Calc. for $C_{13}H_{13}AuN_4S{\cdot}CH_2Cl_2$: C, 31.18; H, 2.80; N, 10.39. Found: C, 31.44; H, 2.61; N, 10.10%.

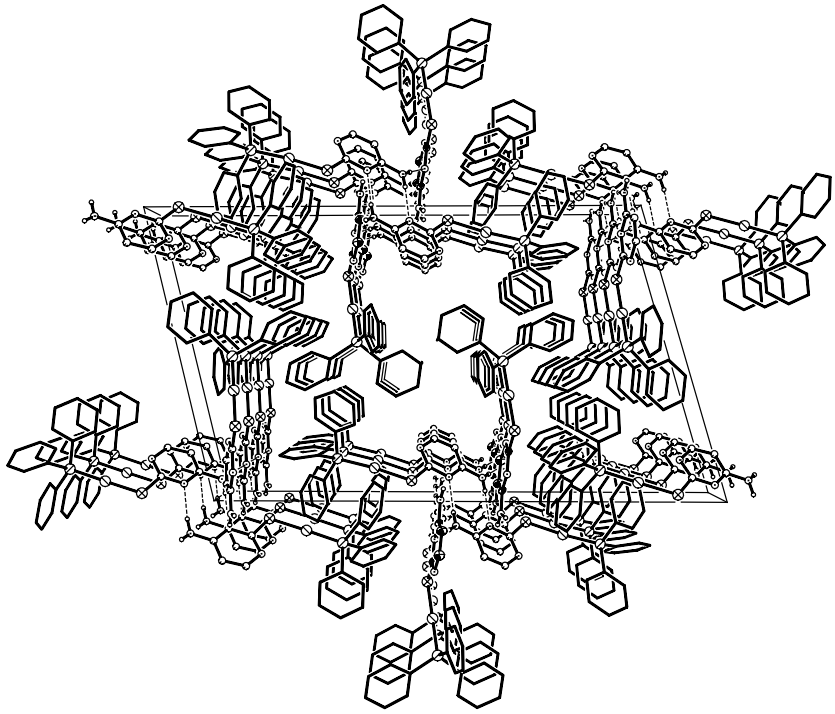


Fig. 4. The molecules of compound **3** are connected via hydrogen bonding to form strings resembling four-bladed paddle-wheels running parallel to the *a* axis of the cell as shown in this projection. The columns of triarylphosphines are interlocked to fill the space. Voids remaining in this packing are filled by the solvent molecules (not shown).

*2.7. (dppm)[Au(2-SPym-4-NH$_2$)]$_2$ (**6**)*

An MeOH suspension (5 ml) of 4-amino-2-pyrimidine-thiol (30 mg, 0.24 mmol) and sodium methoxide (14 mg, 0.26 mmol) was added dropwise to a stirred solution of [(dppm)(AuCl)$_2$] (100 mg, 0.12 mmol) in CH_2Cl_2 (15 ml). After stirring for 2 h, all solvent was removed and the solid triturated in water (25 ml). The colorless product was filtered, washed with water (20 ml), MeOH (10 ml) and pentane (20 ml) and dried. Yield: 67% (83 mg). MS (FAB) $m/z = 905$, 100% $[M - SR]^+$, 580, 7% $[(dppm)Au]^+$. $^{31}P\{^1H\}$-NMR (CD_2Cl_2, ppm): δ 32.1. Anal. Calc. for $C_{33}H_{30}Au_2N_6P_2S_2$: C, 38.46; H, 2.93; N, 8.15. Found: C, 38.86; H, 3.08; N, 8.12%.

*2.8. (dppf)[Au(2-SPym-4-NH$_2$)]$_2$ (**7**)*

An MeOH suspension (5 ml) of 4-amino-2-pyrimidine-thiol (25 mg, 0.20 mmol) and sodium methoxide (12 mg, 0.22 mmol) was added dropwise to a stirred solution of [(dppf)(AuCl)$_2$] (100 mg, 0.10 mmol) in CH_2Cl_2 (15 ml). After stirring for 2 h, the solvent volume was reduced until precipitation of the pale orange product had occurred. This was washed with water (10 ml), methanol (10 ml) and pentane (20 ml) and dried. Yield: 87% (102 mg). MS (FAB) $m/z = 1075$, 100% $[M - SR]^+$, 751, 17% $[(dppf)Au]^+$. $^{31}P\{^1H\}$-NMR (MeOH/CD_2Cl_2, ppm): δ 30.0. Anal. Calc. for $C_{42}H_{36}Au_2FeN_6P_2S_2$: C, 42.02; H, 3.02; N, 7.00. Found: C, 41.61; H, 3.00; N, 6.90%.

*2.9. [(Ph$_3$PAu)$_2$(2-SPym-4-NH$_2$)]BF$_4$ (**8**)*

The oxonium salt $[(Ph_3PAu)_3O]BF_4$ (100 mg, 0.068 mmol), amino-2-pyrimidine-thiol (12.9 mg, 0.102 mmol) and $NaBF_4$ (20 mg, 0.182 mmol) were dissolved

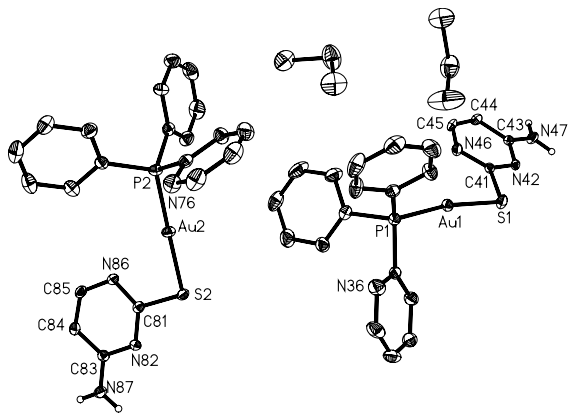


Fig. 5. Molecular structures of the two independent complex molecules and two dichloromethane molecules in the asymmetric unit of crystals of compound **4**. (ORTEP, 50% probability ellipsoids, hydrogen atoms with arbitrary radii.) Selected bond lengths (Å) and angles (°): Au1–P1, 2.2610(8); Au1–S1, 2.3083(8); P1–Au1–S1, 170.89(3); Au1–S1–C41, 105.0(1); Au2–P2, 2.2536(8); Au2–S2, 2.3068(8); P2–Au2–S2, 175.18(3); Au2–S2–C81, 102.0(1).

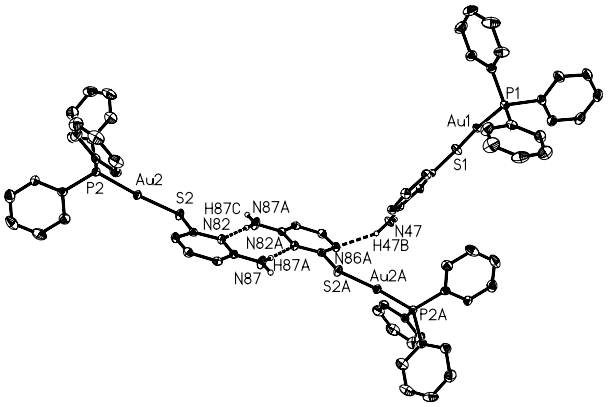


Fig. 6. Connectivity pattern for complex **4** showing the bifurcated double-bridging between a pair of symmetry-related molecules (with Au2 as the metal centers) and the single-bridging with neighboring molecules (with Au1 as the metal centers). The extension of this pattern leads to a three-dimensional network.

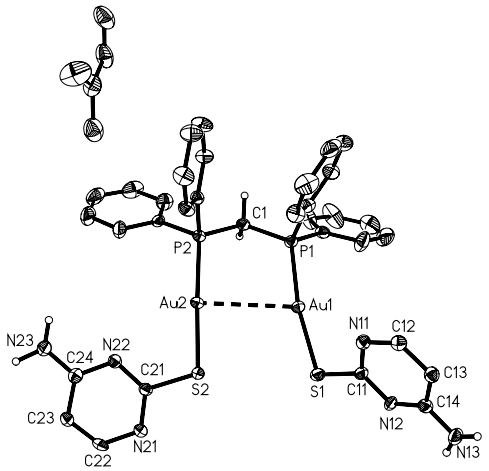


Fig. 7. Molecular structure of the independent dinuclear complex **6** and a dimethylformamide molecule in the asymmetric unit of the crystals. (ORTEP, 50% probability ellipsoids, hydrogen atoms with arbitrary radii.) Selected bond lengths (Å) and angles (°): Au1–Au2, 3.3317(2); Au1–P1, 2.261(1); Au1–S1, 2.309(1); P1–Au1–S1, 168.25(4); Au1–S1–C11, 103.7(1); Au2–P2, 2.2591(9); Au2–S2, 2.3052(9); P2–Au2–S2, 175.66(4); Au2–S2–C21, 106.3(1); P1–C1–P2, 115.6(2); Au1–P1–C1, 119.2(2); Au2–P2–C1, 111.3(1).

in a mixture of CH_2Cl_2 (15 ml) and MeOH (5 ml). The reaction mixture was stirred for 2 h and all solvent removed. The crude product was dissolved in CH_2Cl_2 (15 ml) and filtered through diatomaceous earth. Diethyl ether (20 ml) was added to precipitate the colorless product which was washed with Et_2O (20 ml) and dried. Yield: 87% (110 mg). MS (FAB) $m/z = 1045$, 100% $[M]^+$, 782, 26% $[M - PPh_3]^+$, 721, 37% $[Au(PPh_3)_2]^+$, 586, 19% $[M - AuPPh_3]^+$, 459, 90% $[AuPPh_3]^+$. $^{31}P\{^1H\}$-NMR (CD_2Cl_2, ppm): δ 32.3. ^1H-NMR (CD_2Cl_2, ppm): δ 4.91 (s, 2H, NH_2), 6.60 (d, 1H, H^5, $J_{HH} = 6.4$ Hz), 7.11, 7.57 (m × 2, 31H, $C_6H_5 + H^{3,5}C_6H_3$). Anal. Calc. for $C_{40}H_{34}Au_2BF_4N_3P_2S$: C, 42.46; H, 3.03; N, 3.71. Found: C, 42.17; H, 2.92; N, 3.69%.

2.10. X-ray crystallography

Specimens of suitable quality and size of compounds **2**–**4** and **6** were mounted on the ends of quartz fibers in F06206R oil and used for intensity data collection on a Nonius DIP2020 diffractometer, employing graphite-monochromated Mo–K_α radiation. The structures were solved by a combination of direct methods (SHELXS-97) and difference-Fourier syntheses and refined by full-matrix least-squares calculations on F^2 (SHELXL-97). The thermal motion was treated anisotropically for all non-hydrogen atoms. All C–*H* atoms were calculated and allowed to ride on their parent atoms with fixed isotropic contributions, whereas all N–*H* atoms were located. Further information on crystal data, data collection and structure refinement are summarized in Table 1. Important interatomic distances and angles are shown in the corresponding figure captions.

3. Results and discussion

Complexes **1**–**4** and **6**–**8** were isolated as the only phosphine-containing species from reaction of the (phosphine)gold(I) halide starting materials with 4-amino-2-pyrimidine-thiol, as indicated by the singlet resonances observed in the ^{31}P-NMR spectra. The empirical composition of the products was confirmed by microanalysis and FAB mass spectrometry. The molecular ion was generally the fragment with the highest m/z value, however, in some cases a fragmentation attributable to [2M-(2-SPym-4-NH_2)] was observed. As expected, the 4-amino-2-pyrimidine-thiolate ligand gave rise to three resonances in the ^1H-NMR spectrum. A singlet at 4.7 ppm was assigned to the amino group, while the pyrimidine protons were represented by doublet resonances at 6.0 and 7.8 ppm ($J_{HH} = 5.7$ Hz). Four singlets were observed in the ^{13}C-NMR spectrum for the 4-amino-2-pyrimidine thiolate ligand at 179.3 (C^2), 162.1 (C^4), 155.4 (C^6) and 99.9 (C^5) ppm. The only one of these to display a shift from the free ligand resonance is that for C^6. Characteristic spectroscopic data were obtained for the PR_3, dppm and dppf ligands. The presence of the 2,6-dimethylphenylisocyanide ligand in the complex [(2,6-$C_6H_3Me_2NC$)Au(2-SPym-4-NH_2)] (**5**) was confirmed by resonances in the ^1H-NMR spectrum attributed to the methyl groups (s, 2.40 ppm) and *meta*/*para* aryl protons (7.11 and 7.27 ppm, $J_{HH} = 7.7$ Hz). A strong ν(CN) absorption was observed in the infrared spectrum at 2201 cm^{-1}. Compounds **2**–**4** provided suitable single crystals for structural studies to be undertaken. These revealed hydrogen-bonding networks of considerable complexity.

The dinuclear species (dppm)[Au(2-SPym-4-NH_2)]$_2$ (**6**) and (dppf)[Au(2-SPym-4-NH_2)]$_2$ (**7**) proved to be highly insoluble in di- and trichloromethane, tetrahydrofuran, methanol and in acetone, once precipitated from the reaction mixture. Their composition was given by microanalysis. The major ions in the FAB mass spectra were assigned to fragmentation through loss of one thiolate ligand. ^{31}P- and ^{1}H-NMR spectra of compound **6** were recorded in dimethylfomamide. A singlet resonance at 32.1 ppm in the ^{31}P-NMR spectrum indi-

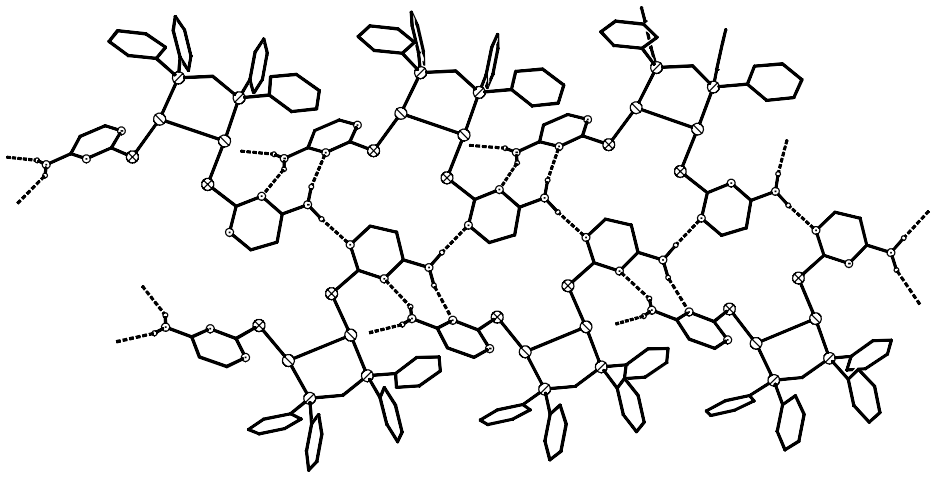


Fig. 8. Hydrogen bonding pattern in a double-strand of complex molecule **6**.

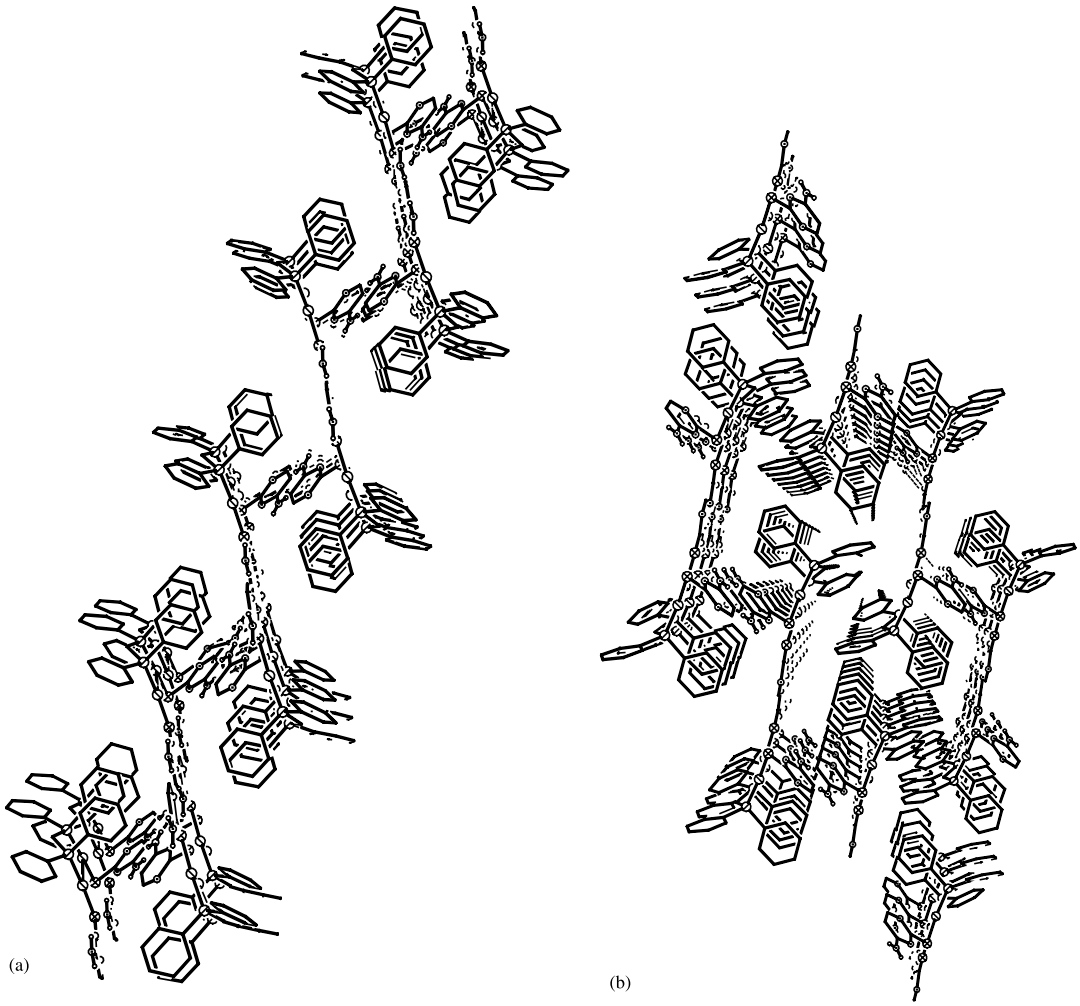


Fig. 9. (a) Projection parallel to a corrugated sheet formed by aggregation of complex molecule **6**. (b) Interlocking (indenting) of these sheets.

Table 2
Hydrogen bonds in compounds **2**–**4** and **6**

	D–H	H···A	D–H···A	D···A	A	Symmetry
Compound ***2***						
N13–H131	0.95	2.17	147.3	3.01	N22	$-X-0.5,\ Y-0.5,\ Z+0.5$
N13–H132	1.05	2.05	147.3	2.99	N32	$X+0.5,\ Y,\ Z$
N23–H231	0.69	2.31	163.1	2.97	N41	$X,\ Y,\ Z$
N23–H232	0.89	2.15	168.7	3.02	N12	$-X-0.5,\ Y+0.5,\ Z-0.5$
N33–H331	0.94	2.18	140.4	2.96	N11	$X-0.5,\ -Y-1.5,\ Z$
N33–H332	0.89	2.19	149.7	2.99	N42	$X,\ Y,\ Z$
N43–H431	0.85	2.11	167.8	2.94	N21	$X+0.5,\ -Y-1.5,\ Z$
N43–H432	1.11	1.89	155.4	2.94	N31	$X,\ Y,\ Z$
Compound ***3***						
N13–H131	0.85	2.23	176.1	3.08	N12	$-X,\ -Y+2,\ -Z+1$
N13–H132	0.85	2.20	174.5	3.05	N41	$-X,\ -Y+1,\ -Z+1$
H23–H231	0.90	2.18	173.3	3.07	N22	$-X+1,\ -Y+2,\ -Z$
N23–H232	0.80	2.33	161.2	3.81	N32	$-X+1,\ -Y+2,\ -Z$
Compound ***4***						
N47–H47A	0.88	2.21	162.4	3.06	N42	$-X,\ -Y,\ -Z+1$
N47–H47B	0.88	2.18	155.7	3.00	N86	$-X+1,\ -Y+1,\ -Z+1$
N87–H87A	0.88	2.14	175.7	3.02	N82	$-X+3,\ -Y+1,\ -Z+1$
N87–H87B	0.88	2.15	161.1	3.00	N46	$-X+2,\ -Y+1,\ -Z+1$
Compound ***6***						
N13–H131	0.76	2.26	167.5	2.99	N11	$-X+1,\ Y+0.5,\ -Z+2$
N13–H132	0.71	2.46	151.3	3.09	N22	$X,\ Y+1,\ Z$
N23–H231	0.99	1.92	172.4	2.90	N21	$-X+2,\ -Y-0.5,\ -Z+2$
N23–H232	0.94	2.17	172.3	3.05	N12	$X,\ Y-1,\ Z$

cated a symmetrical molecule, and a crystallographic study was able to confirm that it adopts the 'A-frame' geometry observed for the vast majority of (dppm)gold(I) species [19]. The molecular structure and that of the hydrogen-bonding network around the 2-SPym-4-NH_2 ligands are discussed in the Section 3.1. It proved possible to obtain a ^{31}P-NMR spectrum of compound **7** only from the reaction mixture before precipitation and this displayed a singlet resonance at 30.0 ppm. Thereafter it became insoluble in all common laboratory solvents including dimethylformamide and dimethylsulfoxide.

Reaction of the oxonium salt $[(Ph_3PAu)_3O]BF_4$ with 2-amino-4-pyrimidine-thiol in the presence of $NaBF_4$ led smoothly to the isolation of the dinuclear complex $[(Ph_3PAu)_2(2\text{-}SPym\text{-}4\text{-}NH_2)]BF_4$ (**8**) in excellent yield. The same product can be obtained by treatment of **3** with Ph_3PAuBF_4 prepared in situ though the one-step route leads to better yields. A molecular ion at $m/z =$ 1045 in 100% abundance is present in the FAB mass spectrum along with fragments due to loss of phosphine. No fragment attributable to $[Ph_3PAu(2\text{-}SPym\text{-}4\text{-}NH_2)]^+$ is observed.

3.1. Discussion of structural results

Of the small series of title compounds **1**–**5** structural data are available for the triethylphosphine (**2**), triphenylphosphine (**3**) and diphenyl(2-pyridyl)phosphine (**4**) complexes. None of these three examples shows aurophilic interaction between the gold(I) centers in the crystal. The compounds are all aggregated solely via extensive hydrogen bonding networks. The absence of metallophilic interactions is probably not due to steric shielding of the metal atoms by the tertiary phosphines and the thiolate ligands. Several other triethyl- and triphenylphosphine complexes were found to aggregate via short gold–gold contacts, where this mode of aggregation is not in competition with other intermolecular interactions. Quite frequently hydrogen bonding was identified as the overruling competitor, and the dominance of hydrogen bonding appears to be a general feature also in the present series. Arene stacking is also known to contribute considerably to the lattice organization of (arylphosphine)gold(I) complexes, but there is no evidence for this type of interaction in the present structures (**3** and **4**). Details are summarized in the following brief discussion.

Crystals of triethylphosphine complex **2** are orthorhombic, space group $Pna2_1$, with $Z = 16$ molecular units in its large unit cell. The asymmetric unit contains no less than four independent molecules which are similar in their configurational and conformational details (Fig. 1). The Au–P and Au–S distances and the P–Au–S angles are all as expected from standard reference data with only minor variations. Interactions between neighboring molecules are established through

the aminopyrimidinethiolate ligands with the amino groups as the proton donor and the pyrimidine ring nitrogen atoms as the proton acceptors. Through two of these parallel interactions, employing one of the two amino hydrogen atoms of each partner molecule and the pyrimidine nitrogen atoms adjacent to the amino groups the usual bifurcated pairing is generated (cf. e.g. center of Fig. 6). The second hydrogen atom of the same amino groups is attached to a donor atom (the second pyrimidine ring nitrogen atom) of another neighbouring unit in different directions. In total, the resulting complicated network is three-dimensional as shown in a projection in Fig. 2.

Crystals of the triphenylphosphine complex **3** grown from dichloromethane solution are triclinic, space group $P\bar{1}$ with $Z = 8$ complex molecules and four solvent molecules in the unit cell. The asymmetric unit thus again contains no less than four independent molecules with similar molecular geometries and two dichloromethane molecules as shown in Fig. 3. The molecules are aggregated via hydrogen bonds of a similar type as described for compound **2**, but a different connectivity pattern leads to strings resembling four-bladed paddle-wheels running parallel to the x axis and mutually indented as shown in Fig. 4.

Crystals of the diphenyl(2-pyridyl)phosphine complex **4** obtained from dichloromethane solution are also triclinic, space group $P\bar{1}$ with $Z = 4$ complexes and four dichloromethane molecules in the unit cell. The asymmetric unit contains two independent complex molecules (and two solvent molecules) which are shown in Fig. 5. The molecular structures are similar to those of the triphenylphosphine analogues (above) because the PPh_3 unit has about the same steric requirements as the Ph_2PyP unit. There is no conspicuous preference in the orientation of the pyridyl rings as compared to the phenyl rings. Optimum space filling appears to be the guiding principle. The typical bifurcated connectivity of two symmetry-equivalent molecules and the attachment of this unit to neighboring molecules to give an extended structure is shown in Fig. 6.

The dinuclear dppm complex **6** has two gold centers held in close proximity, and therefore it is to be expected that these molecules feature short intramolecular aurophilic interactions. These interactions require a *cis*- or *Z*-conformation regarding the orientation of the two diphenylphosphino groups at the bridging methylene unit, but this has been shown to be the standard conformation for all (dppm)digold complexes. The crystal structure of **6** confirms this assumption.

Crystals of the dppm compound **6** obtained from dimethylformamide are monoclinic, space group $P2_1$ with $Z = 2$ complex molecules and two solvent molecules in the unit cell. The asymmtric unit has one independent dinuclear complex molecule, the structure of which is shown in Fig. 7. The intramolecular Au–Au distance is 3.3317(2) Å, well in the range of standard aurophilic bonding. The fact that the gold atoms are drawn together is in fact obvious from the significant bending of the P1–Au1–S1 unit [168.25(4)°] which deviates by 11.75° from linearity. The angle P2–Au2–S2 is reduced to 175.66(4)°. There are sharp bendings at the thiolate sulfur atoms [Au1–S1–C11, 103.7(1)°; Au2–S2–C21, 106.3(1)°] and very different torisonal angles P1–Au1–S1–C11 [73.4(2)°] and P2–Au2–S2–C21 [$-120.8(5)$°]. This leads to two different connectivities through hydrogen bonding in several directions.

The dinuclear complexes are arranged in strings in which the molecules are intimately connected via the bifurcated type of hydrogen bonding illustrated already above for other complexes of this type. In this bonding one hydrogen atom of each amino group and the adjacent nitrogen atom of the pyrimidine ring are engaged. These strings of molecules are associated to give double-stands through hydrogen bonding originating from the second hydrogen atom at one of the two amino groups of each dinuclear complex and reaching out to the second ring nitrogen of a pyrimidine unit in the neighboring string. The second hydrogen atom of the second amino group finally reaches out to a pyrimidine nitrogen atom of another double-strand (Fig. 8). Through this connectivity corrugated sheets are produced (Fig. 9a), which are staked in such a way that efficient space filling is reached through intimate indenting of the columns of phenyl groups covering the sheets above and below (Fig. 9b).

A survey of the above structures (**2**–**4**, **6**) shows that the packing of the molecules is governed solely by hydrogen bonding. The hydrogen bonds in these complexes are listed in Table 2. Intermolecular aurophilic bonding or arene stacking play no role. However, the connectivity varies quite strongly indicating that there is considerable flexibility in the hydrogen-bonding network. The framework can thus be easily adjusted to the sub-structure of the tertiary phosphine ligand which is to be accommodated in such a way that space-filling is most efficient. The absolute dominance of hydrogen bonding in the present structures is probably due to the multifunctionality of the amino-pyrimidine system which can adapt to a manifold of connectivity patterns and thus optimize the packing energy of the lattice.

4. Conclusions

The auration of polyfunctional ligands provides a useful means to study the combined use of hydrogen-bonding and aurophilic interactions in the design of supramolecular networks. Due to the amino protons and nitrogen atoms of the pyrimidine ring, 4-amino-2-

mercaptopyrimidine has proved a highly suitable ligand with which to probe the design of hydrogen-bonding interactions. These results open up the possibility of employing more highly functionalized ligands to create systems of ever greater complexity based on gold–gold contacts and hydrogen bonding.

5. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC nos. 172601–172604 for compounds **2**–**4** and **6**, respectively. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

Acknowledgements

Support of this work by the Deutsche Forschungsgemeinschaft, the Volkswagenstiftung, the Alexander von Humboldt Stiftung (J.D.E.T.W.-E.), and by the Fonds der Chemischen Industrie is gratefully acknowledged. The authors are also indebted to Degussa AG and Heraeus GmbH for the donation of chemicals.

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