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Structural diversity in gold(I) complexes of 4-sulfanylbenzoic acid

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Treatment of the gold(I) halide species AuLCl (where L = PMe_3, PEt_3, PPh_3, $PPh_2(C_5H_4N\text{-}2)$ or $SPPh_3$) and $(AuCl)_2$(P–P) (where P–P = 1,4-bis(diphenylphosphino)butane or 1,1′-bis(diphenylphosphino)ferrocene) with 4-sulfanylbenzoic acid (1 or 2 equivalents as required) in the presence of sodium methoxide provided the corresponding phosphine gold(I) thiolate complexes $AuL(4\text{-}SC_6H_4CO_2H)$ and $[Au(4\text{-}SC_6H_4CO_2H)]_2$(P–P), respectively. Addition of two equivalents of the acid (in the presence of NaOMe) to $[N(PPh_3)_2][AuCl_2]$ yielded the dithiolate species $[N(PPh_3)_2][Au(4\text{-}SC_6H_4CO_2H)_2]$. A polyaurated product $[(Ph_3PAu)_2(4\text{-}SC_6H_4CO_2H)]BF_4$ was obtained on treating the acid with the oxonium complex $[(Ph_3PAu)_3O]BF_4$. The species $AuL(4\text{-}SC_6H_4CO_2H)$ (L = PEt_3, PPh_3 or $PPh_2(C_5H_4N\text{-}2)$) have been investigated crystallographically and reveal diverse structures incorporating aurophilic contacts, Au · · · S interactions and hydrogen bonding.

Introduction

Gold thiolates are an extremely important class of gold compounds. Complexes of the type Au(SR) or AuL(SR) (R = alkyl, aryl, *etc.*; L = neutral donor ligand) are contained in most "liquid golds" for the glass and ceramics industry, in gold pastes used in the electrical industry and microelectronics, and in gold drugs for chemotherapy.[1] Gold thiolate functions are the key connectivities between the surface of bulk gold and the substrate films in self-assembly monolayer (SAM) nanotechnology.[2] The high affinity of gold for the heavy chalcogen elements (sulfur, selenium and tellurium) allows the synthesis of many Au/S (Se,Te) preparations from gold salts and thioles or thiolates, *etc.*,[3] although most of these compounds are thermodynamically unstable relative to gold metal and organic disulfides.

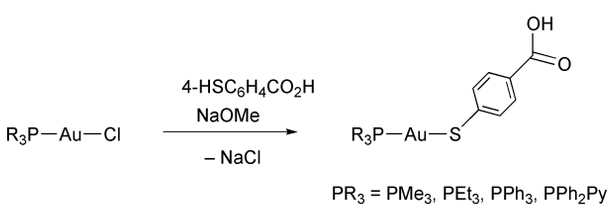
Many gold(I) thiolates (AuSR) and gold(I) thiolate complexes AuL(SR) are known to aggregate either *via* intermolecular aurophilic contacts (*i.e.* Au · · · Au closed-shell interactions) or intermolecular gold–sulfur coordination (Au · · · S) depending on the electronic or steric nature of the substituents. These interactions lead to interesting supramolecular structures often associated with intriguing photophysical properties. Theoretical work has predicted that Au · · · Au contacts should be particularly strong with sulfide or thiolate substituents,[4] but structural data do not always follow this pattern because Au · · · S contacts are also able to compete efficiently and a delicate balance between the two types of interactions often leads to unexpected results.[5]

In the design of a structural pattern, crystal engineering, other weak forces can be combined with Au · · · Au/Au · · · S interactions, and recent attempts to incorporate hydrogen bonding have been particularly successful.[6,7] Ligands which offer both thiolate and carboxylate functions were shown to be instrumental in the construction of multidimensional arrays of gold(I) complexes.[8] Other systems probed successfully in this context were those based on hydroxyphosphine/phosphinate,[9] imidazole/imidazolate[10] and phosphinophenol/phosphinophenolate[11] complexes.

Our initial studies with 2-sulfanylbenzoic acid[7] have now been extended to include gold(I) 4-sulfanylbenzoic acid complexes, in which a different geometrical orientation of the substituents induces entirely different connectivity patterns.

Preparative studies

(Phosphine)gold(I) complexes of 4-sulfanylbenzoic acid are easily obtained from reactions of this acid with coordination compounds of the type $Au(R_3P)Cl$ in methanol with an equivalent amount of sodium methanolate. Four different tertiary monophosphines were employed with R = Me (**1**), Et (**2**) or Ph (**3**), and $R_3 = Ph_2(C_5H_4N\text{-}2)$ (**4**) (Scheme 1). Two examples of



Scheme 1

complexes bearing bisphosphines, $[Au(4\text{-}SC_6H_4CO_2H)]_2$(dppb) **5** [dppb = 1,4-bis(diphenylphosphino)butane] and $[Au(4\text{-}SC_6H_4CO_2H)]_2$(dppf) **6** [dppf = 1,1′-bis(diphenylphosphino)ferrocene], were prepared in a similar manner using two equivalents of the acid and NaOMe from $(AuCl)_2$(dppb) and $(AuCl)_2$(dppf), respectively (Scheme 2). Two examples in which gold is bound solely to sulfur were also investigated. In a similar manner to the examples reported by Nakamoto and coworkers,[12] the compound $[N(PPh_3)_2][Au(4\text{-}SC_6H_4CO_2H)_2]$ **7** was obtained from the reaction of $[N(PPh_3)_2][AuCl_2]$ with 2 equivalents of 4-sulfanylbenzoic acid in the presence of sodium methoxide. The species $Au(Ph_3P{=}S)Cl$ was also found to react with the same acid in the presence of NaOMe to yield $Au(Ph_3P{=}S)(4\text{-}SC_6H_4CO_2H)$ **8**. A polyaurated product $[(Ph_3PAu)_2(4\text{-}SC_6H_4CO_2H)]BF_4$ **9** was obtained on treatment of the acid with the oxonium salt $[(Ph_3PAu)_3O]BF_4$.

All products were isolated in good yields as colourless or pale yellow (in the case of **6**) crystalline solids which were characterised by NMR spectroscopy (^1H, ^{31}P) and FAB mass spectrometry (where possible) and gave satisfactory elemental analyses (see Experimental). The compounds **1**–**4** and **9** are soluble in both dichloromethane and chloroform, and **5**–**8** dissolve in (d^6) dimethyl sulfoxide. The NMR spectra of these solutions

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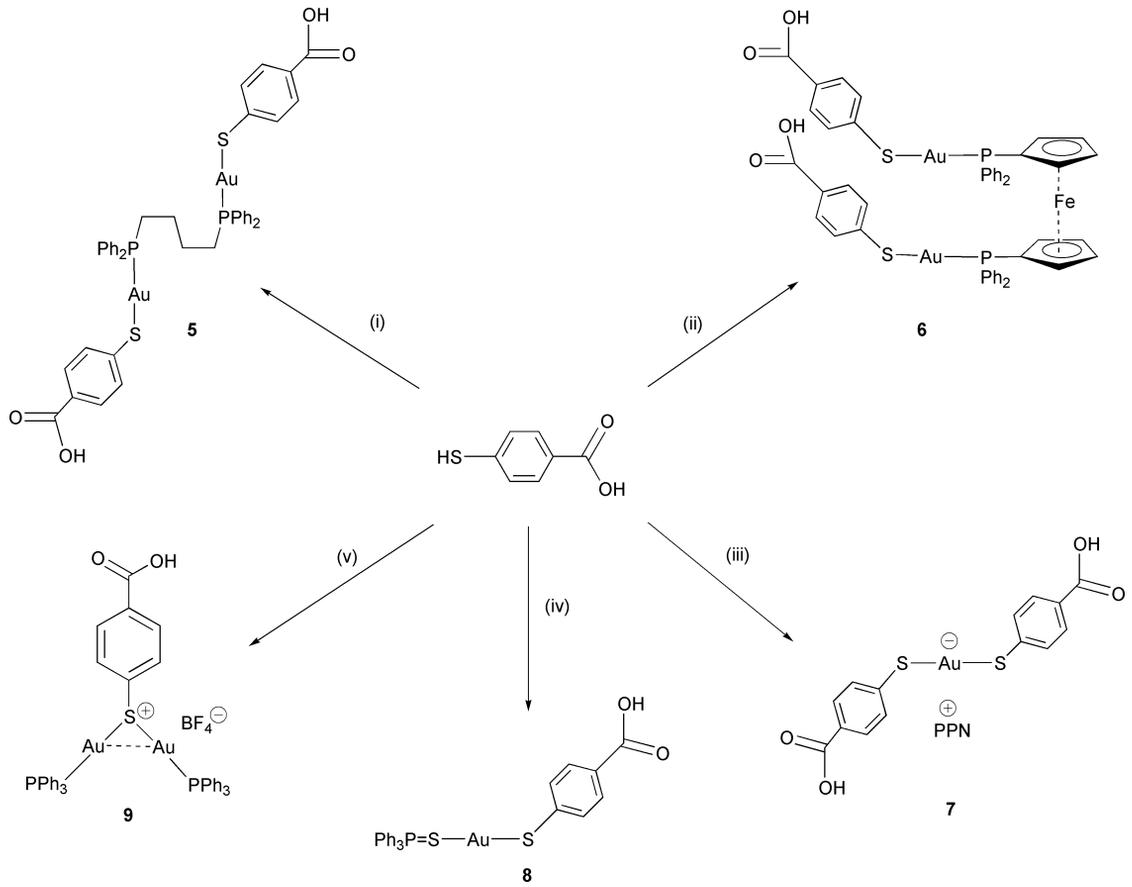

Scheme 2 (i) $(dppb)(AuCl)_2$, NaOMe; (ii) $(dppf)(AuCl)_2$, NaOMe; (iii) [PPN][$AuCl_2$], NaOMe [PPN = $N(PPh_3)_2^+$]; (iv) $(Ph_3P{=}S)AuCl$, NaOMe; (v) $[(Ph_3PAu)_3O]BF_4$, $NaBF_4$.

show singlet signals for $^{31}P\text{-}\{^1H\}$ and the expected sets of resonances in the ^1H spectra.

The FAB mass spectra of complexes **1**–**4** showed the molecular ions $[M]^+$ preceded by the cation $[M + PR_3]^+$, probably generated in the ionization process of the aggregates present in the solid (below). Not surprisingly, therefore, cations $[Au(PR_3)_2]^+$ are also present in the spectra with significant intensity. Of the remaining compounds, only **5** and **9** were sufficiently soluble to allow useful mass spectra to be obtained. Compound **5** showed a molecular ion in the negative FAB mass spectrum at *m*/*z* 503, however **9** displayed no molecular ion but gave a peak at *m*/*z* 722 for $[M - SC_6H_4CO_2H]^+$.

Compounds **2**–**4** could be obtained as single crystals from chloroform or dichloromethane through layering with pentane, however **1**, **7** and **9** failed to yield crystals of sufficient quality. The complexes **5**, **6** and **8** are insoluble in all common laboratory solvents apart from dimethyl sulfoxide and did not yield crystals suitable for structural analysis.

Structural studies

Crystals of compound **2** (obtained from dichloromethane–pentane) are monoclinic, of space group $P2_1/n$, with $Z = 4$ formula units in the unit cell. There are no solvent molecules in the lattice. The individual mononuclear units (Fig. 1) form chains along the *c* axis of the crystal and show contacts between Au–S groups at one end and paired hydrogen bonding of the carboxylic acid groups at the other (Fig. 2).

The coordination of the gold atoms in compound **2** is close to linear [P–Au–S 176.57(4)°] and the Et_3P–Au–S units of neighbouring molecules are aligned head to tail to form parallelograms with edges Au–S 2.313(1), Au · · · S* 3.565(1) Å and a diagonal Au · · · Au* of 3.629(1) Å. The intermolecular Au · · · Au* contacts are therefore of about the same length as the intermolecular Au · · · S* contacts. Since the sum of the van

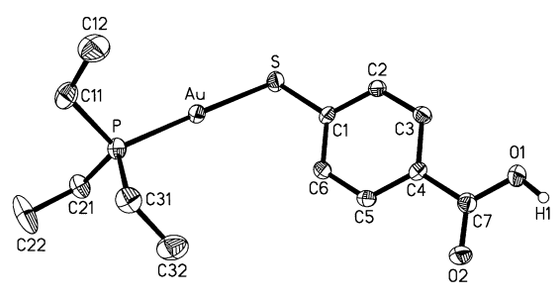

Fig. 1 Molecular structure of the monomeric unit of complex **2** (ORTEP, 50% probability ellipsoids, hydrogen atoms omitted except for carboxylic acid) and atomic numbering. Selected bond lengths [Å] and angles [°]: Au–P 2.268(1), Au–S 2.313(1), P–C11 1.824(4), P–C31 1.817(4), P–C51 1.816(4) and S–C1 1.761(4); P–Au–S 176.57(4), C11–P–C31 105.6(2), C31–P–C51 106.2(2), C11–P–C51 103.9(2) and Au–S–C1 104.5(1).

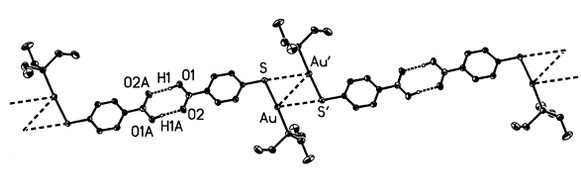

Fig. 2 Chains of molecules **2** joined together through Au · · · S′/Au · · · Au′ interactions and through carboxylic hydrogen bonding.

der Waals radii is larger for two gold atoms [3.60 Å] than for an AuS pair [3.35 Å], the former contact is more likely to be the dominating contributor to the aggregation. The hydrogen bonding between the two carboxylic acid groups shows no structural anomaly.

Crystals of compound **3** (from dichloromethane–pentane) are triclinic, of space group $P\bar{1}$, with $Z = 4$ mononuclear units and two molecules of dichloromethane. There is also some as

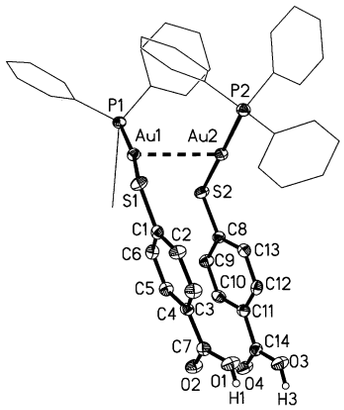

Fig. 3 Molecular structures of two crystallographically independent complexes **3** joined *via* aurophilic interactions Au1 · · · Au2 in **3**·$0.5CH_2Cl_2$ (details as in Fig. 1). Selected bond lengths [Å], bond angles and torsion angles [°]: Au1 · · · Au2 3.0756(2), Au1–P1 2.276(1), Au1–S1 2.315(1), S1–C1 1.765(4), Au2–P2 2.262(1), Au2–S2 2.302(1) and S2–C8 1.751(4); P1–Au1–S1 168.95(4), Au1–S1–C1 108.6(1), P2–Au2–S2 174.78(4) and Au2–S2–C8 114.4(1); S1–Au1–Au2–S2 117.19(4) and P1–Au1–Au2–P2 105.08(4).

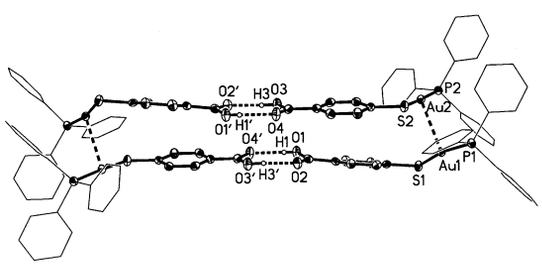

Fig. 4 Macrocyclic tetranuclear unit of complex **3** in the crystal of **3**·$0.5CH_2Cl_2$. The monomeric units are joined *via* aurophilic and paired hydrogen bonding. Atoms are related by a centre of inversion.

yet unidentified additional solvent in the lattice, which was disregarded in the refinement of the structure by pertinent techniques (see Experimental section). The asymmetric unit contains two independent mononuclear units [**3**(I), **3**(II)] with very similar molecular geometry. These two units form dimers *via* a short intermolecular aurophilic contact [Au1 · · · Au2 3.0756(2) Å] between crossed P–Au–S moieties [S1–Au1 · · · Au2–S2 117.2°] (Fig. 3). Note that in compound **3** the intermolecular S1 · · · S2 distance [4.562 Å] is much longer than the Au1 · · · Au2 contact. The crossed arrangement of the P–Au–S units is necessary in order to accommodate the two bulky Ph_3P groups next to each other. In a parallel organization (head-to-tail and in particular head-to-head) no short Au1 · · · Au2 contact would be possible and the system would probably have to undergo a shift of the units similar to that detected in compound **2** to entertain at least Au · · · S contacts.

Through the dimerization of the two molecules the two benzoic acid units become stacked on top of each other, however the phenylene rings are not coplanar and have a distance between their centres of 4.041 Å. The carboxylic acid end groups are able to engage in parallel paired hydrogen bonding with another dinuclear unit. The distance between the stacked hydrogen-bonded systems is 3.617 Å and thus shorter than the distance between the stacked phenylene units (Fig. 4). In total the compound forms *tetramers* through a large elongated macrocycle comprising two pairs of gold atoms and two pairs of thiolato benzoic acid groups. By contrast, the equivalent units of compound **2** form a *polymer*.

Crystals of compound **4** (from chloroform) are triclinic, of space group $P\bar{1}$, with $Z = 4$ molecules of the complex and two molecules of chloroform in the unit cell. The asymmetric unit features two independent gold(I) complexes [**4**(I), **4**(II)] which are very similar in their dimensions and conformations. Each

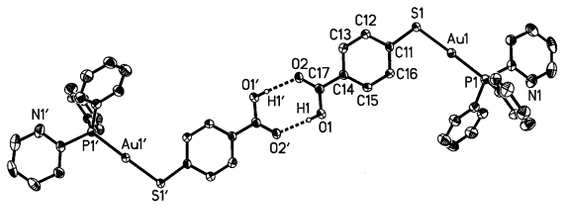

Fig. 5 Two complex molecules **4** linked by paired hydrogen bonds. The two monomers (with gold atom Au1) are related by a centre of inversion (ORTEP, hydrogen atoms omitted except for carboxylic acids). The lattice contains a second independent molecule (with gold atom Au2) with similar dimensions and conformations. Selected bond lengths [Å] and angles [°]: Au1–P1 2.256(1), Au1–S1 2.304(1), S1–C11 1.751(4), Au2–P2 2.259(1), Au2–S2 2.308(1) and S2–C21 1.760(4); P1–Au1–S1 178.40(4), Au1–S1–C11 108.4(1), P2–Au2–S2 177.63(4) and Au2–S2–C21 107.2(1).

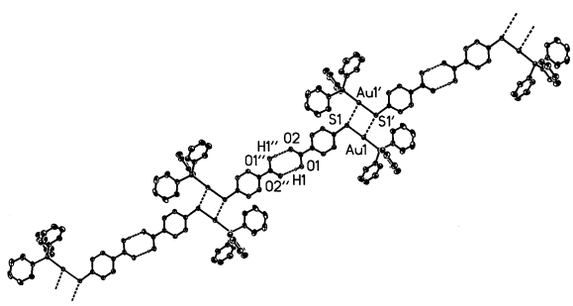

Fig. 6 Association of the dinuclear units shown in Fig. 5 into chains through Au1 · · · S1′/Au1′ · · · S1 interactions. Similar chains are formed from the second set of independent units with gold atom Au2 (see text).

gold atom is attached to a sulfur atom and has coordination number 2 with only a slight bending of the P–Au–S axes [P1–Au1–S1 178.40(4), P2–Au2–S2 177.63(4)°]. The carboxylic acid functions are virtually coplanar with the benzene rings. Each individual monomer [**4**(I) or **4**(II)] is associated with another monomer of its kind related by a crystallographic centre of inversion through hydrogen bonding where the two paired carboxylic acid groups meet. This part is again virtually identical for the two independent molecules (Fig. 5 shows only the molecules with P1–Au1–S1).

Similar to the situation found in compound **2**, the dimers generated through hydrogen bonding are aggregated further into strings of dimers through Au · · · S/Au · · · S contacts at both ends. Au_2S_2 parallelograms are formed which are similar for molecules **4**(I) and **4**(II) but very different from those found in **2**. The variations arise from a different shifting of the S–Au–P units against each other. The intra- and inter-molecular Au–S/Au–S* edges are Au1–S1 2.304(1), Au1 · · · S1* 3.212(1) and Au2–S2 2.308(1), Au2 · · · S2* 3.253(1) Å but the two Au atoms are at the ends of the long diagonals [Au1 · · · Au1* 4.234(1), Au2 · · · Au2* 4.232(1) Å] as compared to Au · · · Au* 3.629(1) Å in **2**.

In total, compound **4** has two independent polymeric chains running parallel with only slightly different coupling patterns at the Au–S end groups. Only one of the two strands is shown in Fig. 6.

Experimental

General information

The experiments were carried out routinely in air. NMR: JEOL GX 400 spectrometer using deuteriated solvents with the usual standards at 25 °C. MS: Varian MAT311A instrument (FAB, *p*-nitrobenzyl alcohol). The 4-sulfanylbenzoic acid was obtained commercially. The complexes $Au(R_3P)Cl$ (R = Me,[14] Et[15] or Ph[14]), $Au[(2\text{-}NC_5H_4)Ph_2P]Cl$,[16] $(AuCl)_2(dppb)$,[17] $[N(PPh_3)][AuCl_2]$,[18] $Au(Ph_3P{=}S)Cl$,[19] $(AuCl)_2(dppf)$[20] and $[(Ph_3PAu)_3O]BF_4$[21] were prepared following literature procedures.

Preparations

Au(Me$_3$P)(4-SC$_6$H$_4$CO$_2$H) 1. A solution of 4-sulfanylbenzoic acid (25 mg, 0.16 mmol) and sodium methoxide (9 mg, 0.17 mmol) in methanol (5 mL) was added dropwise to a stirred solution of Au(Me$_3$P)Cl (50 mg, 0.16 mmol) in dichloromethane (15 mL). After stirring for 2 h, all solvent was removed under vacuum. The residue was dissolved in dichloromethane (10 mL) and filtered through diatomaceous earth to remove NaCl. Pentane (25 mL) was added to precipitate the colourless product in 72% (50 mg) yield. MS (FAB): *m*/*z* = 700, 34, [M + PMe$_3$]$^+$; 427, 60, [M]$^+$; 350, 19, [Au(PMe$_3$)$_2$]$^+$; and 273, 100%, [M − SC$_6$H$_4$CO$_2$H]$^+$. ^{31}P-{^{1}H} NMR (CD$_2$Cl$_2$): δ 0.86 (s). ^{1}H NMR (d^6-dmso): δ 1.61 (d, 9 H, CH$_3$, J_{HP} = 10.2); 7.56, 7.75 (AB system, 4 H, C$_6$H$_4$, J_{HH} = 8.5 Hz). Calc. for C$_{10}$H$_{14}$AuO$_2$PS: C, 28.18; H, 3.31%. Found: C, 27.39; H, 3.48%.

Au(Et$_3$P)(4-SC$_6$H$_4$CO$_2$H) 2. Using the same procedure as for compound **1** with 4-sulfanylbenzoic acid (44 mg, 0.29 mmol), sodium methoxide (16 g, 0.30 mmol) and Au(Et$_3$P)Cl (100 mg, 0.29 mmol) gave a colourless product. Yield: 67% (90 mg). MS (FAB): *m*/*z* = 784, 4, [M + PEt$_3$]$^+$; 469, 12, [M]$^+$; 434, 2, [Au(PEt$_3$)$_2$]; and 315, 20%, [M − SC$_6$H$_4$CO$_2$H]$^+$. ^{31}P-{^{1}H} NMR (CD$_2$Cl$_2$): δ 38.9 (s). ^{1}H NMR (CD$_2$Cl$_2$): δ 1.23 (dt, 6 H, CH$_2$, J_{HP} = 18.7, J_{HH} = 7.6); 1.90 (dq, 9 H, CH$_3$, J_{HP} = 9.9 Hz, J_{HH} = 7.7); 7.57, 7.76 (AB system, 4 H, C$_6$H$_4$, J_{HH} = 8.6 Hz). Calc. for C$_{13}$H$_{20}$AuO$_2$PS: C, 33.34; H, 4.31%. Found: C, 32.99; H, 4.30%.

Au(Ph$_3$P)(4-SC$_6$H$_4$CO$_2$H) 3. Using the same procedure as for compound **1** with 4-sulfanylbenzoic acid (156 mg, 1.01 mmol), sodium methoxide (60 mg, 1.11 mmol) and Au(Ph$_3$P)Cl (500 mg, 1.01 mmol) provided a colourless product. Yield: 92% (570 mg). MS (FAB): *m*/*z* = 1073, 16, [M + PPh$_3$]$^+$; 722, 9, [Au(PPh$_3$)$_2$]$^+$; 614, 38, [M]$^+$; and 460, 100%, [M − SC$_6$H$_4$CO$_2$H]$^+$. ^{31}P-{^{1}H} NMR (CDCl$_3$): δ 40.0 (s). ^{13}C-{^{1}H} NMR (CDCl$_3$): δ 172.0 (s, CO$_2$), 152.3 (s, SC), 134.2 (d, *o*/*m*-C of C$_6$H$_5$, J_{CP} = 13.8), 132.0 (s, *o*/*m*-C of C$_6$H$_4$), 131.9 (d, *p*-C of C$_6$H$_5$, J_{CP} = 2.3), 129.7 (s, *o*/*m*-C of C$_6$H$_4$), 129.3 (d, *o*/*m*-C of C$_6$H$_5$, J_{CP} = 11.5) and 129.1 (d, *ipso*-C$_6$H$_5$, J_{CP} = 58.4 Hz). ^{1}H NMR (CDCl$_3$): δ 7.47–7.59 (m, 15 H, C$_6$H$_5$), 7.67, 7.81 (AB system, 4 H, C$_6$H$_4$, J_{HH} = 8.4 Hz). Calc. for C$_{25}$H$_{20}$AuO$_2$PS: C, 49.03; H, 3.29%. Found: C, 49.07; H, 3.32%.

Au[(2-NC$_5$H$_4$)Ph$_2$P](4-SC$_6$H$_4$CO$_2$H) 4. Using the same procedure as for compound **1** with 4-sulfanylbenzoic acid (31 mg, 0.20 mmol), sodium methoxide (12 mg, 22 mmol) and [Au[(2-NC$_5$H$_4$)Ph$_2$P]Cl] (100 mg, 0.20 mmol) provided a colourless product. Yield: 81% (100 mg). MS (FAB): *m*/*z* = 1075, 9, [M + P(C$_5$H$_4$N)Ph$_2$]$^+$; 724, 5, [Au{P(C$_5$H$_4$N)Ph$_2$}$_2$]$^+$; 615, 26, [M]$^+$; and 461, 68%, [M − SC$_6$H$_4$CO$_2$H]$^+$. ^{31}P-{^{1}H} NMR (CD$_2$Cl$_2$): δ 39.2 (s). ^{1}H NMR (CD$_2$Cl$_2$): δ 7.40–7.85 (m, 17 H, C$_6$H$_5$ + C$_6$H$_4$) and 8.82 (d, C$_5$H$_4$N, 1 H, J_{HH} = 4.7 Hz). Calc. for C$_{24}$H$_{19}$AuNO$_2$PS: C, 46.99; H, 3.12; N, 2.28%. Found: C, 46.59; H, 3.17; N, 2.14%.

[Au(4-SC$_6$H$_4$CO$_2$H)]$_2$(dppb) 5. A solution of 4-sulfanylbenzoic acid (51.9 mg, 0.34 mmol) and sodium methoxide (20 mg, 0.37 mmol) in methanol (5 mL) was added dropwise to a stirred solution of (AuCl)$_2$(dppb) (150 mg, 0.17 mmol) in dichloromethane (15 mL) causing immediate precipitation of a colourless product. After stirring for 1 h, all solvent was removed under vacuum. The residue was filtered off, washed with water (25 mL), acetone (10 mL) and pentane (10 mL) to give a 60% (113 mg) yield. ^{31}P-{^{1}H} NMR (d^6-dmso): δ 36.2 (s). ^{1}H NMR (d^6-dmso): δ 1.76 [s(br), 4 H, CH$_2$], 2.84 [s(br), 4 H, CH$_2$], 7.50, 7.64 (AB system, 8 H, C$_6$H$_4$, J_{HH} = 8.4 Hz); 7.55, 7.74–7.80 (m, 20 H, C$_6$H$_5$). Calc. for C$_{21}$H$_{19}$AuO$_2$PS: C, 44.77; H, 3.40%. Found: C, 44.28; H, 3.37%.

[Au(4-SC$_6$H$_4$CO$_2$H)]$_2$(dppf) 6. Using the same procedure as for compound **5** with 4-sulfanylbenzoic acid (30 mg, 0.20 mmol), sodium methoxide (12 g, 0.22 mmol) and (AuCl)$_2$(dppf) (100 mg, 0.10 mmol) provided a pale yellow product. Yield: 66% (81 mg). ^{31}P-{^{1}H} NMR (d^6-dmso): δ 32.5 (s). ^{1}H NMR (d^6-dmso): δ 4.37, 4.58 (m × 2, 8 H, C$_5$H$_4$); 7.50–7.61 (m, 28 H, C$_6$H$_5$ + C$_6$H$_4$). Calc. for C$_{48}$H$_{38}$Au$_2$FeO$_4$P$_2$S$_2$: C, 45.95; H, 3.05%. Found: C, 45.53; H, 2.96%.

[N(PPh$_3$)$_2$][Au(4-SC$_6$H$_4$CO$_2$H)$_2$] 7. A solution of 4-sulfanylbenzoic acid (71 mg, 0.46 mmol) and sodium methoxide (27 mg, 0.50 mmol) in methanol (5 mL) was added dropwise to a stirred solution of [N(PPh$_3$)$_2$][AuCl$_2$] (150 mg, 0.23 mmol) in dichloromethane (20 mL) causing immediate precipitation of a colourless product. After stirring for 1 h, all solvent was removed under vacuum. The residue was filtered off, washed with water (30 mL), acetone (10 mL) and pentane (10 mL) to give a 77% (150 mg) yield. MS (FAB, negative ion): *m*/*z* = 503, 100% [M]$^-$. ^{31}P-{^{1}H} NMR (d^6-dmso): δ 20.9 (s, N(PPh$_3$)$_2$). ^{1}H NMR (d^6-dmso): δ 7.46–7.70 (m, 38 H, C$_6$H$_5$ + C$_6$H$_4$). Calc. for C$_{50}$H$_{40}$AuNO$_4$P$_2$S$_2$: C, 57.64; H, 3.87, N, 1.34%. Found: C, 57.00; H, 3.95, N, 1.28%.

Au(Ph$_3$P=S)(4-SC$_6$H$_4$CO$_2$H) 8. A solution of 4-sulfanylbenzoic acid (23 mg, 0.15 mmol) and sodium methoxide (9 mg, 0.17 mmol) in methanol (5 mL) was added dropwise to a stirred solution of Au(Ph$_3$P=S)Cl (80 mg, 0.15 mmol) in dichloromethane (10 mL) causing immediate precipitation of a colourless product. Treatment as for compound **7** gave a 75% (73 mg) yield. ^{31}P-{^{1}H} NMR (d^6-dmso): δ 42.7 (s). ^{1}H NMR (d^6-dmso): δ 7.56–7.70 (m, 19 H, C$_6$H$_5$ + C$_6$H$_4$). Calc. for C$_{25}$H$_{20}$AuO$_2$PS$_2$: C, 42.81; H, 3.04%. Found: C, 42.13; H, 2.80%.

[(Ph$_3$PAu)$_2$(4-SC$_6$H$_4$CO$_2$H)]BF$_4$ 9. A solution of 4-sulfanylbenzoic acid (14 mg, 0.09 mmol), [(Ph$_3$PAu)$_3$O]BF$_4$ (200 mg, 0.14 mmol) and NaBF$_4$ (50 mg, 0.46 mmol) in dichloromethane (5 mL) was stirred for 2 h. It was filtered and pentane (20 mL) carefully added to the filtrate to precipitate a colourless product in 69% (163 mg) yield. MS (FAB): *m*/*z* = 722, 56, [M − SC$_6$H$_4$CO$_2$H]; and 459, 85, [Au(PPh$_3$)]$^+$. ^{31}P-{^{1}H} NMR (CDCl$_3$): δ 35.2 [s(br)]. ^{1}H NMR (CDCl$_3$): δ 7.33–7.51, 7.57–7.60 (m, 30 H, C$_6$H$_5$), 7.78, 8.08 (AB system, 4 H, C$_6$H$_4$, J_{HH} = 8.4 Hz). Calc. for C$_{43}$H$_{35}$Au$_2$BF$_4$O$_2$P$_2$S: C, 44.58; H, 3.05%. Found: C, 44.56; H, 3.20%.

X-Ray crystallography

Specimens of suitable quality and size of compounds **2**, **3**, and **4** were mounted on the ends of quartz fibres in F06206R oil and used for intensity data collection on a Nonius DIP2020 diffractometer employing graphite-monochromated Mo-Kα radiation. Intensity data were corrected for absorption effects (DELABS from PLATON).[23] The structures were solved by a combination of direct methods (SHELXS 97)[23] and Fourier-difference syntheses and refined by full matrix least-squares calculations on F^2 (SHELXL 97).[24] 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 O-*H* atoms were located and refined isotropically. Crystals of compound **3** contained some additional disordered and unidentified solvent in the lattice which was not included in the refinement but was handled using the 'SQUEEZE' procedure (from PLATON).[22] The volume occupied by the solvent is 112 Å^3, and the number of electrons per unit cell deduced by SQUEEZE is 19 corresponding to half-occupancy by disordered dichloromethane or tetrahydrofuran. Further information on crystal data, data collection and structure refinement is summarized in Table 1.

CCDC reference numbers 155654–155656.

Table 1 Crystal data, data collection and structure refinement for compounds **2**, **3**·0.5CH_2Cl_2 and **4**·2$CHCl_3$

	2	**3**·0.5CH_2Cl_2	**4**·2$CHCl_3$
Empirical formula	$C_{13}H_{20}AuO_2PS$	$C_{25.50}H_{21}AuClO_2PS$	$C_{25}H_{20}AuCl_3NO_2PS$
M	468.29	654.87	732.77
Crystal system	Monoclinic	Triclinic	Triclinic
Space group	$P2_1/n$	$P\bar{1}$	$P\bar{1}$
a/Å	7.2190(1)	12.0102(2)	8.3563(1)
b/Å	14.0220(1)	13.3450(3)	17.4820(3)
c/Å	15.4040(1)	17.0602(3)	19.2000(3)
α/°		74.062(1)	104.530(1)
β/°	93.094(5)	71.819(1)	90.423(1)
γ/°		86.963(1)	102.696(3)
U/Å^3	1556.99(3)	2496.37(8)	2642.92(7)
Z	4	4	4
μ(Mo-Kα)/cm^{-1}	96.8	61.68	60.3
T/K	143	143	143
Measured reflections	26047	36359	59270
Unique reflections	4807 [R_{int} = 0.0427]	9408 [R_{int} = 0.0335]	15978 [R_{int} = 0.0531]
Refined parameters	163	576	621
$R1$ [$I > 2\sigma(I)$]	0.0313	0.0266	0.0420
$wR2$	0.0707	0.0629	0.0884

See http://www.rsc.org/suppdata/dt/b1/b100113m/ for crystallographic data in CIF or other electronic format.

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