Gold clustering at the methylthiolate anion

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By reaction with the aurating agents $[Au(PMe_3)]BF_4/O_3SCF_3$ or $[\{(Me_3P)Au\}_3O]BF_4$ in molar ratios 1 : 1, 1 : 2 or 1 : 3, sodium methylthiolate NaSMe is converted into dinuclear $[Au(PMe_3)(SMe)]_2$ 1, tetranuclear $[\{MeS[Au(PMe_3)]_2\}_2X_2]$ (X = BF_4 2a, O_3SCF_3 2b) and the novel trinuclear $[MeS\{Au(PMe_3)\}_3][O_3SCF_3]_2$ 3 complexes.

The phenomenon of gold clustering at boron, carbon, and the pnicogens, chalcogens and halogens has been studied extensively in recent years.[1] A large variety of stoichiometries and structures of gold clusters with interstitial main-group elements has been established and the bonding rationalized in terms of cluster theory with significant contributions from interactions between closed-shell gold(I) centres.[1–3] Parallels based on the isolobal principle,[4] which relates units LAu^+ with the proton H^+, were also instrumental as a guiding principle, and the discovery of *e.g.* the oxygen-centred cationic species $[(LAu)_3O]^+$ and $[(LAu)_4O]^{2+}$ was quickly accepted[5] because of the analogy to $[H_3O]^+$ and the elusive $[H_4O]^{2+}$,[6] as was $[(LAu)_5C]^+$ because of its analogy to $[CH_5]^+$ (L = donor ligand).[7,8]

We now report the synthesis of gold clusters resembling the products of the protonation of a simple mercaptan, *i.e.* MeSH, $[MeSH_2]^+$ and even $[MeSH_3]^{2+}$. Protonated alcohols and mercaptans have often been considered as intermediates or transition states of reaction mechanisms,[6] but there is little hard experimental evidence especially for the dications.

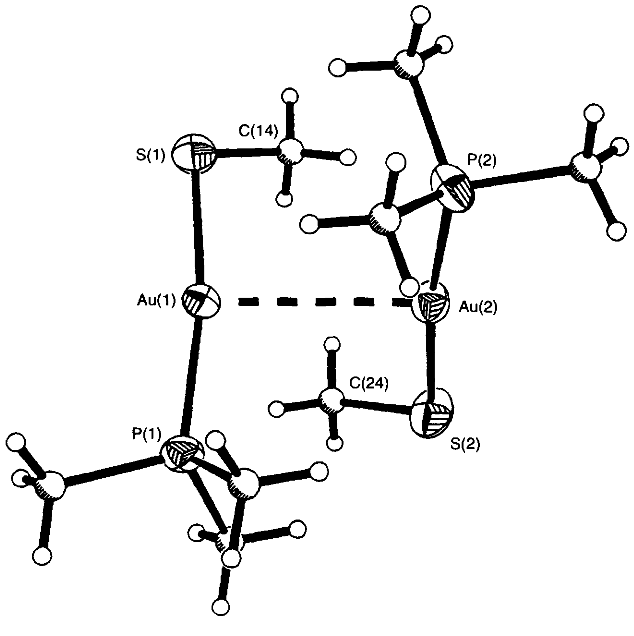

Fig. 1 Molecular structure of the dimer of compound **1** with atomic numbering (ORTEP, hydrogen atoms omitted). Selected bond lengths (Å) and angles (°): Au(1)···Au(2) 3.158(1), Au(1)–S(1) 2.285(6), Au(2)–S(2) 2.285(6), Au(1)–P(1) 2.263(6), Au(2)–P(2) 2.270(5); S(1)–Au(1)–P(1) 171.0(2), S(2)–Au(2)–P(2) 171.1(2), A(1)–S(1)–C(14) 105.5(8), Au(2)–S(2)–C(24) 110.0(9).

Treatment of $[AuCl(PPh_3)]$ with 1 equiv. of NaSMe gives the neutral $[Au(PPh_3)(SMe)]$ **1** as stable colourless crystals.† According to an X-ray diffraction study,‡ the individual complex molecules have the standard quasi-linear coordination geometry at gold and a bending at sulfur (Fig. 1). The compound is associated into dimers with a 'crossed' orientation of the monomers and a short Au···Au contact of 3.240(1) Å. Note how the slight bendings at the gold atoms [171.1° (av.)] shortens this metal–metal contact.

The reaction of **1** with 1 equiv. of $[Au(PMe_3)]BF_4$, or of NaSMe with 2 equiv. of this reagent or of the corresponding oxonium salt, affords the binuclear complex salt **2a** (Scheme 1).† The product is readily identified by its spectroscopic data, in particular by the molecular ion $[MeS(AuPMe_3)_2]^+$ in its FD or FAB mass spectra.†

Treatment of NaSMe with an excess (1 : 3) of the reagent $[Au(PMe_3)]OSO_2CF_3$ yields a set of products consisting largely of the dinuclear species **2b**, but containing also significant amounts of a trinuclear species **3** (Scheme 1).† The existence of compound **3** was first suggested by the detection of the cation

$$NaSMe + [Au(PMe_3)]BF_4 \rightarrow [Au(PMe_3)(SMe)] \quad \mathbf{1}$$

$$NaSMe + 2\,[Au(PMe_3)]BF_4 \rightarrow [MeS\{Au(PMe_3)\}_2]BF_4 \quad \mathbf{2a}$$

$$NaSMe + [\{(Me_3P)Au\}_3O]BF_4 \rightarrow [MeS\{Au(PMe_3)\}_2]BF_4 \quad \mathbf{2a}$$

$$NaSMe + 2\,[Au(PMe_3)]O_3SCF_3 \rightarrow [MeS\{Au(PMe_3)\}_2]O_3SCF_3 \quad \mathbf{2b}$$

$$NaSMe + 3\,[Au(PMe_3)]O_3SCF_3 \rightarrow [MeS\{Au(PMe_3)\}_3](O_3SCF_3)_2 \quad \mathbf{3}$$

Scheme 1

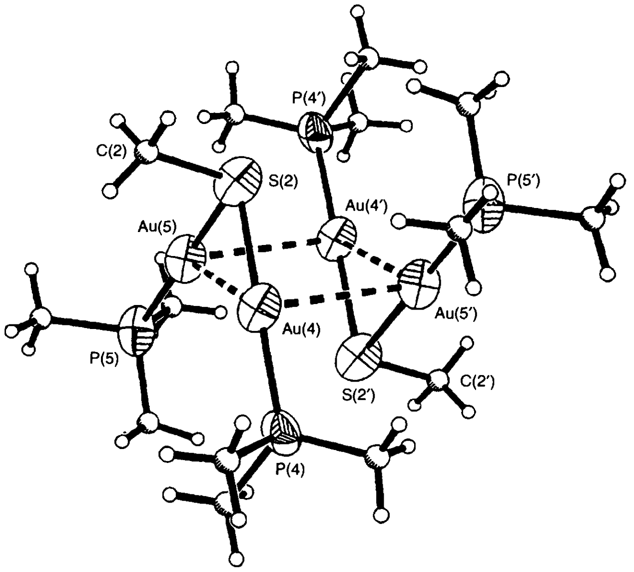

Fig. 2 Molecular structure of the dication of compound **2b** in crystals of **2b** + **3** (ORTEP for heavy atoms; only one of two disordered orientations of the centrosymmetrical dimer is shown). Selected bond lengths (Å) and angles (°): Au(4)···Au(5) 3.033(1), Au(4)···Au(5') 3.060(2); Au(4)···Au(5)···Au(4') 90.50(6), Au(5)···Au(4)···Au(5') 89.50(6).

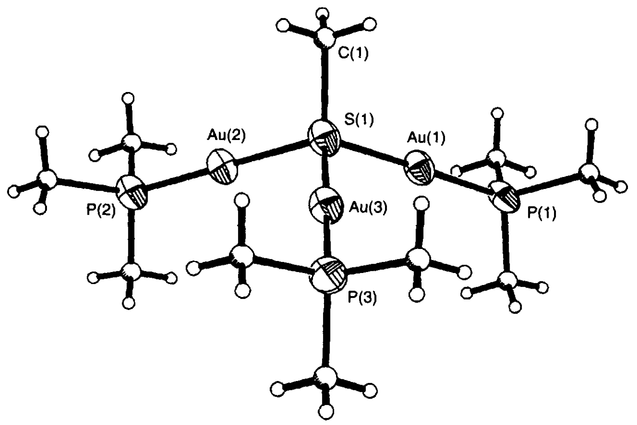

Fig. 3 Molecular structure of the dication of compound **3** in the crystal of **2b** + **3** (ORTEP for heavy atoms). Selected bond lengths (Å) and angles(°): Au(1)–S(1) 2.323(5), Au(2)–S(1) 2.328(5), Au(3)–S(1) 2.319(5), C(1)–S(1) 1.92(2), Au(1)–P(1) 2.257(5), Au(2)–P(2) 2.260(5), Au(3)–P(3) 2.246(6) Au(1)–S(1)–Au(2) 109.2(2), Au(1)–S(1)Au(3) 109.2(2), Au(2)–Au(3) 108.0(2), C(1)–S(1)–Au(1) 111.1(6), C(1)–S(1)–Au(2) 109.7(5), C(1)–S(1)–Au(3) 109.0(6), S(1)–Au(1)–P(1) 178.7(2), S(1)–Au(2)–P(2) 178.1(2), S(1)–Au(2)–P(3) 178.9(2).

$[\{MeS(AuPMe_3)_3\}OSO_2CF_3]^+$ at m/z = 1015.4 in the FD mass spectrum. Quite serendipitously it was then observed that compound **3** co-crystallizes readily with **2b**, and a structure analysis of these crystals revealed the structures of both complexes.†

The cations of **2b** are associated into centrisymmetrical dimers through intimate Au···Au contacts at the edges of an only slightly distorted square. These dimers are disordered in the lattice [Au(4)···Au(5) 3.033(1), Au(4)···Au(5′) 3.060(1) Å; Au(4)···Au(5)···Au(4′) 90.50(6)° for the more abundant orientation; Fig. 2].

The dication of **3** is a novel species. The four-coordination of sulfide sulfur (S^{2-}) is unknown in organic chemistry, and is also unprecedented in coordination chemistry outside a sulfide lattice, and unsupported by ligand clamps or cluster formation. Not accidentally, the only exception is another unusual gold(I) complex, $[S(AuPPh_3)_4][BF_4]_2$, recently synthesized by Laguna and coworkers.[9] However, this dication features a square-pyramidal structure with sharp Au–S–Au angles and short basal Au···Au contacts.

By contrast, the sulfur atom in compound **3** is in the centre of a trigonal pyramid of almost perfect C_{3v} symmetry with the methyl group in the apical position (Fig. 3). The stability of the dication of **3** thus rests solely on the radial bonding to the sulfur atom.

It should be noted that the bonding situation of the thiolate groups in compounds **2** and **3** may resemble quite closely the orientation of the long-chain thiols on the surface of gold metal as produced in 'self assembled monolayers' (SAMs),[10] currently attracting considerable interest.

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Footnotes

† *Compound* **1**: A solution of $[AuCl(PMe_3)]$ (0.12 g, 0.39 mmol) in chloroform (5 cm³) was stirred with a solution of NaSMe (0.03 g, 40 mmol) in water (10 cm³) for 4 h at 20 °C. The organic phase was separated and the product precipitated by addition of pentane (5 cm³); 0.08 g (64%), decomp. 141 °C, $^{31}P\{^1H\}$ NMR ($CDCl_3$) δ −0.6 (s); ^1H NMR δ 1.50 (d, J_{PH} 10.9 Hz, 3 H, PMe_3), 2.4 (s, 3 H, SMe); $^{13}C\{^1H\}$ NMR δ 10.6 (s, SMe), 16.0 (d, J_{PC} 35.8 Hz, PMe_3); FABMS m/z 321 (M^+), 593 $[MeS(AuPMe_3)_2]^+$, 851 $[MeS(AuPMe_3)_3]^+$ (Found: C, 15.20; H, 3.78; S, 10.01; $C_4H_{12}AuPS$ requires C, 15.00; H, 3.73; S, 9.88%).

Compound **2a**: To a solution of $[O\{Au(PMe_3)\}_3BF_4]$ (0.25 g, 0.27 mmol) were added at 20 °C, with stirring, $NaBF_4$ (0.10 g, 0.91 mmol) and a solution of NaSMe (0.03 g, 0.40 mmol) in thf (10 cm³). After 2 h the solvents were removed in a vacuum, the residue taken up in CH_2Cl_2 (10 cm³), and the product **2a** precipitated slowly with Et_2O; 0.095 g (35%). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, −60 °C) δ −4.10 (s); ^1H NMR (−60 °C) δ 1.63 (d, J_{PH} 11.3 Hz, PMe_3), 2.60 (s, SMe). FABMS m/z 592 $[MeS(AuPMe_3)_2]^+$.

Crystals **2b** + **3**: A solution of $[AuCl(PMe_3)]$ (0.41 g, 0.13 mmol) in thf (30 cm³) was treated with $AgOSO_2CF_3$ (0.34 g, 0.13 mmol) at 0 °C. After 10 min the AgCl precipitate was removed by filtration and the filtrate added to a solution of NaSMe (0.03 g, 0.04 mmol) in thf (6 cm³). Subsequently the solvent was removed *in vacuo*, and the residue taken up in dichloromethane (20 cm³). After filtration, diethyl ether was added slowly to the filtrate to precipitate crystals of **2b** + **3**, which decompose slowly upon heating; 0.015 g (20%). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, −60 °C) δ −3.37 (br s); ^1H NMR (−60 °C): δ 1.65 (br d, J_{PH} 11.3 Hz, PMe_3), 2.76 (br s, SMe). FDMS m/z 1015.4 $[MeS(AuPMe_3)_3O_3SCF_3]^+$, 593.3 $[MeS(AuPMe_3)_2]^+$.

‡ *Crystal data*: **1** $C_4H_{12}AuPS$, M_r = 320.13, monoclinic, space group $P2_1/n$, a = 11.631(2), b = 11.614(1), c = 12.618(2) Å, β = 99.29(1)°, Z = 8, U = 1682.0(4) Å³, D_c = 2.55 g cm⁻³, $F(000)$ = 1168.0; crystal dimensions 0.15 × 0.25 × 0.30 mm, Enraf Nonius CAD4 diffractometer, Mo-Kα radiation (λ = 0.71069 Å), T = −62 °C. Data were corrected for Lorentz and polarization effects as well as for absorption [empirical, T_{min} = 0.2687, T_{max} = 0.9962, μ(Mo-Kα) = 178.30 cm⁻¹]. 4232 Reflections measured, 3726 unique, 3279 'observed' [$F_o \geqslant 4\sigma(F_o)$]. Hydrogen atoms were calculated in idealized geometry and included with isotropic contributions [U_{iso} = 0.08 Å²]. Non-H atoms were refined with anisotropic displacement parameters. 127 Refined parameters, $R(R_w)$ = 0.0787(0.0931). ρ_{final} = +4.86, −4.77 e Å⁻³.

2 + **3**: $C_{12}H_{30}Au_3F_6O_6P_3S_3 \cdot C_8H_{21}Au_2F_3O_3P_2S_2$, M_r = 1906.59, triclinic, space group $P\bar{1}$, a = 12.134(1), b = 14.656(2), c = 15.022(3) Å, α = 90.27(1), β = 94.27(1), γ = 114.14(1)°, Z = 2, U = 2429.2(7) Å³, D_c = 2.61 g cm⁻³, $F(000)$ = 1748.0; crystal dimensions 0.15 × 0.20 × 0.25 mm. Data collection as above [empirical, T_{min} = 0.6081, T_{max} = 0.9992, μ(Mo-Kα) = 154.97 cm⁻¹]. 7120 Reflections measured, 7115 unique, 5138 'observed' [$F_o \geqslant 4\sigma(F_o)$]. Hydrogen atoms treated as above [riding model, $U_{iso[H]}$ = 1.5 U_{eq} of C]. Non-H atoms were refined with anisotropic displacement parameters [except C(3), C(41), C(42), C(43), C(51), C(52), C(53), C(61), C(62), C(63), C(71), C(72), C(73) of the disordered cation of **2** and all atoms of one disordered CF_3SO_3]. 515 Refined parameters, $wR_2(R)$ = 0.1513(0.0616), ρ_{final} = +3.84, −2.62 e Å⁻³. The structures were solved by direct methods and refined by full-matrix least-squares refinement. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Information for Authors, Issue No. 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 182/153.

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