A New Class of $Au^I_2Ag^I$ Cluster

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The reaction of the gold(I) ylide complex $[(AuPPh_3)_2\{\mu\text{-}C(PPh_3)(C_5H_4N\text{-}2)\}]ClO_4$ with $AgNO_3$ yields the mixed metal complex $[(AuPPh_3)_2\{\mu\text{-}C(PPh_3)(C_5H_4N\text{-}2)\}\{\mu\text{-}Ag(\eta^2\text{-}O_2NO)(OClO_3)]$, the central moiety of which consists of a loose Au_2Ag cluster with metal–metal contacts *ca.* 3 Å.

The only gold(I)–silver(I) cluster complexes structurally characterized contain an Au_2Ag_2 ring involving two AuX_2 units bridged by two AgL_n moieties; the complexes are tetranuclear $[(AuX_2)_2(\mu\text{-}AgL_n)_2]$ (*e.g.* X = C_2Ph, L = PPh_3, n = 1;[1] X = R_3PCH_2, L = ClO_4, n = 2[2]) or polymeric $[(AuX_2)(\mu\text{-}AgL)]_n$ (*e.g.* X = C_6F_5, L = tetrahydrothiophene or C_6H_6[3]). In the polymers, and in many other gold(I) complexes, weak attractive Au···Au interactions of *ca.* 3 Å are observed.[4,5] These interactions, arising in part from relativistic effects,[6] can be compared in strength to a typical hydrogen bond (7–8 kcal mol^{-1}; 1 cal = 4.184 J).[7] The tendency of LAu^+ units to form metal atom aggregates has been termed 'aurophilicity'.[5] In this paper we report the synthesis of complexes containing weak Au···Au and Au···Au···Ag interactions. Although the three metal atoms in the latter cluster are connected by bridging ligands, the energy involved in the metal–metal bonds seems to be essential in determining the structure of the complex.

We have previously reported the synthesis of the ylide complexes $[(AuEPh_3)_2\{\eta\text{-}C\{C(O)R\}(PPh_3)\}]^+$ (R = OEt, E = P, As; R = OMe, E = P;[8] R = Me, Ph, E = P; R = Me, E = As[9]), by the acid–base reaction between $[Au(acac)(EPh_3)]$ and phosphonium salts $[Ph_3PCH_2C(O)R]^+$ in a 2:1 molar ratio (Hacac = pentane-2,4-dione). When phosphonium salts $[R_3PCH_2C_5H_4N\text{-}2]ClO_4$ react with $[Au(acac)(L)]$ in a 1:3 molar ratio, complexes **1** and **2** can be obtained. Complex **1** reacts with $AgNO_3$ (1:1) to give complex **3** (Scheme 1).†

The crystal structure of **2** shows the two AuL moieties bridged by the atom C(1) (Fig. 1) with a short Au···Au contact of 2.949(1) Å, similar to that found in $[(AuPPh_3)_2\{\mu\text{-}C(PPh_3)(CO_2Et)\}]ClO_4$[8] [2.892(2) Å] and in other related complexes.[4,5,7,10] The pyridine ring is perpendicular to the Au_2C plane (dihedral angle 91°) with an *anti*-orientation of the N lone pair with respect to the Au_2 group. This conformation resembles that found in the doubly phosphido-substituted ylide $Me_3P = C(PPh_2)_2$, which has a *syn–anti* orientation of the lone pairs both in solution and in the crystalline state.[7] However, the complex $[Me_3P = C(PPh_2)_2(AuCl)_2]$ displays a *syn–syn* orientation, because the Au···Au interaction acts as a conformation-determining force.

$$2[Au(acac)(L)] + [R_3PCH_2C_5H_4N\text{-}2]ClO_4 \rightarrow 2Hacac + [(AuL)_2\{\mu\text{-}\{C(PR_3)(C_5H_4N\text{-}2)\}\}]ClO_4$$

$$\mathbf{1};\ L = PPh_3,\ R = Ph$$

$$\mathbf{2};\ L = P(C_6H_4OMe\text{-}4)_3,\ R = C_6H_4Me\text{-}4$$

$$\mathbf{1} + AgNO_3 \rightarrow [(AuL)_2\{\mu\text{-}\{C(PR_3)(C_5H_4N\text{-}2)\}\}\{\mu\text{-}Ag(\eta^2\text{-}O_2NO)(OClO_3)\}]$$

$$\mathbf{3};\ L = PPh_3,\ R = Ph$$

Scheme 1

Similarly, complex **1** (which we assume to have an analogous structure to **2**), changes its configuration from *anti* to *syn* on forming the adduct **3** (Fig. 2) with $AgNO_3$ (as confirmed by the X-ray structure determination of **3**), whereby the formation of two weak Au···Ag bonds could be the cause of the change of orientation. The Ag···Au bonds are similar in nature to weak Au···Au bonds, at least in terms of the bond distances [2.926(1), 3.006(1) Å in **3** are significantly longer than in the Au_2Ag_2 clusters,[2,3] 2.702(2)–2.792(2) Å]. They are similar to those reported for $[\{Au(C_2Ph)_2\}_2(\mu\text{-}AgPPh_3)_2]$ [2.894(1), 2.913(1) Å].[1] To distinguish clusters with weak interactions from conventional clusters where some or all metal atoms are tightly bonded, we prefer to denote the former as 'loose clusters.'

The coordination at silver may be regarded as distorted octahedral or distorted trigonal prismatic [end faces Au(1), Au(2), N(2); O(1), O(2), O(7)]. However, it is possible to consider the Au_2 group as occupying only one coordination position. Recently, the isolobal relationship of this group with

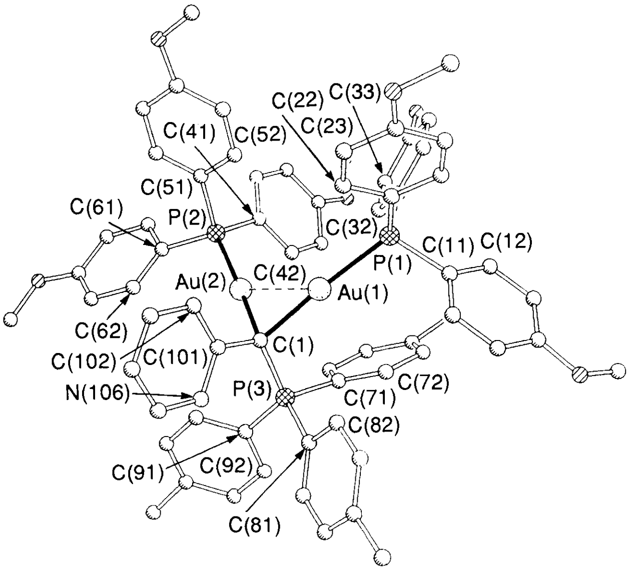

Fig. 1 The structure of the cation of complex **2** in the crystal. Radii are arbitrary, H atoms omitted for clarity. Only one position of the disordered methoxy group is shown. *Crystal data* for **2** at 178 K: $C_{69}H_{67}Au_2ClNO_{10}P_3$, monoclinic, $P2_1/c$, a = 12.855(5), b = 15.186(6), c = 33.203(11) Å, β = 94.06(3)°, U = 6465 $Å^3$, Z = 4, D_c = 1.636 mg m^{-3}, μ = 4.7 mm^{-1}. 11585 reflections were measured to $2\theta_{max}$ 45° (Mo-Kα radiation), of which 8445 were independent (R_{int} 0.018 after absorption corrections based on ψ-scans) and 5586 observed [$F > 4\sigma(F)$]. The structure was solved by heavy-atom methods and refined to R 0.047 (R_w 0.047); Au, P, Cl and O anisotropic, idealised isotropic phenyl groups, twofold disorder for C(37).

[†] **1**: m.p. 218 °C (decomp.); Λ_M = 130 Ω^{-1} cm^2 mol^{-1} in acetone. Selected NMR data: ^1H (200 MHz, $CDCl_3$, $SiMe_4$), δ 6.64 (apparent triplet: 't,' 1H; 5-H of py); ^{31}P (80 MHz, $CDCl_3$, H_3PO_3), δ 37.9 (d, Au*P*Ph₃, $^3J_{PP}$ 2 Hz) and 33.4 (t, C*P*Ph₃). **2**: m.p. 133 °C (decomp); Λ_M = 142 Ω^{-1} cm^2 mol^{-1} in acetone. Selected NMR data: ^1H, δ 7.71 ('d,' 1H; 6-H of py), 7.57 ('d,' 1H; 3-H of py), 7.38 ('t,' 1H; 4-H of py), 6.61 ('t,' 1H; 5-H of py), 3.82 (s, 6H; OCH_3) and 2.37 (s, 3H, $C_6H_4CH_3$); ^{31}P, δ 34.1 (d, Au*P*Ph₃, $^3J_{PP}$ 2 Hz) and 31.8 (t, C*P*Ph₃). **3**: m.p. 140 °C (decomp.); Λ_M = 156 Ω^{-1} cm^2 mol^{-1} in acetone. Selected NMR data: ^1H, δ 8.35 ('d,' 1H; 6-H of py) and 6.73 ('d,' 1H; 3-H of py); ^{31}P, δ 37.6 (d, Au*P*Ph₃, $^3J_{PP}$ 5 Hz) and 24.9 (t, C*P*Ph₃).

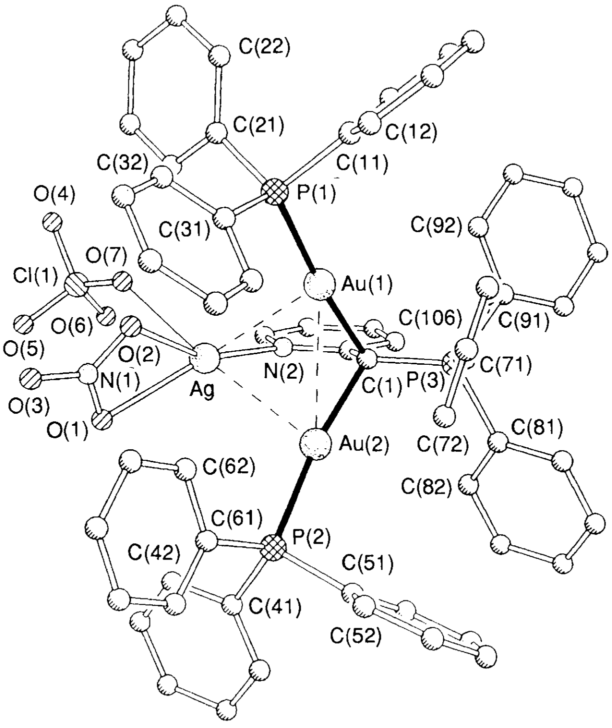

Fig. 2 The structure of complex **3** in the crystal. Radii are arbitrary, H atoms omitted for clarity. *Crystal data* for **3**$\cdot CH_2Cl_2\cdot H_2O$ at 178 K: $C_{61}H_{53}AgAu_2Cl_3N_2O_8P_3$, monoclinic, $P2_1/n$, a = 11.199(2), b = 23.980(7), c = 21.552(6) Å, β = 91.01(2)°, U = 5787 Å^3, Z = 4, D_c = 1.886 mg m^{-3}, μ = 5.7 mm^{-1}. 13601 reflections were measured to $2\theta_{max}$ 50° (Mo-Kα radiation), of which 10184 were independent (R_{int} 0.035 after absorption corrections based on ψ-scans) and 7310 observed. The structure was solved by heavy-atom methods and refined to R 0.046 (R_w 0.050); Au, Ag, N, P, Cl and O anisotropic, idealised isotropic phenyl groups. Further details of both crystal structure investigations may be obtained from the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlichtechnische Information mbH, W-7514 Eggenstein-Leopoldshafen 2 (Germany) on quoting the deposition number CSD 55 735, the names of the authors, and the journal citation. Atomic coordinates, bond lengths and angles, and thermal parameters have also been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

H_2[11] has been discussed for some gold clusters, and it can act in some cases as a two-electron donor analogous to CO or PhC_2Ph; thus, $[(Ph_3PAu)_2\{\mu\text{-}Fe(CO)_4\}]$ or $[Ru_3(\mu_2\text{-}NPh)\{\mu_3\text{-}(AuPPh_3)_2\}(CO)_9]$ are isostructural with $[Fe(CO)_5]$ or $[Ru_3(\mu_2\text{-}NPh)(\mu_3\text{-}CO)(CO)_9]$,[11] respectively, and $[(Ph_3PAu)_2\{\mu\text{-}PtCl(PEt_3)\}]^+$ with $[PtCl(PR_3)(PhC_2Ph)]^+$.[12]

The coordination of the η^1-perchlorato ligand [Ag–O(7): 2.663(9) Å] is significantly weaker than that of the η^2-nitrato ligand [Ag–O(1): 2.442(8); Ag–O(2): 2.396(8) Å], which is consistent with the observation that **3** is a 1 : 1 electrolyte in acetone.

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