The First Example of a Direct Formal Gold(I)–Gold(III) Bond. Synthesis and Structure of [{$Au(CH_2)_2PPh_2$}$_2Au(C_6F_5)_3$]

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The reaction of $[Au(CH_2)_2PPh_2]_2$ with $Au(C_6F_5)_3{\cdot}OEt_2$ affords the trinuclear gold complex [{$Au(CH_2)_2PPh_2$}$_2Au(C_6F_5)_3$]; the Au^I–Au^{III} bond length is 2.572(1) Å.

Short non-bonded $Au^I \cdots Au^I$ contacts of less than 3 Å are well documented, and numerous gold clusters and gold(II) complexes (containing Au^{II}–Au^{II} bonds) have been described.[1] However, no gold complex displaying only a single direct gold–gold bond, unbridged by any other ligand, has been reported until now.

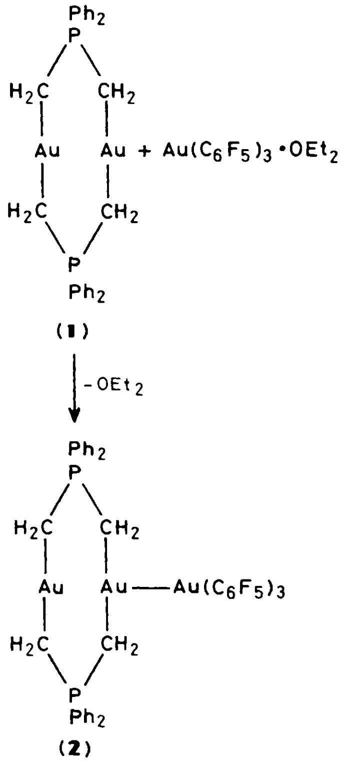
We have recently[2—5] reported heteronuclear complexes containing Au_2Ag_2 rings with unbridged Au–Ag bonds, but the starting gold complexes $[Au(C_6F_5)_2]^-$ and $[Au(CH_2PR_3)_2]^+$ seem to be unable to react with gold centres, such as $[Au(C_6F_5)_3{\cdot}OEt_2]$, to give a gold–gold bond; instead, ligand (C_6F_5 or CH_2PR_3) migration takes place, forming monomeric products $[Au(C_6F_5)_4]^-$ or $[Au(C_6F_5)_3(CH_2PR_3)]$.[6] We therefore selected a different starting complex, μ,μ′-bis(diphenylphosphinium)bis(methylido)gold(I) (**1**), which has been structurally characterized by Fackler *et al.*[7] and fully described by Schmidbauer *et al.*[8] (**1**) contains two Au^I centres doubly bridged by the strong ligand $[Ph_2P(CH_2)_2]^-$ and should thus possess excess electron density at the gold atoms without being too susceptible to ligand migration.

A colourless dichloromethane solution of (**1**) turned red on the addition of colourless solid $Au(C_6F_5)_3{\cdot}OEt_2$[9] (molar ratio 1:1). After five min stirring, evaporation of the solvent *in vacuo* yielded complex (**2**) (equation 1), which is non-conducting in acetone solution and monomeric in chloroform [isopiestic method; M.W. 1638 (calc. 1519)].

The structure of (**2**) was established by a single crystal *X*-ray study (Figure 1).† The two Au^I centres, which were 2.977(1) Å apart in (**1**),[7] approach to 2.769(1) Å in (**2**), which is shorter than the shortest $Au^I \cdots Au^I$ contact previously known (2.776 Å[10]) and not much longer than the longest Au^{II}–Au^{II} bonds.[1,7] One of the Au^I centres is bonded to the Au^{III} of the starting material $Au(C_6F_5)_3{\cdot}OEt_2$, with a very short bond of 2.572(1) Å, comparable to the shortest Au^{II}–Au^{II} bonds.[1,11] The shortest known Au–Au bond of 2.553(1) Å is observed in the Au^{II} species [{$Au(CH_2PPh_2S)$}$_2Cl_2$].[11a]

The assignment of oxidation states to the gold atoms of (**2**) is to some extent a matter of taste. If the bonding interaction between Au(1) and Au(2) is associated with appreciable transfer of electron density from Au(2) to Au(1) (oxidation states I and III, respectively, in the starting materials), then this bonding system could be described as Au^{II}–Au^{II}, and would be the first such system without a supporting bridging ligand. Mössbauer spectroscopy might provide useful information as to the 'true' oxidation states.

The ^1H ($CDCl_3$) and ^{31}P n.m.r. spectra of (**2**) display some differences with respect to the starting compound (**1**);[8] [(**1**): ^1H n.m.r. δ 1.30 (A_2XY', d, *N* 13 Hz, 8H), 7.15—7.82 (m, 20 H); ^{31}P-{^1H} n.m.r. δ 34.2(s) p.p.m.; (**2**): ^1H n.m.r. δ 1.38 (A_2XX', d, *N* 12.9 Hz, 4H), 1.63 (A_2XX', d, *N* 11.3 Hz, 4H), 7.2—7.6 (m, 20H); ^{31}P-{^1H} n.m.r. δ 29.65(s) p.p.m.] *i.e.*, the equivalent H atoms in the four methylene groups of the starting complex (**1**) are distributed in two sets of four H atoms in (**2**).


(**1**)

(**2**)

(1)

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† *Crystal data* for (**2**): $C_{46}H_{28}Au_3F_{15}P_2$, *M* = 1518.6, triclinic, space group $P\bar{1}$, *a* = 11.770(4), *b* = 13.287(6), *c* = 18.261(6) Å, α = 94.35(5), β = 107.88(3), γ = 114.54(3)°, *U* = 2403 Å^3, *Z* = 2, D_x = 2.10 Mg m^{-3}, *F*(000) = 1412, λ(Mo-K_α) = 0.71069 Å, μ = 9.2 mm^{-1}. Data were collected on a Stoe-Siemens four-circle diffractometer, crystal size 0.4 × 0.35 × 0.3 mm (amber-coloured block), $2\theta_{max.}$ 50°, 9270 profile-fitted intensities,[12] 8429 unique ($R_{int.}$ 0.03), 5905 with $F > 4\sigma(F)$ used for all calculations (program system SHELX). Absorption correction based on ψ-scans (transmissions 0.57—0.82). Cell constants refined from 2θ values of 40 reflections in the range 20—23°. Structure solution by heavy-atom method, full-matrix refinement on *F* to *R* = 0.051, R_w = 0.047. Non-H atoms anisotropic, H atoms included using a riding model, 596 parameters, weighting scheme $w^{-1} = \sigma^2(F) + 0.0004(F^2)$, *S* 1.6, max. residual electron density 2 e Å^{-3}.

Complete crystallographic details have been deposited at the Fachinformationszentrum Energie Physik Mathematik, 7514 Eggenstein-Leopoldshaften 2, Fed. Rep. of Germany. Any request for this material should quote a full literature citation and the reference number CSD 53023.

Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

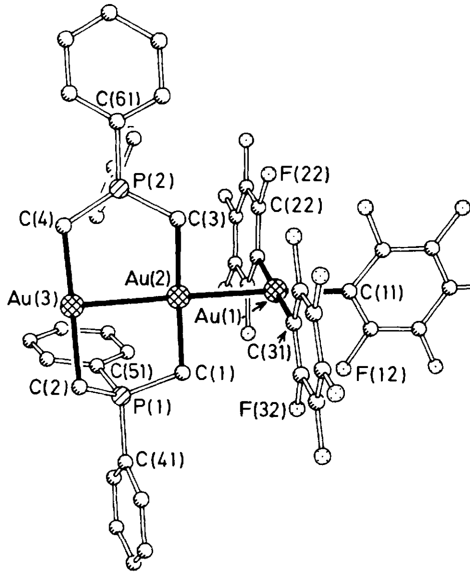
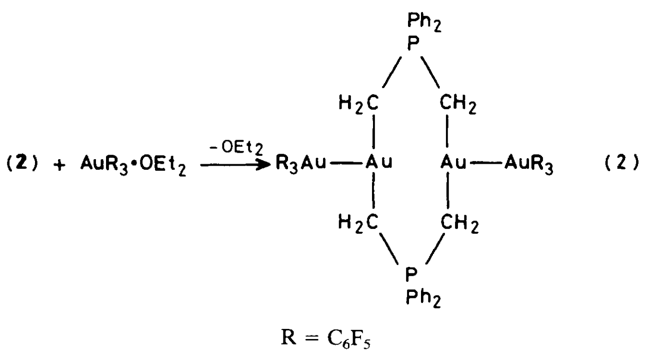


Figure 1. The molecule of complex (**2**) in the crystal (radii arbitrary, H atoms omitted). Selected bond lengths (Å): Au(1)–Au(2) 2.572(1), Au(2)–Au(3) 2.769(1), Au(1)–C(11) 2.021(10), Au(1)–C(21) 2.076(11), Au(1)–C(31) 2.048(11), Au(2)–C(1) 2.106(11), Au(2)–C(3) 2.102(11), Au(3)–C(2) 2.095(12), Au(3)–C(4) 2.046(13).

It is naturally tempting to add another $Au(C_6F_5)_3$ moiety to the 'free' gold(I) atom of (**2**), either by repeating the reaction of equation 1 with molar ratio 1 : 2 or by the process of equation 2. In both cases deep red solutions are formed, from which a red–brown solid (**3**) is obtained upon evaporation of the solvent. Compound (**3**) analyses according to the expected stoicheiometry; it is non-conducting in acetone, and its molecular weight in chloroform is 2372 (calc. 2217). However, its ^1H n.m.r. spectrum is incompatible with the symmetric structure of Equation 2 [δ 1.42 (A_2XX', d, N 10.2 Hz, 4H), 1.87 (A_2XX', d, N 13.7 Hz, 4H), 7.4—7.8 (m, 20H); ^{31}P-{^1H} n.m.r. δ 22.64 p.p.m.] We have not yet been able to obtain crystals suitable for *X*-ray studies.

Silver salts ($AgClO_4$) or complexes ($O_3ClOAgPPh_3$) also react with complex (**1**) to give black solids of the presumed stoicheiometry $[\{Au(CH_2)_2PPh_2\}_2AgOClO_3]$ and $[\{Au(CH_2)_2PPh_2\}_2Ag(OClO_3)(PPh_3)]$, respectively. The insolubility of these complexes precludes spectroscopic investigation, but the analyses are consistent with the suggested formulae.



We thank the Fonds der Chemischen Industrie and the C.A.I.C.Y.T. (Spain) for financial support.

Received, 27th January 1988; Com. 8/00295I

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