Trigold triacetylides: polymerization through gold···gold bonding or bridging ligands

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The new trigold(I) triacetylide [$C_6H_3(C{\equiv}CAu)_3$-1,3,5] reacts with monodentate ligands, L = isocyanide, phosphite or phosphine, to give [$C_6H_3(C{\equiv}CAuL)_3$-1,3,5] complexes which form polymeric solids with intermolecular Au···Au bonding; it also reacts with bidentate ligands to give covalently linked network polymers of the formula [{$C_6H_3(C{\equiv}CAu)_3$-1,3,5}$_2$(μ-L–L)$_3$], L–L = diisocyanide or diphosphine.

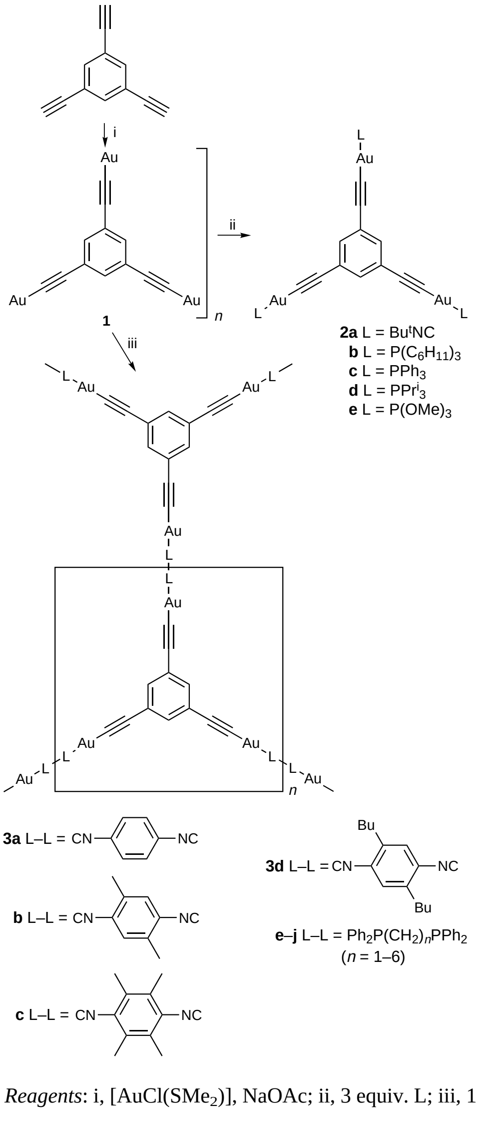
Linear digold(i) complexes have the interesting tendency to polymerize, either through weak intermolecular gold···gold binding, as in compounds with the chain structure derived from PhC≡C–Au–LL–Au–C≡CPh,[1,2] or through covalent binding of bridging bidentate ligands, as in the linear rigid-rod polymers (–LL–Au–C≡C–Ar–C≡C–Au–)$_n$, where L–L = diphosphine or diisocyanide and Ar = 1,4-C_6H_4 or a similar spacer group.[2] The former compounds are unique to gold chemistry, while the latter find an analogy in the well known polymers *trans*-[M(PBu_3)$_2$-(–C≡C–Ar–C≡C–)]$_n$ (M = Ni, Pd, Pt) and in related complexes[3] whose conjugated structures might lead to materials applications.[4] There is currently much interest in extending this chemistry beyond the one-dimensional polymers, by using trifunctional core molecules, and the triacetylene 1,3,5-triethynylbenzene appears particularly well suited for this purpose.[5,6] In this article we report trigold(i) complexes of the type [C_6H_3(C≡C–Au–L)$_3$], which can form loose polymers by intermolecular gold···gold association, as well as covalently linked polymers of the stoichiometry [{C_6H_3(C≡C–Au)$_3$}$_2$-(L–L)$_3$].

Reaction of [AuCl(SMe_2)] in tetrahydrofuran–methanol with 1,3,5-triethynylbenzene and sodium acetate as base gave in high yield the insoluble, bright yellow solid [C_6H_3(C≡CAu)$_3$] **1** (Scheme 1) which is expected to have a polymeric structure with bridging alkynyl groups.[7] (**CAUTION:** the pure complex **1** detonates easily and should be handled with extreme care and in small quantities only.) Reaction of 3 equiv. of ligand L (L = isocyanide, phosphite or phosphine) with a suspension of **1** in dichloromethane at room temperature yields the soluble complexes [C_6H_3(C≡C–Au–L)$_3$] **2** in good yield. Complexes **2** are white or pale yellow, air-stable, analytically pure solids which are soluble in organic solvents. All have been characterized spectroscopically and those with L = $Bu^tN{\equiv}C$ **2a** and P(OMe)$_3$ **2e** by X-ray diffraction as well.† The last two appear to be the first complexes of the $C_6H_3(C{\equiv}C^-)_3$ ligand with any metal, as well as the first trigold triacetylides, to be characterised crystallographically.

The molecular structures of **2a** and **2e**, shown in Fig. 1, are closely similar. Each contains a planar $C_6H_3(C{\equiv}CAuX)_3$ nucleus (X = C or P) which displays approximate D_{3h} symmetry. C–Au–X angles deviate from linearity by 8°.

In the solids of both compounds molecules related by lattice translations are interlinked through weakly attractive Au···Au interactions [3.234(1) Å in **2a**, 3.316(1) Å in **2e**] to form crinkled tapes which extend throughout the crystals (Fig. 1). The gold atoms involved in these interactions [Au(1) and Au(2) in **2a**, Au(1) and Au(3) in **2e**] thereby attain the T-shaped coordination geometry, with Au···Au–X (X = C, P) angles ranging from 73 to 103°.

In **2a** the shortest Au···Au separations between molecular tapes are 3.723(1) Å for Au(1) atoms related by inversion centres and 3.950(1) Å for Au(2) and Au(3) atoms in molecules related by translation along the *a*-axis; in **2e** the two-fold screw axes give rise to intermolecular Au(1)···Au(2) contacts of 3.973(1) Å. Although these inter-tape separations are larger than both the van der Waals diameter of gold (3.60 Å)[8,9] and the range of distances generally regarded as typical of normal $Au^I\cdots Au^I$ attractive interactions (2.90–3.50 Å),[2,8,9] they provide geometrically similar environments for the gold atoms, in which



Scheme 1 *Reagents*: i, [AuCl(SMe_2)], NaOAc; ii, 3 equiv. L; iii, 1.5 equiv. L–L

the Au···Au–X (X = C, P) angles are 62–120° and the Au···Au···Au angles 135–151°. This directionality of the mutual approach of the gold atoms could be taken as evidence for intertape attractions yielding three-dimensional solids stabilized by cross-linking of ···Au–R–Au···Au–R–Au··· chains [R = $C_6H_3(C{\equiv}C)_3$]. It also appears that weak intermolecular Au···Au interactions leading to the T-shaped geometry, which is considered highly specific for gold(i) complexes,[8] may be a significant factor in driving molecular self-assembly in their solids. It is therefore conceivable that the synthon **A** may prove useful in the design of supramolecular solids with desirable chemical and physical properties.

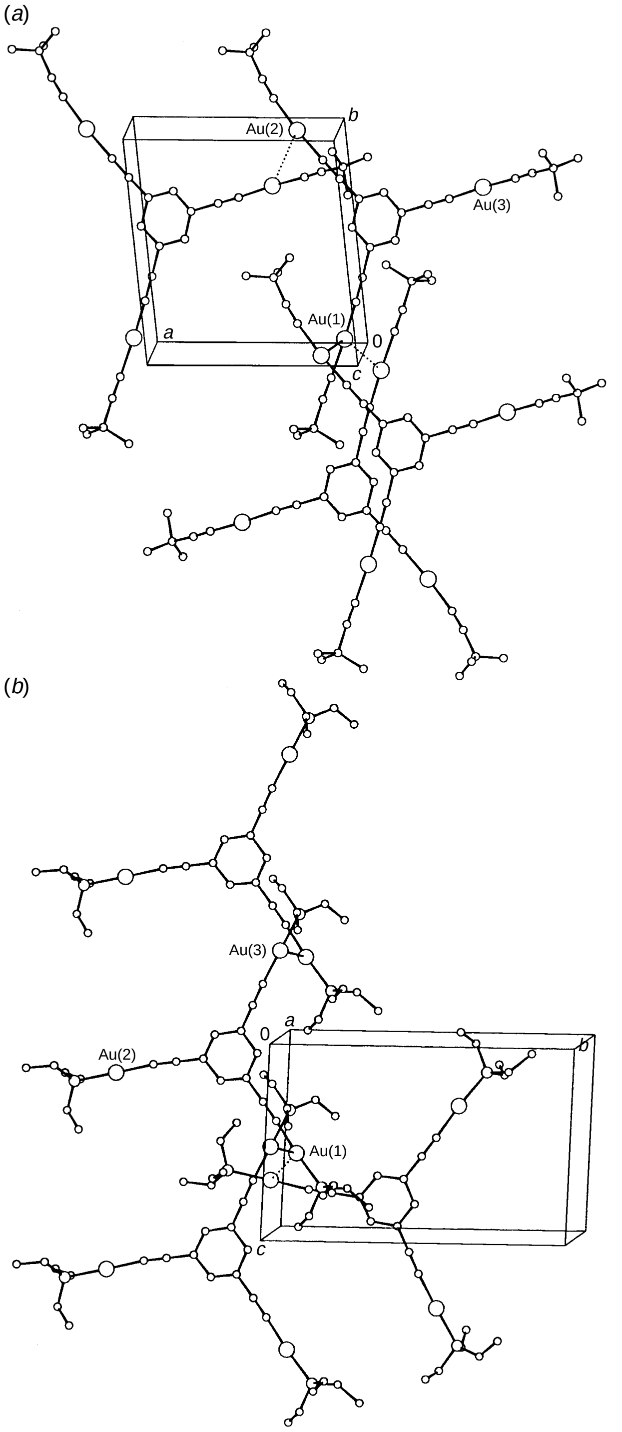


Fig. 1 (*a*) The crystal structure of 1,3,5-($Bu^tNCAuC{\equiv}C)_3C_6H_3{\cdot}C_2H_4Cl_2$ **2a**·$C_2H_4Cl_2$, with the solvent molecules omitted for clarity. Labels are shown for the gold atoms in the reference molecule only, the Au···Au interactions within the molecular tapes are shown by full lines, and those involving the gold atoms in different tapes, by dashed lines. Selected interatomic distances (Å) and angles (°): Au(1)–Au(1^{i}) 3.723(1), Au(1)–Au(2^{ii}) 3.234(1), Au(2)–Au(3^{iii}) 3.950(1). The symmetry transformations applied are: i −*x*, −y, 1 − *z*; ii *x*, *y* − 1, *z*; iii 1 + *x*, *y*, *z*; iv *x*, 1 + *y*, *z*; (v) *x* − 1, y, *z*. (*b*) The crystal structure of 1,3,5-[$(MeO)_3PAuC{\equiv}C]_3C_6H_3$ **2e**. Selected interatomic distances (Å) and angles (°): Au(1)–Au(2^{i}) 3.973(1), Au(1)–Au(3^{ii}) 3.316(1). The symmetry transformations applied are: i 2 − *x*, 1/2 + *y*, 1 − *z*; ii *x*, *y*, 1 + *x*; (iii) 2 − *x*, −1/2 + *y*, 1 − *z*; iv *x*, *y*, *z* − 1. Disorder involving phosphite methoxy groups is not shown for clarity.

Covalently bridged polymers were readily prepared by reaction of **1** (addition) or **2a** (displacement of the $Bu^tN{\equiv}C$ ligands) with bidentate ligands [L–L = diisocyanide CN–Ar–CN, Ar = C_6H_4, $C_6H_2Me_2$, C_6Me_4, C_6H_2 Bu^t_2, or diphosphine $Ph_2P(CH_2)_nPPh_2$, *n* = 1–6] in acetone at room temperature. They precipitated as pale yellow solids which were insoluble in common organic solvents, and analysed as $[\{C_6H_3(C{\equiv}C\text{–}Au)_3\}_2(L\text{–}L)_3]_n$ **3**. Their proposed structures (Scheme 1) are supported by comparison of their IR and XPS data with those of the corresponding model compounds **2**.

In summary, the first trigold triacetylide complexes have been prepared and shown to have elegant planar molecular structures with approximate D_{3h} symmetry. They can act as a core of loosely linked polymers formed by weak intermolecular gold···gold binding, or they can react with bidentate ligands to form covalently-linked network polymers.

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Footnote

† *Crystallographic data*: **2a**·$C_2H_4Cl_2$: $C_{27}H_{30}Au_3N_3{\cdot}C_2H_4Cl_2$, *M* = 1086.39, space group $P\bar{1}$, *a* = 10.340(1), *b* = 11.539(1), *c* = 16.444(1) Å, α = 75.01(1), β = 80.11(1), γ = 81.33(1)°, *U* = 1855.5(2) Å^3, *Z* = 2.

Intensities were measured at 20 °C with Mo-Kα radiation, λ = 0.710 73 Å. The mean intensity of three standard reflections decreased by 27% during the experiment. The data were corrected for crystal decomposition and for absorption. Refinement on F^2 of 287 parameters, using 5082 observations, converged at R_1 = 0.054, wR_2 = 0.140 for 2825 reflections with $I > 2\sigma(I)$, $|\Delta\rho| < 1.31$ e Å^{-3}. The unit cell contains two molecules of the gold complex, one ordered and one disordered $C_2H_4Cl_2$ solvate molecules.

For **2e**: $C_{21}H_{30}Au_3O_9P_3$, *M* = 1110.26, monoclinic, space group $P2_1$, *a* = 0.979(2), *b* = 15.630(2), *c* = 10.453(2) Å, β = 111.57(2)°, *U* = 1516.2(5) Å^3, *Z* = 2.

The data were corrected for absorption. Refinement of F^2 of 320 parameters using 5242 observations converged at R_1 = 0.043, wR_2 = 0.080 for 2613 reflections with $I > 2\sigma(I)$, $|\Delta\rho| < 1.43$ e Å^{-3}. The Flack absolute structure parameter χ = −0.015(13). Two oxygen and two carbon atoms of $P(OMe)_3$ ligands are disordered.

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 182/321.

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