[2] T. J. Sworski, *J. Chem. Phys.* **1948**, *16*, 550.
[3] Several types of dehydroannulenes have been studied extensively. For a review see: M. Nakagawa, *Cyclic Acetylenes* in *The Chemistry of Carbon Carbon Triple Bond, Part II.* (Ed.: S. Patai), Wiley, Chichester, **1978**, Chapter 15.
[4] Y. Kuwatani, N. Watanabe, I. Ueda, *Tetrahedron Lett.* **1995**, *36*, 119.
[5] For a review see: K. C. Nicolaou, W.-M. Dai, *Angew. Chem.* **1991**, *103*, 1453; *Angew. Chem. Int. Ed. Engl.* **1991**, *30*, 1387.
[6] K. J. H. Kruithof, R. F. Schmitz, G. W. Klumpp, *Tetrahedron* **1983**, *39*, 3073.
[7] This compound was prepared from 3-bromo-2-propyne-1-ol under standard conditions (treatment with $t\mathrm{BuMe_2SiCl}$ and $\mathrm{NEt_3}$ in the presence of 4-dimethylaminopyridine in $\mathrm{CH_2Cl_2}$).
[8] K. Sonogashira, Y. Tohda, N. Hagihara, *Tetrahedron Lett.* **1975**, 4467; S. Takahashi, Y. Kuroyama, K. Sonogashira, N. Hagihara, *Synthesis* **1980**, 627.
[9] D. B. Dess, J. C. Martin, *J. Am. Chem. Soc.* **1991**, *113*, 7277; *J. Org. Chem.* **1983**, *48*, 4155.
[10] A. S. Raw, S. F. Pederson, *J. Org. Chem.* **1991**, *56*, 830; A. G. Myers, P. S. Dragovich, *J. Am. Chem. Soc.* **1992**, *114*, 5859. In this procedure, it is important to use THF as the solvent.
[11] The direct coupling of **9** to give **11** by the McMurry reaction failed.
[12] A related strategy, the use of cyclic diynediols as precursors of cyclic enediyne systems, was reported: M. F. Semmelhack, J. Gallagher, *Tetrahedron Lett.* **1993**, *34*, 4121.
[13] M. Iyoda, Y. Kuwatani, M. Oda, *J. Am. Chem. Soc.* **1989**, *111*, 3761.
[14] The low yield of this transformation came from the first step in which an electron transfer occurred. Like quinone, dione **5** is susceptible toward reduction.
[15] J.-L. Luche, *J. Am. Chem. Soc.* **1978**, *100*, 2226; A. L. Gemel, J.-L. Luche, *ibid.* **1981**, *103*, 5454; J.-L. Luche, L. Rodriquez-Hahn, P. Crabbe, *J. Chem. Soc. Chem. Commun.* **1978**, 601.
[16] Related transformations have been reported: M. Iyoda, Y. Onishi, M. Nakagawa, *Tetrahedron Lett.* **1981**, *22*, 3645.
[17] The yields of **4c** and **4d** were not determined because of their instability.

A Gold(I) [2]Catenane[**]

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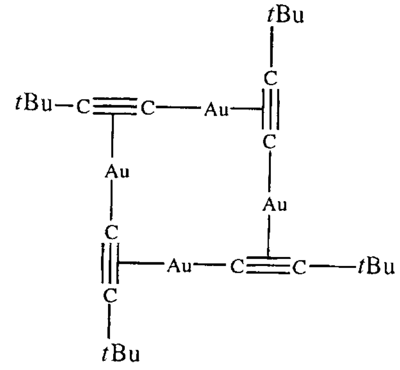
Recently we have described the charcterization of some linear gold(I) complexes with nitrogen donor ligands,[1-3] which are very labile and therefore provide excellent precursors for the development of the coordination and organometallic chemistry of gold. When $[\mathrm{Au(NH_3)_2}]^+$ [2] is treated with $\mathrm{PhC{\equiv}CH}$ the colorless crystalline compound **1** is obtained in excellent yield

$[(\mathrm{H_3N})\mathrm{Au(C{\equiv}CPh)}]$ **1**

and has been characterized by elemental analyses and IR spectroscopy. When the reaction is repeated with $t\mathrm{BuC{\equiv}CH}$ the resultant compound is yellow and the elemental analysis suggests that the ammonia is no longer coordinated to the gold and that it is best formulated as $[\mathrm{Au(C{\equiv}C}t\mathrm{Bu)}]_n$. Coates and Parkin[4] have reported an identical compound and proposed that it is probably polymeric and have tentatively suggested the tetrameric structure shown in Scheme 1.

Single crystals of $[\mathrm{Au(C{\equiv}C}t\mathrm{Bu)}]_n$ can be obtained from EtOH from the above-mentioned synthesis, starting from $[\mathrm{Au(NH_3)_2}]^+$. The yellow color of the crystals is unusual for linear gold(I) ethynyl compounds, the compound also has $\nu(\mathrm{C{=}C})$ stretching modes at 2002, 1983, and 1964 $\mathrm{cm^{-1}}$ suggesting three inequivalent triple bond environments.



Scheme 1. Possible structure of a $[\mathrm{Au(C{\equiv}C}t\mathrm{Bu)}]$ oligomer.

The single-crystal X-ray crystallographic analysis of the oligomer[5] has demonstrated that it actually has a novel catenane structure based on two interlocked rings each containing six gold atoms and thus has the formula $[\{\mathrm{Au(C{\equiv}C}t\mathrm{Bu)}\}_6]_2$ (**2**) (Fig. 1). A crystallographically imposed C_2 axis passes through the midpoint of the Au(1)–Au(1A) vector. The ethynyl ligands in **2** adopt both η^1 and η^2 coordination modes, a feature which has been noted previously in Group 11 ethynyl complexes.[6] Each ring of (**2**) contains pairs of gold(I) atoms with the different ligand arrangements and formal charges (Scheme 2) because

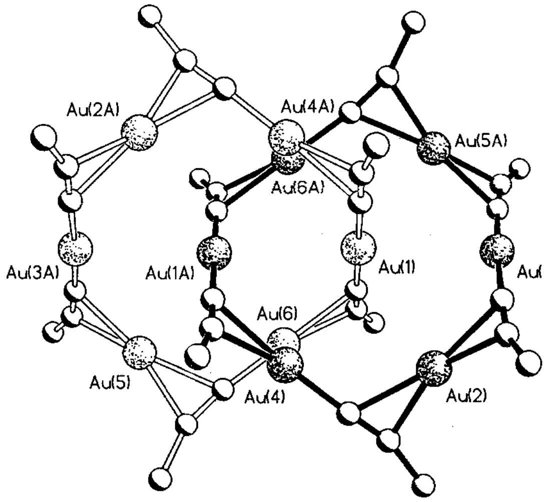
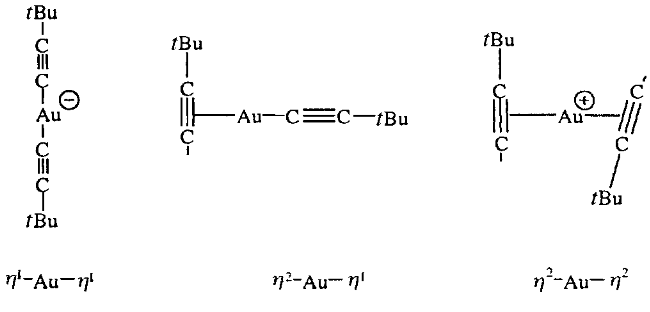


Fig. 1. Molecular structure of [2]catenane-$[\{\mathrm{Au(C{\equiv}C}t\mathrm{Bu)}\}_6]_2$. For reasons of clarity the methyl groups have been excluded. The crystallograhic C_2 axis is perpendicular to the page and passes through the mid-point of Au(1)–Au(1A).



Scheme 2.

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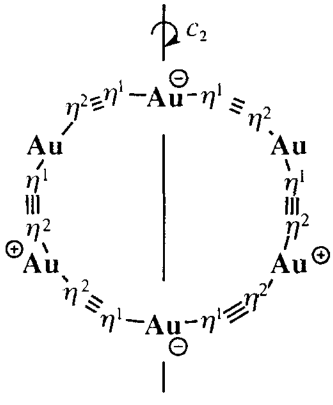

Scheme 3.

some of the ethynyl ligands in [Au(C≡C*t*Bu)] have migrated in the oligomerization process. The arrangement of these coordination modes around the ring is shown in Scheme 3.

Within each ring the gold atoms form an almost regular hexagon (Au–Au contacts between 3.304(2)–3.361(2) Å) and define a plane (maximum deviation 0.1 Å). The two interlocking rings make a dihedral angle of 64.5° and inter-ring gold–gold contacts lie in the range between 3.215(2)–3.351(2) Å, leading to a symmetrical [2]catenane structure. The individual rings have approximately C_2 symmetry as a result of the ethynyl ligand bonding modes described above, and if one ignores the ligands the central Au_{12} core has approximately D_2 symmetry.

The η^2-η^2 coordination mode, not previously observed in gold(I) chemistry, results in the ethynyl ligands being mutually perpendicular in a manner similar to that reported previously for [Pt^0(ethyne)$_2$] complexes.[7] The utilization of orthogonal C≡C π orbitals is also evident in the η^1-η^1 and η^2-η^1 coordination centers, (see Fig. 1).

The gold–gold distances within the rings and between the rings are significantly longer than those in the bulk metal (2.88 Å) but are nonetheless in the range where weak "aurophilic"[8] interactions may occur. The narrow range of the Au–Au contacts and the symmetrical nature of the structure suggests that the "aurophilic" interactions may contribute significantly to the self-assembly of the catenane.

The manner in which the basic [Au(C≡C*t*Bu)] fragments rearrange their coordination environments in solution and self-assemble in order to realize the observed solid-state structure remains a mystery. IR studies on the [2]catenane in solution have indicated that the three ν(C≡C) bands observed in the solid are also observed in solution (IR (CCl_4): ν(C≡C) 2003, 1985, 1965 cm^{-1}) suggesting that the ring structure is maintained in solution. Two ^1H resonances for the *t*Bu groups in the ratio of 2:1 in the ^1H NMR spectrum at room temperature (see experimental) are also consistant with the C_2 symmetry of the individual rings.

The observation of such an interesting catenane structure based on such simple homoleptic organometallic complex is really most unexpected and novel. Previous examples of [2]catenane complexes have the metal atoms involved in much more complex polyaromatic nitrogen ligand systems[9] and in some cases two different metal ions.[10] We are currently investigating similar compounds in order to establish the extent to which the "aurophilicity" of the gold atoms is contributing to the spontaneous formation of the [2]catenane.

Experimental Procedure

1: PhC≡CH (0.025 mL, 0.228 mmol) was added dropwise to [Au(NH_3)$_2$]BF_4 (0.065 g, 0.204 mmol) dissolved in pre-dried, degassed acetonitrile (10 mL). The colorless solution was allowed to stir for 1 h, after about 10 minutes a white microcrystalline solid separated, which was eventually collected by filtration, washed with acetonitrile (3 × 5 mL), and dried under reduced pressure. Yield 94%; elemental analysis for C_8H_8AuN; found: C 30.0, H 2.4, N 4.4; calcd: C 30.5, H 2.6, N 4.5; IR(KBr): ν(NH) bands at 3318 and 3239 cm^{-1}, ν(CH) at 3078, 3050, and 3030 cm^{-1} and ν(C≡C) at 2112 cm^{-1}.

2: *t*BuC≡CH (0.06 mL, 0.487 mmol) was added dropwise to [Au(NH_3)$_2$]BF_4 (0.10 g, 0.487 mmol) dissolved in pre-dried, degassed acetonitrile (10 mL). After about 30 min a pale yellow solution was observed, the solution was then allowed to stir for a further 30 min, after which time the volume was concentrated under reduced pressure to give a dark yellow precipitate. This was filtered, dissolved in a minimum volume of hot EtOH and left in a refrigerator at about 4 °C, to give pale yellow cubes after about 2 days. Yield 65%; elemental analysis for [$(C_6H_9Au)_6$]$_2$; found: C 25.6, H 2.4; calcd: C 25.9, H 3.2; IR(KBr): ν(CH) bands at 2966, 2945, 2922, 2895, and 2864 cm^{-1} and ν(C≡C) at 2002, 1983 and 1964 cm^{-1}; ^1H NMR (270 MHz, C_6D_6, 25 °C, TMS): δ = 1.2 (S, 36H; 4*t*Bu), 0.5 (s, 18H; 2*t*Bu).

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[1] D. M. P. Mingos, J. Yau, *J. Organomet. Chem.* **1994**, *479*, C16–C17.
[2] D. M. P. Mingos, J. Yau, S. Menzer, D. J. Williams, *J. Chem. Soc. Dalton Trans.* **1995**, 319–320.
[3] J. Yau, D. M. P. Mingos, H. Powell, *Polyhedron* **1995**, in press.
[4] G. E. Coates, C. Parkin, *J. Chem. Soc.* **1962**, 3220–3226.
[5] Crystal data for **2**: monoclinic, $a = 29.378(4)$, $b = 13.112(2)$, $c = 25.805(3)$ Å, $\beta = 117.14(1)°$; $V = 8846(2)$ Å^3; space group $C2/c$; $Z = 4$; $\rho = 2.506$ g cm^{-3}; $\mu(Mo_{K\alpha}) = 19.847$ mm^{-1}; Siemens P4/PC diffractometer, ω scans, graphite monochromated $Mo_{K\alpha}$ radiation; data corrected for absorption. The structure was solved by the heavy-atom method. All six *tert*-butyl groups are severely disordered, however, only three of these could be split into pairs with alternative partial occupancy orientations. All the *tert*-butyl groups were refined subject to C–C distance constraints. Least-squares refinement based on F^2 with the gold atoms anisotropic, and the remaining non-hydrogen atoms isotropic, gave $R_1 = 0.0722$ and $wR_2 = 0.1879$ for 3350 independent observed data [$|F_0| > 4\sigma |F_0|$, $2\theta <= 45°$]. Further details of the crystal study can be obtained from the Director of the Cambridge Crystallographic Data Centre, 12 Union Road, GB-Cambridge, CB12 1EZ, (UK), on quoting the full literature citation.
[6] G. E. Coates, M. L. H. Green, K. Wade, *Organometallic Compounds - Transition Elements Vol 2*, 3rd ed., Methuen, London, **1968**, pp. 271–287.
[7] N. M. Boag, M. Green, D. M. Grove, J. A. K. Howard, J. L. Spencer, F. G. A. Stone, *J. Chem. Soc. Dalton Trans.* **1980**, 2170–2181.
[8] H. Schmidbaur, *Gold Bull.* **1990**, *32*, 11–21.
[9] C. Dietrich-Buchecker, J.-P. Sauvage, *Bull. Soc. Chim. Fr.* **1992**, *129*, 113–120; J.-C. Chambron, C. Dietrich-Buchecker, J.-P. Sauvage, *Top. Curr. Chem.* **1993**, *165*, 131–162.
[10] C. Piquet, G. Bernardinelli, A. F. Williams, B. Bocquet, *Angew. Chem.* **1995**, *107*, 618–621; *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 582–584.

Novel Networks of Unusually Coordinated Silver(I) Cations: The Wafer-Like Structure of [Ag(pyz)$_2$][Ag$_2$(pyz)$_5$](PF$_6$)$_3$·2G and the Simple Cubic Frame of [Ag(pyz)$_3$](SbF$_6$)**

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The crystal engineering of two- (2D) and three-dimensional (3D) coordination polymers is of great current interest,[1–3] both for the theoretical aspects related to the topologies of novel networks, and for their potential physicochemical properties, such as electrical conductivity,[4] magnetism,[5] and applications in host–guest chemistry,[1,6] and catalysis.[7] In the supramolecular chemistry of hydrogen-bonded organic molecules,[8] coordination polymers offer a higher potential because of the variety of coordination modes and the peculiarities of the metallic cen-

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[**] pyz = pyrazine, G = CH_2Cl_2, $CHCl_3$, CCl_4.