Au–Au Interactions

Self-Assembly in Gold(I) Chemistry: A Double-Stranded Polymer with Interstrand Aurophilic Interactions**

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There has been remarkable progress and interest in the design and synthesis of hybrid organic–inorganic molecular materials, and a key strategy is to design simple building blocks that can be induced to form complex molecular structures by self-assembly.[1] Gold(I) centers are particularly versatile as components of such building blocks based on their tendency for linear coordination,[2,3] their high reactivity towards ligand substitution,[2] and their ability to form secondary aurophilic bonds that can be used to direct the self-assembly.[2–9] These properties have made it possible to design macrocycles, molecular triangles, catenanes, and polymers with gold(I) centers coordinated to a phosphane and a nitrogen or carbon donor ligand.[2–10] The gold–carboxylate linkage is important in self-assembled monolayers on gold colloids[11] and is well known in simple complexes,[2,12] but it has not yet been exploited in molecular materials. Here we show that a simple condensation procedure can lead to the self-assembly of a cyclic dimer or trimer, or of a linear polymer for gold(I) complexes of the three isomers of diphenylphosphanylbenzoic acid, and that the polymer forms a remarkable double-stranded structure through aurophilic attractions. The ligands themselves are already known to give interesting gold compounds[13,14] and bimetallic compounds,[15] and this work further highlights their potential in the field of hybrid organic–inorganic molecular materials.

The synthetic strategy was to eliminate HCl from the *ortho* (**1**), *meta* (**2**), and *para* (**3**) isomers of $[AuCl(Ph_2PC_6H_4CO_2H)]$,[13,14] to yield the corresponding oligomers or polymers $[\{Au(Ph_2PC_6H_4CO_2)\}_n]$, with the expectation that the degree of aggregation would be different for the different isomers. Preliminary experiments with $[AuCl(4\text{-}Ph_2PC_6H_4CO_2H)]$ (**3**), which forms a hydrogen-bonded dimer in the solid state (Figure 1), were unsuccessful since the complex was resistant to dehydrochlorination with mild bases and was decomposed by stronger ones. However, success was achieved by a two-step reaction involving abstraction of the chloride ligand from each complex **1**–**3** using silver(I) trifluoroacetate to form the corresponding gold(I) trifluoroacetate complex, which was not isolated but was treated in situ with a base to eliminate trifluoroacetic acid and give the product, as outlined in Scheme 1. Complex **1** gave a mixture of dimer **4** and trimer **5**, while complex **2** gave only a molecular triangle **6**, and complex **3** gave an insoluble polymer **7**.

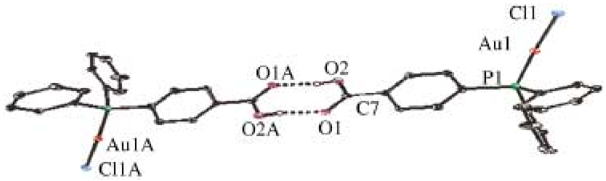

Figure 1. A view of the hydrogen-bonded dimeric structure of **3**.

The soluble complexes **4**–**6** were characterized in solution by NMR spectroscopy and ESI mass spectrometry. Complex **6** gave a singlet in the ^{31}P NMR spectrum (in $CDCl_3$) at $\delta = 28.8$ ppm and a peak at $m/z = 1639$ in the ESI-MS (in CH_2Cl_2/CH_3CN, with CsI present to enhance ionization), which corresponds to the $[\{Au(Ph_2PC_6H_4CO_2)\}_3]\cdot Cs^+$ ion, and indicates the presence of the molecular triangle structure only. Complexes **4** and **5** formed an equilibrium mixture in solution. Thus, the ^{31}P NMR spectrum gave two resonances at $\delta = 33.0$ (trimer) and 27.9 ppm (dimer) while the ESI-MS contained two major ions at $m/z = 1639$ and 1137 corresponding to $[\{Au(Ph_2PC_6H_4CO_2)\}_n]\cdot Cs^+$, with $n = 3$ or 2, respectively. Crystallization of the mixture gave the molecular triangle complex **5**, whose structure is shown in Figure 2. The 18-membered macrocycle contains three linear gold(I) units with gold atoms separated by 3.56–4.31 Å, which is too long to be indicative of aurophilic bonding. Molecular modeling indicates that the dimer **4** has more ring strain than **5** but that this is compensated by the presence of a shorter Au···Au contact of approximately 2.9 Å. In solution, **4** will also be favored with respect to **5** through entropic effects.

Complex **7** was insufficiently soluble for characterization in solution, but the remarkable structure shown in Figure 3 was determined using crystals that were grown by the diffusion of 2,2′-bipyridyl into a solution of $[Au(O_2CCF_3)(4\text{-}Ph_2PC_6H_4CO_2H)]$ in $CHCl_3$. The structure (Figure 3) contains infinite polymer chains $[\{Au(4\text{-}Ph_2PC_6H_4CO_2)\}_n]$; there is a degree of helicity in these chains arising from the usual

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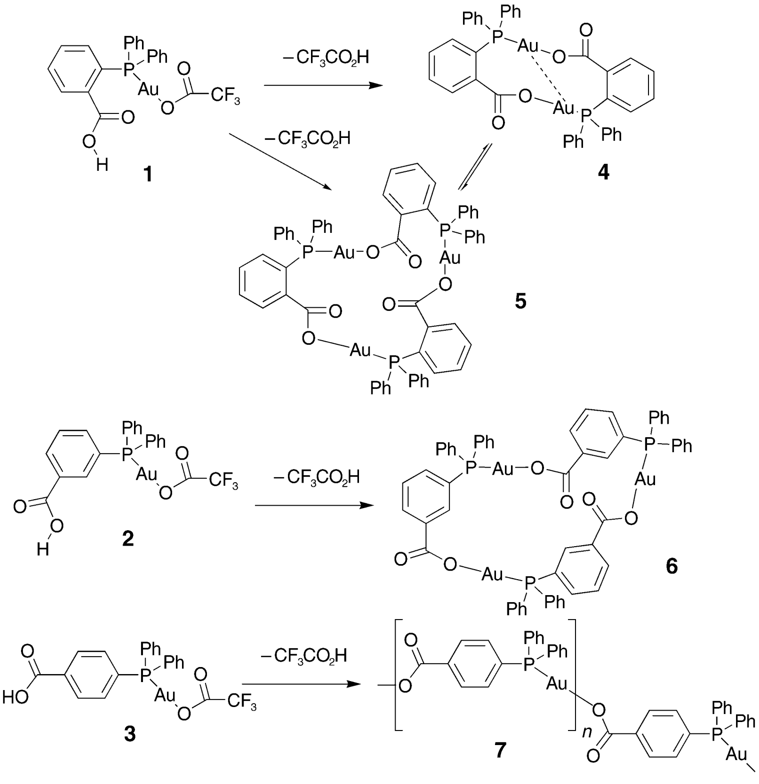
[**] We thank NSERC (Canada) for financial support. R.J.P. holds a Canada Research Chair.

DOI: 10.1002/ange.200353127



Scheme 1. Self-assembly processes from monomers **1**–**3**.

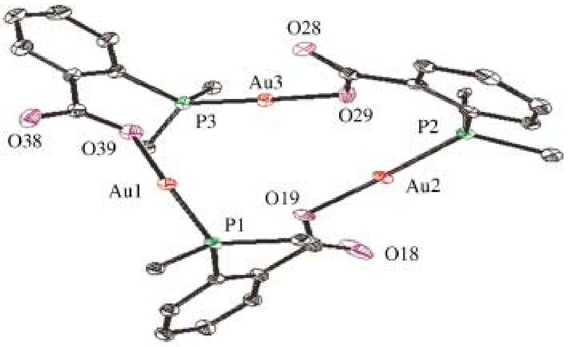


Figure 2. A view of the molecular triangle structure of **5**.

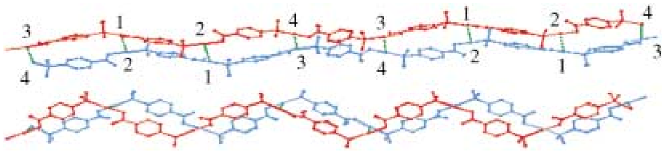


Figure 3. Two views of the double-stranded polymeric structure of **7**. Only the gold atoms are labeled with the labels 1–4 representing Au(1)–Au(4), respectively, and only the *ipso* carbon atoms of the phenyl groups are shown for clarity.

propeller-like arrangement of phenyl groups at the phosphorus centers, and all units within the same polymer chain have the same helicity *P* or *M*. The polymer chains associate in pairs primarily through gold–gold aurophilic contacts (Au(1)···Au(2) = 3.1643(9) Å) to give a racemic *P*,*M* double-helical structure. Complex **7** appears to be the first example of a hybrid organic–inorganic double-chain polymer of this type. However, there is a related inorganic double-chain polymer containing $[\mathrm{AuSe}_5]_n^{n-}$ ions, in which chains are connected through aurophilic interactions (Au···Au = 2.950(3) Å).[16] In addition, the antiarthritic drug gold thiomalate contains a classic chiral double-helical structure with chains connected through interchain aurophilic bonds (Au···Au = 3.227(5) Å).[17] Together, these structures demonstrate the remarkable ability of gold(I) centers to form several classes of double-stranded polymeric structures through aurophilic bonding.

Experimental Section

4, **5**: A solution of $[\mathrm{AuCl(2\text{-}Ph_2PC_6H_4CO_2H)}]$ (0.050 g, 0.093 mmol) in CH_2Cl_2 (10 mL) was treated with AgO_2CCF_3 (0.021 g, 0.095 mmol) for 0.5 h. The solution was filtered through celite. Et_3N (0.010 g, 0.099 mmol) was then added to the filtrate, the volume was reduced to 5 mL, and pentane (20 mL) was added to precipitate the product as a pale-yellow solid. Yield: 54%. ^{31}P NMR ($CDCl_3$): $\delta = 33.0$ (**5**); 27.9 ppm (**4**). IR (KBr disk): $\tilde{\nu} = 1635$ (s, C=O), 1336 cm^{-1} (s, C−O); ESI-MS (*m*/*z*): 1639 [**5**+Cs]$^+$, 1137 [**4**+Cs]$^+$; elemental analysis (%) calcd for $C_{19}H_{14}AuO_2P$: C 45.4, H 2.8, found: C 45.2, H 2.9.

6: This complex was prepared similarly from $[\mathrm{AuCl(3\text{-}Ph_2PC_6H_4CO_2H)}]$. Yield: 40%. ^{31}P NMR ($CDCl_3$): $\delta = 28.8$ ppm; IR (KBr disk): $\tilde{\nu} = 1627$ (s, C=O), 1334 cm^{-1} (s, C−O); ES-MS (*m*/*z*): 1639 [**6**+Cs]$^+$; elemental analysis (%) calcd for $C_{19}H_{14}AuO_2P$: C 45.4, H 2.8, found: C 45.1, H 2.5.

7: This was prepared similarly from $[\mathrm{AuCl(4\text{-}Ph_2PC_6H_4CO_2H)}]$, but precipitated on addition of Et_3N, and was isolated at that stage by filtration. Yield: 65%. IR (KBr disk): $\tilde{\nu} = 1625$ (s, C=O), 1334 cm^{-1} (s, C−O); elemental analysis (%) calcd for $[C_{19}H_{14}AuO_2P \cdot 0.25\,CH_2Cl_2]$: C 44.8, H 2.8, found: C 44.6, H 2.8.

X-ray structure analysis:[18] Nonius Kappa-CCD diffractometer ($Mo_{K\alpha}$ radiation), data collection and refinement SHELXTL-NT V6.1, empirical absorption correction. CCDC-221124–6 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB21EZ, UK; fax: (+44)1223-336-033; or deposit@ccdc.cam.ac.uk).

Received: October 21, 2003 [Z53127]

Keywords: gold · macrocycles · polymers · self-assembly · supramolecular chemistry

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[18] **3**: $C_{19}H_{15}AuClO_2P$, $M_r = 538.70$, triclinic, space group $P\bar{1}$, $Z = 4$, $a = 12.0996(3)$, $b = 12.4632(3)$, $c = 13.7806(3)$ Å, $\alpha = 112.200(1)$, $\beta = 91.268(1)$, $\gamma = 108.774(1)°$, $V = 1797.04(7)$ Å^3, $T = 148(2)$ K, $\mu(Mo_{K\alpha}) = 8.432\ mm^{-1}$, 18665 reflections, 8195 independent reflections, $R_1\ [I > 2\sigma(I)] = 0.069$, $wR_2 = 0.160$. **5**·3.25 acetone: $C_{66.75}H_{61.5}Au_3O_{9.25}P_3$, $M_r = 1695.47$, monoclinic, space group $P2_1/c$, $Z = 4$, $a = 13.6996(2)$, $b = 19.7912(3)$, $c = 23.1202(3)$ Å, $\beta = 97.756(1)$, $V = 6211.3(1)$ Å^3, $T = 150(2)$ K, $\mu(Mo_{K\alpha}) = 7.202\ mm^{-1}$, 62032 reflections, 10958 independent reflections, $R_1\ [I > 2\sigma(I)] = 0.044$, $wR_2 = 0.110$. **7**·6.5 $CHCl_3$: $C_{82.5}H_{62.5}Au_4Cl_{19.5}O_8P_4$, $M_r = 2784.85$, monoclinic, space group $P2_1/c$, $Z = 4$, $a = 34.8469(3)$, $b = 12.6874(1)$,$c = 23.3187(2)$ Å, $\beta = 108.645(1)°$, $V = 9768.5(1)$ Å^3, $T = 150(2)$ K, $\mu(Mo_{K\alpha}) = 6.638\ mm^{-1}$, 86413 reflections, 16218 independent reflections, $R_1\ [I > 2\sigma(I)] = 0.074$, $wR_2 = 0.151$.