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Polymers and rings in gold(I) diphosphine complexes: linking gold rings through aurophilic interactions

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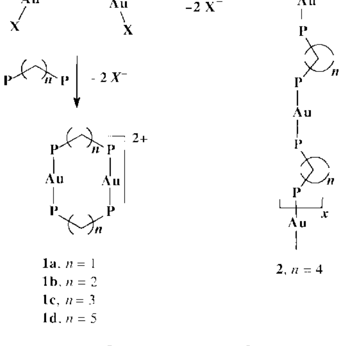
Gold(I) complex cations of empirical formula $Au[Ph_2P(CH_2)_nPPh_2]^+$ crystallize as rings $[Au_2\{Ph_2P(CH_2)_nPPh_2\}_2]^{2+}$ when $n = 3$ or 5 but as a polymer $[\{Au[Ph_2P(CH_2)_nPPh_2]\}_x]^{x+}$ when $n = 4$. In favorable cases, the ring complexes can be connected through aurophilic bonding by addition of $[Au(CN)_2]^-$, and crystals contain pentagold units when $n = 3$ or polymeric pleated chains when $n = 5$.

In the context of the rapidly developing field of coordination polymers,[1] and of gold(I) diphosphine complexes that may have interesting photophysical and biological properties,[2] this article reports two new one-dimensional polymers containing gold(I) diphosphine units, one being the first polymer containing linear gold(I) centres with only diphosphine ligands and the other the first to contain gold rings stitched together by using aurophilic attractions.[1,3] The factors that are important in giving self-assembly of polymeric structures are elucidated.

The complexes of empirical formula $AuX[Ph_2P(CH_2)_nPPh_2]$ have been suggested to exist as ring complexes $[Au_2\{\mu\text{-}Ph_2P(CH_2)_nPPh_2\}_2]^{2+}(X^-)_2$,[4] though more complex structures may be formed in cases when the anion X^- is also a ligand to give a higher coordination number than two at gold(I).[1,4] However, it is now shown that the derivatives with X = CF_3CO_2, prepared as in Scheme 1, exist as rings **1** when $n = 1$, 2, 3 or 5 but as a unique polymeric chain complex **2** when $n = 4$.

The ring complexes **1** give sharp singlet resonances in the ^{31}P NMR spectra while **2** gives several overlapping and broader resonances.† The complexes were isolated as the trifluoroacetate salts, and complexes **1c** and **2** were characterized by X-ray structure determination (Fig. 1).‡

Why does complex **2** have a structure that is different from the others? The answer is not obvious but can be analyzed in terms of two effects. First, when $n = 1$ or 2, the ring structure is favored because transannular Au···Au attractions are possible[1–4] and this effect is dominant in these cases. Second, there is a relative preference for the *anti*, rather than *syn*, orientation of the two PPh_2 groups, and hence formation of chains rather than rings, when n is an even integer.[1] Only when $n = 4$ does the preference for the *anti* conformation prevail and lead to the novel polymeric structure of **2** (Fig. 1). The NMR data suggest, but do not prove, that the solid state structures are maintained in solution.



Scheme 1 P = PPh_2.

Can the rings **1** (Scheme 1) be linked to form polymers? The complexes **1** were reacted with potassium dicyanoaurate in the expectation that both ionic and aurophilic attractions between the cationic and anionic gold(I) centres in **1** and $[Au(CN)_2]^-$ would promote association. In solution, these reactions lead to mixtures containing the original ions and the neutral diphosphine gold(I) cyanide complexes **3** (Scheme 2) as established by NMR [^1H, ^{13}C on ^{13}CN enriched samples, ^{31}P; complexes **3** are readily identified by the large coupling $^2J(PC)$].† Crystallization from these solutions gave **3** when $n = 1$ or 2, but the linked ring complex **4** when $n = 3$ and the novel polymer **5** when $n = 5$ (Scheme 2). Both **4** and **5** crystallized as the dicyanoaurate salts and so also contain free $[Au(CN)_2]^-$ anions.‡

The structures of **4** and **5** are shown in Fig. 2. In complex **4** two rings are connected by an $[Au(CN)_2]^-$ ion through aurophilic interactions to give the unit $[\{Au_2(\mu\text{-}Ph_2PCH_2CH_2CH_2PPh_2)_2\}_2\{Au(CN)_2\}]^{3+}$, with only one of the two AuP_2^+ centres of each ring involved in Au···Au bonding. However, in complex **5** all the AuP_2^+ centres are involved in

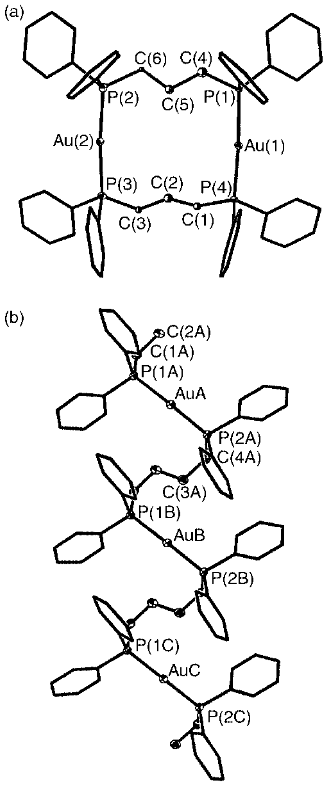


Fig. 1 Structures of the cationic units in (a) the ring complex **1c** and (b) the polymeric complex **2**. For clarity, thermal ellipsoids are not shown for phenyl carbon atoms.

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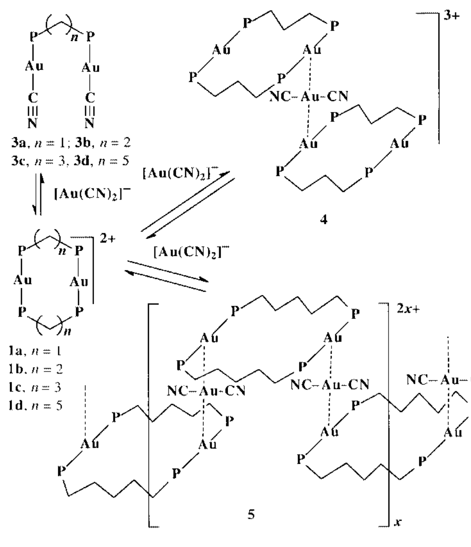

Scheme 2 P = PPh$_2$.

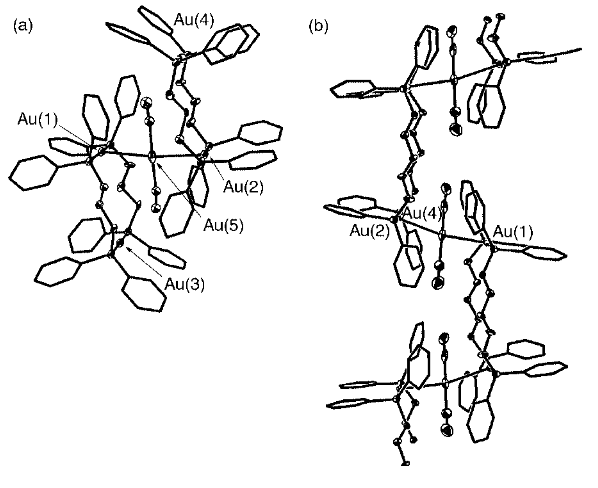

Fig. 2 Structures of the linked ring complex cations in (a) complex **4** and (b) complex **5**. The parameters corresponding to aurophilic attractions are: for complex **4**, Au(1)–Au(5) 3.059(3) Å, Au(2)–Au(5) 3.034(3) Å; Au(1)–Au(5)–Au(2) 172.1(1)°. For complex **5**, Au(1)–Au(4) 2.9906(8), Au(2)–Au(4) 3.0665(8) Å, Au(1)–Au(4)–Au(2) 165.26(3)°.

Au···Au bonding and so the pleated-chain polymeric structure $[\{Au_2[\mu\text{-}Ph_2P(CH_2)_5PPh_2]_2\}_2\{Au(CN)_2\}_2]_x^{2x+}$ results. By inspection of Fig. 2, it is immediately clear that the structure observed for **5** would not be possible for **4** because the transannular Au···Au distance is too short to allow both gold atoms to be linked to approximately collinear $[Au(CN)_2]^-$ units. Phenyl–phenyl repulsions prevent bridging in other ways to link units of **1a**, **1b** or **1c**.

The complexes **4**, **2** and **5**, as the dicyanoaurate salts, give rather similar solid state emission spectra, with maxima at 419, 414 and 411 nm, respectively. This indicates that the extended structures present in **2** (n = 4) and **5** (n = 5) do not greatly affect the photophysical properties of the complexes, when compared to the more limited association in **4**.

The ability to control the self-assembly of extended structures is becoming increasingly important. This article shows how conformational differences in simple, commonly used diphosphine ligands can be used to control whether ring or polymeric structures will be formed in gold(I) complexes and, for the ring compounds, how the distance between phosphorus donors is critical in determining if the rings can be linked to give extended structures.

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Notes and references

† *Selected data*: for **1** and **2**: $\delta(^{31}P)$ in CD$_3$OD: **1a**, 38.3; **1b**, 41.1; **1c**, 44.3; **1d**, 45.6; **2**, 44.7. For **3a**: $\delta(^{13}CN)$ 155.7; $\delta(^{31}P)$ 34.9. For **3b**: $\delta(^{13}CN)$ 155.9 [J(PC) 132 Hz]; $\delta(^{31}P)$ 33.5. For **3c**: $\delta(^{13}CN)$ 157.2 [J(PC) 123 Hz]; $\delta(^{31}P)$ 31.9. For **3d**: $\delta(^{13}CN)$ 157.7 [J(PC) 124 Hz]; $\delta(^{31}P)$ 35.8.

Complexes were prepared in methanol solution, NMR data were obtained in CD_2Cl_2/CD_3OD solution, and crystals were grown by slow diffusion of pentane into these solutions.

‡ *Crystal data*: for **1c**·2CH$_2$Cl$_2$: $C_{60}H_{56}Au_2Cl_4F_6O_4P_4$, M = 1586.61, orthorhombic, space group $Pna2_1$, a = 22.7641(8), b = 13.3249(3), c = 19.5994(8) Å, V = 5945.1(3) Å^3, Z = 4, $R1$ = 0.0739 and $wR2$ = 0.1787 for 12645 reflections with $I > 2\sigma(I)$ at 150 K.

For **2**: $C_{30}H_{28}AuF_3O_2P_2$, M = 736.43, monoclinic, space group Pc, a = 6.7570(1), b = 11.7756(3), c = 20.3694(5) Å, β = 93.629(1)°, V = 1617.50(6) Å^3, Z = 2, $R1$ = 0.0752 and $wR2$ = 0.2057 for 8807 reflections with $I > 2\sigma(I)$ at 300 K.

For **3a**: $C_{27}H_{22}Au_2N_2P_2$, M = 830.34, monoclinic, space group $C2/c$, a = 22.039(1), b = 7.4488(3), c = 18.3838(6) Å, β = 122.193(2)°, V = 2554.0(2) Å^3, Z = 4, $R1$ = 0.0364 and $wR2$ = 0.0883 for 3723 reflections with $I > 2\sigma(I)$ at 200 K.

For **3b**: $C_{28}H_{24}Au_2N_2P_2$, M = 844.36, monoclinic, space group $P2_1/n$, a = 12.597(1), b = 11.4020(9), c = 19.258(1) Å, β = 108.34(6)°, V = 2625.5(4) Å^3, Z = 4, $R1$ = 0.0641 and $wR2$ = 0.1676 for 4262 reflections with $I > 2\sigma(I)$ at 298 K.

For **4**: $C_{58}H_{52}Au_4N_4P_4$, M = 1716.78, monoclinic, space group $P2_1/n$, a = 26.860(1), b = 17.425(1), c = 28.026(1) Å, β = 96.439(4)°, V = 13034(1) Å^3, Z = 10, $R1$ = 0.1357 and $wR2$ = 0.3699 for 15165 reflections with $I > 2\sigma(I)$ at 200 K.

For **5**: $C_{62}H_{60}Au_4N_4P_4$, M = 1772.89, monoclinic, space group $P2_1/c$, a = 13.7149(3), b = 25.056(1), c = 19.4449(8) Å, β = 97.46(2)°, V = 6625.5(4) Å^3, Z = 5, $R1$ = 0.0561 and $wR2$ = 0.1633 for 13231 reflections with $I > 2\sigma(I)$ at 296 K.

CCDC 164205–164210. See http://www.rsc.org/suppdata/cc/b1/b103020p/ for crystallographic data in CIF or other electronic format.

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