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Preliminary communication

Inclusion and aggregation properties of organogold complexes: crystal structures of $C_2\{Au[P(C_6H_4R\text{-}3)_3]\}_2 \cdot nC_6H_6$ ($R = H$, $n = 2$; $R = Me$, $n = 0$ and 1)

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Abstract

The digold acetylides $C_2\{Au[P(C_6H_4R\text{-}3)_3\}_2$ ($R = H$ or Me) form inclusion complexes in which two molecules ($R = H$) or one ($R = Me$) are present in cavities formed by the aryl groups; both complexes show unusual aggregation behaviour in the vapour phase, tetrameric ions being found in their FAB mass spectra.

The so-called 'wheel-and-axle' [1] or 'spacer' molecules [2], such as $CPh_2(OH)C{\equiv}CC{\equiv}CCPh_2(OH)$, have attracted attention on account of their clathrating ability, most recently demonstrated in the formation of inclusion compounds by solid-state reactions [3]. The 'guest' molecules reside in channels which are defined by the long molecular axis, the bulky end groups acting as spacers; hydrogen-bonding to the OH groups is also a feature of these structures.

Whilst exploring the chemistry of the compounds $C_2\{Au(PR_3)\}_2$ [4], which contain a similar linear six-atom rod-like fragment, we have found that the PPh_3 and $P(C_6H_4Me\text{-}3)_3$ derivatives have a remarkable affinity for benzene, but that the nature of the inclusion is fundamentally different from that found in the diynes studied earlier. Thus, solutions of the two organogold complexes in ethanol or dichloromethane rapidly deposit highly refractive sparkling crystals when a few drops of benzene are added. The crystal structures of both the solvent-free (**1**) and clathrate (**2**) complexes containing $P(C_6H_4Me\text{-}3)_3$, and of the clathrate of the PPh_3 complex (**3**), have been determined by X-ray diffraction: the three crystals are isomorphous [5 *].

The asymmetric unit for **1**, and in part for **2**, comprises a $(C_7H_7)(PAuC)_{1/3}$ moiety of which the P, Au and C atoms are located on a crystallographic three-fold

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* A reference number with an asterisk indicates a note in the list of references.

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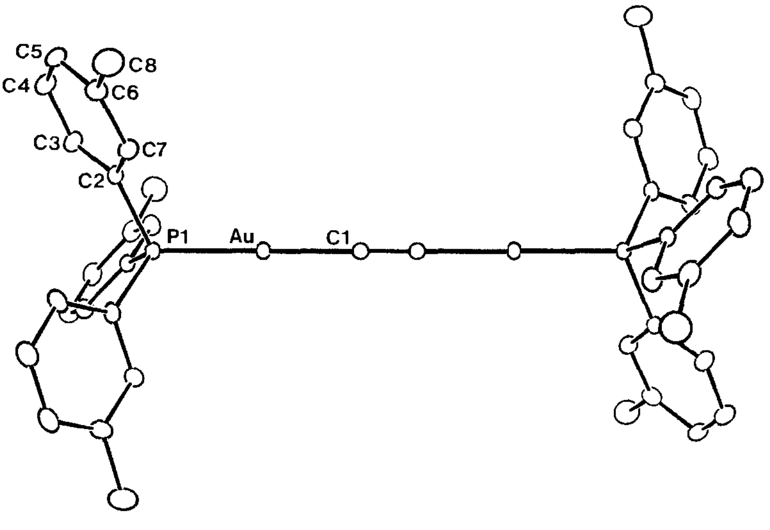

Fig. 1. A plot of one molecule of $C_2\{Au[P(C_6H_4Me\text{-}3)_3]\}_2$ as found in **1** in **2**; the molecule in **3** is similar, lacking the methyl groups (C(8)). Bond distances for **1**, **2** and **3**: Au–P 2.270(4), 2.284(3), 2.280(3); Au–C 2.02(1), 2.002(9), 2.00(1); C≡C 1.13(2), 1.19(2), 1.19(2) Å.

axis; the $(C_7H_7)_3PAuC$ species thus generated is situated about a centre of inversion (located at (0,0,0)). In consequence, the PAuC≡CAuP system is constrained to linearity; the molecule is shown in Fig. 1. In the solvated complex **2**, the asymmetric unit is completed by a C atom of the solvent benzene molecule, situated about a site of symmetry $\bar{3}$ located at $(0,0,\frac{1}{2})$. The benzene molecule thus generated is very nearly planar (the maximum deviation of the symmetry related C atoms is 0.001 Å from the least-squares plane). The unit-cell of **2** is 90.7 $Å^3$ (2.2%) larger than that of **1**.

In **2**, the benzene molecules reside in cavities defined by six methyl groups from six tertiary phosphine ligands of six symmetry-related dinuclear units. The regular octahedral hole (Fig. 2a) is situated about the site of symmetry $\bar{3}$; the mid-point of the C_6H_6 molecule is 4.68 Å from each of the six methyl carbon atoms, C(8), although the molecules are held in place by normal Van der Waals H...H contacts. The outer confines of the cavity are defined by six substituted phenyl rings which are disposed in positions approximately perpendicular to the plane of the benzene ring. The cavity may thus be described as being shaped as a 'wine-barrel' with the methyl groups defining the 'tops' and the phenyl rings the 'staves'.

The related PPh_3 complex forms solvent-free crystals with difficulty, and none have yet proved suitable for X-ray studies. The structure of the di-benzene solvate (**3**) has been determined, the organo-gold molecules being virtually identical (apart from the absence of the Me groups) with those found in **1** and **2**; the C_6H_6 molecules are apparently essential for the formation of the cubic lattice [5*]. Although the host lattices for **1**, **2** and **3** are isomorphous, the cavities in the latter (which are aligned along the crystallographic 3-fold axis) differ from those in **2** in containing two benzene molecules, and in being capped at either end by the PPh_3 groups (Fig. 2b). The sides of the elongated cavities are defined by six phenyl groups, one from each of six distinct digold molecules.

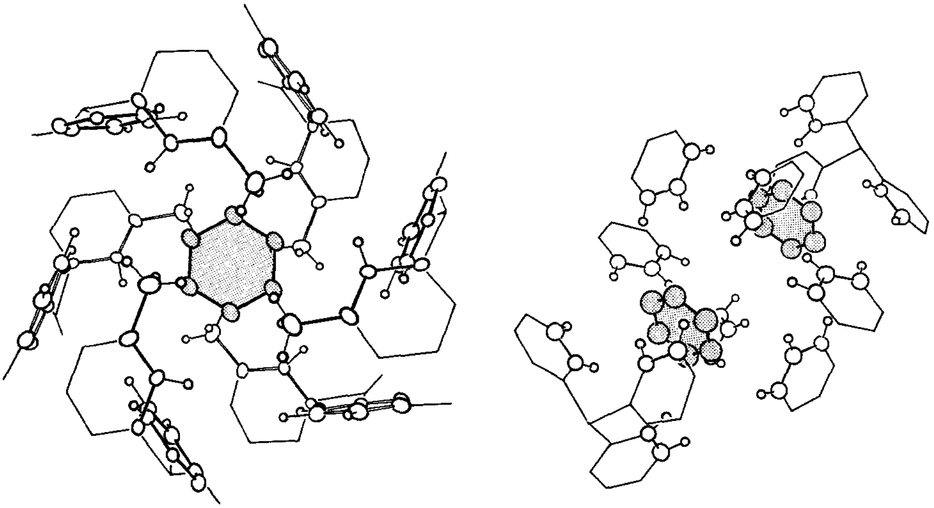

Fig. 2. (a) The octahedral cavity in **2**, viewed perpendicular to the C_6H_6 plane. (b) The elongated cavity in **3**. In each case, the included C_6H_6 molecule(s) is(are) hatched.

A further point of interest in the chemistry of these compounds is the high degree of association revealed in their fast atom-bombardment mass spectra [6]. The highest mass ions so far measured occur between m/z 4000–4500, and correspond to $[M_4 + Au_2C_2]^+$ $[M = C_2\{Au(PR_3)\}_2]$. Indeed, the major ions found in these spectra correspond to the series $[M_n + Au]^+$, $[M_n + Au(PR_3)]^+$ and $[M_n + Au_2C_2]^+$ ($n = 1$–4). The nature of the aggregation process is not clear at present; in the crystal, there are no Au–Au interactions, as found, for example, in $Au(C_2Ph)(PPh_3)$ [7], and there is no evidence that the clathrated benzene molecules found in the solid state are involved in the aggregation processes occurring in the mass spectrometer. Interestingly, the ions $[M_n + Au(PR_3)]^+$ are isolobal analogues of the oft-observed $[M + H]^+$ ions in organic compounds; further application of the analogy reduces these ions to protonated poly(alkynes).

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5 Intensity data ($1° \leqslant \theta \leqslant 22.5°$) were measured on an Enraf–Nonius CAD4 diffractometer (T 293 K) with Mo-K_α radiation (λ 0.7107 Å) and the $\omega/2\theta$ scan technique. The structures were solved by Patterson methods and refined by a full-matrix least-squares procedure (SHELX76). Anisotropic thermal parameters for non-H atoms and H atoms were included in the models at their calculated positions. After the inclusion of a weighting scheme of the form, $w = k/[\theta^2(F) + g|F|]$, the refinements were continued until convergence in each case.

Crystal data. **1**: $C_2\{Au[P(C_6H_4Me\text{-}3)\}_2 = C_{44}H_{42}Au_2P_2$, $M = 1026.7$, cubic space group $Pa3$ (T_h^6, No 205), a 16.092(5) Å, U 4167.1 Å^3, D_c ($Z = 4$) 1.637 g cm^{-3}, μ 70.95 cm^{-1}, analytical absorption correction, max/min transmission factors 0.2299, 0.0551 respectively, 3616 reflections collected (917 unique), final $R = 0.038$, $R_w = 0.044$, $k = 0.47$ and $g = 0.0077$ for 721 reflections which satisfied $I \geqslant 2.5\sigma(I)$. **2**: $C_2\{Au[P(C_6H_4Me\text{-}3)_3]\}_2 \cdot C_6H_6 = C_{44}H_{42}Au_2P_2 \cdot C_6H_6$, $M = 1104.8$ cubic, space group $Pa3$, a 16.208(5) Å, U 4257.8 Å^3, D_c ($Z = 4$) 1.724 g cm^{-3}, μ 69.47 cm^{-1}, max/min transmission factors 0.2734, 0.1966 respectively, 3669 reflections collected (929 unique), final $R = 0.020$, $R_w = 0.021$, $k = 0.89$ and $g = 0.0004$ for 659 reflections. **3**: $C_2\{Au(PPh_3)\}_2 \cdot 2C_6H_6 = C_{38}H_{30}Au_2P_2 \cdot 2C_6H_6$, $M = 1098.8$, cubic, space group $Pa3$, a 16.126(4) Å, U 4193.5 Å^3, D_c ($Z = 4$) 1.740 g cm^{-3}, μ 70.54 cm^{-1}, max/min transmission factors 0.3540, 0.2565 respectively, 4158 reflections collected (922 unique), final $R = 0.030$, $R_w = 0.025$, $k = 3.4$ and $g = 0.0003$ for 672 reflections. Tables of atomic coordinates and of bond lengths and angles will be deposited with the Cambridge Crystallographic Data Centre.

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