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Crystal Structure of a New Ethylenic Gold Complex, $[Ph_3PAuC(CF_3)]_2$

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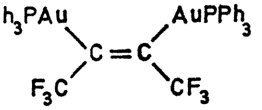
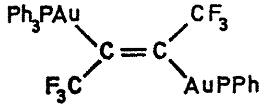
Summary Structure determination by *X*-ray diffraction shows that the compound $(Ph_3P)_2Au_2C_2(CF_3)_2$ is *cis*-1,2-bis(triphenylphosphinegold)-1,2-bis(trifluoromethyl)-ethylene, the first ethylenic compound in which both carbon atoms are σ-bonded to the metal atom of an organometallic ligand.

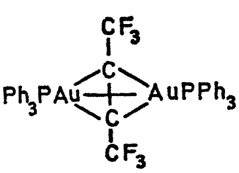
Reaction of hexafluorobut-2-yne with methyl(triphenylphosphine)gold at 55 °C or under u.v. radiation yields a binuclear gold complex $(Ph_3PAu)_2C_2(CF_3)_2$.[1] Three possible structures (I), (II), and (III) have been proposed. Our crystallographic examination established (I) as the correct structure, the compound is a rare example of direct σ-bonding, *via* the metal, between an organometallic ligand and an ethylenic carbon atom and, we believe, the first compound in which both ethylenic carbon atoms are so linked.



(I)



(II)

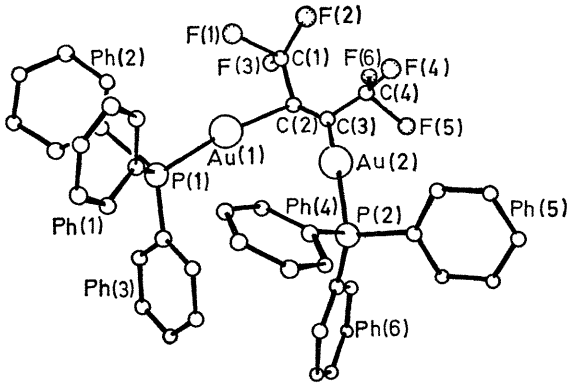


(III)

Crystals of $C_{40}H_{30}Au_2F_6P_2$ are colourless, monoclinic, $a = 13{\cdot}78$, $b = 14{\cdot}28$, $c = 21{\cdot}91$ Å, $\beta = 112{\cdot}3°$, space group $P2_1/c$. The intensities of 1842 unique reflections were measured on a Buerger–Supper–Pace two-circle auto-diffractometer. The elucidation of the structure was much hampered by problems of pseudo-symmetry, as the gold, phosphorus, and ethylenic carbon atoms all lie on the glide plane at $y = \frac{1}{4}$; this gives rise to a pseudo-translation of $\frac{1}{2}c$, effectively reducing the c dimension to half its value and converting the glide into a mirror plane. With such an extreme proportion of the scattering power of the unit cell occupying special positions, location of the remaining light atoms was very difficult, and was in fact only achieved by a combination of Fourier methods, trial and error, and rigid-body refinement of phenyl- and trifluoromethyl-groups. At convergence, $R = 0{\cdot}084$ (R' 0·104).

A perspective view of the determined structure is given in the Figure. The molecule is seen to be a *cis*-substituted ethylene, with triphenylphosphinegold- and trifluoromethyl-groups σ-bonded to an ethylenic skeleton. The P–Au–C=C–Au–P moiety is substantially planar and of C_{2v} symmetry. The gold atoms adopt linear two-co-ordination [P–Au–C = 170(7)°], with mean Au–P and Au–C distances of 2·28(1) and 2·05(6) Å respectively. The Au···Au distance of 3·343(8) Å is too large for any appreciable interaction to be possible if the gold atoms are univalent; neither is any interaction necessary. Indeed, assuming normal ethylenic geometry, the Au···Au distance is expected to be 3·33 Å.

If we take the covalent radius of Au^I to be 1·32 Å [2] and of tetrahedral phosphorus to be 1·10 Å, it is seen that the Au–P bond is some 0·14 Å shorter than the sum of the covalent radii, probably as a result of d_π–d_π Au—P interaction. Similarly short Au–P bond lengths have been reported in $Ph_3PAuW(CO)_3C_5H_5$ (2·25 Å);[3] in $Ph_3PAuMn(CO)_4P(OPh)_3$ (2·33 Å);[4] and in $Ph_3PAuCo(CO)_4$ (2·23 Å).[2] Whether there is also d_π–p_π interaction in the Au–C bond is not clear because of the limited accuracy of



the bond lengths. In principle the d_{xz} gold orbitals, although diffuse, could donate into unfilled π^* orbitals on the ethylenic moiety, to give a lengthening of the ethylenic bond; it would be interesting to have bond lengths accurate enough to establish this point significantly. In neither $CF_2{=}CF[Mn(CO)_5]$[5] nor in $[C_5H_5(CO)_2(CH)_2]_2$[6,7] was this possible.

The triphenylphosphine ligand shows no departure in its geometry from that of the unco-ordinated molecule; the trifluoromethyl groups are poorly resolved, but we ascribe this to their high thermal activity.

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