A New Type of Organogold Compound. The Molecular Structure of $[(\pi\text{-}C_5H_5)Fe(\pi\text{-}C_5H_4)Au_2(PPh_3)_2]^+[BF_4]^-$

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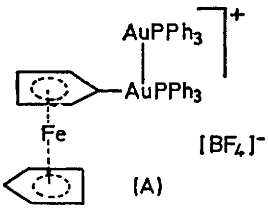
Summary In the cation $[(\pi\text{-}(C_5H_5)Fe(\pi\text{-}C_5H_4)Au_2(PPh_3)_3]^+$ metal atoms form an Au–Au–Fe chain and one carbon atom of the ferrocene cyclopentadienyl ring acts as a bridge between both gold atoms.

As shown previously, reaction of HBF_4 with ferrocenyltriphenylphosphinegold, $C_5H_5FeC_5H_4AuPPh_3$, leads to an ionic complex of a composition $[C_5H_5FeC_5H_4Au_2(PPh_3)_2]^+$-$[BF_4]^-$ (I). On the basis of i.r., ^1H n.m.r., and u.v. spectra this complex was initially ascribed structure (A). We have determined the structure of this new organogold compound unambiguously by *X*-ray crystallography. Crystal data: $C_{46}H_{39}Au_2FeP_2BF_4$, M = 1190·5, monoclinic, space group $P2_1/a$; $a = 14{\cdot}460(11)$, $b = 30{\cdot}539(27)$, $c = 9{\cdot}509(12)$ Å, $\beta = 92{\cdot}61(5)°$, $D_m = 1{\cdot}86$, $D_c = 1{\cdot}89$ g cm^{-3} for $Z = 4$.



(A)

Intensities of 2182 independent non-zero reflexions were measured on a four-circle Hilger and Watts diffractometer (Mo-K_α radiation with a graphite monochromator, ω-scan). The structure was solved, neglecting absorption, by the heavy-atom technique and refined by an isotropic least-squares method to $R = 0{\cdot}112$.

The proposed structure (A) proved to be incorrect as in the cation one of gold atoms is also bonded to iron and one of C_5H_5 rings acts as a bridging ligand between both gold atoms (Figure). The co-ordination around Au(1) is distorted trigonal-planar and that around Au(2) is distorted square-planar. The C–Au–P fragments are linear, as is typical for molecules with X–Au–P groups (X a one electron donor).

A discussion of individual M–C and, especially C–C distances seems unjustified in view of low accuracy of the determination of the carbon co-ordinates. However, it is evident that both unsubstituted and bridging C_5H_5 rings are bonded to iron through all five ring atoms (Fe–C 2·03—2·15, av. 2·08 Å and 1·96—2·16, av. 2·08 Å respectively). The bridging C(1) atom is displaced outwards from the iron atom by 0·28 Å out of the plane of the four other carbon atoms in the same C_5H_5 ring. The C_5H_5 rings, which are practically eclipsed, form a dihedral angle of 16° and their mean planes are normal to the Au–Au–Fe plane. P(1), P(2), and C(1) are displaced from the latter in the same direction by 0·38, 0·20, and 0·08 Å respectively.

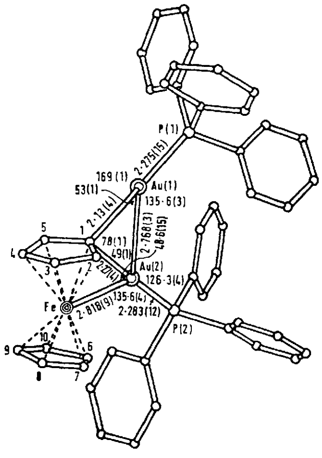


FIGURE. *A general view of the cation of* (I) *showing important distances and angles.*

The Fe–Au bond length (2·818 Å), not determined previously, is close to the sum of the covalent radii (2·782 Å) of Fe (1·34 Å[2]) and Au (taken as half the distance in the metal, 1·442 Å[3]). Au–Au distances in complexes and especially in cluster systems vary considerably.[4] In the complex (I) this distance has an intermediate value of 2·768Å which is close to that in $[PrNCS_2Au]_2$ (2·76 Å[5]). The Au–P (2·28 Å) and P–C (1·83 Å) bond lengths are normal. The significant difference in the Au–C bond distances (2·13 and 2·27 Å) can be ascribed to steric as well as to electronic effects. The anion is tetrahedral with B–F distances in the range 1·35—1·42 Å.

To our knowledge (I) is the first structural study on a ferrocene derivative with a direct Fe–M bond. It presents also the first known example of a cyclopentadienyl ring bridging (*exclusively* through one of its carbons) *two* metal (Au) atoms, comparable with the interesting bridging multicentre bonding systems found for phenyl and benzyne ligands.[6]

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