The Mechanism of Insertion of an Acetylene into the Methylgold Bond: Structure of a Reaction Intermediate

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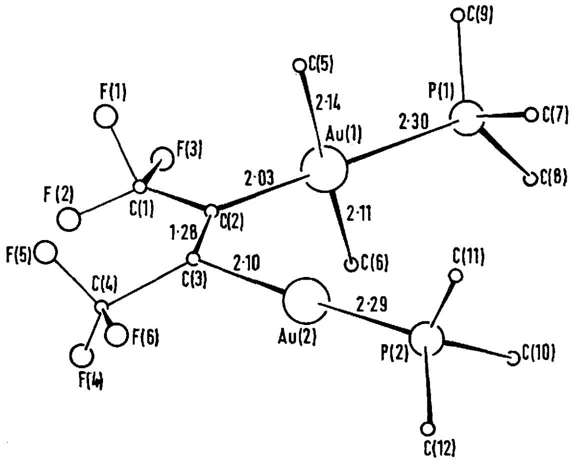
Summary The determination of the structure of a reaction intermediate gives strong evidence for an unusual mechanism of insertion of an acetylene into the methylgold bond.

THE methylgold compounds MeAuL (I; L = tertiary phosphine) react with hexafluorobut-2-yne, C_4F_6, to give intermediate complexes of composition $(MeAuL)_2C_4F_6$, (II).[1] These complexes can then break down either to give the insertion compound *cis*-$LAuC(CF_3) = C(CF_3)CH_3$, (III), or to give ethane and *cis*-$LAuC(CF_3){=}C(CF_3)AuL$, (IV)[1–3]. When L = PMe_2Ph a single isomer, (IIa) is formed but when L = PMe_3 two isomers (IIb) and (IIc) can be isolated.

The complexes (II) were thought to contain two MeAuL units with an acetylene bridge,[1] in which case the two gold atoms in (II) should be identical. However, the ^{197}Au Mössbauer spectra contain two doublets for each isomer rather than the one expected for this formulation and comparison of the Mössbauer parameters with those for



FIGURE

model compounds[4–6] shows that (II) are in fact mixed oxidation state complexes containing both Au^{I} and Au^{III} centres as indicated in the Table.

TABLE. ^{197}Au *Mössbauer spectra*[a]

Compound	I.S. mm s^{-1}	Q.S. mm s^{-1}	Oxidation state
(IIa)	5·11 ± 0·01	9·13 ± 0·04	III
	4·13 ± 0·04	9·44 ± 0·03	I
(IIb)	5·16 ± 0·06	9·27 ± 0·05	III
	4·37 ± 0·04	9·18 ± 0·02	I
(IIc)	5·28 ± 0·26	9·07 ± 0·13	III
	4·14 ± 0·26	9·17 ± 0·10	I

[a] Half width, $\Gamma = 1{\cdot}5$—$2{\cdot}5$ mm s^{-1} for all peaks.

This revised formulation is confirmed by a crystal structure determination for isomer (IIb). *Crystal data* $C_{12}H_{24}Au_2P_2F_6$, $M = 738{\cdot}3$; orthorhombic, $a = 20{\cdot}68(3)$, $b = 19{\cdot}20(1)$, $c = 10{\cdot}47(1)$ Å; space group *Pbca*, $D_c = 2{\cdot}36$, $Z = 8$. Intensities were measured for 1320 reflections and the structure refined to R 0·081. The stereochemistry of the molecule and selected bond lengths are shown in the Figure. The co-ordination of Au(2) is linear and that for Au(1) is square planar with the bonds to C(5) and C(6) roughly perpendicular to the plane defined by the Au and P atoms. This configuration is expected to facilitate π-bonding between Au(1) and C(2). The distance between Au(1) and Au(2) is 3·31 Å. The compound (IIa) has a similar structure but (IIc) differs in having the *cis*-configuration at the square planar Au^{III} centre.

The overall mechanism of reaction of (I) with C_4F_6 can therefore be interpreted as follows: transfer of a methyl group from one gold atom to a second with formation of the C_4F_6 bridge leading to a mixed Au^{I}–Au^{III} complex, (II), followed by reductive elimination from the Au^{III} centre to give the final products. Cleavage of the bonds from Au(1) to C(5) and C(6) gives ethane and (IV), while cleavage of the bonds to C(5) or C(6) and C(2) gives (I) and (III). It is interesting that the configuration about the C=C bond is retained on formation of (III) during the reductive elimination step.[7] This is also the case[8] in the reaction of (IIb) with HCl which gives $AuClPMe_3$ and *cis*-$HC(CF_3){=}C(CF_3)$-[*trans*-$AuMe_3(PMe_2)$].

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