Reactions of Hexafluorobut-2-yne with Alkylgold(I) Complexes. Properties of Intermediate Binuclear Gold(I)–Gold(III) Complexes

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Reactions of alkylgold(I) complexes [AuRL] (R = Me, L = PMe_3, PMe_2Ph, or $PMePh_2$; R = Et, L = $PMePh_2$) with hexafluorobut-2-yne give first the mixed-oxidation-state complexes $[LAu\{(F_3C)C{=}C(CF_3)\}AuR_2L]$, which react further to give either the binuclear gold(I) complexes $[LAu\{(F_3C)C{=}C(CF_3)\}AuL]$ or the products of *cis* insertion of the alkyne into the original Au–C bond, $[AuL\{(F_3C)C{=}CR(CF_3)\}]$. The course of this subsequent reaction is dependent on the nature of L and R and on the solvent, and the reaction mechanisms have been investigated. Hydrogen chloride reacts with $[LAu\{(F_3C)C{=}C(CF_3)\}AuMe_2L]$ (L = PMe_3) to cleave the vinylgold(I) bond and give [AuClL] and $[AuMe_2L\{(F_3C)C{=}CH(CF_3)\}]$, while metal halides $\{HgCl_2, [PtX_2(PMePh_2)_2]\}$ react initially to cleave a methylgold(III) bond. Both electrophilic-cleavage and reductive-elimination reactions involving the vinylgold bond occur with retention of stereochemistry about the C=C bond. Gold-197 Mössbauer spectra of many of the complexes are reported, and show the presence of both Au^I and Au^{III} in some complexes.

REACTIONS of methylgold(I) complexes [AuMeL] (L = tertiary phosphine) with alkenes bearing electronegative substituents give π complexes,[1,2] [AuMeL(tcne)], with tetracyanoethylene or products of insertion into the Au–Me bond, $[Au(CF_2CF_2Me)L]$, with tetrafluoroethylene.[1,3] When L = PPh_3, Mitchell and Stone found that acetylenes, RC≡CR, give rise to binuclear complexes *cis*-[LAu(RC=CR)AuL].[3,4] With less bulky tertiary-phosphine ligands we were later able to isolate intermediate complexes of empirical formula $[(AuMeL)_2(C_4F_6)]$ from hexafluorobut-2-yne (C_4F_6). These complexes were first thought to contain an acetylene bridging between two AuMeL units *via* π bonds,[1] but they were later proved to be mixed-oxidation-state complexes containing both gold(I) and gold(III) centres as shown in structures (1) and (2).[5] We now report details of the synthesis and characterisation of complexes (1) and (2), and a study of their chemical properties.

RESULTS AND DISCUSSION

Preparation and Characterisation of the Mixed-oxidation-state Gold(I)–*Gold*(III) *Complexes*.—Reaction of

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[1] A. Johnson, R. J. Puddephatt, and J. L. Quirk, *J.C.S. Chem. Comm.*, 1972, 938.

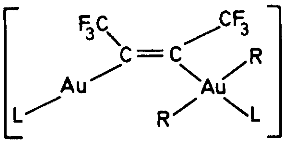
[2] A. Johnson and R. J. Puddephatt, *J.C.S. Dalton*, 1977, 1384.

[3] C. M. Mitchell and F. G. A. Stone, *Chem. Comm.*, 1970, 1264; *J.C.S. Dalton*, 1972, 102.

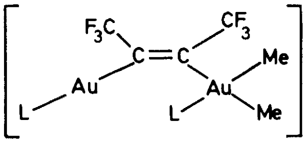
[4] C. J. Gilmore and P. Woodward, *Chem. Comm.*, 1971, 1233.

[5] J. A. J. Jarvis, A. Johnson, and R. J. Puddephatt, *J.C.S. Chem. Comm.*, 1973, 373.

[AuMeL] (L = PMe_3, PMe_2Ph, or $PMePh_2$) with hexafluorobut-2-yne in diethyl ether at room temperature gave complexes (1) or (2) as colourless crystals. Diethyl ether was the preferred solvent since the products were sparingly soluble and precipitated from solution, thus minimising further reactions with hexafluorobut-2-yne (see below). In the case of [$AuMe(PMe_3)$], isomeric complexes (1a) and (2) were formed, differing in the stereochemistry about the gold(III) centre, but in other cases only complexes (1) having the *trans* stereochemistry at Au^{III} were formed. Reaction of [$AuEt(PMePh_2)$] with hexafluorobut-2-yne gave an analogous complex (1d), whose thermal stability was lower than for the methyl derivatives (1a)—(1c). The complexes are all air-stable, although somewhat photosensitive, solids which are soluble in solvents such as benzene, acetone, and dichloromethane but sparingly soluble in diethyl ether, ethanol, and pentane.



	L	R
(1a)	PMe_3	Me
(1b)	PMe_2Ph	Me
(1c)	$PMePh_2$	Me
(1d)	$PMePh_2$	Et



(2) L = PMe_3

Reaction of the complex [$MeAu(Ph_2PCH_2CH_2PPh_2)AuMe$] with hexafluorobut-2-yne gave at first a complex whose analysis corresponded to [$MeAu(Ph_2PCH_2CH_2PPh_2)AuMe$]·$C_4F_6$ and for which we tentatively suggest the structure (7). However, this deposited from solution a highly insoluble white solid which may have the polymeric structure (8). No complex (1) could be isolated from [$AuMe(PPh_3)$] and C_4F_6 but, as reported by Mitchell and Stone,[3] only (3c) was formed.

TABLE 1

Gold-197 Mössbauer spectra of the complexes

Complex	i.s.*/mm s^{-1}	q.s./mm s^{-1}	Oxidation state
[$AuMe(PMe_3)$]	4.90 ± 0.10	10.21 ± 0.20	I
[$AuMe_3(PMe_2Ph)$]	4.84 ± 0.10	9.04 ± 0.20	III
(4a)	4.41 ± 0.20	9.49 ± 0.30	I
(1a)	5.16 ± 0.06	9.27 ± 0.05	III
	4.37 ± 0.04	9.18 ± 0.02	I
(2)	5.28 ± 0.26	9.07 ± 0.13	III
	4.14 ± 0.26	9.17 ± 0.10	I
(1b)	5.11 ± 0.01	9.13 ± 0.04	III
	4.13 ± 0.04	9.44 ± 0.03	I

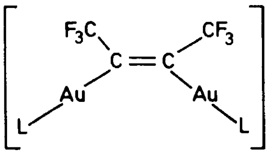
* Reference ^{197}Au–Pt.

The characterisation of the complexes was readily achieved by comparison of the spectroscopic data (i.r., ^1H and ^{19}F n.m.r., and ^{197}Au Mössbauer) with those of (1a) whose structure was determined by single-crystal *X*-ray studies.[5] The first indication that complexes (1) contained both gold(I) and gold(III) centres came from a consideration of the ^{197}Au Mössbauer spectra. The spectra each contained two overlapping doublets indicating the presence of gold in two distinct chemical environments. From the magnitudes of both the isomer shift (i.s.) and quadruple splitting (q.s.) it is possible [6-8] to distinguish between most linear gold(I) and square-planar gold(III) complexes by using empirical

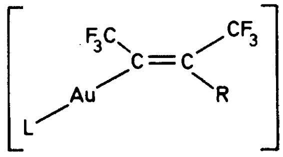
$$\text{Linear gold(I) complexes, q.s.} = \text{i.s.} + 5.6\ \text{mm s}^{-1} \quad \text{(i)}$$

$$\text{Square-planar gold(III) complexes, q.s.} = 2.0\ \text{i.s.} - 0.5\ \text{mm s}^{-1} \quad \text{(ii)}$$

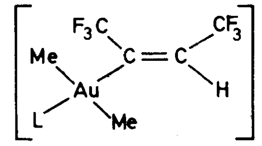
relations [9] (i) and (ii). The data in Table 1 indicate that complexes (1) and (2) contain both linear gold(I) and square-planar gold(III) centres, as expected for the proposed structures.



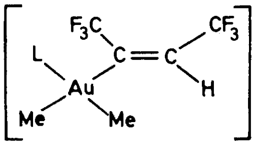
	L
(3a)	PMe_2Ph
(3b)	$PMePh_2$
(3c)	PPh_3



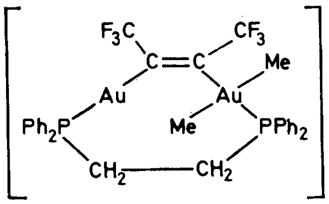
	L	R
(4a)	PMe_2Ph	Me
(4b)	$PMePh_2$	Me
(4c)	$PMePh_2$	Et



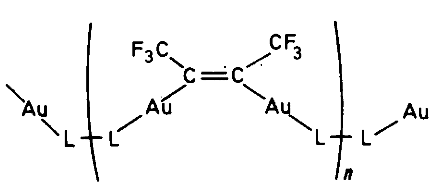
(5) L = PMe_3



(6) L = PMe_3



(7)



(8) L—L = $Ph_2PCH_2CH_2PPh_2$

Hydrogen-1 and ^{19}F n.m.r. data of the complexes are given in Table 2. The distinction between the isomers

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[6] H. D. Bartunik, W. Potzel, R. L. Mössbauer, and G. Kaindl, *Z. Physik*, 1970, **240**, 1.

[7] M. O. Faltens and D. A. Shirley, *J. Chem. Phys.*, 1970, **53**, 4249.

[8] J. S. Charlton and D. I. Nichols, *J. Chem. Soc.* (*A*), 1970, 1484.

[9] R. J. Puddephatt, ' The Chemistry of Gold,' Elsevier, Amsterdam, 1978, ch. 10.

(1a) and (2) could readily be made from the ^{1}H n.m.r. spectra. Thus (1a) gives three doublets in the ^{1}H n.m.r. spectrum of relative intensity 3 : 3 : 2 due to the two non-equivalent trimethylphosphine ligands and the equivalent methylgold groups respectively. On the other hand, the n.m.r. spectrum of (2) combined four doublets with relative intensity 3 : 3 : 1 : 1, the former two peaks being due to the PMe_3 protons and the latter two to the non-equivalent methyl groups of (2). It is difficult to be as certain about the stereochemistry surrounding the C=C bond in (1) and (2). For (1a), where the *cis* stereochemistry is known from *X*-ray work,[5] the ^{19}F n.m.r. spectrum contains a very complex, unsymmetrical, group of peaks due to the CF_3 groups. This arises because the CF_3 groups are in similar chemical environments and form an A_3B_3 spin system, with further splittings due to coupling with the two non-equivalent ^{31}P atoms of (1). We have not been able to analyse the spectrum in detail, but the ^{19}F n.m.r. spectra of all the complexes (1) and (2) are very similar in appearance. A different form of spectrum would be expected if any of the complexes contains mutually *trans* CF_3 groups since the value of ^{5}J(FF) is known to be much less when the CF_3 groups are *trans* than when *cis* to each other about the C=C bond.[10] Hence, it is very likely that all the complexes have the *cis* stereochemistry about the C=C bond as shown in structures (1) and (2).

TABLE 2

Hydrogen-1 and ^{19}F n.m.r. spectra of the complexes

Complex	Solvent	δ(AuR) p.p.m.	^{3}J(PH) Hz	δ(PMe) p.p.m.	^{2}J(PH) Hz	δ(CF_3) [a] p.p.m.	^{4}J(PF) Hz	^{5}J(FF) Hz	^{3}J(FH) Hz	Other
(1a)	$(D_3C)_2CO$	0.18(d)	7.1	1.29(d)	8.5	51.7(m)				
				1.49(d)	9.8					
(2)	$CDCl_3$	0.77(d) [b]	8.2	1.93(d)	9.8	52.4(m)				
		1.44(d) [c]	9.4	1.98(d)	10.0					
(1b)	$(D_3C)_2CO$	0.16(d)	7.0	1.57(d)	10.6					
				1.59(d)	9.1					
	C_6H_6	0.59(d)	7.0	0.97(d)	9.1	53.9(m)				
				1.13(d)	10.6					
(1c)	$(D_3C)_2CO$	0.05(d)	7.0	1.70(d)	10.0	50.8(m)				
				1.85(d)	8.6					
(1d)	$(D_3C)_2CO$	0.80(m)		1.74(d)	10.2	53.1(m)				
				1.88(d)	8.8					
(3a)	C_6H_6			0.98(d)	8.7	50.5(d)	1.5			
(3b)	C_6H_6			1.92(d)	9.5	52.9(d)	3			
(4a)	C_6H_6			1.15(d)	9.5	50.4(qqd) [d]	6.2	14.6		δ(CMe) 2.52(q), ^{5}J(HF) 2.4
						60.8(q) [e]		14.6		
(4b)	CH_2Cl_2			2.01(d)	9.3					δ(MeC) 2.21(q), ^{5}J(HF) 2
(4c)	C_6H_6			1.90(d)	9.5	47.6(qd) [d]	8	14.7		δ(CMe) 1.06(t), ^{3}J(HH) 7.8
						56.9(q) [e]		14.7		δ(CH_2) 2.40(q), ^{3}J(HH) 7.8
(5)	C_6H_6	0.42(d)	6.6	0.95(d)	11.4	53.9(qd) [d]	10.8	10.8		δ(CH) 5.90(q)
						58.4(qd) [e]		10.8	9.4	
(6)	$(D_3C)_2CO$	0.47(d)	8.6	1.59(d)	11.0	52.3(q) [d]	0	11.6		δ(CH) 6.10(q)
		0.76(d)	9.0			57.3(qdd) [e]	1.4 [f]	11.6	9.4	

[a] From $CFCl_3$ reference. [b] Me *trans* to C. [c] Me *trans* to P. [d] CF_3 α to gold. [e] CF_3 β to gold. [f] ^{5}J(PF).

Complexes (1) and (2) all gave two medium-intensity bands in the i.r. spectra due to ν(C=C) in the 1 560—1 590 cm^{-1} region. These are rather low values for ν(C=C) and may be compared with values of 1 635—1 640 cm^{-1} for (5) and (6) and *ca.* 1 610 cm^{-1} for (4). Unfortunately the *X*-ray structure of complex (1a) was insufficiently accurate to indicate whether the C=C bond is longer than a typical double bond, so that further discussion of the low ν(C=C) is not justified. The symmetrical complexes (3) did not give an i.r. band due to ν(C=C), so that the characteristic presence of two closely spaced bands in the 1 560—1 590 cm^{-1} region can be taken as evidence for complexes of structure (1) or (2). The initial product of reaction of [Au_2Me_2-(μ-$Ph_2PCH_2CH_2PPh_2$)] with C_4F_6 gave these characteristic ν(C=C) bands, as expected for a complex of structure (7), and, together with the observation of a doublet due to the methylgold protons in the ^{1}H n.m.r. spectrum, constitutes the evidence for this proposed structure. The insoluble product which deposited from solutions of (7) gave no i.r. bands due to ν(C=C), and so it is presumably not a mixed-oxidation-state complex.

Further Reactions of (1) *with Hexafluorobut-2-yne.*—Complexes (1) are thermally stable in solution, but they react with hexafluorobut-2-yne to give further products. For example, (1c) in $(D_3C)_2CO$ was stable for 6 months but in the presence of C_4F_6 reaction to give largely (4b) was complete in 24 h. Since (1c) was prepared from [AuMe($PMePh_2$)] and C_4F_6, these reagents ultimately give (4b).

In some cases the nature of the final products was dependent on the solvent. For example, reaction of [AuMe(PMe_2Ph)] with C_4F_6 in diethyl ether gave (4a) but in acetone solvent the product was (3a) and ethane. Both products (3) and (4) are probably formed by reductive elimination from the gold(III) centre of the mixed-oxidation-state complexes (1) as indicated by the

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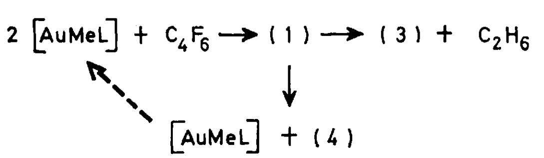
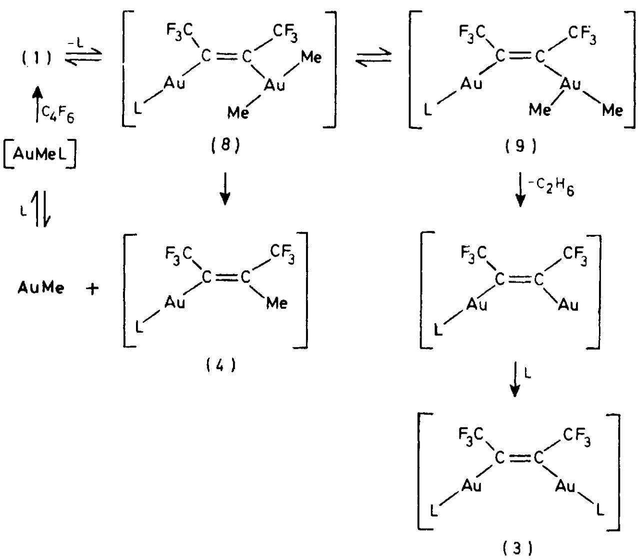
[10] H. C. Clark and W. S. Tsang, *J. Amer. Chem. Soc.*, 1967, **89**, 529, 533.

overall Scheme 1. Reductive elimination of two methyl groups to give ethane and (3) is simple, but, by analogy with the known mechanism of reductive elimination from other trialkylgold(III) complexes,[11] a preliminary dissociation of the phosphine ligand from Au^{III} would be expected and the resulting T-shaped three-co-ordinate gold(III) species would need to undergo isomerisation so that the two methyl groups occupied mutually *cis* positions (Scheme 2).



SCHEME 1



SCHEME 2

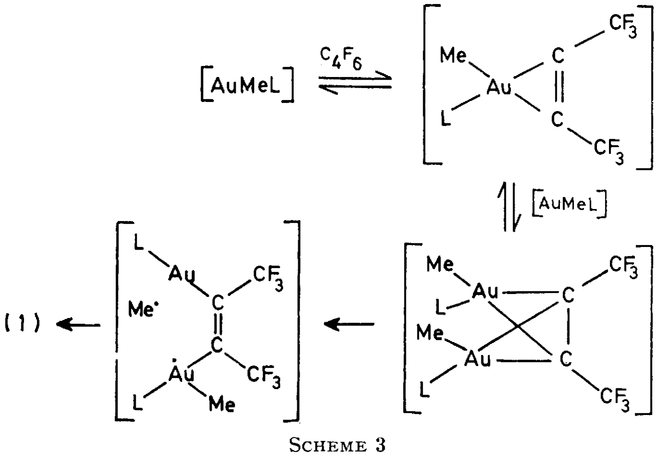
Formation of (4) involves reductive elimination from (1) with cleavage of a gold(III)–methyl bond and a gold(III)–vinyl bond which are already mutually *cis* in (1). Also formed will be [AuMeL] which would then react rapidly with C_4F_6 to regenerate (1) in a cyclic system shown in Scheme 2. The effect of the solvent on the final products may act either by influencing the relative amounts of the intermediates (8) and (9) in solution, or more likely by influencing whether reductive elimination from (8) to give (4) occurs more rapidly than isomerisation to (9) which would ultimately give (3) and ethane. Of course intermediates (8) and (9) would be solvated in polar solvents.

According to Scheme 2, the hexafluorobut-2-yne acts as a catalyst for the reductive elimination from (1), but the mechanism of action is not clear. It is possible that C_4F_6 simply acts as a scavenger for trace amounts of tertiary phosphine, which strongly retard reductive elimination from Au^{III}.[11] Hexafluorobut-2-yne is known to react very rapidly with tertiary phosphines.[12] Alternatively it is possible that C_4F_6 aids phosphine dissociation by co-ordination to either the gold(I) or gold(III) centre of (1), although if such intermediates are formed they are not present in sufficient concentration to be detectable by i.r. or n.m.r. spectroscopy.

Whatever the role of C_4F_6, it is clear that reductive elimination from the gold(III) centre of (1) to give (4) occurs with retention of stereochemistry about the C=C bond, as would be expected for a concerted mechanism of reductive elimination. The mutually *cis* orientation of the CF_3 groups in (4) is readily shown by the magnitude of the coupling constants ^5J(FF) (Table 2). It is worth noting that (4) is the product of *cis* insertion of C_4F_6 into the methylgold bond of [AuMeL] and that the mechanism of this apparent insertion reaction is unparalleled in organometallic chemistry.

Since the formation of mixed-oxidation-state complexes (1) is unusual, we have attempted to discover the reaction mechanism. The reaction of [AuMe(PMePh$_2$)] with C_4F_6 to give first (1c) and then (3b) and (4b) was not inhibited by the free-radical scavenger galvinoxyl, nor was the reaction of (1c) with C_4F_6 inhibited. Thus neither the formation of (1c) nor its further reaction with C_4F_6 occurs by a free-radical chain mechanism. Reaction of [AuMe(PMe$_3$)] or [AuMe(PMePh$_2$)] with C_4H_6 in the presence of the spin trap Bu^{t}NO led to formation of Bu^t(Me)NO radicals identified by e.s.r. spectroscopy. No radicals were formed from [AuMeL] and Bu^{t}NO in the absence of C_4F_6.[13] Thus some methyl radicals appear to be formed during the reaction, although the spin-trapping technique is incapable of determining whether the major part of the reaction occurs by a radical process. A mechanism which is consistent with the available data is shown in Scheme 3.

This is an example of a free-radical non-chain process and hence explains the above observations.[14] It also explains why the product (1) contains mutually *cis* CF_3 groups, and why binuclear products such as (1) are



SCHEME 3

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[11] S. Komiya, T. A. Albright, R. Hoffmann, and J. K. Kochi, *J. Amer. Chem. Soc.*, 1976, **98**, 7255.

[12] W. R. Cullen and D. S. Dawson, *Canad. J. Chem.*, 1967, **45**, 2887.

[13] A. Johnson and R. J. Puddephatt, *J.C.S. Dalton*, 1975, 115.

[14] M. F. Lappert and P. W. Lednor, *J.C.S. Chem. Comm.*, 1973, 948.

formed from acetylenes, which can π bond to two gold atoms, but not from alkenes which can π bond to only one gold atom. Preliminary formation of a complex $[AuMeL(C_4F_6)]$ is reasonable, since an analogous alkene complex [AuMeL(tcne)] has been isolated previously.[1,2]

Reactions of Complexes (1) *and* (2) *with Other Electrophilic Reagents.*—Complex (1a) or (2) reacted with hydrogen chloride in diethyl ether to cleave the gold(I)–carbon bond and give $[AuCl(PMe_3)]$ and (5) or (6) respectively. The stereochemistry about the C=C bond and the gold(III) centre was retained during the reactions, as shown by the n.m.r. spectra of (5) and (6) (Table 2).

In contrast, reactions of (1c) with $[PtX_2(PMePh_2)_2]$ (X = Cl, I, or NO_3) proceeded according to equation (iii).

$$(1c) + [PtX_2(PMePh_2)_2] \longrightarrow [AuX(PMePh)_2] + (4b) + trans\text{-}[PtX(Me)(PMePh_2)_2] \quad \text{(iii)}$$

The rate of reaction followed the series *cis*-$[Pt(NO_3)_2(PMePh_2)_2]$ > $[PtI_2(PMePh_2)_2]$ (*cis–trans* mixture) > *cis*-$[PtCl_2(PMePh_2)_2]$ which is the same as the rate of cleavage of a Au–Me bond from $[AuMe_3(PMePh_2)]$.[15] Thus it seems that reaction occurs by exchange of X and Me groups between platinum and Au^{III} to give *trans*-$[PtX(Me)(PMePh_2)_2]$ and the binuclear complex $[(Ph_2MeP)Au\{(F_3C)C{=}C(CF_3)\}AuX(Me)(PMePh_2)]$ followed by rapid reductive elimination from the gold(III) centre to give the final products. We had hoped that cleavage of the Au^{I}–C bond would occur (as with the reactions with hydrogen chloride described above) to give a mixed platinum(II)–gold(III) complex but none of this product was observed. Similarly, mercury(II) chloride with (1b) gave HgCl(Me), $[AuCl(PMe_2Ph)]$, and (4a). It is not clear why hydrogen chloride and metal halides attack different centres in complexes (1).

EXPERIMENTAL

Methylgold(I) complexes were prepared as described earlier.[13,16] Hexafluorobut-2-yne was a commercial sample and was not further purified. It was added to reaction mixtures in measured quantities using standard vacuum-line techniques. Gold-197 Mössbauer spectra were obtained from P.C.M.U., Harwell, and the deconvolution of spectra was also carried out at P.C.M.U.

Reactions of Hexafluorobut-2-yne.—*With methyl(trimethylphosphine)gold*(I). Hexafluorobut-2-yne (8.2 mmol) was condensed into a solution of $[AuMe(PMe_3)]$ (8.2 mmol) in diethyl ether (10 cm^3) contained in a conical flask (25 cm^3) cooled in liquid nitrogen. The flask was sealed and the mixture allowed to warm to room temperature. After 1 h the solution was left to stand for 48 h in a refrigerator when colourless crystals of *cis*-$[(Me_3P)Au\{(F_3C)C{=}C(CF_3)\}$*trans*-$AuMe_2(PMe_3)]$ (1a) separated, yield 40%, m.p. 133—140 °C (decomp.) (Found: C, 19.65; H, 3.15; F, 15.25. Calc. for $C_{12}H_{24}Au_2F_6P_2$: C, 19.5; H, 3.2; F, 15.4%). Infrared spectrum: 501 and 512 [ν(AuMe)]; 1 084, 1 122, 1 208, and 1 222 [ν(CF)]; 1 590 and 1 568 cm^{-1} [ν(C=C)].

The mother liquor was then treated with light petroleum (b.p. 30—40 °C, 5 cm^3) and set aside for 24 h in the refrigerator. Crystals of the isomeric *cis*-$[(Me_3P)Au\{(F_3C)C{=}C(CF_3)\}$*cis*-$AuMe_2(PMe_3)]$ (2) then separated, yield 40%, m.p. 95—105 °C (decomp.) (Found: C, 19.55; H, 3.2; F, 15.2%). Infrared spectrum: 520 and 535 [ν(AuMe)]; 1 084, 1 120, 1 200, and 1 225 [ν(CF)]; 1 560 and 1 580 cm^{-1} [ν(C=C)].

With (dimethylphenylphosphine)methylgold(I). (*a*) Treatment of $[AuMe(PMe_2Ph)]$ (9.6 mmol) with C_4F_6 (14 mmol) in diethyl ether (10 cm^3) as above gave, after 24 h, *cis*-$[(PhMe_2P)Au\{(F_3C)C{=}C(CF_3)\}$*trans*-$AuMe_2(PMe_2Ph)]$ (1b), yield 68%, m.p. 125—127 °C [Found: C, 30.4; H, 3.5; F, 14.0%; *M* (benzene) 932. Calc. for $C_{22}H_{28}Au_2F_6P_2$: C, 30.6; H, 3.3; F, 13.3%; *M* 862]. Infrared spectrum: 502 [ν(AuC)]; 1 095, 1 115, 1 209, and 1 223 [ν(CF)]; 1 565 and 1 586 cm^{-1} [ν(C=C)].

(*b*) Hexafluorobut-2-yne (10 mmol) was condensed into a Carius tube containing $[AuMe(PMe_2Ph)]$ (7 mmol) in acetone (10 cm^3). The tube was sealed and left to stand at room temperature for 6 d. It was then opened, the solution was filtered to remove some metallic gold, and the solvent was evaporated to give a pale yellow oil. This was dissolved in diethyl ether (10 cm^3) and the solution was cooled to −78 °C when colourless crystals of *cis*-$[(PhMe_2P)Au\{(F_3C)C{=}C(CF_3)\}Au(PMe_2Ph)]$ (3a) deposited, yield 54%, m.p. 156—158 °C [Found: C, 29.0; H, 2.8; F, 13.9%; *M* (benzene) 813. Calc. for $C_{20}H_{22}Au_2F_6P_2$: C, 28.8; H, 2.6; F, 13.7%; *M* 832]. Infrared spectrum: 1 100, 1 125, and 1 225 cm^{-1} [ν(CF)]. Another experiment in which this reaction was carried out in a sealed n.m.r. tube in $(D_3C)_2CO$ solvent showed that this product was formed essentially quantitatively and that ethane was also formed (δ 0.67 p.p.m.).

(*c*) A solution of $[AuMe(PMe_2Ph)]$ (2 mmol) and C_4F_6 (5 mmol) in diethyl ether (10 cm^3) contained in a sealed Carius tube was allowed to stand for 2 weeks at room temperature. The initial precipitate redissolved to give a clear solution. The tube was opened and the solvent evaporated to give *cis*-$[Au(PMe_2Ph)\{(F_3C)C{=}CMe(CF_3)\}]$ (4a) as a colourless oil, which was purified by chromatography on a column of silica gel eluting with light petroleum–dichloromethane (Found: C, 30.1; H, 2.5; F, 21.6. Calc. for $C_{13}H_{14}AuF_6P$: C, 30.5; H, 2.7; F, 22.2%). Infrared spectrum: 1 110, 1 125, 1 200, 1 225, and 1 240 [ν(CF)]; 1 610 cm^{-1} [ν(C=C)].

With methyl(methyldiphenylphosphine)gold(I). Hexafluorobut-2-yne (6 mmol) was condensed into a solution of $[AuMe(PMePh_2)]$ (4 mmol) in diethyl ether (10 cm^3) contained in a Carius tube. The tube was sealed and left to stand in the refrigerator for 24 h. Colourless crystals of *cis*-$[(Ph_2MeP)Au\{(F_3C)C{=}C(CF_3)\}$*trans*-$AuMe_2(PMePh_2)]$ (1c) which formed were filtered off, washed with diethyl ether, and dried *in vacuo*, yield 77%, m.p. 125—128 °C (decomp.) (Found: C, 38.9; H, 3.2; F, 11.7. Calc. for $C_{32}H_{32}Au_2F_6P_2$: C, 38.9; H, 3.25; F, 11.6%). Infrared spectrum: 513 [ν(AuMe)]; 1 100, 1 130, 1 210, and 1 225 [ν(CF)]; 1 568 and 1 587 cm^{-1} [ν(C=C)].

With ethyl(methyldiphenylphosphine)gold(I). As above, $[AuEt(PMePh_2)]$ (2.2 mmol) with C_4F_6 (10 mmol) gave *cis*-$[(Ph_2MeP)Au\{(F_3C)C{=}C(CF_3)\}$*trans*-$AuEt_2(PMePh_2)]$ (1d), m.p. 95 °C (decomp.) (Found: C, 39.9; H, 3.25; F, 11.4. Calc. for $C_{34}H_{36}Au_2F_6P_2$: C, 40.2; H, 3.55; F, 11.2%). Infrared spectrum: 510 [ν(AuEt)]; 1 100 and 1 220 [ν(CF)]; 1 570 and 1 582 cm^{-1} [ν(C=C)].

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With μ-[1,2-*Bis(diphenylphosphino)ethane*]-*bis*[*methylgold*(I)]. Into a solution of [$Au_2Me_2(\mu\text{-}Ph_2PCH_2CH_2PPh_2)$] (0.38 mmol) in dichloromethane (10 cm^3) contained in a Carius tube was condensed C_4F_6 (2 mmol). After 24 h at room temperature the solution was filtered and the solvent evaporated from the filtrate to give a cream solid tentatively identified as [$Au_2Me_2(Ph_2PCH_2CH_2PPh_2)(C_4F_6)$]. It was recrystallised from dichloromethane–light petroleum (Found: C, 38.85; H, 2.95; F, 11.4. Calc. for $C_{32}H_{30}Au_2F_6P_2$: C, 39.0; H, 3.05; F, 11.6%). Infrared spectrum: 515 [ν(AuMe)]; 1 105, 1 125, and 1 225 [ν(CF)]; 1 568 and 1 582 cm^{-1} [ν(C=C)].

Reaction of Hydrogen Chloride.—With (1a). Hydrogen chloride (1 mmol as a standard solution in diethyl ether) was added slowly to a solution of (1a) (1.0 mmol) in dichloromethane (10 cm^3). After 30 min, diethyl ether was added to precipitate [$AuCl(PMe_3)$] (m.p. 230—231 °C; lit.,[17] 230—231 °C) and the solvent was removed from the filtrate to give *cis*-[*trans*-$AuMe_2(PMe_3)\{(F_3C)C{=}CH(CF_3)\}$] (6) as a colourless oil (Found: C, 24.0; H, 3.5; F, 24.7. Calc. for $C_9H_{16}AuF_6P$: C, 23.2; H, 3.4; F, 24.5%). ν(C=C) at 1 635 cm^{-1}.

With (2). Similarly, this reaction gave *cis*-[*cis*-$AuMe_2(PMe_3)\{(F_3C)C{=}CH(CF_3)\}$] (5) as a colourless oil (Found: C, 22.9; H, 3.3; F, 24.2. Calc. for $C_9H_{16}AuF_6P$: C, 23.2; H, 3.4; F, 24.5%). ν(C=C) at 1 640 cm^{-1}.

Reaction of (1c) *with Hexafluorobut-2-yne.*—A solution of (1c) (0.10 mmol) in $(D_3C)_2CO$ (0.5 cm^3) was sealed *in vacuo* in an n.m.r. tube. After 6 months there was no decomposition. The tube was opened, C_4F_6 (1 mmol) was condensed into it, and then the tube was resealed. After 24 h the ^1H and ^{19}F n.m.r. spectra showed that reaction to give *cis*-[$Au(PMePh_2)\{(F_3C){=}CMe(CF_3)\}$] (4b) was complete. The tube was opened, the solvent was evaporated, and the *product* was recrystallised from dichloromethane–light petroleum, m.p. 110 °C (decomp.) (Found: C, 38.2; H, 2.8; F, 18.0. Calc. for $C_{18}H_{16}AuF_6P$: C, 38.4; H, 2.8; F, 18.4%).

Reaction of (1d) *with Hexafluorobut-2-yne.*—In a similar reaction the product was largely *cis*-[$Au(PMePh_2)\{(F_3C)C{=}CEt(CF_3)\}$] (4c) although a small amount of *cis*-[$(Ph_2MeP)Au\{(F_3C)C{=}C(CF_3)\}Au(PMePh_2)$] (3b) could be identified from the ^{19}F n.m.r. spectrum of the crude product. The major product was purified as above (Found: C, 38.0; H, 2.9. Calc. for $C_{19}H_{18}AuF_6P$: C, 38.8; H, 3.0%).

Reaction of (1c) *with* [$PtI_2(PMePh_2)_2$].—The complex [$PtI_2(PMePh_2)_2$] (0.5 mmol, *cis–trans* mixture) was added to a solution of (1c) (0.5 mmol) in dichloromethane (5 cm^3). After 24 h the reaction was complete and the n.m.r. spectrum indicated the presence of *trans*-[$PtI(Me)(PMePh_2)_2$] [15] [δ(MePt) 0.01 (t) p.p.m., ^3J(PH) 7.0, ^2J(PtH) 79.2 Hz; δ(MeP) 2.42 (t) p.p.m., ^2J(PH) + ^4J(PH) 7.0, ^3J(PtH) 31.4 Hz], [$AuI(PMePh_2)$] [15] [δ(MeP) 2.07 (d) p.p.m., ^2J(PH) 10.4 Hz], and (4b). Ethanol (10 cm^3) was added and the mixture was set aside for 24 h. Crystallisation of the precipitate gave first [$AuI(PMePh_2)$] (Found: C, 30.4; H, 2.6; I, 22.5. $C_{13}H_{13}AuIP$ requires C, 29.8; H, 2.5; I, 24.2%) and then, from the mother liquor, *trans*-[$PtI(Me)(PMePh_2)_2$] identical (m.p. and n.m.r.) with an authentic specimen. Complex (4b) could not be isolated in pure form from the mixture.

Similar reactions of (1c) with *cis*-[$Pt(NO_3)_2(PMePh_2)_2$] and *cis*-[$PtCl_2(PMePh_2)_2$] gave in 3 h or 7 d respectively (4b) with *trans*-[$PtX(Me)(PMePh_2)_2$] and [$AuX(PMePh_2)$] ($X = NO_3$ or Cl respectively). When $X = NO_3$ the products were ' quenched ' with sodium iodide and the resulting *trans*-[$PtI(Me)(PMePh_2)_2$] and [$AuI(PMePh_2)$] were isolated.

E.S.R. Studies.—A solution of [$AuMe(PMe_3)$] (0.05 mmol) and Bu^tNO (0.005 g) in benzene (0.2 cm^3) contained in an e.s.r. tube was degassed by several freeze–pump–thaw cycles. Hexafluorobut-2-yne (0.25 mmol) was condensed into the tube which was then sealed and allowed to warm to room temperature. The characteristic e.s.r. signal of $Bu^t(Me)NO$ was observed as a triplet of quartets with a_N 1.50 and a_H 1.15 mT.[18]

N.M.R. Studies.—(*a*) Hexafluorobut-2-yne (0.3 mmol) was condensed into an n.m.r. tube containing [$AuMe(PMePh_2)$] (0.03 mmol) and galvinoxyl (5×10^{-3} mmol) in benzene (0.4 cm^3) and the tube was sealed. In a blank experiment the same reagents but without the scavenger galvinoxyl were sealed into a second n.m.r. tube. The n.m.r. spectra were monitored for 7 h at 35 °C. The rates of reaction in the two tubes were essentially equal and the same products, ethane, (4b), and (3b) were ultimately formed and identified by their ^1H and ^{19}F n.m.r. spectra.

(*b*) In a similar reaction in $(D_3C)_2CO$ solvent, galvinoxyl was shown to have no effect on the rate of reaction of complex (1c) with C_4F_6. In this case the only product was (4b).

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