Reactions of Low-Valent Metal Complexes with Fluorocarbons. Part XXII.[1] Tertiary Phosphine Gold Complexes

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Methyl(triphenyl- and diphenylmethyl-phosphine)gold react with tetrafluoroethylene on u.v. irradiation to give $Au(L)CF_2{\cdot}CF_2Me$ ($L = PPh_3$ or PPh_2Me), and with perfluoropropene to give $Au(L)CF(CF_3){\cdot}CF_2Me$. Chlorotrifluoroethylene and $Au(PPh_3)Me$ yield $Au(PPh_3)CFCl{\cdot}CF_2Me$. In contrast with the formation of these mononuclear gold compounds, hexafluoroacetone reacts with the methyl(phosphine)gold compounds to give binuclear complexes $LAu{\cdot}O{\cdot}C(CF_3)_2{\cdot}AuL$. Side products of these reactions are the non-organometallic compounds $LAu{\cdot}O{\cdot}C(CF_3)_2{\cdot}O{\cdot}AuL$; formed in high yield by treating $Au(L)Me$ with hexafluoroacetone hydrate.

Hexafluorobut-2-yne reacts with methyl(triphenylphosphine)gold either thermally or on u.v. irradiation to give *cis*-$(Ph_3PAu)C(CF_3){:}C(CF_3)(AuPPh_3)$. The thermal reaction is accompanied by formation of the phosphorane $Ph_3\overline{PC(CF_3){:}C(CF_3)C(CF_3){:}C}(CF_3)$. Reactions of $Au(PPh_3)Me$ with perfluorocarboxylic acids are also described.

PREVIOUSLY we have described reactions of the oxidative–addition type between unsaturated fluorocarbons and iridium(I) (d^8) and platinum(0) d^{10} complexes.[2,3] Since gold(I) complexes also have a d^{10} configuration it was of interest to study the analogous reactions of the compounds $Au(L)Me$ ($L = PPh_3$ or PPh_2Me).[4]

The complexes $Au(L)Me$ did not react with tetrafluoroethylene when heated in benzene, but on irradiation with u.v. light the insertion products $Au(L)CF_2CF_2Me$ (I, II) formed in over 60% yield. The ^{19}F n.m.r. spectra of the two complexes are similar, comprising two multiplets of equal intensity. Thus the spectrum of (I) ($L = PPh_3$) shows multiplets at 100·5 and 102·8 p.p.m. (rel. to CCl_3F at 0·0 p.p.m.), assigned to the CF_2 groups α and β to the metal, respectively.[5] The lower field signal appears as a doublet of sextets [J_{PF_α} 27; $J_{F_\alpha H}$ 3; $J_{F_\alpha F_\beta}$ 3 Hz], that at highest field a quartet of quartets [J_{HF_β} 18; J_{PF_β} 3; $J_{F_\alpha F_\beta}$ 3 Hz]. Double resonance of the signal due to the α-CF_2 group caused the signal due to the β-CF_2 group to collapse to a quartet of doublets. The ^1H spectrum showed the expected signal for the CH_3 protons at τ 8·33 [t of t, $J_{F_\beta H}$ 18; $J_{F_\alpha H}$ 3 Hz].

An interesting feature of the ^{19}F spectra is revealed by a comparison with the spectrum of the compound $Re(CO)_5CF_2CF_2Me$.[6] In the latter, as in the spectra of transition metal–fluoroalkyl derivatives in general,[5] a large downfield shift is found with the absorption due to the CF_2 group bonded to the metal (52·9 p.p.m. for the rhenium compound). No shift of such magnitude is observable in the spectra of the polyfluoroalkylgold compounds (I) and (II) and in this respect the behaviour of gold parallels that of main group metals such as tin.[5]

An analogous insertion into carbon–gold σ-bonds occurs in reactions between $Au(L)Me$ and hexafluoropropene. Although two isomers $Au(L)CF(CF_3)CF_2Me$ or $Au(L)CF_2CF(CF_3)Me$ are possible, the nature of the n.m.r. spectra of the respective products [(III) and (IV)] is indicative of the formation of a single isomer in each case. Thus the ^1H spectrum of (III; $L = PPh_3$) showed only one resonance attributable to a methyl group, at τ 8·17. This signal was a triplet [$J_{F_\beta H}$ 20 Hz], characteristic of a CF_2CH_3 group,[6,7] in accord with the structure $Au(PPh_3)CF(CF_3)CF_2Me$ for (III). Moreover, the ^{19}F spectrum showed only one set of multiplets of relative intensity 3 : 2 : 1 at 68·0, 91·2, and 194·5 p.p.m. Attempts to decouple the spectrum were unsuccessful.

The fluorocarbon–gold complexes (I)—(IV) (Table) are air-stable, soluble in polar solvents, and monomeric in benzene. Complex (I) undergoes a simple ligand-exchange reaction with diphenylmethylphosphine to give (II), but does not react with tetrafluoroethylene or hexafluoroacetone, although the latter readily reacts with $Au(PPh_3)Me$, as described below. Bromine and carbon tetrachloride cleave the gold–carbon bond in (I) to give in high yield, $Au(PPh_3)Br$ and $Au(PPh_3)Cl$, respectively.

Under u.v. irradiation, chlorotrifluoroethylene reacts with methyl(triphenylphosphine)gold to give the compound $Au(PPh_3)CFClCF_2Me$ (V). The ^1H n.m.r. spectrum shows a triplet-of-doublets signal for the methyl protons [$J_{F_\beta H}$ 18·5; $J_{F_\alpha H}$ 2·5 Hz]. Such a signal unambiguously defines the structure of (V) since the pattern is typical of $CH_3CF_2CFX{\cdot}$, and cannot be rationalised in terms of a complex containing the CH_3-$CFClCF_2{\cdot}$ group. The stereospecific nature of the reaction and the particular isomer isolated parallels the behaviour of methyl(pentacarbonyl)manganese which reacts with chlorotrifluoroethylene to form exclusively $Mn(CO)_5CFClCF_2Me$.[7]

As generally observed with chlorofluorocarbon derivatives of metals,[8] complex (V) is markedly less stable than the compounds (I)—(IV). Indeed, (V) decomposes slowly even *in vacuo* in the solid state forming $Au(PPh_3)$-Cl. Interestingly, bromotrifluoroethylene and methyl-

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[3] M. Green, R. B. L. Osborn, A. J. Rest, and F. G. A. Stone, *J. Chem. Soc.* (*A*), 1970, 2525.

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[6] J. B. Wilford and F. G. A. Stone, *Inorg. Chem.*, 1965, **4**, 93.

[7] J. B. Wilford, P. M. Treichel, and F. G. A. Stone, *J. Organometallic Chem.*, 1964, **2**, 119.

[8] J. B. Wilford, A. Forster, and F. G. A. Stone, *J. Chem. Soc.*, 1965, 6519, and references cited therein.

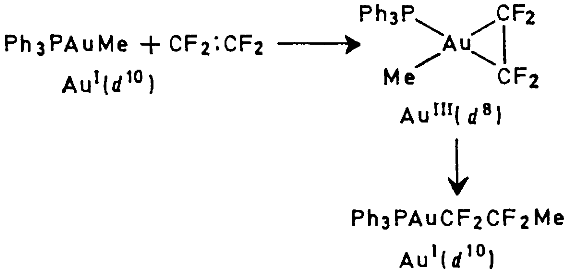
(triphenylphosphine)gold react to give $Au(PPh_3)Br$, presumably *via* initial formation of unstable $Au(PPh_3)$-$CFBrCF_2Me$. Triphenylphosphinegold chloride was formed in nearly quantitative yield in the reaction between $Au(PPh_3)Me$ and 1,2-dichloro-1,2-difluoroethylene. The olefins $CF_2{:}CFH$ and $CH_2{:}CH_2$ did not react either on heating or under u.v. irradiation with methyl(triphenylphosphine)gold.

Analytical data for the complexes

		M.p.	Colour	Analysis (%) [a] C	H	P	F	*M* [b]
(I)	$Au(PPh_3)CF_2CF_2Me$	125—126°	White	44·0 (43·9)	3·1 (3·2)	5·6 (5·4)	13·2 (13·2)	554 (575)
(II)	$Au(PPh_2Me)CF_2CF_2Me$	153—153·5	White	37·3 (37·5)	3·0 (3·2)	6·1 (6·1)	14·9 (14·8)	491 (513)
(III)	$Au(PPh_3)CF(CF_3)CF_2Me$	127—128·5	White	42·2 (42·3)	2·8 (2·9)	5·0 (5·0)	18·3 (18·3)	636 (625)
(IV)	$Au(PPh_2Me)CF(CF_3)CF_2Me$	88—89	White	36·1 (36·3)	2·8 (2·9)	5·7 (5·5)	19·6 (20·3)	520 (563)
(V)	$Au(PPh_3)CFClCF_2Me$ [c]	Decomp.	White	42·4 (42·7)	2·9 (3·1)	5·1 (5·2)	9·8 (9·7)	
(VI)	$[AuPPh_3]_2OC(CF_3)_2$ [d]	125 decomp.	White	42·9 (43·2)	2·7 (2·8)	5·1 (5·7)	10·4 (10·5)	927 (1085)
(VII)	$[AuPPh_2Me]_2OC(CF_3)_2$ [e]	160 decomp.	White	36·2 (36·3)	2·8 (2·7)	6·7 (6·5)	11·9 (11·9)	
(VIII)	$[Au(PPh_3)O]_2C(CF_3)_2,H_2O$ [f]	135 decomp.	Yellow	41·6 (41·6)	2·6 (2·9)	5·5 (5·5)	12·2 (10·2)	
(IX)	$[Au(PPh_2Me)O]_2C(CF_3)_2,H_2O$ [g]	235 decomp.	Yellow	34·9 (35·0)	2·8 (2·8)	5·1 (6·2)	12·4 (11·5)	1060 (994)
(X)	$[AuPPh_3]_2OC(CF_3)(CF_2Cl)$ [h]	125 decomp.	White	41·1 (42·5)	2·7 (2·8)	5·3 (5·6)		
(XI)	$[Au(PPh_3)O]_2C(CF_3)(CF_2Cl),H_2O$ [i]	160 decomp.	Yellow	41·2 (41·3)	2·6 (2·8)	5·3 (5·5)	8·5 (8·4)	
(XII)	$[Au(PPh_3)]_2NHC(CF_3)_2$ [j]	96 decomp.	White	43·2 (43·2)	2·9 (2·9)	5·7 (5·7)	10·5 (10·5)	1000 (1084)
(XIII)	$[Au(PPh_3)]_2C_2(CF_3)_2$	184 decomp.	White	46·3 (44·4)	2·8 (2·8)	5·9 (5·7)	10·5 (10·5)	1100 (1081)
(XIV)	$[Au(PPh_3)]_2C_2Me_2$	115 decomp.	White	49·5 (49·4)	3·8 (3·7)	6·4 (6·4)		

[a] Calculated values in parentheses. [b] Mechrolab vapour pressure osmometer, benzene or chloroform solutions. [c] Found: Cl, 6·1. Reqd.: Cl, 6·0%. [d] Found: Au, 34·6. Reqd.: 36·3%. [e] Found: Au, 40·5. Reqd.: 41·0%. [f] Found: Au, 34·1. Reqd.: 35·2%. [g] Found: Au, 38·6. Reqd.: 39·6%. [h] Found: Au, 35·6. Reqd.: 35·8%. [i] Found: Au, 34·7. Reqd.: 34·7. [j] Found: N, 0·7; Au, 36·2. Reqd.: N, 1·3; Au, 36·3%.

In view of earlier work with d^{10} complexes,[1,3] it is tempting to account for the formation of (I), and the related insertion products, in terms of oxidative-addition followed by an intra-molecular reductive step: *e.g.*



In such a mechanism the methyl group would migrate to the least sterically hindered carbon atom, thereby accounting for the nature of the products from hexafluoropropene and chlorotrifluoroethylene. However, since the insertion reactions only occur under u.v. irradiation it seems more likely that a free-radical mechanism is involved,[9] and this is supported by the nature of the products from reactions between $Au(L)Me$ and hexafluoroacetone or hexafluorobut-2-yne, described below.

A rapid reaction occurs at room temperature between a benzene solution of methyl(triphenylphosphine)gold and hexafluoroacetone to yield a white, crystalline and air-stable complex (VI). Formation of a similar binuclear gold complex (VII) is observed with methyl(diphenylmethylphosphine)gold. The latter reaction occurs more rapidly, and will even proceed at —10°. The ^{19}F n.m.r. spectra of the products show sharp singlets at 81·05 (VI) and 80·93 (VII) p.p.m. Pyrolysis of (VII) *in vacuo* afforded hexafluoroacetone, with traces of an unidentified fluorocarbon.

Isolation of (VI) and (VII) rather than the simple insertion products $Au(L){\cdot}C(CF_3)_2{\cdot}OMe$ is surprising. Moreover, it is very unlikely that the latter are intermediates in the reactions since subsequent formation of (VI) and (VII) from them would involve the breaking of carbon–oxygen bonds. It is difficult to visualise how (VI) and (VII) might form *via* a gold(III) (d^8) intermediate $Ph_3P(Me)\overline{AuC(CF_3)_2O}$, and in view of the tendency of hexafluoroacetone to participate in free-radical reactions[10] it is possible that a free radical mechanism is involved in these reactions also. The

$$LAuMe + (CF_3)_2CO \longrightarrow LAu(CF_3)_2CO{\cdot} + Me{\cdot}$$
$$LAuMe + Me{\cdot} \longrightarrow LAu{\cdot} + Me_2$$
$$LAu{\cdot} + LAu(CF_3)_2CO{\cdot} \longrightarrow \text{(VI) or (VII)}$$

reactivity pattern might thus be similar to that established[11] for certain reactions of the d^7 complex $Co(CN)_5^{3-}$ which proceed *via* a free-radical mechanism.

The reaction of hexafluoroacetone with the complexes $Au(L)Me$ is accompanied by formation of a dense brown oil. This was found to be indicative of an interesting side reaction. Extraction of each oil led to the isolation of two similar complexes (VIII) and (IX), their spectroscopic properties suggesting similar structures, differing only in the nature of the phosphine ligands. Indeed, this was firmly established by treatment of (VIII) with diphenylmethylphosphine when a simple ligand exchange occurred to give (IX). The structures of (VIII) and (IX) remained an enigma until

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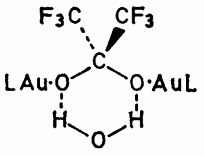
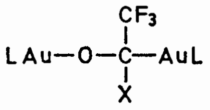
[9] G. W. Parshall and J. J. Mrowca, *Adv. Organometallic Chem.*, 1968, **7**, 194.

[10] E. G. Howard, P. B. Sargeant, and C. G. Krespan, *J. Amer. Chem. Soc.*, 1967, **89**, 1422.

[11] J. Halpern, *Accounts Chem. Res.*, 1970, **3**, 386.

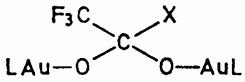
it was recognised that, even under ' anhydrous ' conditions, hexafluoroacetone contains traces of its acidic (pK_a 6·58 [12]) hydrate $(CF_3)_2C(OH)_2$. Indeed, (VIII) formed in good yield on treatment of $Au(PPh_3)Me$ with hexafluoroacetone hydrate. Both analytical and spectroscopic evidence are in accord with the structures proposed, but require that one molecule of water be co-ordinated perhaps by hydrogen bonding, *viz.*



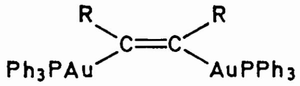


$LAu{-}O{-}C(CF_3)(X){-}AuL$

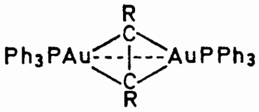
(VI) L = PPh_3, X = CF_3
(VII) L = PPh_2Me, X = CF_3
(X) L = PPh_3, X = CF_2Cl



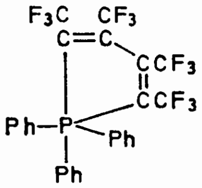
(VIII) L = PPh_3, X = CF_3
(IX) L = PPh_2Me, X = CF_3
(XI) L = PPh_3, X = CF_2Cl



(XIIIa) R = CF_3
(XIVa) R = Me



(XIIIb) R = CF_3
(XIVb) R = Me



(XV)

A broad absorption typical of an OH group is apparent at 3100—3000 cm^{-1} in the i.r. of both complexes, and the presence of water has been demonstrated by n.m.r. spectroscopy. The ^1H n.m.r., in addition to signals attributable to the phosphine ligands show sharp singlets at τ 3·80 (VIII) and 3·34 (IX). These singlet resonances disappear on shaking the solutions with a few drops of D_2O; indicative of co-ordinated water. The ^{19}F spectra show singlets at 83·36 (VIII) and 83·33 (IX) p.p.m.

Chloropentafluoroacetone behaves in a manner entirely analogous to hexafluoroacetone and reacts with $Au(PPh_3)Me$ to form compounds (X) and (XI). The reaction, however, is considerably slower as might be expected from this less reactive fluoroketone and the products are markedly less stable.

The binuclear gold complex (VI) undergoes an unusual exchange reaction with hexafluoroisopropylideneamine to afford $[Au(PPh_3)]_2NHC(CF_3)_2$ (XII), characterised by elemental analysis and spectroscopic studies. Attempts to replace hexafluoroacetone in (VI) with C_2F_4, $(CF_3)_2CNMe$, or $CF_3C_2CF_3$ were unsuccessful. Interestingly, treatment of $Au(PPh_3)Me$ with $(CF_3)_2C{:}NH$ results in rapid reduction to metallic gold and no fluoro-complex was isolated. However, when a mixture of the imine (90%) and hexafluoroacetone (10%) are employed, complex (XII) is formed in good yield; reaction presumably proceeding *via* (VI). Pyrolysis of (XII) affords metallic gold and hexafluoroisopropylideneamine, identified by its i.r. spectrum. The ^{19}F n.m.r. spectrum shows a sharp singlet at 83·28 p.p.m. and the ^1H spectrum a complex multiplet at τ 2·48 (C_6H_5P). The N*H* proton could not be detected.

Hexafluorobut-2-yne reacts with $Au(PPh_3)Me$ either on u.v. irradiation or on heating to give a binuclear gold complex $(Ph_3PAu)_2(CF_3C_2CF_3)$, rather than the anticipated simple insertion product $Ph_3PAuC(CF_3){:}C(CF_3)Me$. Complex (XIII) is stable in air, and may be heated to 180° before decomposition occurs. The two most likely structures for this complex are (XIIIa) (or its *trans*-isomer) or (XIIIb). Although no absorption in the i.r. of (XIII) could be found corresponding to the presence of the C:C group structure (XIIIb) seemed unlikely in view of the isolation of complexes such as (VI). A single-crystal *X*-ray diffraction study [13] of complex (XIII) has firmly established structure (XIIIa). The gold–gold distance of 3·34 Å is too long for any metal–metal bond, and the bond angles at the carbon atoms are normal for an ethylene molecule *cis*-substituted by two gold atoms.

The ^{19}F n.m.r. spectrum of (XIIIa) shows a multiplet at 54 p.p.m. with a pattern typical of an $X_3AA'X'_3$ system but poorly resolved so that the coupling constants could not be evaluated. However, either $J_{AA'}$ or $J_{XX'}$ is *ca.* 50 Hz, and the magnitude of this coupling establishes that it is the phosphorus nuclei which are coupled and not the CF_3 groups. Due to the positioning of the phenyl groups the phosphorus atoms are in different magnetic environments.[13]

Treatment of methyl(triphenylphosphine)gold with but-2-yne at 50° affords complex (XIV) in low yield. Presumably this compound has a structure (XIVa) similar to its fluorocarbon analogue.

When $Au(PPh_3)Me$ and $CF_3C_2CF_3$ are heated togther the cyclic phosphorane (XV) is formed in addition to (XIIIa). Compound (XV) does not form when hexafluorobut-2-yne and triphenylphosphine are heated together, or when hexafluorobut-2-yne and methyl(triphenylphosphine)gold are subjected to u.v. irradiation, (XIIIa) being the sole product under the latter conditions.

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[12] W. J. Middleton and R. V. Lindsey, *J. Amer. Chem. Soc.*, 1964, **86**, 4948.

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

The phosphorane (XV) is an air-stable yellow crystalline solid which is readily soluble in organic solvents. Its molecular weight was firmly established by mass spectrometry. In the i.r., (XV) showed a band at 1555 cm^{-1} assignable to the carbon–carbon double bonds. The ^{19}F n.m.r. spectrum consisted of four complex multiplets of equal intensity centred at 41·19, 49·39, 55·58 and 59·23 p.p.m., suggesting the presence of four non-equivalent trifluoromethyl groups and requiring a non-planar C_4P ring. This is reasonable if the two $P-C(CF_3)$ bonds are not equivalent, occupying axial and equatorial position; as would be expected for a five-co-ordinated phosphorus atom bonded to groups with different electronegativities.[14] Formation of compound (XV) has been observed [15] in other reactions involving hexafluorobut-2-yne and triphenylphosphine transition-metal complexes.

Protolysis of the compounds Au(L)Me with $(CF_3)_2C(OH)_2$ to give (VIII) and (IX) prompted us to examine reactions of $Au(PPh_3)Me$ with fluorinated carboxylic acids as a route to fluorocarbon–gold complexes. Both trifluoroacetic and perfluorobenzoic acids afforded the corresponding perfluorocarboxylates $R_FCO_2Au(PPh_3)$ [$R_F = CF_3$ (XVI), C_6F_5 (XVII)] with evolution of gas, presumably methane. In these reactions use of excess of the acids results in complete decomposition and formation of metallic gold. Compounds (XVI) and (XVII) are white crystalline solids which are soluble in polar solvents and monomeric and undissociated in benzene. The ^{19}F spectrum of (XVI) shows a sharp singlet at 74·4 p.p.m., while that of (XVII) shows three multiplets at 141·2, 163·0, and 156·2 p.p.m. (rel. int. 2 : 2 : 1) typical of the C_6F_5 group, with $J_{F\text{-}meta,\,F\text{-}para}$ 18·8 and $J_{F\text{-}ortho,\,F\text{-}para}$ 2·0 Hz.[16,17]

Complex (XVII) releases carbon dioxide smoothly at its melting point to afford the previously known compound [18,19] $Au(PPh_3)C_6F_5$ in essentially quantitative yield. In agreement with Vaughan and Sheppard [19] we find that pentafluorophenyl(triphenylphosphine)gold melts without decomposition at 170°. Attempts to decarbonylate (XVI) to give $Au(PPh_3)CF_3$ were unsuccessful. The perfluoroacetate decomposed above its melting point to give metallic gold.

We have also studied cleavage of the methyl group from $Au(PPh_3)Me$ with some reagents containing only weakly protonic hydrogen. For example, phenylacetylene which is known to form zinc phenylacetylide compounds by cleavage of ethyl groups,[20] reacts to give $Au(PPh_3)C{\equiv}CPh$ (XVIII). Similarly, $Au(PPh_3)Me$ reacts with pentacarbonyl(hydrido)manganese to give the known compound $Au(PPh_3)Mn(CO)_5$,[21] and with $HOs(CO)_4SiMe_3$ to give $Au(PPh_3){\cdot}Os(CO)_4SiMe_3$.[22]

EXPERIMENTAL

^1H and ^{19}F N.m.r. spectra were recorded on a Varian Associates H.A. 100 spectrometer at 100 and 94·1 MHz, respectively. Chemical shifts are relative to Me_4Si (τ 10·00) and CCl_3F (0·00 p.p.m.). I.r. spectra were recorded with a Perkin-Elmer 257 spectrophotometer; except where otherwise stated hexachlorobutadiene mulls were used. The phosphinegold halides were prepared as described elsewhere,[23] and the methyl derivatives obtained by reaction of the compounds Au(L)Cl with methyl-lithium. All solvents were dried by refluxing them over lithium aluminium hydride, and all reactions were carried out under nitrogen. U.v. irradiation was provided by a 250 W mercury lamp held some 30 cm from the reactants.

Reactions of Methyl(triphenylphosphine)gold

(a) *With Tetrafluoroethylene.*—Tetrafluoroethylene (0·6 g, 6·0 mmol) was condensed into a Carius tube containing methyl(triphenylphosphine)gold (0·4 g, 0·84 mmol) in benzene (25 ml). The reactants were irradiated with u.v. light for 23 h, during which time the solution gradually became deep yellow. Removal of solvent *in vacuo* left an oily residue which was extracted with methanol giving white *crystals* (from methanol) of (I) (0·3 g, 62%) $\nu_{max.}$ 3070w, 3047w, 2994w, 1481s, 1446sh, 1436s, 1384s, 1328w, 1313w, 1300w, 1268s, 1248sh, 1226m, 1200s, 1161s, 1146s, 1100s, 1072sh, 1066s, 1026m, 956s, 926s, 870s, 755s, 750s, 740s, 713s, 708s, 695s, and 639s cm^{-1}.

(b) *With Hexafluoropropene.*—In a similar manner, hexafluoropropene (0·75 g, 5·0 mmol) with methyl(triphenylphosphine)gold (0·25 g, 0·53 mmol) in benzene (25 ml) for 20 h afforded a yellow reaction mixture, from which white *needles* of (III) (from methanol) were obtained (0·19 g, 59%); $\nu_{max.}$ 3085w, 3070w, 3015w, 2939vw, 2860vw, 1484m, 1442s, 1388m, 1332w, 1310sh, 1292s, 1249s, 1203s, 1150s, 1119m, 1107s, 1073w, 1060w, 1030m, 1018m, 919m, 908m, 880m, 755s, 729m, 718m, and 698s cm^{-1}.

(c) *With Chlorotrifluoroethylene.*—U.v. irradiation of chlorotrifluoroethylene (0·5 g, 4·3 mmol) and methyl(triphenylphosphine)gold (0·4 g, 0·84 mmol) in benzene (25 ml) for 40 h gave (V) (0·35 g, 70%), from methanol; $\nu_{max.}$ 3088w, 3060w, 3010w, 2940w, 2860w, 1485s, 1440s, 1382m, 1330w, 1315w, 1309w, 1250m,br, 1202m, 1195s, 1185m, 1150s, 1110s, 1101s, 1075w, 1032m, 1011s, 1002s, 965m, 936s, 922m, 785s, 760s, 755s, 750s, 720s, 719s, 705s, and 695sh cm^{-1}. The ^{19}F n.m.r. spectrum of (V) could not be recorded because of the instability of the compound.

(d) *With Bromotrifluoroethylene.*— Methyl(triphenylphosphine)gold (0·3 g, 0·63 mmol) and bromotrifluoroethylene (0·5 g, 6·9 mmol) were allowed to react in benzene (25 ml) for 90 h under u.v. irradiation. Removal of solvent afforded triphenylphosphinegold bromide (0·31 g, 90%), from benzene, identified by i.r. spectroscopy and analysis (Found: C, 40·4; H, 2·2. Calc. for $C_{18}H_{15}AuBrP$: C, 40·1; H, 2·8%).

(e) *With 1,2-Dichloro-1,2-difluoroethylene.*—In a similar manner $Au(PPh_3)Me$ (0·25 g, 0·53 mmol) and CFCl:CFCl

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(0·5 g, 3·8 mmol) in benzene (30 ml) gave $Au(PPh_3)Cl$ (0·16 g, 63%), identified by its i.r. spectrum.

(f) *With Hexafluoroacetone.*—After purification by fractionation through a trap at −95° on a vacuum line, hexafluoroacetone (0·7 g, 4·2 mmol) was condensed into a Carius tube containing methyl(triphenylphosphine)gold (0·5 g, 1 mmol) in benzene (55 ml). After 15 h at room temperature, the solution was decanted and the colourless oil remaining after evaporation of the solvent was washed with diethyl ether. *Crystals* of complex (VI) (0·16 g, 28%) precipitated from the ether on evaporation; $\nu_{max.}$ 3072w, 3059w, 3010w, 2990w, 1480m, 1438s, 1330w, 1312sh, 1296s, 1278m, 1146s, 1110s, 1103s, 1029w, 1000m, 958s, 755s, 749s, 728s, and 700s cm^{-1}.

The black oil remaining in the Carius tube was dissolved in dichloromethane. Addition of hexane yielded yellow *crystals* of (VIII) (0·1 g, 17%); $\nu_{max.}$ (Nujol) 3500—2600m,br, 1480m, 1468s, 1305m, 1200s,br, 1100s, 1085sh, 1071m, 1029vw, 1000w, 960m, 751m, 725m, 717m, and 698s cm^{-1}.

(g) *With Hexafluoroacetone Hydrate.*—Methyl(triphenylphosphine)gold (0·4 g, 0·84 mmol) in benzene (50 ml) was added dropwise to a benzene solution of hexafluoroacetone hydrate (0·37 g, 2·0 mmol). The reaction mixture darkened immediately, and was stirred for 15 h at room temperature. This afforded a black oil and a colourless benzene phase which was decanted. The oil was treated with dichloromethane, filtered, and the filtrate reduced in volume (3 ml) to give *crystals* of (VIII) (0·21 g). The benzene solution afforded additional *crystals* (24 mg) so that the total yield was 47%. The compound was identified by i.r. spectroscopy (see above).

(h) *With Chloropentafluoroacetone.*— Methyl(triphenylphosphine)gold (0·4 g, 0·84 mmol) in benzene (50 ml) was treated with chloropentafluoroacetone (0·5 g, 2·7 mmol) in a Carius tube to yield a two-phase reaction mixture. Following the same procedure as for (VI) above, the major product was *compound* (X) (0·2 g, 22%), $\nu_{max.}$ 3070m, 3050m, 3005w, 2983w, 1480s, 1438s, 1330w, 1312sh, 1285m,br, 1270sh, 1198s, 1152s, 1140sh, 1100s, 1072sh, 1025m, 997s, 900sh, 888s, 750s,br, 711s, 690s, and 675m; ^{19}F n.m.r. 62·41 (q, 2F, CF_2; J_{FF} 10·2 Hz), and 78·07 (t, 3F, CF_3; J_{FF} 10·2 Hz), ^1H n.m.r.: τ 2·75 (m, C_6H_5).

The minor product was isolated as yellow *crystals* (XI) (0·13 g, 14%) from the oily layer; recrystallised from dichloromethane–diethyl ether; $\nu_{max.}$ 3070vw, 3010vw,br, 2500—2700m,br, 1480m, 1439s, 1285w, 1187s, 1104s, 1080m, 1029w, 908w, 751m, 717m, 699s; ^{19}F n.m.r. 67·17 (q, 2F, CF_2; J_{FF} 10·2 Hz) and 81·04 (t, 3F, CF_3; J_{FF} 10·2 Hz); ^1H n.m.r. τ 2·9 (m, C_6H_5) and 3·64 (s, OH).

(i) *With Hexafluorobut-2-yne.*—A Carius tube containing methyl(triphenylphosphine)gold (0·34 g, 0·72 mmol), hexafluorobut-2-yne (0·75 g, 1·3 mmol), and benzene (50 ml) was heated at 60° for 18 h. A yellow solution formed and metallic gold was observed. Filtration of the reaction mixture, and evaporation of solvent, left an oil which was extracted with hexane. The extracts upon evaporation afforded feathery yellow *crystals* of (XV) (0·13 g, 31%), m.p. 154—155° [Found: C, 53·0; H, 2·4; F, 38·8; P, 5·3%; *M* (mass spec.), 584. $C_{30}H_{15}F_{24}P$ requires C, 53·2; H, 2·6; F, 38·9; P, 5·3%; *M*, 586]; $\nu_{max.}$ 3075vw, 3039vw, 1790w, 1542s, 1499w, 1484w, 1453w, 1444s, 1440m, 1409s, 1349vw, 1324w, 1285m, 1242s, 1240s, 1201s, 1190s, 1178s, 1159s, 1139s, 1112s, 1095s, 1072s, 1060s, 1012s, 1004s, 926m, 760s, 751s, 740m, 730m, 720w, 709s, 701m, 695s, and 687m cm^{-1}.

That part of the residue remaining after washing with hexane afforded, from benzene–hexane, *crystals* of (XIII) (0·15 g, 38%), $\nu_{max.}$ (Nujol) 3080w, 3060w, 1481m, 1439s, 1230vs, 1214s, 1171w, 1160w, 1122s, 1100s, 1071sh, 1030w, 1000w, 840vw, 759m, 751m, 720m, 715sh, 700s, and 686m cm^{-1}.

In another experiment, hexafluorobut-2-yne (0·5 g, 0·87 mmol) and methyl(triphenylphosphine)gold (0·25 g, 0·53 mmol) in benzene (40 ml). were irradiated with u.v. light for 42 h. The solution remained colourless but a purple deposit of colloidal gold formed. Filtration, followed by evaporation of solvent afforded (XIII) (20 mg, 5%); this was separated from $Au(PPh_3)Me$ (0·18 g) by crystallisation (benzene–hexane). There was no evidence for formation of (XV).

(j) *With But-2-yne.*—In a similar experiment to that which gave (XIII), methyl(triphenylphosphine)gold (0·4 g, 0·84 mmol), but-2-yne (0·5 g, 9·2 mmol) in benzene (50 ml) gave white *crystals* (XIV) (0·28 g, 68%), from benzene–hexane.

(k) *With Trifluoroacetic Acid.*—Methyl(triphenylphosphine)gold (0·4 g, 0·84 mmol) in benzene (40 ml) was treated dropwise with trifluoroacetic acid (0·15 g, 0·88 mmol). A vigorous evolution of gas was accompanied by formation of a brown solution. Solvent was removed, and the oily residue was extracted with diethyl ether. Reduction of volume of the extract afforded white *crystals* (XVI) (0·29 g, 61%), m.p. 133—134° (Found: C, 41·8; H, 2·6; Au, 34·4; F, 10·2; P, 5·6. $C_{20}H_{15}AuF_3O_2P$ requires C, 42·0; H, 2·6; Au, 34·4; F, 10·0; P, 5·4%), $\nu_{max.}$ 1695 cm^{-1} (CF_3CO_2).

(l) *With Perfluorobenzoic Acid.*—In a similar manner, methyl(triphenylphosphine)gold (0·4 g, 0·84 mmol), pentafluorobenzoic acid (0·18 g, 0·84 mmol), and benzene (40 ml) gave white *crystals* (XVII), from dichloromethane–hexane (0·17 g, 30%), m.p. 123—124° decomp. (Found: C, 45·0; H, 2·3; Au, 29·6; F, 14·2; P, 4·7. $C_{25}H_{15}AuF_5O_2P$ requires C, 44·8; H, 2·3; Au, 29·4; F, 14·2; P, 4·6%), $\nu_{max.}$ 1661 cm^{-1} ($C_6F_5CO_2$).

A sample of $Au(CO_2C_6F_5)(PPh_3)$ [0·3 g, 0·45 mmol] was heated in an evacuated tube at 130° for 30 min. Carbon dioxide was evolved and identified by its i.r. spectrum. Pentafluorophenyl(triphenylphosphine)gold [18,19] was extracted from the residue with diethyl ether and recrystallised (0·24 g, 85%), m.p. 170° (lit.,[19] 170°), from diethyl ether–hexane (Found: C, 46·1; H, 2·4. Calc. for $C_{24}H_{15}AuF_5P$: C, 46·0; H, 2·4%).

(m) *With Phenylacetylene.*—The acetylene (0·4 g, 3·9 mmol) and a solution of methyl(triphenylphosphine)gold (0·4 g, 0·84 mmol) in benzene (50 ml) were sealed in a Carius tube and heated (80°/64 h). The contents of the tube were filtered and the solvent and excess of phenylacetylene were removed under reduced pressure. The residue was fractionally crystallised (benzene–hexane) to give (XVIII) (50 mg, 10%), m.p. 162—163° (lit.,[24] 163°); $\nu_{max.}$ 2126 cm^{-1} ($C\equiv C$).

Reactions of Methyl(diphenylmethylphosphine)gold

(a) *With Tetrafluoroethylene.*—Tetrafluoroethylene (0·5 g, 5 mmol) and methyl(diphenylmethylphosphine)gold (0·2 g, 0·49 mmol) in benzene (30 ml) were irradiated for 24 h. Removal of solvent yielded *complex* (II) (0·16 g, 65%), from benzene–hexane, $\nu_{max.}$ 3080w, 3059w, 2999w, 2959w,

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2924w, 1487s, 1439s, 1420m, 1388s, 1338m, 1314m, 1282s, 1207s, 1154s, 1108s, 1090m, 1070sh, 1052s,br, 1030sh, 1014s, 902s, 895s, 766s, 758s, 749s, and 700s cm^{-1}; ^{1}H n.m.r. τ 2·48 (m, 10H, C_6H_5), 7·98 (d, 3H, CH_3-P), and 8·4 (t of t, 3H, $CH_3{\cdot}CF_2$; $J_{F\beta H}$ 19, $J_{F\alpha H}$ 3 Hz); ^{19}F n.m.r. 100·7 (d of sextets, 2F, β-CF_2; $J_{PF\alpha}$ 28, $J_{F\beta F\alpha}$ 3, $J_{HF\alpha}$ 3 Hz) and 102·7 (q of q, 2F, β-CF_2; $J_{HF\beta}$ 19, $J_{F\alpha F\beta}$ 3, $J_{PF\beta}$ 3 Hz).

(b) *With Hexafluoropropene.*—The reactants, $CF_3CF{:}CF_2$ (0·7 g, 4·7 mmol) and $Au(PPh_2Me)Me$ (0·25 g, 0·84 mmol), in benzene (35 ml) for 12 h in the presence of u.v. light afforded a yellow oily residue after removal of solvent. After washing with hexane, the product was extracted with diethyl ether as *needles* (IV) (0·13 g, 35%), from diethyl ether; $\nu_{max.}$ 3080w, 3065w, 3019w, 2930w, 1486m, 1441s, 1424m, 1390s, 1339w, 1315sh, 1300m, 1282s, 1250s, 1200s, 1189s, 1151s, 1109s, 1077w, 1085w, 1019s, 1004m, 964m, 910s, 904s, 880s, 762m, 748s, 730s, 712m, 703s, 740m; ^{1}H n.m.r. τ 8·18 (apparent t, 3*H*, CH_3CF_2; $J_{F\beta H}$ 20 Hz), 7·92 (d, 3*H*, CH_3–P; J_{PH} 10 Hz) and 2·46 (m, 10*H*, C_6H_5); ^{19}F n.m.r. 68·0 (3F, CF_3), 91·18 (2F, β-CF_2), and 193·9 (1F, α-CF).

(c) *With Hexafluoroacetone.*—Methyl(diphenylmethylphosphine)gold (0·3 g, 0·73 mmol), hexafluoroacetone (0·5 g, 3 mmol), and benzene (40 ml) were sealed in a tube. A brown colour appeared as the mixture warmed to room temperature. After 16 h the tube was opened, a black oil having separated from the benzene phase. The two phases were separated by decantation. The yellow benzene phase was reduced to an oily residue by removal of solvent. After washing with ether, the solid which had thus formed was extracted with benzene to give *crystals* (VII) (0·11 g, 32%) $\nu_{max.}$ 3060m, 2980m, 2918m, 1482m, 1435s, 1334m, 1305sh, 1290s, 1270sh, 1130s, 1098s, 1030w, 1000m, 910sh, 895s, 752s, 742s, 726s, and 695s,br cm^{-1}.

The black tar constituting the oily phase was dissolved in dichloromethane and the volume was reduced. Addition of diethyl ether precipitated yellow *crystals* (IX) (0·1 g, 28%); $\nu_{max.}$ 3500—2500m,br, 1484m, 1438s, 1421m, 1370m,br, 1334m, 1310s,br, 1150s, 1136s, 1104s, 1080s,br, 1028w, 1000m, 924w, 907m, 892s, 883s, 760m, 745s,br, 725s, 710sh, 695s, and 685m cm^{-1}.

Complex (IX) was also formed (0·15 g, 55%), recrystallised from dichloromethane–hexane, by treating (VIII) (0·3 g, 0·27 mmol) in dichloromethane (20 ml) with diphenylmethylphosphine (0·25 g, 1·3 mmol).

Reaction of Complex (VI) *with Hexafluoroisopropylideneamine.*—A suspension of $[Au(PPh_3)]_2OC(CF_3)_2$ (0·12 g, 0·11 mmol) in benzene (40 ml) was sealed in a Carius tube with $(CF_3)_2C{:}NH$ (0·4 g, 2·4 mmol). On warming to room temperature immediate reaction occurred to give a clear yellow solution. Removal of solvent and extraction with diethyl ether gave a solution which on cooling (0°) gave *needles* of (XII) (30 mg, 26%); $\nu_{max.}$ 3080vw, 3060vw, 3019vw, 1480m, 1439s, 1305w,br, 1184s,br, 1103s, 1030vw, 757m, 725m, 717m, and 700s cm^{-1}.

Compound (XII) (0·17 g, 50%) was also prepared along with (VIII) (40 mg, 11%) by treating methyl(triphenylphosphine)gold (0·3 g, 0·63 mmol) in benzene (40 ml), with $(CF_3)_2C{:}NH$ (0·4 g, 2·4 mmol) containing 10% hexafluoroacetone.

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