Reactions of Methylgold Complexes with Unsaturated Reagents

By **Antony Johnson and Richard J. Puddephatt,** * Donnan Laboratories, The University of Liverpool, Liverpool L69 3BX

Both [AuMeL] and [$AuMe_3L$] react with SO_2 and with $CF_3C{\equiv}CH$ to give [$Au(SMeO_2)L$], *cis*-[$AuMe_2(SMeO_2)L$], [$Au(C{\equiv}CCF_3)L$], and *cis*-[$AuMe_2(C{\equiv}CCF_3)L$] respectively (L = a tertiary phosphine ligand). The complexes [AuMeL] react with tetracyanoethylene (tcne) to give solvated complexes [AuMeL(tcne)] and with $MeO_2CC{\equiv}CCO_2Me$ and C_2F_4 to give products of insertion into the methylgold bond. The complexes [$AuMe_3L$] are unreactive towards alkenes and non-terminal alkynes, and reasons for this are discussed.

CONTINUING our investigations into the reactivity of transition-metal alkyls, we have investigated reactions of the complexes [AuMeL] and [$AuMe_3L$] (L = tertiary phosphine) with some unsaturated reagents. It was of particular interest to compare the reactivities of the gold(I) and gold(III) methyl derivatives with a wide variety of reagents. Thus cleavage of a methylgold bond by mercury(II) chloride takes place by electrophilic attack at the methyl group (S_E2 open), and the rates are similar for the gold(I) and gold(III) derivatives.[1] Cleavage by transition-metal halides is thought to occur by the S_E2 cyclic mechanism and the methylgold(I) complexes react faster than the trimethylgold(III) analogues.[2] The gold(I) complexes react rapidly with hexafluorobut-2-yne to give [$LAu\{C(CF_3){=}C(CF_3)\}$-

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[1] B. J. Gregory and C. K. Ingold, *J. Chem. Soc.* (*B*), 1969, 276.

[2] R. J. Puddephatt and P. J. Thompson, *J.C.S. Dalton*, 1975, 1810.

$AuMe_2L$] but trimethylgold(III) complexes are unreactive.[3,4] In this case it is thought that the acetylene interacts with the electron-rich gold(I) centre as the first step, but that the *d* orbitals in the gold(III) complex are of too low energy to interact with the electrophilic acetylene derivative. A similar difference in reactivity of the methyl-gold(I) and -gold(III) derivatives towards cleavage of a methylgold bond by benzenethiol has been observed.[5,6] In this case the gold(I) complexes appear very reactive to attack by $SPh^{\bullet}$ radicals to give gold(II) intermediates, whereas the similar attack on Au to give a gold(IV) intermediate is not possible.

Thus a general trend may be that if an electrophilic reagent attacks the methyl group in a methylgold complex the gold(I) and gold(III) complexes will have similar reactivity. The reactions with $HgCl_2$ appear to fall into this category.[1] On the other hand, with the gold(I) complexes it is also possible for the electrophile to attack the electron-rich gold centre as the first step. This may then provide a lower-energy route to eventual cleavage of the methylgold bond, and may be assumed to operate in cases where there is a great difference in reactivity between the methylgold(I) and trimethylgold(III) derivatives. Reactions with hexafluorobut-2-yne,[3,4] benzenethiol,[5] benzeneselenol,[6] and trifluoroiodomethane [7] may fall into this category. Such reactions may be considered to involve intermediate oxidative addition at the gold(I) centre.[7]

TABLE 1

Analytical data and melting points of the complexes

Complex	M.p. (θ_c/°C)	Analysis (%) * C	H	Other
$[Au(SMeO_2)(PMe_3)]$	102—104 (decomp.)	13.3 (13.6)	3.0 (3.4)	S, 9.1 (8.4)
$[Au(SMeO_2)(PMe_2Ph)]$	90 (decomp.)	25.9 (26.1)	3.5 (3.4)	S, 7.6 (7.7)
cis-$[AuMe_2(SMeO_2)(PMe_2Ph)]$	97—99	29.5 (29.7)	4.5 (4.5)	S, 7.1 (7.2)
$[AuMe(PMe_3)(tcne)]\cdot 0.3C_6H_5Me$		32.9 (33.1)	3.3 (3.3)	N, 12.5 (12.4)
$[AuMe(PMe_2Ph)(tcne)]\cdot thf$	45—47 (decomp.)	41.3 (41.4)	4.2 (4.0)	N, 10.5 (10.2)
$[Au\{C(CO_2Me)=C(CO_2Me)Me\}(PMe_3)]$	82—85	27.0 (27.6)	3.8 (4.1)	
cis-$[AuMe_2\{C(CO_2Me)=C(CO_2Me)Me\}(PMe_3)]$	99—101	31.5 (31.0)	6.9 (5.2)	
$[Au(C\equiv CCF_3)(PMe_2Ph)]$	98—100	30.9 (30.8)	2.6 (2.6)	F, 13.1 (13.3)
cis-$[AuMe_2(C\equiv CCF_3)(PMe_2Ph)]$		34.3 (34.1)	3.6 (3.7)	F, 12.1 (12.4)

* Calculated values are given in parentheses.

To extend this series, reactions of methylgold(I) and trimethylgold(III) derivatives with some electrophilic unsaturated reagents have been studied, with particular emphasis on the relative reactivities of the gold(I) and gold(III) species. A preliminary report of some of this work has been published.[3]

RESULTS AND DISCUSSION

Reactions with Sulphur Dioxide.—When sulphur dioxide was condensed at −196 °C on to the solid complexes [AuMeL] (L = PMe_3, PMe_2Ph, or $PMePh_2$) a deep red colouration was produced. On allowing the mixture to warm, the SO_2 melted to give a bright red solution. This colour soon faded and a pale yellow solution was obtained. The process was not reversible, so that cooling the solution again to −196 °C did not regenerate the red colour. In each case the product isolated was $[Au(SMeO_2)L]$, and this was characterised by elemental analysis (Table 1) and by the i.r. and n.m.r. spectra (Table 2). In particular, the i.r. spectra in the ν(SO) region clearly indicate that the *S*- rather than *O*-sulphinato-derivatives are formed.[8]

Similarly $[AuMe_3(PMe_2Ph)]$ in liquid SO_2 rapidly gave *cis*-$[AuMe_2(SMeO_2)(PMe_2Ph)]$, again characterised as the *S*-sulphinato-derivative. In this case, however, the intermediate intense red colouration was not observed. On leaving the product in liquid SO_2 in an n.m.r. tube at room temperature, further reaction took place as evidenced by changes in the n.m.r. spectrum. Among the products, ethane and dimethylphenylphosphine sulphide were identified.

The *S*-sulphinato-derivatives were all rather unstable to moist air, blackening over a period of several days. In solution in solvents other than liquid SO_2 decomposition was very rapid. From a reaction with dichloromethane solvent, $[Au(SMeO_2)(PMe_3)]$ gave $[AuCl(PMe_3)]$.

Attempts to isolate the bright red intermediates formed from the methylgold(I) complexes with SO_2 were unsuccessful. At −60 °C, the lowest temperature at which a satisfactory n.m.r. spectrum could be obtained, the insertion step was already complete in the reaction of $[AuMe(PMe_3)]$ with SO_2 and so the n.m.r. spectrum of the intermediate could not be recorded. The intermediate may be a sulphur dioxide complex $[AuMe(SO_2)(PMe_3)]$ analogous to the intensely coloured green $[Pt(SO_2)(PPh_3)_2]$ or red-brown $[Pt(SO_2)(PPh_3)_3]$ formed by the isoelectronic platinum(0) species,[9,10] and the sulphur dioxide insertion into the methylgold bond may then occur by intramolecular rearrangement of the intermediate.[8] The insertion reactions take place at similar rates for the complexes $[AuMe(PMe_2Ph)]$ and

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

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[$AuMe_3(PMe_2Ph)$], and both are considerably faster than for square-planar alkylplatinum(II) complexes.[11] Other examples of reactions of SO_2 with organogold complexes have been reported recently.[12,13]

TABLE 2

Infrared and n.m.r. data for the *S*-bonded sulphinato-complexes [a]

Complex	$\nu_{asym}(SO_2)$	$\nu_{sym}(SO_2)$	δ(MeP)	^2J(PH)	δ(MeS)
	cm^{-1}		p.p.m.	Hz	p.p.m.
[$Au(SMeO_2)(PMe_3)$]	1 170	1 044	1.94 (d)	10.8	3.05 (s)
[$Au(SMeO_2)(PMe_2Ph)$]	1 168	1 044	1.62 (d)	10.7	2.47 (s)
[$Au(SMeO_2)(PMePh_2)$]	1 170	1 044	2.63 (d)	10.7	3.20 (s)
cis-[$AuMe_2(SMeO_2)(PMe_2Ph)$] [b]	1 185	1 048	1.85 (d)	11.0	2.53 (s)

[a] N.m.r. solvent SO_2. d = doublet, s = singlet. [b] δ(MeAu) 0.77 (d) [^3J(PH) 8.6] and 0.98 (d) p.p.m. [^3J(PH) 8.0 Hz].

Reactions with Tetracyanoethylene (*tcne*).—Reaction of tetracyanoethylene with complexes [AuMeL] (L = PMe_3 or PMe_2Ph) at room temperature gave an intermediate black colour and no pure materials could be isolated. However if solutions of the methylgold(I) complex and tcne in tetrahydrofuran (thf) were mixed at −78 °C yellow crystals were obtained. For the reaction with [$AuMe(PMe_2Ph)$] the product crystallised from solution as yellow needles of [$AuMe(PMe_2Ph)$]·tcne·thf, and with [$AuMe(PMe_3)$] toluene was added to the reaction mixture to precipitate [$AuMe(PMe_3)$]·tcne·0.3C_6H_5Me. In each case the presence of solvent of crystallisation was indicated by the analytical data and confirmed by the n.m.r. spectra. The tcne adducts could be stored at −78 °C, but decomposed rapidly to black oils at room temperature.

TABLE 3

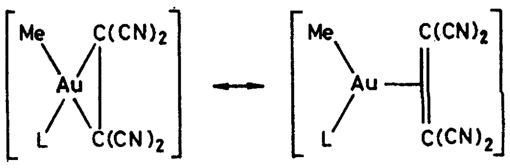
Infrared and n.m.r. data for the tetracyanoethylene complexes

Compound	ν(CN)	ν(C=C)	ν(MeAu)	δ(MeAu)	δ(MeP)
		cm^{-1}		p.p.m.	
tcne	2 262 2 215	1 562			
tcne$^{-\cdot}$	2 209 2 183	1 371			
[$Pt(PMe_3)_2(tcne)$]	2 220 2 165	1 191			
[$AuMe(PMe_3)(tcne)$]	2 225 2 220	1 178	516	0.30 (d) [a]	0.88 (d) [b]
[$AuMe(PMe_2Ph)(tcne)$]	2 230	1 191	528	0.85 (s) [c]	1.9 (s)

[a] Solvent CH_2Cl_2 at −60 °C, δ(C_6H_5Me) 2.3 p.p.m. [^3J(PH) 6.0 Hz]. [b] ^2J(PH) 10.8 Hz. [c] Solvent $(CD_3)_2CO$ at −60 °C, δ(thf) 1.8 and 3.6 p.p.m.

The i.r. and n.m.r. spectra of the complexes (Table 3) are best interpreted in terms of the structure (1). Thus the i.r. spectra show the presence of a methylgold bond, with ν(AuMe) being at lower frequency than in the parent methylgold(I) complex. The CN stretching region contained two closely spaced sharp peaks in each case. The frequencies are intermediate between those for tcne and tcne$^-$ indicating strong back bonding from *d* orbitals on gold to π* orbitals of tcne. These features are typical of tcne complexes of metals in this region of the Periodic Table,[14] but are inconsistent with products arising from insertion of tcne into the methylgold bond [15] or with simple charge-transfer complexes of tcne.[16] From the extent of the lowering of ν(CN) and ν(C=C) from the values for free tcne, the amount of back bonding appears comparable with that in the isoelectric [$Pt(PMe_3)_2(tcne)$].[17] A similar structure as for the platinum(0) species is therefore proposed, although some asymmetry in the Au(tcne) group is expected due to the differing *trans* influences of the methyl and tertiary phosphine ligands on gold.

The ^1H n.m.r. spectrum of [$AuMe(PMe_3)(tcne)$] in dichloromethane at −60 °C contained two doublets due to methylgold and methylphosphorus protons, but these peaks broadened on warming to −40 °C. This process was irreversible and cooling to −60 °C did not give the original spectrum. Thus significant decomposition appears to take place at −40 °C. A similar effect was observed with [$AuMe(PMe_2Ph)(tcne)$] in [$^2H_6$]acetone solution, when the methylgold and methylphosphorus peaks appeared as broad singlets even at −60 °C.



(1)

The decomposition of [$AuMe(PMe_3)(tcne)$] was studied by allowing a solution in thf to warm slowly in the probe of an e.s.r. spectrometer. At −100 °C the e.s.r. spectrum of the radical anion tcne$^{-\cdot}$ could be observed.[18]

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The signal became more intense and then decayed slowly on warming to room temperature. Evidence for decomposition to tcne$^{-\cdot}$ was also obtained by i.r. spectroscopy. Thus the i.r. spectrum of $[AuMe(PMe_3)(tcne)]$ as a Nujol mull changed as the complex decomposed. The initial sharp CN stretching peaks decayed and broader peaks arose at 2 184 and 2 196 cm^{-1}, close to those for $Li^+tcne^{-\cdot}$ at 2 183 and 2 209 cm^{-1}. Thus it appears that the tcne complex decomposes by electron transfer to give tcne$^{-\cdot}$ and presumably $[AuMe(PMe_3)]^{+\cdot}$ which is then expected to decompose further. The observation is of interest since it has been shown that tcne complexes may be formed after *initial* electron transfer, as in equation (1).[19]

$$\begin{aligned} &[Co(CNMe)_5]^+ + tcne \rightleftharpoons \\ &\qquad [Co(CNMe)_5]^{2+} + tcne^{-\cdot} \\ &\qquad \downarrow \\ &\qquad [Co(CNMe)_4(tcne)]^+ + MeNC \quad (1) \end{aligned}$$

A similar process apparently operates in the reaction of $[Pt(PPh_3)_4]$ with tcne.[20] In both cases the metal atom is co-ordinatively saturated. Although dissociation of $[Pt(PPh_3)_4]$ to $[Pt(PPh_3)_3]$ occurs in solution, the product is a sterically congested molecule. Thus when direct attack of tcne on the metal centre is not possible it seems that the initial step is the electron transfer, whereas with the linear gold(I) complexes, in which little steric hindrance is expected, the π complex is formed first and then decomposes to give tcne$^{-\cdot}$. This is then more comparable to the behaviour of tcne with organic electron donors, when formation of charge-transfer complexes precedes complete electron transfer to give tcne$^{-\cdot}$.

The complex $[AuMe_3(PMe_2Ph)]$ reacted only slowly with tcne at room temperature, with blackening of the solution. The only isolated product was gold(I) cyanide in very low yield. The relatively low reactivity compared with the methylgold(I) complexes is presumably due to the lower electron density on gold in the gold(III) derivative. For the same reason, chlorogold(I) complexes also fail to react with tcne.[21]

Reactions with Alkynes.—Reactions of [AuMeL] (L = tertiary phosphine) with hexafluorobut-2-yne have been described previously,[3,4,22] and give either $[LAu\{C(CF_3)=C(CF_3)\}AuL]$ or $[Au\{C(CF_3)=C(CF_3)Me\}L]$ by decomposition of the intermediate gold(I)–gold(III) complexes $[L(Me)_2Au\{C(CF_3)=C(CF_3)\}AuL]$. Attempts to prepare similar complexes from other alkynes have been unsuccessful. Thus dimethyl acetylenedicarboxylate reacted with $[AuMe(PMe_3)]$ in benzene solution to give some decomposition to metallic gold, and forming $[Au\{C(CO_2Me)=C(CO_2Me)Me\}(PMe_3)]$ (2) and *cis*-$[AuMe_2\{C(CO_2Me)=C(CO_2Me)Me\}(PMe_3)]$ (3) in relative proportion 3 : 1. Separation of these products from other minor products was achieved by column chromatography. Complex (2) is the product of insertion of the acetylene into the methylgold bond of $[AuMe(PMe_3)]$ [equation (2)]. The formation of (3) is surprising, however, and must be accompanied by formation of gold [equation (3)]. Complexes (2) and (3) were

$$\begin{aligned} &[AuMe(PMe_3)] + MeO_2CC{\equiv}CCO_2Me \longrightarrow \\ &\qquad [Au\{C(CO_2Me)=C(CO_2Me)Me\}(PMe_3)] \quad (2) \end{aligned}$$

characterised by elemental analysis, and i.r., n.m.r., and mass spectra. The spectroscopic data do not give the

$$\begin{aligned} &3[AuMe(PMe_3)] + MeO_2CC{\equiv}CCO_2Me \longrightarrow \\ &\qquad cis\text{-}[AuMe_2\{C(CO_2Me)=C(CO_2Me)Me\}(PMe_3)] + \\ &\qquad\qquad 2Au + 2PMe_3 \quad (3) \end{aligned}$$

stereochemistry about the C=C bond of (2) and (3) however.

Mitchell and Stone[22] showed that phenylacetylene reacted with $[AuMe(PPh_3)]$ to give $[Au(CCPh)(PPh_3)]$. Similarly we find that 3,3,3-trifluoropropyne cleaves a methylgold bond in both $[AuMe(PMe_2Ph)]$ and $[AuMe_3(PMe_2Ph)]$ to give methane and $[Au(C{\equiv}CCF_3)(PMe_2Ph)]$ and *cis*-$[AuMe_2(C{\equiv}CCF_3)(PMe_2Ph)]$ respectively. The C≡C stretching frequencies were at 2 130 and 2 148 cm^{-1} for the gold(I) and gold(III) derivatives respectively, perhaps indicating stronger back bonding in the gold(I) complex.

The complex $[AuMe(PMe_3)]$ did not react with tetrafluoroethylene at room temperature, but under u.v. irradiation the product of insertion of C_2F_4 into the methylgold bond, $[Au(CF_2CF_2Me)(PMe_3)]$, was formed. Its n.m.r. spectrum was similar to that of $[Au(CF_2CF_2Me)(PPh_3)]$.[22] In diethyl ether solvent a further product which could not be separated from $[Au(CF_2CF_2Me)(PMe_3)]$ was also formed and was tentatively identified as *cis*-$[Au\{CF=CF(OEt)\}(PMe_3)]$ from spectroscopic data. Certainly the presence of an ethoxy-group, presumably derived from the solvent, was established from the n.m.r. spectrum. This supports the contention of Mitchell and Stone[22] that free radicals are involved in the photochemical reaction.

No reaction took place at room temperature between $[AuMe(PMe_2Ph)]$ or $[AuMe_3(PMe_2Ph)]$ and carbon monoxide, *p*-tolyl isocyanide, carbon disulphide, or phenyl isothiocyanate. *N*-Sulphinylaniline reacted with $[AuMe(PMe_3)]$ but the product decomposed rapidly to gold.

Conclusions.—There is good evidence that some unsaturated reagents can interact with the gold centre in methylgold(I) but not in methylgold(III) complexes. Thus the formation of tcne complexes of methylgold(I) complexes is demonstrated, and it is likely that sulphur dioxide complexes of Au^I are also formed at low temperature. The tetracyanoethylene complexes may be considered as models for the likely initial intermediates in reactions of other alkenes and alkynes with methylgold(I) complexes, although it is still not possible to predict what the final products of these reactions will be. In accord with this theory, the methylgold(I) complexes

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[21] G. L. McClure and W. H. Baddley, *J. Organometallic Chem.*, 1971, **27**, 155.

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were very much more reactive towards alkenes and alkynes than the methylgold(III) complexes. In contrast, the ability of SO_2 to form a complex with the methylgold complexes does not appear to affect the reactivity towards insertion of SO_2 into the metal–carbon bond. It is possible therefore that direct attack by SO_2 on the methyl group, as in reactions of SO_2 with co-ordinatively saturated transition-metal alkyls,[8] may occur readily irrespective of whether a sulphur dioxide complex is formed or not.

EXPERIMENTAL

Organogold complexes were prepared as described previously.[2,5,7,23]

Methyl(trimethylphosphine)gold(I) *with* SO_2.—Sulphur dioxide (0.5 cm^3) was condensed into an n.m.r. tube containing $[AuMe(PMe_3)]$ (0.28 mmol). The tube was sealed. A bright red colouration was observed which faded slowly as the tube was allowed to warm. The course of reaction was monitored by recording the n.m.r. spectrum. The solvent was evaporated *in vacuo* to give white (methanesulphinato-*S*)(trimethylphosphine)gold(I) in quantitative yield. Attempts at recrystallisation led to decomposition. Other reactions with SO_2 were carried out in a similar way.

(*Dimethylphenylphosphine*)*methylgold*(I) *with Tetracyanoethylene* (*tcne*).—Solutions of $[AuMe(PMe_2Ph)]$ (0.22 g) and tcne (0.08 g) in tetrahydrofuran (thf) (4 cm^3) were cooled to −78 °C and then mixed. After 3 h at −78 °C the golden-yellow needles of $[AuMe(PMe_2Ph)(tcne)]\cdot thf$ which formed slowly were separated by decanting off the solvent, washed with thf at −78 °C, and dried *in vacuo* at −20 °C, yield 0.18 g.

Methyl(trimethylphosphine)gold(I) *with Dimethyl Acetylenedicarboxylate*.—A solution of $[AuMe(PMe_3)]$ (1.68 mmol) and $MeO_2CC\equiv CCO_2Me$ (1.68 mmol) in benzene (15 cm^3) was allowed to stand at room temperature for 4 weeks. The product mixture was then separated by chromatography through a column of silica eluting with light petroleum, then diethyl ether, and finally methanol. The ether fractions gave *cis*-$[AuMe_2\{C(CO_2Me)=C(CO_2Me)Me\}(PMe_3)]$ (3) (0.41 mmol); n.m.r. in C_6H_6, δ(MeAu) 0.30 (d) [^3J(PH) 8.7], 1.12 (d) [^3J(PH) 9.4], δ(MeP) 0.75 (d) [^2J(PH) 9.9 Hz], δ(MeO) 3.35 (s), 3.44 (s), and δ(MeC) 1.78 (s) p.p.m. The mass spectrum did not give a parent ion at *m/e* 460, but an intense peak at *m/e* 445 due to loss of a methyl group was observed. The methanol fractions gave $[Au\{C(CO_2Me)=C(CO_2Me)Me\}(PMe_3)]$ (2) (0.14 mmol); n.m.r. in C_6H_6, δ(MeP) 0.35 (d) [^2J(PH) 10.1 Hz], δ(MeO) 3.22 (s), 3.52 (s), and δ(MeC) 2.32 (s) p.p.m. The mass spectrum gave a parent ion at *m/e* 430.

$[AuMe(PMe_2Ph)]$ *with* 3,3,3-*Trifluoropropyne*.—3,3,3-Trifluoropropyne (3 mmol) was condensed into a solution of $[AuMe(PMe_2Ph)]$ (0.21 g) in diethyl ether (10 cm^3) in a Carius tube. The tube was sealed and allowed to stand at room temperature for 3 d. The white crystals of $[Au(C\equiv CCF_3)(PMe_2Ph)]$ which precipitated were filtered off, washed with diethyl ether, and dried *in vacuo*, yield 0.15 g; n.m.r. in $CDCl_3$, δ(MeP) 1.77 (d) [^2J(PH) 9.8] and δ(CF_3) 33.1 (d) p.p.m. [^5J(PF) 47 Hz] from CF_3CCl_3 reference. ν(C≡C) at 2 130 cm^{-1}.

$[AuMe_3(PMe_2Ph)]$ *with* 3,3,3-*Trifluoropropyne*.—3,3,3-Trifluoropropyne (3 mmol) was condensed into a solution of $[AuMe_3(PMe_2Ph)]$ (0.24 g) in diethyl ether in a Carius tube. After 2 weeks at room temperature, evaporation of the solvent and recrystallisation from diethyl ether–light petroleum gave *cis*-$[AuMe_2(C\equiv CCF_3)(PMe_2Ph)]$ (0.09 g); n.m.r. in $(CD_3)_2CO$, δ(MeAu) 0.23 (d) [^3J(PH) 9.2, *trans* to $C\equiv CCF_3$], 0.74 (d) [^3J(PH) 9.0, *trans* to PMe_2Ph], δ(MeP) 1.44 (d) [^2J(PH) 13.2], and δ(CF_3) 46.30 (d) p.p.m. [^5J(PF) 3.5 Hz] (reference CF_3CCl_3). ν(C≡C) at 2 148 cm^{-1}.

$[AuMe(PMe_3)]$ *with Tetrafluoroethylene*.—Tetrafluoroethylene (6.8 mmol) was condensed into a solution of $[AuMe(PMe_3)]$ (3.4 mmol) in diethyl ether (5 cm^3) in a silica tube. The tube was sealed and irradiated with a mercury lamp at 25 °C for 4 h. Some metallic gold was formed during this time. The solution was filtered and the solvent was evaporated to give a colourless oil. This was shown by t.l.c. to contain two components but separation by column chromatography or by vacuum distillation could not be achieved. The distilled mixture contained $[Au(CF_2CF_2Me)(PMe_3)]$; n.m.r. in C_6H_6, δ(MeP) 1.54 (d) [^2J(PH) 10.2], δ(MeC) 1.60 (tt) [^3J(FH) 18.2, ^4J(FH) 2.4], δ($AuC\mathit{F}_2$) 100.7 (d of sxt) [^3J(PF) 29.6, ^3J(FF) 2.4], and δ($MeC\mathit{F}_2$) 103.9 (qq) p.p.m. [^4J(PF) 2.4 Hz]. The other component was tentatively identified as *cis*-$[Au\{CF=CF(OEt)\}(PMe_3)]$; n.m.r. in C_6H_6, δ(MeC) 3.64 (q) [^3J(HH) 7.0], δ($MeC\mathit{H}_2$) 1.14 (t), δ(F) −102.8 (dd) [^3J(FF) 11.5, ^3J(PF) 28.0], and −123.0 (dd) p.p.m. [^3J(FF) 11.5, ^4J(PF) 3.3 Hz] (reference $CFCl_3$).

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