Reactions of the Gold–Methyl Bond

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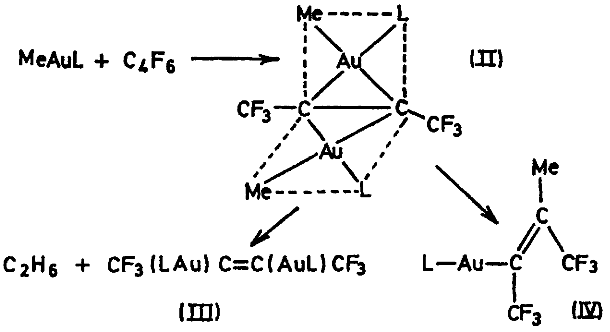
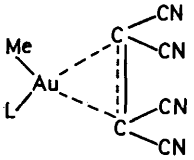
Summary Olefin and acetylene complexes of a methylgold(I) compound have been isolated; they are believed to be important intermediates in further reactions of the methylgold bond.

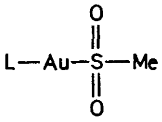
The methylgold(I) complex $MeAuPPh_3$ reacts with tetrafluoroethylene, C_2F_4, to give the insertion compound, $MeCF_2CF_2AuPPh_3$, but with hexafluorobut-2-yne, C_4F_6, ethane is eliminated and $CF_3(Ph_3PAu)C{=}C(AuPPh_3)CF_3$ is formed.[1,2] Previous work with methylplatinum complexes suggested that intermediates in these reactions, which are important as models for transition-metal catalysis, might be isolated if a less bulky phosphine ligand were used.[3]



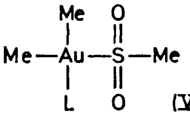
This has now been achieved using the ligand dimethylphenylphosphine, L.

MeAuL (I; L = PMe_2Ph) reacts rapidly with C_4F_6 to give a stable 2:1 adduct $(MeAuL)_2C_4F_6$, (II). Analytical† and spectroscopic (i.r., ^{1}H and ^{19}F n.m.r.) data suggest that (II) is an unusual π-complex in which the acetylene acts as a bridging ligand.[4,5] Thus the ^{1}H n.m.r. spectrum of (II) in $CDCl_3$ contained peaks due to methylgold, δ (MeAu) 0·79 p.p.m. [d, ^3J (PH) 7·1 Hz], and methylphosphorus, δ (MeP) $-2{\cdot}05$ p.p.m. [d, ^2J (PH) 9·5 Hz], peaks, with relative areas in the expected ratio of 1 : 2. In benzene or perdeuterioacetone the methylphosphorus peaks appeared as two doublets confirming that there is no plane of symmetry containing the phosphorus–gold bonds.[3] The ^{19}F n.m.r. spectrum contains an unsymmetrical multiplet centred at δ 52·4 p.p.m. from $CFCl_3$, suggesting that the CF_3 groups are non-equivalent, and hence that the *cis*-configuration about the bridging acetylene is present in (II), since in the *trans*-configuration the CF_3 groups would be identical. The i.r. spectrum of (II) contains a band at 502 cm^{-1} due to the methylgold stretching vibration [compare the value of 528 cm^{-1} in (I)], and weak peaks at 1565 cm^{-1} and 1586 cm^{-1} which can be assigned to the C≡C stretching mode of the bridging acetylene.[6]


(V)


(VII)

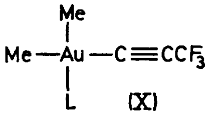
$$\mathrm{L-Au-\underset{\underset{O}{\|}}{\overset{\overset{O}{\|}}{S}}-Me}$$


(VIII)

$$\mathrm{Me-\underset{\underset{L}{|}}{\overset{\overset{Me}{|}}{Au}}-\underset{\underset{O}{\|}}{\overset{\overset{O}{\|}}{S}}-Me}$$

$\mathrm{L-Au-C\equiv C-CF_3}$

(IX)


(X)

$$\mathrm{Me-\underset{\underset{L}{|}}{\overset{\overset{Me}{|}}{Au}}-C\equiv CCF_3}$$

A solution of (II) in acetone containing excess of C_4F_6 slowly decomposed by eliminating ethane to give $(LAu)_2C_4F_6$ (III), but in ether solution the major product was that of *cis*-insertion into the methylgold bond (IV).

In contrast, C_2F_4 reacts to give insertion only,[1] presumably because it can complex to only one methylgold unit. We have been unable to isolate such a complex, but the stronger π-acid tetracyanoethylene does form an unstable 1 : 1 adduct with (I). The structure (V) which is predicted by analogy with the structures of isoelectronic Pt^0 complexes[7] is consistent with the spectroscopic properties of the compound.

In contrast to this behaviour, the gold(III) derivative Me_3AuL (VI; L = PMe_2Ph) is quite unreactive towards C_2F_4 and C_4F_6 presumably because, in this higher oxidation state, the filled *d*-orbitals on gold are too stable to interact with the π-acids C_2F_4 and C_4F_6 so that stable intermediate π-complexes cannot be formed.[8] If the π-complexes were not intermediates in these reactions, the gold(I) and gold(III) derivatives should be about equally reactive towards electrophiles.[9] This type of reactivity is observed in reactions of SO_2 and $CF_3C{\equiv}CH$ which give the insertion compounds (VII) and (VIII) and the alkynylgold compounds (IX) and (X), respectively.

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† Satisfactory C,H,F analyses were obtained. Mol. wt. in benzene: calc. 862, found 932.

[1] C. M. Mitchell and F. G. A. Stone, *Chem. Comm.*, 1970, 1264; *J.C.S. Dalton*, 1972, 102.
[2] C. J. Gilmore and P. Woodward, *Chem. Comm.*, 1971, 1233.
[3] H. C. Clark and R. J. Puddephatt, *Inorg. Chem.*, 1970, **9**, 2670; 1971, **10**, 18.
[4] O. S. Mills and B. W. Shaw, *J. Organometallic Chem.*, 1968, **11**, 595.
[5] J. L. Boston, D. W. A. Sharp, and G. Wilkinson, *J. Chem. Soc.*, 1962, 3488.
[6] A. I. Gusev and Yu. T. Struchkov, *J. Struct. Chem.*, 1970, **11**, 340.
[7] A. McAdam, J. N. Francis, and J. A. Ibers, *J. Organometallic Chem.*, 1971, **29**, 149.
[8] B. W. Davies, N. C. Payne, and R. J. Puddephatt, *Canad. J. Chem.*, in the press.
[9] B. J. Gregory and C. K. Ingold, *J. Chem. Soc.* (*B*), 1969, 276.