Reactions of Trifluoromethyl Iodide with Methylgold(I) Complexes. Preparation of Trifluoromethyl-gold(I) and -gold(III) Complexes

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Trifluoromethyl iodide reacts with [AuMeL] to give $[\mathrm{AuMe_2(CF_3)L}]$ and [AuIL] (L = $\mathrm{PMe_3}$ or $\mathrm{PMe_2Ph}$), or $[\mathrm{Au(CF_3)L}]$ and MeI (L = $\mathrm{PPh_3}$), or a mixture of these products (L = $\mathrm{PMePh_2}$). In some cases reaction of $[\mathrm{AuMe(PMe_3)}]$ with $\mathrm{CF_3I}$ gives $[\mathrm{AuMe(CF_3)I(PMe_3)}]$. Evidence is presented that the reactions proceed, at least in part, by a free-radical chain mechanism.

REACTIONS of methyl iodide with the complexes [AuMeL] (L = $\mathrm{PMe_3}$, PMePh, $\mathrm{PMePh_2}$, or $\mathrm{PPh_3}$) have been reported previously.[1-3] In all cases the initial reaction took place according to equation (1), the products

$$2[\mathrm{AuMeL}] + \mathrm{MeI} \longrightarrow [\mathrm{AuMe_3L}] + [\mathrm{AuIL}] \tag{1}$$

arising from rapid methyl for halogen exchange between the product of oxidative addition of [AuMeL] with MeI, namely *cis*-$[\mathrm{AuMe_2IL}]$ and unchanged [AuMeL] [equation (2)]. However, a slower subsequent reaction then took

$$cis\text{-}[\mathrm{AuMe_2IL}] + [\mathrm{AuMeL}] \longrightarrow [\mathrm{AuMe_3L}] + [\mathrm{AuIL}] \tag{2}$$

place which was dependent on the nature of the ligand L. Thus when L = $\mathrm{PPh_3}$ the complex $[\mathrm{AuMe_3L}]$ underwent reductive elimination of ethane to give ultimately the products of equation (3), while when L = $\mathrm{PMe_3}$ or

$$[\mathrm{AuMeL}] + \mathrm{MeI} \longrightarrow [\mathrm{AuIL}] + \mathrm{C_2H_6} \tag{3}$$

$\mathrm{PMe_2Ph}$ the complex $[\mathrm{AuMe_3L}]$ was stable to reductive elimination and the reverse reaction of equation (2) took place instead to give finally the product of equation (4). When L = $\mathrm{PMePh_2}$, a mixture of the products of equations (3) and (4) was formed.

$$[\mathrm{AuMeL}] + \mathrm{MeI} \longrightarrow cis\text{-}[\mathrm{AuMe_2IL}] \tag{4}$$

We now report an extension of this work to reactions of $\mathrm{CF_3I}$ with methylgold(I) complexes. We were interested in these reactions for the following reasons. (*i*) They give a possible route to trifluoromethylgold complexes which have not been reported previously. (*ii*) We wished to investigate if the products were determined by the nature of the ligands L, as with the reactions with methyl iodide. (*iii*) There has been some controversy about whether oxidative-addition reactions of MeI proceed by nucleophilic attack of an electron-rich metal centre at the carbon atom of MeI or by a free-radical mechanism.[4-6] The carbon atom of $\mathrm{CF_3I}$ is not susceptible to nucleophilic attack, while $\mathrm{CF_3I}$ takes part in many free-radical reactions and in oxidative-addition reactions. We were interested in comparing the products and mechanisms of reaction of MeI and $\mathrm{CF_3I}$ with methylgold(I) complexes, believing that a free-radical mechanism was more likely with $\mathrm{CF_3I}$ than with MeI.

RESULTS AND DISCUSSION

Trifluoromethyl iodide reacted with the complexes [AuMeL] to give a variety of products, depending on the nature of the ligand L and on the reaction conditions. Thus when L = $\mathrm{PMe_3}$ or $\mathrm{PMe_2Ph}$ reaction took place according to equation (5) (with exceptions under certain

$$2[\mathrm{AuMeL}] + \mathrm{CF_3I} \longrightarrow [\mathrm{AuMe_2(CF_3)L}] + [\mathrm{AuIL}] \tag{5}$$

conditions when L = $\mathrm{PMe_3}$, see below). By comparison with the similar reactions with MeI, it is likely that reaction occurs in the two stages shown in equations (6) and (7).

$$[\mathrm{AuMeL}] + \mathrm{CF_3I} \longrightarrow [\mathrm{AuMe(CF_3)IL}] \tag{6}$$

$$[\mathrm{AuMe(CF_3)IL}] + [\mathrm{AuMeL}] \longrightarrow [\mathrm{AuMe_2(CF_3)L}] + [\mathrm{AuIL}] \tag{7}$$

The $[\mathrm{AuMe_2(CF_3)L}]$ was formed as a mixture of the *cis* and *trans* isomers which could readily be distinguished by their n.m.r. spectra (Table), but the relative proportions of the isomers formed was strongly dependent on the solvent. Thus for L = $\mathrm{PMe_3}$, in $\mathrm{CF_3I}$ solvent the *cis* isomer was formed almost exclusively, in perdeuterioacetone the *cis–trans* ratio was 2 : 1, in diethyl ether the *cis–trans* ratio was 0.8 : 1, and in dichloromethane the *trans* isomer was formed exclusively. Once formed the isomers did not interconvert, so that the change in isomer ratio of the product with solvent is due to a mechanistic effect rather than to a simple solvent dependence on the equilibrium constant. There was also a dependence of the *cis–trans*-isomer ratio on the ligand, L, so that, in $\mathrm{(CD_3)_2CO}$ as solvent, when L = $\mathrm{PMe_3}$, the *cis–trans* ratio was 2 : 1, when L = $\mathrm{PMe_2Ph}$ it was 0.3 : 1, and when L = $\mathrm{PMePh_2}$ none of the *cis* isomer was formed. In all the reactions in $\mathrm{(CD_3)_2CO}$ solvent, $[\mathrm{AuMe_3L}]$ was formed in detectable concentration at intermediate stages of the reaction, although it was not always among the final products. Thus the course of the reaction may be more complex than as represented in equations (6) and (7).

The reaction of $[\mathrm{AuMe(PMe_3)}]$ with $\mathrm{CF_3I}$ in dichloromethane was studied closely by conducting the reaction in a sealed n.m.r. tube and monitoring the n.m.r. spectrum at regular intervals. Reaction was complete in *ca.* 1 d at room temperature, but occasionally the reaction was very rapid (<5 min) and the product was

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Hydrogen-1 and ^{19}F n.m.r. spectra of the trifluoromethyl gold complexes [a]

Complex	Solvent	$\delta(CH_3Au)$ p.p.m.	$^3J(PH)$ Hz	$\delta(CH_3P)$ p.p.m.	$^2J(PH)$ Hz	$\delta(CF_3Au)$[b] p.p.m.	$^3J(PF)$ Hz
$[Au(CF_3)(PMe_3)]$	CH_2Cl_2			1.40	10.0	31.5	48.3
$[Au(CF_3)(PMePh_2)]$	CH_2Cl_2			1.95	9.3	28.8	46.0
$[Au(CF_3)(PPh_3)]$	CH_2Cl_2					30.5	46.0
cis-$[AuMe_2(CF_3)(PMe_3)]$	CH_2Cl_2	0.32 [c]	8.5	1.42	10.6	31.5	7.1
		0.81 [d]	8.9				
trans-$[AuMe_2(CF_3)(PMe_3)]$	CH_2Cl_2	0.14	5.6	1.48	11.3	32.5	65.9
cis-$[AuMe_2(CF_3)(PMe_2Ph)]$	$(CD_3)_2CO$	0.57 [c]	8.7	1.85	10.3	30.3	8.4
		1.16 [d]	9.0				
trans-$[AuMe_2(CF_3)(PMe_2Ph)]$	$(CD_3)_2CO$	0.45	5.6	1.90	11.3	32.0	65.2
trans-$[AuMe_2(CF_3)(PMePh_2)]$	CH_2Cl_2	0.45	5.4	1.76	11.4	32.5	66.0
$[Au^cMe^b(CF_3)^aI^d(PMe_3)]$	CH_2Cl_2	1.78	6.0	1.96	12.0	23.1	68.8

[a] All the peaks appeared as 1 : 1 doublets. Relative to $CFCl_3$ as internal reference. [c] Methyl group *cis* to phosphorus. [d] Methyl group *trans* to phosphorus.

$[AuMe(CF_3)I(PMe_3)]$ formed according to equation (6). Clearly the oxidative addition was so rapid that all the $[AuMe(PMe_3)]$ was consumed before the exchange process of equation (7) could take place. This same product, $[AuMe(CF_3)I(PMe_3)]$, was formed by reaction of *trans*-$[AuMe_2(CF_3)(PMe_3)]$ with hydrogen chloride in the presence of excess of sodium iodide, but we were unable to reproduce reliably its preparation from $[AuMe(PMe_3)]$ and CF_3I.

A quite different reaction took place between CF_3I and $[AuMe(PPh_3)]$ to give $[Au(CF_3)(PPh_3)]$ and MeI [equation (8), $L = PPh_3$]. When $L = PMePh_2$, a

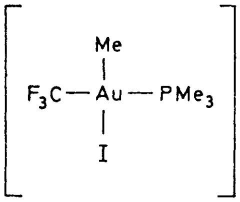
$$[AuMeL] + CF_3I \longrightarrow [Au(CF_3)L] + MeI \quad (8)$$

mixture of the products of equations (5) and (8) was formed with the product ratio $[Au(CF_3)(PMePh_2)]$: *trans*-$[AuMe_2(CF_3)(PMePh_2)]$ being *ca.* 5 : 1. Reaction of CF_3I with $[AuEt(PMePh_2)]$ gave a mixture consisting mostly of $[Au(CF_3)(PMePh_2)]$ and some $[AuI(PMePh_2)]$. No gold(III) complexes were detected, but considerable decomposition to metallic gold took place.

Overall then, it can be seen that the effect of the ligand, L, on the course of reaction of [AuMeL] with CF_3I is comparable to its effect in the reactions with MeI. Thus when $L = PMe_3$ or PMe_2Ph stable trifluoromethylgold(III) species are formed, when $L = PPh_3$ only a trifluoromethylgold(I) complex is formed, while when $L = PMePh_2$ a mixture of trifluoromethyl-gold(I) and -gold(III) species is formed.

Characterisation of Trifluoromethylgold Complexes.—The trifluoromethylgold complexes were all air and water stable, and were easily purified by crystallisation, column chromatography, or vacuum sublimation (when $L = PMe_3$ only). After heating a *cis–trans* mixture of $[AuMe_2(CF_3)(PMe_3)]$ to 160 °C for 1 h, the *cis* isomer was recovered unchanged although the *trans* isomer decomposed to metallic gold. The same mixture partially decomposed to $[Au(CF_3)(PMe_3)]$ after storage for several months at room temperature in the light.

The complexes were characterised by elemental analysis and by the ^1H and ^{19}F n.m.r. spectra (Table) which, for some of the complexes, have been discussed previously.[7] In the methyl(trifluoromethyl)gold(III) complexes, the magnitude of the coupling constant between ^{31}P and the methylgold protons does not vary much whether the methyl group is *cis* or *trans* to the phosphine (although the signs differ), but the coupling constant between phosphorus and the fluorine atoms of the CF_3 group is strongly dependent on stereochemistry, with $^3J(PF)$ for $[AuMe_2(CF_3)(PMe_3)]$ being 66 Hz in the *trans* isomer but only 7.2 Hz in the *cis* isomer. The complex $[AuMe(CF_3)I(PMe_3)]$ had $^3J(PF)$ 68.8 Hz indicating that the CF_3 group is *trans* to phosphorus and so defining the stereochemistry as (I). This is the product of *cis* oxidative addition of CF_3I to $[AuMe(PMe_3)]$.



(I)

Mechanistic Investigations.—The possibility that the reactions may proceed by free-radical mechanisms was investigated by the techniques of spin trapping, and by addition of free-radical scavengers and initiators to the reaction mixtures, but the results were not conclusive. For example, CF_3I underwent reaction with Bu^{t}NO in the absence of methylgold complexes to give the radical $CF_3(Bu^t)NO^{\bullet}$, identified by its e.s.r. spectrum, so that, although the same radical was formed in the presence of $[AuMe(PMe_3)]$, no conclusions about the reaction mechanism are possible.

A solution of $[AuMe(PMe_3)]$ and CF_3I in dichloromethane was added to two n.m.r. tubes one of which contained the radical scavenger galvinoxyl, which was shown by u.v. spectroscopy not to react with $[AuMe(PMe_3)]$ or with CF_3I separately. The tubes were sealed *in vacuo* and the reaction was monitored by recording the spectra. The solution without galvinoxyl reacted faster in all cases, and in one experiment gave the complex $[AuMe(CF_3)I(PMe_3)]$ within 5 min at room temperature. In the presence of galvinoxyl the products were always *trans*-$[AuMe_2(CF_3)(PMe_3)]$ and $[AuI(PMe_3)]$ and the reaction took *ca.* 1 d to reach completion, without the colour of the scavenger being discharged.

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The very rapid reaction in the absence of scavenger is almost certainly a radical-chain reaction therefore, but the mechanism of the slower reaction in the presence of galvinoxyl is not known. It could possibly involve a free-radical non-chain process as has been proposed for some oxidative-addition reactions to isoelectronic platinum(0) complexes.[5,6] The propagation steps in the radical-chain mechanism of oxidative addition are shown in equations (9) and (10). Unless this is very fast, further reaction of $[AuMe(CF_3)IL]$ with $[AuMeL]$ then takes place according to equation (7). The reason for the lack of reproducibility in the rate of reaction of $[AuMe(PMe_3)]$ with CF_3I is not clear, but is not uncommon in free-radical chain reactions.

$$CF_3^{\bullet} + [AuMeL] + \longrightarrow [AuMe(CF_3)L]^{\bullet} \quad (9)$$

$$[AuMe(CF_3)L]^{\bullet} + CF_3I \longrightarrow [AuMe(CF_3)IL] + CF_3^{\bullet} \quad (10)$$

The formation of trifluoromethylgold(I) complexes in the reactions when $L = PPh_3$ or $PMePh_2$ can be accommodated by this mechanism if the complexes $[AuMe(CF_3)IL]$ undergo rapid reductive elimination of MeI with these ligands. Alternatively, the proposed gold(II) intermediate $[AuMe(CF_3)L]^{\bullet}$ formed in equation (9) could eliminate a methyl radical, which then abstracts iodide from CF_3I [equations (11) and (12)]. The $CF_3^{\bullet}$ radicals then continue the chain. This mechanism involves homolytic substitution of a methyl group from gold by a trifluoromethyl group, and such reactions have been shown to take place readily in similar systems.[8,9] The formation of $[AuMe_3L]$ in some reactions can be explained if the reaction of equation (11) is followed by (13), and then by reaction of $[AuMe_2IL]$ with $[AuMeL]$ according to equation (2).

$$[AuMe(CF_3)L]^{\bullet} \longrightarrow [Au(CF_3)L] + Me^{\bullet} \quad (11)$$

$$Me^{\bullet} + CF_3I \longrightarrow MeI + CF_3^{\bullet} \quad (12)$$

$$Me^{\bullet} + [AuMeL] \rightleftharpoons [AuMe_2L]^{\bullet} \xrightarrow{CF_3I} [AuMe_2IL] + CF_3^{\bullet} \quad (13)$$

The formation of different proportions of the isomers of $[AuMe_2(CF_3)(PMe_3)]$ in the reaction of $[AuMe(PMe_3)]$ with CF_3I is worthy of comment. In the reaction in dichloromethane the product was the *trans* isomer only, as expected if $[AuMe(CF_3)I(PMe_3)]$ of configuration (I) undergoes the reaction (7) with retention of configuration about Au^{III}. Retention of configuration is generally expected in such exchange reactions,[10-13] and this has been checked independently by reaction of (I) with $[AuMe(PMe_3)]$ to give *trans*-$[AuMe_2(CF_3)(PMe_3)]$. It is likely therefore that the observed isomer ratio reflects the solvent dependence of the stereochemistry of the initial oxidative addition of CF_3I to $[AuMe(PMe_3)]$, this being *cis* in dichloromethane, *trans* in CF_3I, and a mixture of these in diethyl ether and acetone.

EXPERIMENTAL

General techniques and the preparation of starting materials have been described previously.[2,8] All reactions were studied first in sealed n.m.r. tubes, so that the product mixtures could be analysed directly from the n.m.r. spectra. A typical procedure is given.

Methyl(trimethylphosphine)gold(I) *with* CF_3I.—(a) *In dichloromethane.* Solutions of $[AuMe(PMe_3)]$ (0.08 mmol) in dichloromethane (0.5 cm^3) were placed in two n.m.r. tubes A and B. To tube A was added galvinoxyl (3×10^{-4} mmol). Each solution was degassed on the vacuum line and into each tube was condensed CF_3I (0.32 mmol). The tubes were sealed *in vacuo*, allowed to warm to room temperature, and the n.m.r. spectra were recorded. The reaction in tube B was complete within 5 min at 35 °C and the product was identified as $[AuMe(CF_3)I(PMe_3)]$ by comparison with an authentic sample. Reaction in tube A was complete in 24 h at 35 °C giving $[AuI(PMe_3)]$ and *trans*-$[AuMe_2(CF_3)(PMe_3)]$, which was subsequently isolated by crystallisation from diethyl ether, m.p. 97—100 °C.

(b) *In diethyl ether.* Trifluoromethyl iodide (1.2 mmol) was condensed into a solution of $[AuMe(PMe_3)]$ (0.55 mmol) in diethyl ether (10 cm^3) in a Pyrex tube. The tube was sealed, allowed to warm to room temperature, and shaken for 10 d. The tube was opened and the solution cooled to −78 °C when $[AuI(PMe_3)]$ crystallised (m.p. 209—214 °C; lit.,[14] 210—214 °C). The solvent was evaporated from the filtrate to give a mixture of *cis*- and *trans*-$[AuMe_2(CF_3)(PMe_3)]$ (identified by the n.m.r. spectra) as a colourless oil which could not be crystallised. This was purified by vacuum sublimation, which gave a white solid. Separation of the isomers was not achieved (Found: C, 19.3; H, 4.1; F, 15.1. Calc. for $C_6H_{15}AuF_3P$: C, 19.4; H, 4.0; F, 15.3%).

Iodo(methyl)(trifluoromethyl)(trimethylphosphine)gold(III).—Solutions of *trans*-$[AuMe_2(CF_3)(PMe_3)]$ (0.29 mmol) and sodium iodide (0.63 mmol), each in acetone (5 cm^3), were mixed, and a solution of HCl (0.29 mmol) in diethyl ether was added dropwise. The solvent was evaporated and the product separated from sodium halides by extraction with diethyl ether. The *product* crystallised on adding light petroleum, m.p. 125—130 °C (decomp.) (Found: C, 12.7; H, 2.75; F, 11.0. Calc. for $C_5H_{12}AuF_3IP$: C, 12.4; H, 2.5; F, 11.8%).

(*Dimethylphenylphosphine*)*methylgold*(I) *with* CF_3I.—Trifluoromethyl iodide (0.3 mmol) was condensed into an n.m.r. tube containing $[AuMe(PMe_2Ph)]$ (0.11 mmol) in $[^2H_6]$acetone (0.5 cm^3). The tube was sealed *in vacuo*. The course of the reaction was monitored by recording the ^1H and ^{19}F n.m.r. spectra. The reaction was complete in 1 d, giving $[AuI(PMe_2Ph)]$, *cis*-$[AuMe_2(CF_3)(PMe_2Ph)]$, and *trans*-$[AuMe_2(CF_3)(PMe_2Ph)]$ in the proportions 1 : 0.23 : 0.77 determined by integration of the ^1H and ^{19}F n.m.r. spectra. The tube was opened, the solvent evaporated, and the product extracted with diethyl ether in which $[AuI(PMe_2Ph)]$ was insoluble. The $[AuMe_2(CF_3)(PMe_2Ph)]$ was

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purified by chromatography over silica gel with dichloromethane as eluant, giving a colourless oil. Separation of the isomers was not achieved (Found: C, 29.7; H, 3.9; F, 12.5. Calc. for $C_{11}H_{17}AuF_3P$: C, 30.4; H, 3.9; F, 13.1%).

Methyl(methyldiphenylphosphine)gold(I) *with* CF_3I.—To a solution of [AuMe($PMePh_2$)] (0.28 mmol) in dichloromethane (10 cm^3) in a Pyrex tube was added CF_3I (0.56 mmol). The tube was sealed *in vacuo*, allowed to warm to room temperature, and set aside for 48 h. The tube was opened and an n.m.r. spectrum of the solution was recorded to identify the products. The complex mixture was chromatographed over silica using dichloromethane, diethyl ether, and then methanol as eluants. This gave [Au(CF_3)($PMePh_2$)] which was recrystallised from diethyl ether, m.p. 125—127 °C (Found: C, 35.9; H, 2.9; F, 12.0. Calc. for $C_{14}H_{13}AuF_3P$: C, 36.1; H, 2.8; F, 12.2%), and then [AuI($PMePh_2$)], m.p. 140—142 °C (Found: C, 30.1; H, 2.6. Calc. for $C_{13}H_{13}AuIP$: C, 29.8; H, 2.5%); [$AuMe_3$($PMePh_2$)] and *trans*-[$AuMe_2$(CF_3)($PMePh_2$)] were identified by n.m.r. in the initial mixture but were not isolated.

Methyl(triphenylphosphine)gold(I) *with* CF_3I.—To a solution of [AuMe(PPh_3)] (0.08 mmol) in dichloromethane (0.5 cm^3) in an n.m.r. tube was added CF_3I (0.32 mmol). The tube was sealed *in vacuo*, warmed to room temperature, and n.m.r. spectra were recorded. After 45 min at 35 °C the doublet due to the $AuCH_3$ protons had disappeared and a singlet due to MeI appeared. The tube was opened and the solvent evaporated to give [Au(CF_3)(PPh_3)] in quantitative yield, m.p. 150 °C (decomp.) (Found: C, 42.9; H, 2.7; F, 10.0. Calc. for $C_{19}H_{15}AuF_3P$: C, 43.1; H, 2.8; F, 10.8%).

[6/132 *Received*, 20*th January*, 1976]