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OXIDATIVE ADDITION REACTIONS OF METHYL IODIDE WITH SOME METHYLGOLD(I) COMPOUNDS

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Summary

Reactions of methyl iodide with MeAuL (L = PMe_3, PMe_2Ph or $PMePh_2$) rapidly give an equimolar mixture of Me_3AuL and IAuL. A slower reaction then takes place to give *cis*-Me_2AuIL when L = PMe_3 or PMe_2Ph and a mixture of *cis*-Me_2AuIL (and the products of its subsequent reaction with methyl iodide) and IAuL + C_2H_6 when L = $PMePh_2$. The kinetics of the reactions when L = PMe_3 have been studied, and possible mechanisms are discussed.

Introduction

Reactions of alkyl halides with methylgold(I) compounds were first studied by Shiotani and Schmidbaur [1]. These authors showed that reaction took place according to eqn. (1), L = tertiary phosphine:

$$\text{MeAuL} + \text{MeI} \rightarrow \text{IAuL} + C_2H_6 \qquad (1)$$

Soon afterwards Tamaki and Kochi [2] showed that when L = PPh_3 the reaction took place in several steps (eqns. 2-4):

$$\text{MeAuL} + \text{MeI} \xrightarrow{k_2} cis\text{-}Me_2\text{AuIL} \qquad (2)$$

$$cis\text{-}Me_2\text{AuIL} + \text{MeAuL} \rightleftharpoons Me_3\text{AuL} + \text{IAuL} \qquad (3)$$

$$Me_3\text{AuL} \rightarrow C_2H_6 + \text{MeAuL} \qquad (4)$$

The reaction of eqn. (3) was rapid so that the initial product of oxidative addition *cis*-Me_2AuIL was not observed as a product. However, Me_3AuL could be isolated from the reaction mixture at intermediate stages because the subsequent reductive elimination step (eqn. 4) was slow.

During our studies of the reactions of methylgold(I) compounds with alkynes [3, 4] we isolated some mixed oxidation state gold(I)—gold(III) complexes whose formation and subsequent decomposition were considered to involve oxidative addition and reductive elimination reactions respectively, and this led us independently to seek further examples of oxidative addition reactions of methylgold(I) complexes (for example with alkyl halides).

In a preliminary communication [5] we noted that when L = PMe_3 the initial reaction of MeAuL with MeI gave a 1/1 mixture of Me_3AuL and IAuL according to eqns. (2) and (3) but then a slow subsequent reaction occurred to give *cis*-Me_2AuIL (eqn. 5) rather than the product IAuL which is formed when L = PPh_3.

$$Me_3AuL + IAuL + MeI \rightarrow 2\ cis\text{-}Me_2AuIL \tag{5}$$

We suggested that the reaction of eqn. (3) was reversible and that *cis*-Me_2AuIL was formed by the reactions of Scheme 1 (eqns. 6 and 2).

SCHEME 1

$$Me_3AuL + IAuL \xrightleftharpoons[k_{-6}]{k_6} cis\text{-}Me_2AuIL + MeAuL \tag{6}$$

$$MeAuL + MeI \xrightarrow{k_2} cis\text{-}Me_2AuIL \tag{2}$$

The observation of different overall reactions when L = PMe_3 or PPh_3 is then due to the lower tendency of Me_3AuL to undergo reductive elimination of ethane when L is the smaller, stronger σ-donor ligand PMe_3.

Tamaki and Kochi [6] independently observed this reaction and reached a similar conclusion about the mechanism. They also suggested an alternative mechanism (Scheme 2), though this was considered less likely.

SCHEME 2

$$IAuL + MeI \xrightleftharpoons[k_{-7}]{k_7} MeAuI_2L \tag{7}$$

$$MeAuI_2L + Me_3AuL \xrightarrow{k_8} 2\ cis\text{-}Me_2AuIL \tag{8}$$

In an attempt to distinguish between these possible mechanisms we have studied the kinetics of the reaction of $MeAuPMe_3$ and MeI. We have also studied reactions of methyl iodide with the compounds MeAuL where L = PMe_2Ph and $PMePh_2$ in order to see if these give the reaction characteristic of the trimethylphosphine or triphenylphosphine complexes.

Results and discussion

A. Reactions with methyl iodide

The reaction of MeAuL with MeI were conveniently followed by NMR spectroscopy. The methylgold peaks in both starting materials and products appear as 1/1 doublets due to coupling with ^{31}P, and are quite characteristic for different compounds since the chemical shifts are sensitive to changes in other substituents on gold (Table 1) [6-10]. In all cases the initial reaction led to formation of Me_3AuL and IAuL within two hours at 33°, but the slower subsequent reaction was critically dependent on the nature of the ligand L. When L = PMe_3 or PMe_2Ph the final product was *cis*-Me_2AuIL only and when L = PPh_3 the product was IAuL and C_2H_6 only. When L = PMe_3 the reaction was complete in 18 days at 33° in neat methyl iodide solution, and when L = PMe_2Ph the reaction was complete in 25 days under similar conditions. When L = $PMePh_2$ however the final products after 14 days at 33° in neat methyl iodide were C_2H_6, IAuL, *cis*-Me_2AuIL, $(Me_2AuI)_2$ and $(Me_2Ph_2P)^+I^-$. These products are probably formed in the following ways. The initial product Me_3AuL appears to react 66% by reductive elimination of ethane to give finally IAuL and C_2H_6 (as when L = PPh_3) and 33% by the alternative reaction to give *cis*-Me_2AuIL (as when L = PMe_3 or PMe_2Ph). The *cis*-Me_2AuIL then slowly dissociates phosphine to give $(Me_2AuI)_2$ and the phosphine further reacts with MeI to give dimethyldiphenylphosphonium iodide. After 14 days about 33% of the *cis*-Me_2AuIL had been converted to $(Me_2AuI)_2$ and $(Me_2Ph_2P)^+I^-$.

TABLE 1

NMR SPECTRA OF THE GOLD COMPLEXES[a]

Compound	Solvent	δ(MeAu) (ppm)	^3J(PH) (Hz)	δ(MeP) (ppm)	^2J(PH) (Hz)
$IAu(PMe_3)$	$(CD_3)_2CO$			2.08	11.0
$IAu(PMe_2Ph)$	$(CD_3)_2CO$			2.15	10.5
$IAu(PMePh_2)$	CH_2Cl_2			2.55	10.3
$MeAu(PMe_3)$	CH_3I	0.90	8.4	2.30	9.0
	$(CD_3)_2CO$	0.07	8.4	1.36	9.0
$MeAu(PMe_2Ph)$	$(CD_3)_2CO$	0.16	8.2	1.90	8.4
$MeAu(PMePh_2)$	CH_2Cl_2	0.76	8.4	2.36	8.8
$Me_3Au(PMe_3)$	CH_3I	0.88[b]	7.2	[d]	
		1.56[c]	9.2		
	$(CD_3)_2CO$	−0.06[b]	7.2	1.42	10.2
		0.58[c]	9.2		
$Me_3Au(PMe_2Ph)$	$(CD_3)_2CO$	0.20[b]	7.2	2.02	10.3
		0.96[c]	9.2		
$Me_3Au(PMePh_2)$	CH_3I	0.85[b]	7.2	[d]	
		1.84[c]	9.2		
	CH_2Cl_2	0.42[b]	7.2	2.50	9.4
		1.38[c]	9.2		
cis $Me_2AuI(PMe_3)$	CH_3I	2.05[c]	9.6	2.65	10.8
		2.25[b]	8.4		
cis $Me_2AuI(PMe_2Ph)$	CH_3I	2.06[b]	8.5	2.82	10.1
		2.17[c]	9.0		
cis $Me_2AuI(PMePh_2)$	CH_3I	1.92[b]	8.6	[d]	
		2.24[c]	9.0		
	CH_2Cl_2	1.50[b]	8.6	2.90	10.2
		1.80[c]	9.0		
$(Me_2AuI)_2$	CH_2Cl_2	1.88[e]			
$[Me_2PPh_2]^+I^-$	CH_2Cl_2			3.10	13.7

[a] All peaks appear as 1/1 doublets unless specified otherwise. [b] Methyl group *cis* to phosphorus. [c] Methyl group *trans* to phosphorus. [d] Peak obscured. [e] Singlet.

Thus the overall reaction of methyl iodide with MeAuL gives *cis*-Me_2AuIL when L = PMe_3 or PMe_2Ph, IAuL when L = PPh_3 and a mixture of these products when L = $PMePh_2$. The overall rate of reaction follows the series L = PPh_3 > $PMePh_2$ > PMe_3 > PMe_2Ph, while the rate for the initial reaction (eqns. 2 and 3) was lowest for L = PPh_3 and highest for L = PMe_3. Thus the dependence of the overall reaction products on the nature of the ligand appears to be due primarily to a marked increase in the rate of reductive elimination of ethane from the intermediate Me_3AuL as the bulk of the ligand L increases. Since Tamaki, Magennis and Kochi [11] have shown that this reductive elimination reaction takes place from the species Me_3Au, which is formed by prior dissociation of the ligand L, the critical factor appears to be the greater ease of dissociation of L from Me_3AuL as the bulk of the ligand L increases. Confirmation that the ligand $PMePh_2$ dissociates more readily than PMe_3 or PMe_2Ph from the complex *cis*-Me_2AuIL is obtained from its reaction with methyl iodide to give $(Me_2AuI)_2$ and LMe^+I^- when L = $PMePh_2$ but not when L = PMe_2Ph or PMe_3.

B. Kinetic studies

In order to gain further insight into the mechanism of reaction we have studied the kinetics of the reaction of MeI with $MeAuPMe_3$. The initial reaction to give Me_3AuPMe_3 and $IAuPMe_3$ was followed by NMR spectroscopy by monitoring the disappearance of the methylgold peak of $MeAuPMe_3$ in benzene solution. High concentrations of methyl iodide were needed to give a reaction rate suitable for kinetic studies. If the reaction takes place according to eqns. (2) and (3) the rate is expected to be given by:

$$-\frac{d}{dt}[MeAuL] = 2k_2[MeAuL][MeI]$$

At the high concentrations of MeI used the reactions followed pseudo-first order kinetics with the observed rate constants approximately proportional to the methyl iodide concentration as shown in Fig. 1 and Table 2. Considering

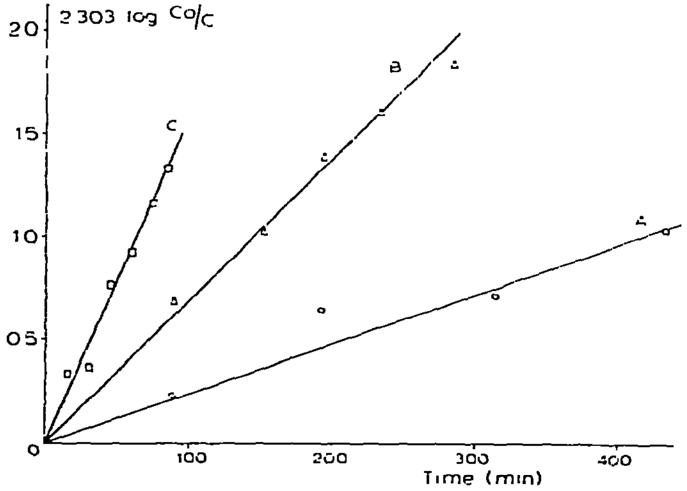


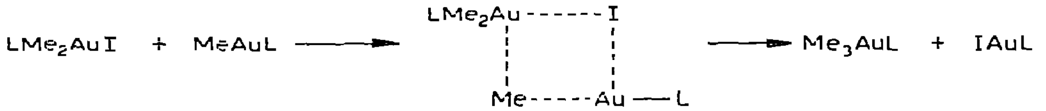
Fig. 1. First-order plots for the reaction of MeI with $MeAuPMe_3$. A, [MeI] = 2.11 *M*; B, [MeI] = 5.25 *M*; C, [MeI] = 16.0 *M*. C_0 and *C* refer to the concentration of $MeAuPMe_3$.

TABLE 2

RATE CONSTANTS FOR THE REACTION OF METHYL IODIDE WITH METHYL(TRIMETHYLPHOSPHINE)GOLD(I) IN BENZENE AT 33°

[MeI] (mol l^{-1})	$10^3 k_{obs}$ (min^{-1})	$10^4 k_2 = 10^4 k_{obs}/2[\text{MeI}]$ (l mol^{-1} min^{-1})
2.11	2.38 ± 0.6	5.6 ± 1.3
4.64	6.05 ± 0.4	6.5 ± 0.4
5.25	6.88 ± 0.8	6.6 ± 0.8
16.0	15.5 ± 2.7	4.8 ± 0.8

that the solvent polarity will change with methyl iodide concentration and that the methyl iodide activity and concentration will not be directly related at such high concentrations, the results are fully consistent with the proposed mechanism. We have independently showed that the reaction of eqn. (3) is fast (complete within 10 min at 33°). The rate of the reaction of MeAuL with MeI is not affected by addition of the free-radical scavenger galvinoxyl, so that the reaction is not a free-radical chain process. An ionic mechanism of reaction similar to that proposed in related systems [e.g. with the isoelectronic $\text{Pt(PPh}_3)_2$] [12] seems likely for the reaction of eqn. (2), though a free-radical non-chain mechanism [13] is also possible. The methyl—iodo exchange of eqn. (3) probably takes place via a 4-centre transition state (eqn. 9) [14]:



$$\text{LMe}_2\text{AuI} + \text{MeAuL} \longrightarrow \begin{array}{ccc} \text{LMe}_2\text{Au} & \cdots & \text{I} \\ \vdots & & \vdots \\ \text{Me} & \cdots & \text{Au}-\text{L} \end{array} \longrightarrow \text{Me}_3\text{AuL} + \text{IAuL} \qquad (9)$$

The subsequent reaction of eqn. (5) followed pseudo-second order kinetics in neat methyl iodide at 33° as shown in Fig. 2 [k_{obs} = (1.63 ± 0.05) × 10^{-3} l mol^{-1} min^{-1}], but we have been unable to obtain satisfactory kinetic plots using methyl iodide solutions in benzene so that the order of the reaction with respect to methyl iodide could not be determined.

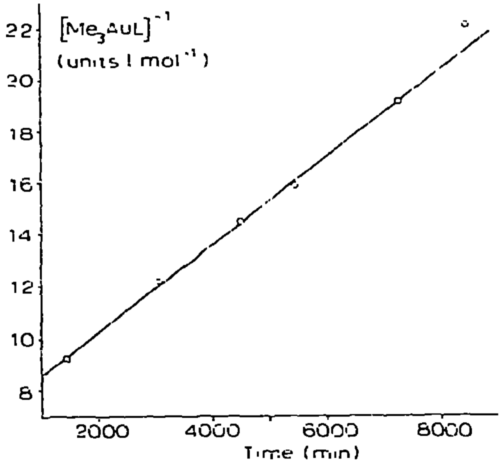


Fig. 2. Second-order plot for the reaction of eqn. (5), L = PMe_3, in neat methyl iodide at 33°.

If the reaction proceeds according to Scheme 1, and the steady state approximation is made for [MeAuL], the rate should be given by:

$$-\frac{\mathrm{d}}{\mathrm{d}t}[\mathrm{Me_3AuL}] = \frac{k_2k_6[\mathrm{Me_3AuL}][\mathrm{IAuL}][\mathrm{MeI}]}{k_{-6}[\mathrm{Me_2AuL}] + k_2[\mathrm{MeI}]}$$

Since [Me_3AuL] = [IAuL], second order kinetics should be observed if $k_2[\mathrm{MeI}] \gg k_{-6}[\mathrm{Me_2AuIL}]$. This is expected since it has already been shown that the reaction of methyl iodide with $MeAuPMe_3$ is very fast compared with this subsequent reaction. The rate of reaction is then simply equal to the rate of the forward reaction of eqn. (6).

If the reaction proceeds according to Scheme 2, and the steady state approximation is made for [$MeAuI_2L$], the rate should be given by:

$$-\frac{\mathrm{d}}{\mathrm{d}t}[\mathrm{Me_3AuL}] = \frac{k_7k_8[\mathrm{Me_3AuL}][\mathrm{IAuL}][\mathrm{MeI}]}{k_{-7} + k_8[\mathrm{Me_3AuL}]}$$

Thus second order kinetics will be followed only if $k_{-7} \gg k_8[\mathrm{Me_3AuL}]$. However, independent experiments in which $MeAuX_2L$ was generated in the presence of methylgold compounds (by reactions of AuX_3L with MeAuL) suggests that the exchange reaction (eqn. 8) should be fast with respect to the reductive elimination of the back reaction of eqn. (7) [14].

Thus the combined chemical [6] and kinetic data are more consistent with the mechanism of Scheme 1. An unequivocal decision could be made if the dependence of the rate on [MeI] could be determined, since according to Scheme 1 the second-order rate should be independent of [MeI] while according to Scheme 2 the rate should increase linearly with [MeI].

Experimental

^{1}H NMR spectra were recorded using a Perkin—Elmer R12-B spectrometer. Chemical shifts are given in ppm downfield from external TMS.

$MeAuPMe_3$ and $MeAuPMePh_2$ were prepared as descibed earlier [15]. Methyl iodide was distilled from copper wire before use.

Methyl(dimethylphenylphosphine)gold(I) was prepared by treating $BrAuPMe_2Ph$ [16] with methyllithium in ether at —80°. After allowing to warm to room temperature, the mixture was hydrolysed and the dried ether layer yielded the product as a colourless oil. Crystals could be obtained from petroleum spirit. M.p. 30°. $\nu(\mathrm{AuCH_3})$ 537 cm^{-1}. (Found: C, 30.6; H, 4.2. $C_9H_{14}AuP$ calcd.: C, 30.9; H, 4.0%.)

Iodo(dimethylphenylphosphine)gold(I) was prepared by treating $BrAuPMe_2Ph$ with sodium iodide in acetone solution, and was recrystallised from CH_2Cl_2/methanol. Yield 75%. M.p. 138-140°. (Found: C, 20.6; H, 2.1. $C_8H_{11}AuIP$ calcd.: C, 20.8; H, 2.35%.)

Trimethyl(dimethylphenylphosphine)gold(III) was prepared by reaction of $(AuBr_3)_2$ in ether at —80° with methyllithium (3 mol) followed by addition of PMe_2Ph (1 mol). After warming to room temperature and hydrolysing, the dried ether layer was evaporated under vacuum to give the crude product which was purified by chromatography through silica gel eluting with diethyl ether. It was a colourless oil ν(AuMe) 540, 500 cm^{-1}.

Methyl(trimethylphosphine)gold(I) with methyl iodide

A. $MeAuPMe_3$ was dissolved in methyl iodide and the mixture allowed to stand at room temperature for 3 h. Crystals of $IAuPMe_3$, m.p. 210-212° (lit. 210-214°) [17] precipitated. The filtrate contained Me_3AuPMe_3 which was identified by its NMR spectrum, and by comparison with an authentic specimen.

B. $MeAuPMe_3$ was dissolved in methyl iodide and the mixture left for 3 weeks at room temperature. Evaporation of the methyl iodide and recrystallisation from chloroform/petroleum spirit gave *cis*-$Me_2AuI(PMe_3)$. M.p. 77-80° (lit. 79-80°) [8]. (Found: C, 14.4; H, 3.7. $C_5H_{15}AuIP$ calcd.: C, 14.0; H, 3.5%.)

C. Kinetic studies. The reaction was followed by monitoring the disappearance of the methylgold resonance in the NMR spectrum of $MeAuPMe_3$ in benzene containing methyl iodide and toluene as internal standard. The system was calibrated with known concentrations of $MeAuPMe_3$ and toluene in benzene.

The kinetics of the subsequent reaction to give *cis*-$Me_2AuI(PMe_3)$ was followed by treating $MeAuPMe_3$ with neat MeI in an NMR tube which was sealed under vacuum. The rate was followed by monitoring the decay of the high-field methylgold peak of Me_3AuPMe_3. Concentrations were obtained by comparing the peak height with the height of the ^{13}C satellite of the MeI peak. Again a previous calibration was made.

$MeAu(PMe_3)$ with cis-$Me_2AuI(PMe_3)$

$MeAu(PMe_3)$ (0.062 mmol) and *cis*-$Me_2AuI(PMe_3)$ (0.062 mmol) were dissolved in benzene (0.5 ml) in an NMR tube. The reaction to give $IAu(PMe_3)$ and $Me_3Au(PMe_3)$ was complete in 10 min at 33°, as determined by the NMR spectrum.

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