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OXIDATIVE ADDITION IN THE COUPLING OF ALKYLGOLD(I) WITH ALKYL HALIDES

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Summary

MeAu(PPh$_3$) reacts with MeI to afford C_2H_6 and I(PPh$_3$)Au by a multistep mechanism involving: (i) oxidative addition to form an intermediate Me$_2$-AuI(PPh$_3$) species, which (ii), undergoes iodide—methyl exchange with another MeAu(PPh$_3$) species to afford Me$_3$Au(PPh$_3$), followed by (iii), reductive elimination of C_2H_6 and reformation of MeAu(PPh$_3$). The more reactive trimethylphosphine derivative also readily undergoes (i) oxidative addition and (ii) methyl exchange. However, Me$_3$Au(PMe$_3$) is more stable than the PPh$_3$ analog and does not undergo (iii) reductive elimination. Instead, it is involved in (iv), a further very slow reaction with IAu(PMe$_3$) and MeI to afford Me$_2$AuI-(PMe$_3$) in high yields. C_2H_5Au(PPh$_3$) specifically affords n-C_4H_{10} at 0° in MeI. Reactions of other alkylgold(I) complexes with alkyl halides are also reported, and fit into a general mechanistic pattern desribed by reactions (i) - (iv).

Introduction

Methyl derivatives of gold(I) and gold(III) are known, especially when they contain nitrogen, phosphorus or sulfur-containing ligands [1 - 6]. In a preliminary report [7], we examined the oxidative addition of methyl iodide to methyl(triphenylphosphine)gold(I) to form trimethyl(triphenylphosphine)gold(III), [reaction (a)] which underwent subsequent reductive elimination [reaction (b)]. The reactions (a) and (b) taken together constitute a catalytic process for the formation of ethane. We believe that this system serves as a model system for the catalytic coupling of alkyl groups by metal complexes [8], and thus merits a detailed examination.

$$2CH_3AuL + CH_3I \rightarrow (CH_3)_3AuL + IAuL \qquad (a)$$

(where L = PPh$_3$)

$$(CH_3)_3AuL \rightarrow CH_3CH_3 + CH_3AuL \qquad (b)$$

The methylgold complexes offer further advantages for mechanistic studies, since the diamagnetism of these complexes does allow reaction intermediates to be readily probed by examination of the ^1H NMR spectra. Thus, methyl(triphenylphosphine)gold shows a well-resolved doublet (δ 1.35 ppm, J 8.0 Hz)* in the NMR spectra due to splitting of the CH_3 group by phosphorus [4a]. Trimethyl(triphenylphosphine)gold in CH_3I shows two sets of doublets attributable to the CH_3 group *trans* to phosphorus (δ 1.92 ppm, J 9.1 Hz) and the CH_3 groups *cis* to phosphorus (δ 0.87 ppm, J 7.0 Hz) in these square-planar complexes [4a,5a]. The latter are also highly characteristic of a variety of alkylgold(III) complexes containing *cis*- and *trans*-CH_3 groups and can be reliably and conveniently used for their identification.

Triphenylphosphine ($L = PPh_3$) and trimethylphosphine ($L' = PMe_3$) complexes of methylgold(I) and methylgold(III) show different reactivities in oxidative addition reactions and in alkyl exchange reactions. As a result, their overall behavior appears to be different, despite the similar reactions they undergo at varying rates. In the following presentation we first discuss the reactions of methyl(triphenylphosphine)gold in methyl iodide, followed by a treatment of methyl(trimethylphosphine)gold under the same conditions. Although different overall reactions pertain in these two systems, we wish to show that both methylgold(I) complexes undergo oxidative addition of methyl iodide as the initial reaction, followed by alkyl exchange and/or reductive elimination of methylgold(III) intermediates. Analogous reactions of other alkylgold derivatives with various alkyl halides are also described.

Results and discussion

Methyl(triphenylphosphine)gold(I) and methyl iodide

Methyl(triphenylphosphine)gold(I) on dissolution in methyl iodide afforded ethane and iodo(triphenylphosphine)gold(I) after 48 h at room temperature according to the stoichiometry shown in eqn. (1) (L = triphenylphosphine).

$$CH_3AuL + CH_3I \rightarrow CH_3CH_3 + IAuL \qquad (1)$$

The course of reaction (1) could be readily followed continuously by examination of the ^1H NMR spectrum of the solution. Thus, the methyl group in CH_3AuPPh_3 appeared in the NMR spectrum as a doublet (J 8.0 Hz) centered at δ 1.35 ppm, but it disappeared in the methyl iodide solution after 8 h, and was replaced by a new doublet (J 7.0 Hz) at higher field (δ 0.87 ppm). The latter coincided with the resonances of the methyl groups which are *cis* to triphenylphosphine in trimethyl(triphenylphosphine)gold(III). The resonance at lower field due to the *trans*-methyl ligand in $(CH_3)_3AuPPh_3$ (δ 1.92 ppm, J 9.1 Hz) was hidden under the signal due to the $H—^{13}C$ coupling in methyl iodide. However, both signals were clearly observed** when the reaction of CH_3AuPPh_3 was carried out in perdeuteriomethyl iodide [*cis*-$(CH_3)_2$: δ 0.88

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* All NMR chemical shifts are reported relative to external TMS.

** This observation indicates extensive scrambling of methyl groups in $(CH_3)_3AuPPh_3$ during the course of its formation and/or subsequent alkyl exchange reactions to be discussed later (vide infra).

ppm doublet, J 7.2 Hz; *trans*-CH_3 : δ 1.95 ppm doublet, J 9.3 Hz].

The formation of $(CH_3)_3AuPPh_3$ as an intermediate in the reaction was further proved by carrying out the reaction at 0° for 150 h. Under these conditions $(CH_3)_3AuPPh_3$ was isolated in 87% yield, together with $IAuPPh_3$ in 91% yield (cf. eqn. 1). The $(CH_3)_3AuPPh_3$ was identified by comparison of its NMR [4a,5a] and IR spectra as well as its melting point with those of an authentic sample [3].

The subsequent decomposition of the intermediate $(CH_3)_3AuPPh_3$ was shown to occur in an independent experiment, in which a methyl iodide solution of it afforded, in approximately 40 h, two moles of ethane and one mole of $IAuPPh_3$ according to eqn. (2).

$$(CH_3)_3AuL + CH_3I \rightarrow 2CH_3CH_3 + IAuL \qquad (2)$$

Since the foregoing experiments showed that the gold(III) complex is derived from the gold(I) precursor, we deduced that the first step of reaction (1) occurred by oxidative addition of methyl iodide (eqn. 3) to form $(CH_3)_2$-$AuIPPh_3$.

$$CH_3AuL + CH_3I \rightarrow (CH_3)_2AuIL \qquad (3)$$

The NMR spectrum in chloroform of an authentic sample [9] of *cis*-dimethyliodo(triphenylphosphine)gold* prepared from *cis*-dimethyliodogold(III) and triphenylphosphine showed a pair of doublets for *cis*-CH_3 (δ 1.66 ppm, J 8.2 Hz) and *trans*-CH_3 groups (δ 2.12 ppm, J 8.9 Hz) [4a]. However, we could see no NMR evidence for the presence of $(CH_3)_2AuIPPh_3$ as an intermediate during the reaction between CH_3AuPPh_3 and methyl iodide. This ambiguity was resolved when it could be shown that $(CH_3)_2AuIPPh_3$ is readily converted to $(CH_3)_3AuPPh_3$ by CH_3AuPPh_3 according to eqn. (4). Thus, a pair of new doublets corresponding to those of *cis*- and *trans*-methyl groups in $(CH_3)_3$-$AuPPh_3$ appeared in the NMR spectrum within 5 min, when CH_3AuPPh_3 was added to an equimolar amount of $(CH_3)_2AuIPPh_3$ in deuteriochloroform solution. The signals due to CH_3AuPPh_3 and $(CH_3)_2AuIPPh_3$ disappeared at room temperature within 25 min, which is considerably faster than the reaction between either CH_3AuPPh_3 or $(CH_3)_2AuIPPh_3$ alone with methyl iodide under the same conditions. Work-up of the reaction mixture afforded $(CH_3)_3$-$AuPPh_3$ and $IAuPPh_3$ in excellent yields.

$$cis\text{-}(CH_3)_2AuIL + CH_3AuL \rightarrow (CH_3)_3AuL + IAuL \qquad (4)$$

The overall sequence of steps for reaction (1) can now be described as consisting of the individual processes shown in Scheme 1. Step (4) in this chain sequence is faster than the oxidative addition step (3), so that $(CH_3)_2AuIPPh_3$ does not attain concentrations high enough to be detected by NMR. Step (5) represents reductive elimination of two methyl groups from a gold(III) complex and is described later (vide infra) [10]. Furthermore, the regeneration of CH_3AuPPh_3 in step (5) indicates that the consumption of methyl iodide is catalytic.

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* The *trans*-iodo isomer is not known.

SCHEME 1

$$CH_3AuL + CH_3I \rightarrow (CH_3)_2AuIL \qquad (3)$$

$$(CH_3)_2AuIL + CH_3AuL \underset{\text{fast}}{\rightarrow} (CH_3)_3AuL + IAuL \qquad (4)$$

$$(CH_3)_3AuL \rightarrow CH_3CH_3 + CH_3AuL, \text{etc.} \qquad (5)$$

Methyl(trimethylphosphine)gold(I) and methyl iodide

Methyl iodide reacted faster with CH_3AuPMe_3 than it reacted with CH_3-$AuPPh_3$ Thus, greater than 90% conversion of CH_3AuPMe_3 to $(CH_3)_3AuPMe_3$ was achieved in 2 h at 25° according to reaction (6) (L' = trimethylphosphine).

$$2CH_3AuL' + CH_3I \underset{2\,h}{\rightarrow} (CH_3)_3AuL' + IAuL' \qquad (6)$$

Whereas $(CH_3)_3AuPPh_3$ subsequently underwent reductive elimination at room temperature in methyl iodide solutions (cf. eqn. 1 or eqns. 3 - 5), the rate of the further thermal reaction of $(CH_3)_3AuPMe_3$ in methyl iodide was very slow under the same conditions. The mixture was instead slowly further converted in high yields to *cis*-$(CH_3)_2AuIPMe_3$ on standing over a period of 4 weeks (eqn. 7).

$$(CH_3)_3AuL' + IAuL' + CH_3I \underset{\text{slow}}{\rightarrow} 2(CH_3)_2IAuL' \qquad (7)$$

The formation in eqn. (7) of the oxidative adduct $(CH_3)_2AuIPMe_3$ from $(CH_3)_3AuPMe_3$ is in apparent contradiction to the behavior of $(CH_3)_3AuPPh_3$ described above. However, it could be shown that alkylation of $(CH_3)_2$-$AuIPMe_3$ was obtained within an hour at 25° when an equimolar amount of CH_3AuPMe_3 was simply added to the product of reaction (7) (after removal of the CH_3I solvent and replacement with benzene) (eqn. 8). It could also be demonstrated that the products of reaction (6) made up independently [namely an equimolar mixture of $(CH_3)_3AuPMe_3$ and $IAuPMe_3$], when dissolved in methyl iodide slowly afforded $(CH_3)_2AuIPMe_3$ (80% in 14 days) according to the stoichiometry in eqn. (7).

$$(CH_3)_2AuIL' + CH_3AuL' \xrightarrow{C_6H_6} (CH_3)_3AuL' + IAuL' \qquad (8)$$

These observations can be accounted for by either of the two mechanisms presented in Schemes 2 and 2′. The mechanism in Scheme 2 depends on the reversibility of the methyl exchange between Au^{III} and Au^{I} in eqn. (9), the microscopic reverse of which has been shown to proceed readily in eqn. (8).

SCHEME 2

$$(CH_3)_3AuL' + IAuL' \rightleftharpoons (CH_3)_2AuIL' + CH_3AuL' \qquad (9)$$

$$CH_3AuL' + CH_3I \rightarrow (CH_3)_2AuIL' \qquad (10)$$

The essential reaction in Scheme 2′ involves the oxidative addition of methyl iodide to $IAuPMe_3$ as given in eqn. (11).

SCHEME 2′

$$\mathrm{IAuL' + CH_3I \rightleftharpoons CH_3AuI_2L'} \qquad (11)$$

$$\mathrm{CH_3AuI_2L' + (CH_3)_3AuL' \rightarrow 2(CH_3)_2AuIL'} \qquad (12)$$

Indirect evidence favors Scheme 2. Thus, $(CH_3)_3AuPMe_3$ reacted faster with methyl iodide when an equivalent amount of $IAuPPh_3$ was present rather than $IAuPMe_3$. A high conversion (76%) was attained in 2 days and the presence of both $(CH_3)_2AuIPMe_3$ and $(CH_3)_3AuPPh_3$ could be shown by NMR, and accounted for in the following manner*:

$$\mathrm{(CH_3)_3AuL' + IAuL \rightleftharpoons (CH_3)_2AuIL' + CH_3AuL} \qquad (13)$$

$$\mathrm{CH_3AuL + CH_3I \rightarrow [(CH_3)_2AuIL] \xrightarrow{CH_3AuL} (CH_3)_3AuL + IAuL} \qquad (14)$$

Furthermore, $ClAuAsPh_3$ exerted an even larger rate effect since an 80% yield of $(CH_3)_2AuIPMe_3$ was obtained in 12 h under the same conditions. The ligand exchange of CH_3 and Cl in reaction (15) was extremely rapid in methylene chloride, and 70% of $(CH_3)_3AuPMe_3$ was converted to $(CH_3)_2AuClPMe_3$ in 10 min at room temperature. The overall reaction in the latter example, however, is not clear, and it is probably complicated by the concomitant decomposition of organogoldarsine species.

$$\mathrm{(CH_3)_3AuL' + ClAuAsPh_3 \rightarrow (CH_3)_2AuClL' + CH_3AuAsPh_3} \qquad (15)$$

The foregoing results only provide indirect support for Scheme 2. We cannot at this point rigorously rule out the mechanism in Scheme 2′, since there is some evidence for oxidative addition to halogold(I) species. Thus, the facile reaction of $ClAuPPh_3$ with methyl iodide to produce methyl chloride in quantitative yields may proceed via such a mechanism (eqn. 16). The analogous reaction with $ClAuAsPh_3$ also proceeds readily. Both reactions are similar to the acetate exchange shown in eqn. (17) and reported by Nichols and Charleston [11].

$$\mathrm{ClAu^IL + CH_3I \overset{?}{\rightarrow} [CH_3(I)Au^{III}ClL] \rightarrow CH_3Cl + IAu^IL} \qquad (16)$$

$$\mathrm{R{-}X + CH_3CO_2AuL \rightarrow R{-}OAc + X{-}AuL} \qquad (17)$$

Decomposition of trimethyl(triphenylphosphine)gold in methyl iodide

A solution of trimethyl(triphenylphosphine)gold in methyl iodide evolves ethane quantitatively according to eqn. (18). The solution remains homogeneous and colorless due to the solubility of $IAuPPh_3$ in this medium and the absence of gold(0) species.

$$\mathrm{(CH_3)_3AuL + CH_3I \rightarrow 2CH_3CH_3 + IAuL} \qquad (18)$$

Reaction (18) is a two-stage process, involving first reductive elimination

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*The absence of $IAuPMe_3$, as shown by NMR suggests that phosphine exchange between Au^I and Au^{III} is relatively slow.

to CH_3AuPPh_3 (eqn. 5), then followed by a multistep reaction (eqn. 1) involving oxidative addition as described in the foregoing study. Reductive elimination from $(CH_3)_3AuPPh_3$ in eqn. (5) can be shown independently by carrying out the decomposition of $(CH_3)_3AuPPh_3$ in an inert solvent in which CH_3AuPPh_3 is stable [2b,10].

$$(CH_3)_3AuL \rightarrow CH_3CH_3 + CH_3AuL \qquad (5)$$

$$CH_3AuL + CH_3I \rightarrow CH_3CH_3 + IAuL \qquad (1)$$

The rate of ethane evolution can be readily followed by gas chromatography. However, the kinetics are not first order in $(CH_3)_3AuPPh_3$ because the apparent first-order rate constant for ethane formation (determined in the first 10% reaction) is inversely related to the concentration of $(CH_3)_3AuPPh_3$ as shown in Table 1. Since trimethyl(triphenylphosphine)gold is monomeric and largely undissociated in a nonpolar media (such as benzene), the foregoing kinetic behavior cannot be accounted for by the presence of binuclear gold species*.

The rates of overall ethane formation from various methylgold(I) and -(III) complexes are listed in Table 2. It is apparent from these results that the rates of reactions (5) and (1) are comparable under reaction conditions. The competitive nature of these processes, thus, does not allow the examination of only the step involving the reductive elimination of $(CH_3)_3AuPPh_3$ in this system. The decomposition of trialkyl(triphenylphosphine)gold complexes prepared by an independent method will be discussed in a later report [10].

Thermal reaction of trimethyl(trimethylphosphine)gold with methyl iodide

The decomposition of the trimethylphosphine derivative of trimethylgold(III) differs from the triphenylphosphine analog in that ethane is formed according to the stoichiometry in eqn. (19) in contrast to eqn. (18) shown earlier. The slow decomposition of $(CH_3)_3AuPMe_3$ in the presence of methyl iodide diluted in benzene solution was first reported by Shiotani and Schmid-

TABLE 1

RATES OF ETHANE FORMATION FROM TRIMETHYL(TRIPHENYLPHOSPHINE)GOLD AND METHYL IODIDE AT 31°

$(CH_3)_3AuPPh_3$ (mmol/l)	Rate (% × 10^3/min)
3.97	3.2
7.57	2.6
13.8	2.4
13.8[a]	0.2
21.8	2.1
32.9	1.5
43.5	1.6
75.3	0.84

[a] Contains an equimolar amount of PPh_3.

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* It is noteworthy that the decomposition of $(CH_3)_3AuPPh_3$ is much faster in CH_3I as solvent than it is in hydrocarbon solutions (compare ref. 2b). The difference may be due to auto-inhibition by free PPh_3 liberated during decomposition in the latter solvents. On the other hand, PPh_3 is readily scavenged as $CH_3PPh_3^+I^-$ on spontaneously reacting with CH_3I.

TABLE 2

RATES OF OVERALL ETHANE FORMATION FROM VARIOUS METHYLGOLD COMPLEXES IN METHYL IODIDE AT 31°

Methylgold complex	Concn. ($M \times 10^2$)	Rate constant[a] ($\text{min}^{-1} \times 10^4$)	Time (h) for completion[b]
CH_3AuPPh_3	3.4	5.0	48(100)
$(CH_3)_2(I)AuPPh_3$	2.0	4.3	100(100)
$(CH_3)_3AuPPh_3$	2.1	21.0[c]	40(200)
	3.3	15.0	

[a] Apparent first-order rate constant for first 20% reaction. [b] Percent yield of ethane liberated (in parentheses) based on gold. [c] Apparent rate constant decreases with increasing concentration of trimethylgold(III) with inverse half-order dependence. (See Table 1.)

baur [12], who obtained a 15% conversion to $(CH_3)_2AuIPMe_3$ in 40 days at 20°. The reaction is slightly faster without diluent, proceeding to 27% conversion in 30 days. A mechanism involving oxidative addition can be proposed [12], (eqns. 20 and 21). Based on our foregoing studies, we favor an alternative pathway (eqns. 22 - 23) which avoids the postulation of an unlikely gold(V) intermediate. The further alkylation of $(CH_3)_2AuIPMe_3$ as shown in eqn. (8) would not be significant under these conditions due to the low steady state concentration of CH_3AuPMe_3.

$$(CH_3)_3AuL' + CH_3I \rightarrow (CH_3)_2AuIL' + CH_3CH_3 \tag{19}$$

$$(CH_3)_3AuL' + CH_3I \rightarrow (CH_3)_4Au^{V}IL' \tag{20}$$

$$(CH_3)_4Au^{V}IL' \rightarrow CH_3CH_3 + (CH_3)_2AuIL' \tag{21}$$

$$(CH_3)_3AuL' \xrightarrow[\text{slow}]{} CH_3CH_3 + CH_3AuIL' \tag{22}$$

$$CH_3AuL' + CH_3I \xrightarrow[\text{fast}]{} (CH_3)_2AuIL' \tag{23}$$

Reaction of ethyl(triphenylphosphine)gold with methyl iodide

Ethyl(triphenylphosphine)gold was treated with methyl iodide to serve as a comparison with the reactions of methyl(triphenylphosphine)gold and to extend their generality. Thus, a solution of $C_2H_5AuPPh_3$ in methyl iodide afforded 91% n-butane, 94% ethane and 5% propane at 31°, accounting for 96% of the ethyl groups (butane and propane) and 99% of the methyl groups (ethane and propane) according to eqn. (24).

$$C_2H_5AuL + CH_3I \rightarrow \frac{a}{2}(C_4H_{10} + C_2H_6) + (1 - a)C_3H_8 + IAuL \tag{24}$$

The formation of butane and ethane in different sequential steps can be demonstrated by carrying the reaction out at lower temperatures. When C_2H_5-$AuPPh_3$ is dissolved in methyl iodide at 0°, only n-butane (accompanied by less than 1% propane) is formed in 86 h and the reaction stops as shown in Fig. 1a. However, on warming this solution to 25°, ethane is slowly liberated accompanied by propane (11%) and additional butane (19%) as shown in Fig. 1b.

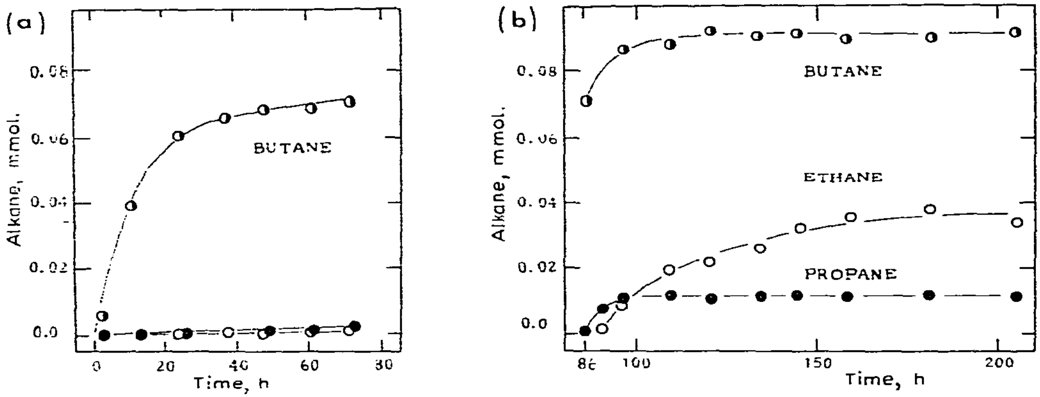

Fig. 1. (a) Reaction of ethyl(triphenylphosphine)gold (0.197 mmol) and methyl iodide at 0°; (b) continuation of (a) at 25°: ◑, n-butane; ○, ethane; ●, propane.

These observations can be accounted for by a mechanism proposed in Scheme 3, which is analogous to that (Scheme 1) proposed for CH_3AuPPh_3.

SCHEME 3

$$C_2H_5AuL + CH_3I \rightarrow C_2H_5(CH_3)AuIL \qquad (25)$$

$$C_2H_5(CH_3)AuIL + C_2H_5AuL \rightarrow (C_2H_5)_2(CH_3)AuL + IAuL \qquad (26)$$

$$(C_2H_5)_2(CH_3)AuL \rightarrow C_4H_{10} + CH_3AuL \qquad (27)$$

$$CH_3AuL + CH_3I \rightarrow C_2H_6 + IAuL \qquad (1)$$

Butane is derived in this mechanism by ready reductive elimination from a diethylgold(III) species shown in eqn. (27)*. Ethane is slowly derived via the more stable $(CH_3)_3AuPPh_3$, the concentration of which is also limited by the oxidative addition of CH_3AuPPh_3 (eqn. 1).

Propane is (most likely) derived by reductive elimination from an ethyldimethylgold species which can be formed from reaction intermediates as shown in eqns. (28) and (29).

$$\left.\begin{array}{l}(CH_3)_2AuIL + C_2H_5AuL\\ C_2H_5(CH_3)IL + CH_3AuL\end{array}\right\} \rightarrow C_2H_5(CH_3)_2AuL + IAuL \qquad (28)$$

$$\downarrow$$

$$C_3H_8 + CH_3AuL, \text{etc.} \qquad (29)$$

The mechanism presented in Scheme 3 is consistent with the NMR spectral changes during the reaction. Thus, a methyl iodide solution of C_2H_5-$AuPPh_3$ at room temperature showed an NMR signal for CH_3AuPPh_3 as early as 20 min after mixing, but it disappeared 5 h later, having been replaced by $(CH_3)_3AuPPh_3$ (NMR: CH_3Au *cis* to P: δ 0.90 ppm, J 7.0 Hz) and a species tentatively assigned to $C_2H_5(CH_3)_2AuPPh_3$ (CH_3Au *cis* to P: δ 0.94 ppm, J 7.1 Hz). Only $(CH_3)_3AuPPh_3$ remained after 23 h. The NMR spectrum of

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* The structural and stereochemical requirements for reductive elimination of trialkylgold(III) complexes will be presented separately.

$(C_2H_5)_2(CH_3)AuPPh_3$ could not be positively identified in the reaction mixture. The diethylgold(III) species is probably a transient intermediate which did not build up.

The exchange of alkyl groups between gold(III) and gold(I) account for some of the minor anomalies observed in this system. Thus, the formation of butane in Fig. 1b suggests that $(C_2H_5)_2Au^{III}$ species were formed in the warming cycle. A similar exchange occurred between $(CH_3)_2AuIPPh_3$ and C_2H_5-$AuPPh_3$ since a chloroform solution evolved n-butane (together with smaller amounts of propane and ethane) even at −20°. This system without exchange is expected to give mainly propane. In an analogous manner $(CH_3)_2AuIPPh_3$ and CD_3AuPPh_3 afforded CH_3AuPPh_3, whose concentration reached a maximum at 50 min, and finally afforded $(CH_3)_3AuPPh_3$ *.

$$(CH_3)_2AuIL + CD_3AuL \rightleftharpoons CH_3(CD_3)AuIL + CH_3AuL, \text{etc} \qquad (30)$$

The reactions of other alkylgold derivatives and alkyl halides are discussed in the Experimental section.

Conclusions

The trimethylphosphine complex of methylgold(I) undergoes oxidative addition of methyl iodide approximately five times faster than the triphenylphosphine analog. The resulting dimethyliodogold(III) adducts in both cases rapidly exchange methyl groups with an additional methylgold(I) to form trimethylgold(III) complexes, the fate of which depends on the phosphine ligand. Trimethyl(triphenylphosphine)gold undergoes ready reductive elimination of ethane, and the resultant CH_3AuPPh_3 undergoes oxidative addition again and is recycled. On the other hand, trimethyl(trimethylphosphine)gold is substantially more stable, which coupled with the higher reactivity of methyl (trimethylphosphine)gold to oxidative addition, leads to ethane and dimethyliodogold(III) as the final products of reaction.

Experimental

Materials

Chloro(dimethylsulfide)gold. $ClAuS(CH_3)_2$ was prepared from hydrogen tetrachloroaurate, $HAuCl_4 \cdot 3H_2O$ [13], and dimethyl sulfide according to procedure by Phillips [14]. Other chlorogold(I) complexes, ClAuL (where L = trimethylphosphine, triphenylphosphine, triethylphosphine, triphenylphosphine sulfide, triphenylarsine and phenylisocyanide) were prepared by stirring $ClAuS(CH_3)_2$ with a slight excess of the ligand in acetone at room temperature.

Chlorodibromo(trimethylphosphine)gold. $ClBr_2AuPMe_3$ was prepared by stirring a mixture of $ClAuPMe_3$ and a slight excess of bromine in chloroform at 0° for one-half hour. The product precipitated as yellow crystals which were washed with cold chloroform (yield 95%). $ClBr_2AuPPh_3$ was prepared by a similar procedure [15].

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* Extensive scrambling of CH_3 and CD_3 groups may be attributed to lack of stereoselectivity during alkyl exchange in either or both reactions (8) and (30).

Methyl(trimethylphosphine)gold. CH_3AuPMe_3 was prepared from $ClAuPMe_3$ and methyllithium [2,3a], and the triphenylphosphine analog was prepared by an analogous procedure. CD_3AuPPh_3 was prepared from $ClAuPPh_3$ and trideuteriomethyllithium, which was generated from trideuteriomethyl iodide and n-butyllithium in hexane at 0°. The precipitate of $(CD_3Li)_4$ was washed once with hexane and dissolved in ether. Trideuteriomethyl iodide was prepared from perdeuteriomethyl alcohol and phosphorus triiodide generated in situ from phosphorus and iodine. The preparation of other alkylgold(I) complexes was described earlier [16].

Trimethyl(trimethylphosphine)gold. $(CH_3)_3AuPMe_3$ was prepared by suspending 2.9 g of $ClBr_2AuPMe_3$ in 30 ml ether under nitrogen and adding 12 ml of methyllithium (1.6 *M*) solution. The mixture was stirred at room temperature for 2 h and excess CH_3Li destroyed with water. Work-up of the ethereal layer after drying with Na_2SO_4 afforded 1.5 g (75%) of $(CH_3)_3$-$AuPMe_3$ as a colorless oil which was further purified by molecular distillation in vacuo [4a].

Trimethyl(triphenylphosphine)gold. $(CH_3)_3AuPPh_3$ was also prepared from $ClBr_2AuPPh_3$ and methyllithium. M.P. 115 - 116° (decomp.) (lit. 3] 119°). A more convenient procedure involves the reaction of lithium dimethyl (triphenylphosphine)gold(I) with methyl iodide [17].

Dimethyliodo(triphenylphosphine). This was prepared by a modification of the procedure [9] for $[(CH_3)_2AuI]_2$, in which triphenylphosphine was added instead of ethylenediamine to the crude product. Substantially higher yields (70%) were obtained by reacting a methylene chloride solution of trimethyl(triphenylphosphine)gold with a stoichiometric amount of iodine dissolved in the same solvent. Concentration of the solution in vacuo afforded colorless crystals which were recrystallized from acetone [10].

Reaction of methyl(triphenylphosphine)gold with methyl iodide

Methyl(triphenylphosphine)gold (40.5 mg) was dissolved in methyl iodide and kept at room temperature. The NMR signal for CH_3Au^I (δ 1.35 ppm doublet, J 8.0 Hz) disappeared in 11 h. Analysis of the vapor phase by gas chromatography indicated the presence of ethane with a trace of methane. After 9 days, iodo(triphenylphosphine)gold was recovered from the solution, recrystallized from acetone (m.p. 212 - 215°), and the IR spectrum compared with an authentic sample.

The same reaction at −20° required 2 days for the CH_3Au^I signal to disappear completely. At the same time another doublet (δ 0.87 ppm, J 7.0 Hz) corresponding to the *cis*-CH_3 groups in $(CH_3)_3AuPPh_3$ appeared in the NMR spectrum and continued to increase with time. The NMR spectrum at lower field could be examined by carrying out the reaction in deuteriomethyl iodide. Under these conditions, a second doublet (δ 1,95 ppm, J 9.3 Hz) corresponding to the *trans*-CH_3 group in $(CH_3)_3AuPPh_3$ grew simultaneously with the doublet resonance at 0.87 ppm. The intensity ratios of the proton signals were: 1.49 (*cis*-CH_3)/0.74 (*trans*-CH_3)/15.0 (Ph), indicating a lack of stereoselectivity in the formation of $(CH_3)_3AuPPh_3$.

The NMR spectrum of a solution containing CH_3AuPPh_3 and excess methyl iodide diluted with chloroform showed no change in 13 h at room temperature.

A preparative run was carried out at 0° with 2.52 g $(CH_3)_3AuPPh_3$ dissolved in 25 ml methyl iodide. The NMR spectrum of the solution showed that CH_3AuPPh_3 was gone after 6 days. The solvent was removed in vacuo and the residue after extraction with n-pentane afforded 1.17 g (87%) of $(CH_3)_3$-$AuPPh_3$, which after recrystallization from pentane melted at 115 - 116°. The IR spectrum was identical with that of authentic $(CH_3)_3AuPPh_3$. The pentane-insoluble $IAuPPh_3$ was isolated in 91% (1.42 g) yield.

Reaction of methyl(trimethylphosphine)gold with methyl iodide

CH_3AuPMe_3 was dissolved in methyl iodide at room temperature. The reaction was followed by examination of the NMR spectrum. The spectrum of CH_3AuPMe_3 (CH_3Au: δ 1.12 ppm doublet, J 8.5 Hz, CH_3P: δ 2.52 ppm, J 8.9 Hz) decreased and the spectra of $(CH_3)_3AuPMe_3$ (CH_3Au: *cis* to P, δ 1.03 ppm, J 7.8 Hz, *trans* to P, δ 1.69 ppm, J 9.3 Hz; CH_3P: δ 2.57 ppm, J 9.9 Hz) and $IAuPMe_3$(CH_3P: δ 2.75 ppm, J 10.9 Hz) appeared and continued to increase according to eqn. (6), and attained 50% conversion in 20 min (94% conversion in 120 min).

Continued examination of the NMR spectrum of the same solution showed that a new species *cis*-$(CH_3)_2IAuPMe_3$ (CH_3Au: *cis* to P, δ 2.19 ppm, J 9.3 Hz; CH_3Au: *trans* to P, δ 2.37 ppm, J 8.6 Hz; CH_3P: δ 2.78 ppm, J 10.4 Hz) subsequently appeared and increased in concentration. After 4 weeks most of the gold consisted of *cis*-$(CH_3)_2IAuPMe_3$, and only traces of $(CH_3)_3$-$AuPMe_3$ and $IAuPMe_3$ were observable.

The solvent was removed in vacuo and the solid (56 mg) redissolved in benzene to afford a solution of $(CH_3)_2IAuPMe_3$, whose NMR spectrum [4b] (CH_3Au: *cis* to P, δ 1.32 ppm, J 8.4 Hz; CH_3Au: *trans* to P, δ 1.65 ppm, J 9.7 Hz; CH_3P: δ 1.25 ppm, J 10.2 Hz) was the same as that of an authentic sample prepared from the iodinolysis of $(CH_3)_3AuPMe_3$ in methylene chloride [10]. (It is noteworthy that the values of the NMR chemical shifts are highly dependent on the concentrations of the benzene solutions.) When an equimolar amount of CH_3AuPMe_3 was added to this benzene solution, a solid ($IAuPMe_3$) began to separate and in an hour only the NMR spectrum of $(CH_3)_3AuPMe_3$ remained.

The reaction of 90.0 mg of $(CH_3)_3AuPMe_3$ and 113.2 mg of $IAuPMe_3$ was carried out in 1 ml methyl iodide at room temperature. A 50% yield of $(CH_3)_2IAuPMe_3$ was obtained in 4 days and 80% after 14 days. After a month, the NMR spectrum of the solution showed the presence of only $(CH_3)_2$-$IAuPMe_3$ and traces of $(CH_3)_3AuPMe_3$ and $IAuPMe_3$. The same reaction with $IAuPPh_3$ (to replace $IAuPMe_3$) required 2 days to convert 76% of $(CH_3)_3$-$AuPMe_3$ to $(CH_3)_2IAuPMe_3$. The presence of $(CH_3)_3AuPPh_3$ was also indicated from the NMR spectrum (CH_3Au: *cis* to P, δ 0.89 ppm, J 7.0 Hz; CH_3Au: *trans* to P, δ 1.86 ppm, J 9.0 Hz). The reaction occurred even more rapidly with $ClAuAsPh_3$ (replacing $IAuPMe_3$ or $IAuPPh_3$), and 84% of $(CH_3)_3$-$AuPMe_3$ was converted to $(CH_3)_2IAuPMe_3$ in 12 h. Unidentified singlet absorptions also appeared in the NMR spectrum near the CH_3Au^{III} resonances. When the foregoing reaction was carried out in methylene chloride solution, a rapid reaction occurred at room temperature, and approximately 70% of the $(CH_3)_3AuPMe_3$ was converted to $(CH_3)_2IAuPMe_3$ in less than 10 min. The dark color of the solution together with unidentified absorptions in the spectrum indicated some decomposition had also occurred.

The reaction of $(CH_3)_3AuPMe_3$ alone was carried out in methyl iodide at room temperature. Its concentration decreased slowly as $(CH_3)_2IAuPMe_3$ appeared in 15% yield after 15 days and 25% after 29 days.

Reaction of methyl(triphenylphosphine)gold with other alkyl halides

Allyl chloride was employed as solvent for the reaction with CH_3AuPPh_3. No reaction was apparent after 3 days at room temperature.

Allyl bromide and CH_3AuPPh_3 afforded an 80% yield of ethane, as well as propylene (20%), 1-butene (4%) and a trace of methane after 1000 h at room temperature. The NMR spectrum of the solution showed that the CH_3—Au^I signal was gone after 17 h. Bromo(triphenylphosphine)gold was isolated from the reaction mixture. [IR spectrum, m.p. 245 - 247° (lit. [3a] 251°).]

Benzyl bromide reacted with CH_3AuPPh_3 in 3 days at room temperature. Under the same conditions acetyl chloride reacted on mixing, although the reaction was slower (20 h) when diluted with deuteriochloroform. Iodobenzene showed no reaction with CH_3AuPPh_3 in 2 days at room temperature or even for 5 days at 50°. The products were not identified in these qualitative reactivity studies.

Reaction of methyl iodide with other alkyl(triphenylphosphine)gold complexes

Ethyl(triphenylphosphine)gold (25.0 mg) was dissolved in 1 ml methyl iodide [16]. The NMR spectrum of the solution immediately after dissolution showed a small doublet signal for CH_3AuPPh_3 (δ 1.39 ppm, J 7.8 Hz). After 5 h the signal disappeared and was replaced by two sets of doublets at higher field (δ 0.94 ppm, J 7.1 Hz and δ 0.90 ppm, J 7.0 Hz). The doublet at 0.94 ppm disappeared after 22 h, and it is tentatively assigned to ethyldimethyl(triphenylphosphine)gold (vide supra for the spectrum in chloroform). The doublet at 0.90 ppm corresponds to that of the *cis*-CH_3 groups in $(CH_3)_3$-$AuPPh_3$. The NMR spectrum of the same reaction at −20° showed similar behavior, except for a much slower rate of reaction.

The gaseous products of the reaction were analyzed after sealing 102.2 mg $C_2H_5AuPPh_3$ and 5.0 ml methyl iodide under a helium atmosphere in a 100 ml flask equipped with a break seal. The reaction mixture was kept for 7 days at 25° and analyzed by gas chromatography (isobutane, internal standard) in a 3 ft. Porapak Q column at 40°. Ethane (97%) and n-butane (78%) were the principal products together with propane (6%) and methane (0.1%). Iodo(triphenylphosphine)gold was isolated in 70% (85.9 mg) yield from the reaction mixture.

The kinetic studies were carried out typically by dissolving 55 mg C_2H_5-$AuPPh_3$ in 5.0 ml methyl iodide contained in a 25 ml flask sealed with a gas-tight rubber serum cap. The internal standard was added and the flask heated in a constant temperature bath. Samples were extracted periodically and analyzed by gas chromatography after careful calibration.

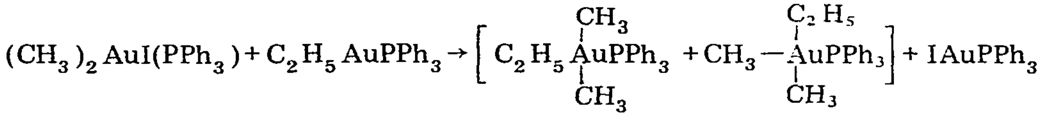
n-Propyl(triphenylphosphine)gold, isopropyl(triphenylphosphine)gold, tert-butyl(triphenylphosphine)gold and neopentyl(triphenylphosphine)gold [16] all reacted with methyl iodide to afford alkylgold^{III} complexes, as indicated by the presence of characteristic NMR doublet resonances for *cis*-CH_3 groups (δ 0.9 ± 0.1 ppm, J 7 ± 0.2 Hz) in methylgold^{III} complexes. Under the same conditions, the NMR spectrum of a solution of $PhAuPPh_3$ [16] in methyl iodide showed no change over prolonged periods. t-$BuAuPPh_3$ when dissolved in carbon tetrachloride, liberated isobutene and tert-butyl chloride.

Reaction of dimethyl(triphenylphosphine)iodogold with alkyl(triphenylphosphine)gold complexes

CH_3AuPPh_3 was mixed with an equimolar amount (0.095 mmol) of $(CH_3)_2AuI(PPh_3)$ in chloroform and the solution kept for 4 days at −20°, or an hour at room temperature. Removal of the solvent followed by pentane extraction afforded $(CH_3)_3AuPPh_3$ which was identified by its IR spectrum.

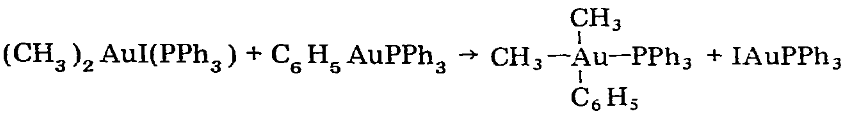
The reaction was repeated with CD_3AuPPh_3 and $(CH_3)_2AuI(PPh_3)$ in $CDCl_3$. The NMR spectrum of the solution after 1 min indicated the presence of both $(CH_3)_3AuPPh_3$ and CH_3AuPPh_3. The former component continued to increase until the reaction was complete, but the concentration of CH_3AuPPh_3 reached a maximum after 5 min. Only $(CH_3)_3AuPPh_3$ remained after 50 min. The intensity of the resonance signal due to *cis*-CH_3 relative to *trans*-CH_3 was 1.7 in the $(CH_3)_3AuPPh_3$ product indicating extensive scrambling of methyl groups.

$C_2H_5AuPPh_3$ and an equimolar amount (0.11 mmol) of $(CH_3)_2AuI(PPh_3)$ were dissolved in deuteriochloroform and kept for 6 days at −20°. The NMR spectra of $(CH_3)_3AuPPh_3$ and CH_3AuPPh_3 were readily observed in the solution in addition to two new species which showed CH_3—Au^{III} resonances at δ 0.59 ppm (J 6.8 Hz) and 0.50 ppm (J 7.0 Hz) for *cis*-CH_3 groups as well as δ 1.65 ppm (J 8.9 Hz) for *trans*-CH_3 groups. Comparison with authentic samples indicated that these signals are associated with *cis* and *trans* ethyldimethyl(triphenylphosphine)gold [16].



$$(CH_3)_2AuI(PPh_3) + C_2H_5AuPPh_3 \rightarrow \left[C_2H_5\underset{CH_3}{\overset{CH_3}{Au}}PPh_3 + CH_3-\underset{CH_3}{\overset{C_2H_5}{Au}}PPh_3 \right] + IAuPPh_3$$

Phenyl(triphenylphosphine)gold also reacted with $(CH_3)_2AuI(PPh_3)$ in chloroform solution in 10 min at room temperature. Only the spectrum (δ 0.72 ppm, J 7.3 Hz; δ 1.17 ppm, J 9.0 Hz) of *cis*phenyldimethyl(triphenylphosphine)gold was observed.



$$(CH_3)_2AuI(PPh_3) + C_6H_5AuPPh_3 \rightarrow CH_3-\underset{C_6H_5}{\overset{CH_3}{Au}}-PPh_3 + IAuPPh_3$$

Neopentyl(triphenylphosphine)gold was treated with an equimolar amount (0.093 mmol) of $(CH_3)_2AuI(PPh_3)$ in $CDCl_3$, but it required more than 3 h for the NMR signals due to $(CH_3)_2AuI(PPh_3)$ to disappear completely. However, at this point only half of the neopentyl(triphenylphosphine)gold (NMR: δ 1.63 singlet; δ 2.08 doublet, J 8.0 Hz) had been consumed and an equivalent amount of $(CH_3)_3AuPPh_3$ was formed. Another portion (0.093 mmol) of $(CH_3)_2AuI(PPh_3)$ was added to this solution. After 10 h most of the neo-$C_5H_{11}Au(PPh_3)$ had disappeared, and $(CH_3)_3AuPPh_3$ as well as a new neopentyl-containing species (probably $C_5H_{11}(CH_3)AuIPPh_3$, NMR: δ 1.39 singlet, partial spectrum) were probably formed according to the following reaction:

$$\text{neo-}C_5H_{11}AuL + 2(CH_3)_2AuIL \rightarrow \text{neo-}C_5H_{11}(CH_3)AuIL + (CH_3)_3AuL + IAuL$$

t-$BuAuPPh_3$ shows a sharp doublet in the NMR spectrum (δ 1.97 ppm, *J* 6.5 Hz, benzene). Addition to a $CDCl_3$ solution containing an equimolar amount (55.0 mg) $(CH_3)_2AuI(PPh_3)$ caused the latter to disappear completely in less than a minute. The resulting NMR spectrum consisted simply of a singlet (δ 1.89 ppm, 7.1 H based on Ph = 30.0 H). The NMR spectrum of *trans*-t-$Bu(CH_3)_2AuPPh_3$ [$(CH_3)_2$ *cis* to P: δ 0.03 ppm, *J* 7.3 Hz; $(CH_3)_3C$: δ 1.59 ppm doublet, *J* 11.4 Hz, in DME] was absent as well as that of CH_3AuPPh_3. The reaction merits further study.

Analysis

The molecular weight of trimethyl(triphenylphosphine)gold was determined in benzene solution with a Mechrochrom 301A vapor pressure osmometer at 37° using benzil as a calibrant. The molecular weights were 498 and 509 using 37.3 mg and 57.4 mg of $(CH_3)_3AuPPh_3$ in 1.2026 mg and 0.8602 mg of benzene, respectively (Calculated for monomeric species, 504.40.)

The hydrocarbon gases were analyzed by gas chromatography (hydrogen flame, Aerograph 500, 50 cm Porapak Q at 90° or a 20 ft. ODPN column). Quantitative analysis was effected by the internal standard method after careful calibration under reaction conditions.

The proton NMR spectra were recorded on a Varian HA-100 spectrometer with a variable temperature probe. All chemical shifts are reported relative to external TMS and are reproducible to ± 0.03 ppm. Chemical shifts vary appreciably with solvent changes.

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